

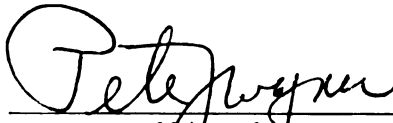




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Factors Influencing the Photochemistry
of Ortho Alkyl Phenyl Ketones

presented by
Martin Sobczak

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Ph.D. degree in Chemistry


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FACTORS INFLUENCING THE
PHOTOCHEMISTRY OF ORTHO ALKYL PHENYL KETONES.

VOLUME I

By

Martin Sobczak

A DISSERTATION

Submitted to
Michigan State University
In partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1997

ABSTRACT

FACTORS INFLUENCING THE PHOTOCHEMISTRY OF ORTHO ALKYL PHENYL KETONES.

By

Martin Sobczak

This thesis research focused on γ -hydrogen abstraction of several ortho alkyl phenyl ketones including substituted trialkyl benzophenones. Modern NMR has allowed me to reinvestigate photoenolization paradigms that have existed for over 35 years. Conducting the photochemical experiments in NMR tubes has revealed the effects that temperature, oxygen and wavelength has on secondary reactions of the initial photoproducts. We now have a firm understanding of the ketone $\rightarrow$ enol $\rightarrow$ benzocyclobutenols chronology.

Variations in the photochemistry of several similar o-alkylphenyl ketones suggest the chemo- and diastereoselectivity of product formation is determined by the geometry of the biradical initially formed by γ -hydrogen abstraction. My findings combined with Park's and independent literature results provide these facts: 2-ethylbenzophenone forms only the E-2-methyl-1-phenyl-1-hydroxy-benzocyclobutenol and only a single Diels-Alder-adduct with maleic anhydride; 2-benzylacetophenone forms no products in deaerated benzene but forms

peroxides and undergoes H/D exchange in methanol- d_4 ; 2-benzylbenzophenone forms a single benzocyclobutenol and a single Diels-Alder adduct. Each of these product distributions reflects the expected chemistry of a population of *o*-xylylenols formed from a twisted triplet biradical. The biradical is coincidentally the triplet state of the *o*-xylylenol such that it has two unpaired electrons in orbitals localized primarily on the exocyclic carbons, with one orbital parallel and the other orthogonal to the π system. The radical conjugating ability and the steric bulk of the substituents on the two exocyclic carbons determines the geometry of the twisted triplet, which determines the geometry of the ground state *o*-xylylenols formed upon decay. The decay modes of the different *o*-xylylenols formed are believed to involve: a facile 1,5-sigmatropic hydrogen shift regenerating starting ketone for the Z-enol(OH in); and an allowed stereoselective conrotatory cyclization for the E-enol(OH out).

Previously we reported that the primary photoproducts of hexaalkylbenzils are α -hydroxyindanones formed from a 1,5-biradical after δ -hydrogen abstraction. The initial hydroxyindanones are photolabile and undergo the Norrish Type I reaction followed by biradical disproportionation to yield ketoaldehydes. My studies have revealed subtleties in this secondary photochemistry, in particular a second disproportionation pathway for the biradical which involves a 1,4 hydrogen transfer rather than a 1,6 transfer. The efficiency for triplet α -cleavage appears to be controlled by a competing photoenolization and singlet quenching.

*In Memory of My Grandmother Mary Sobczak, My Aunt Yvonne Sobczak and My
Canine Companion Beau.*

ACKNOWLEDGMENTS

I would like to thank Dr. Peter J. Wagner: for his guidance, his brain for the archive of photochemistry literature it possesses, the countless discussions that helped mold this thesis, the free tickets to hockey games (even though I should have been in lab!), for the freedom of exploring new ideas, financial support and his help in developing me into a Ph.D. scientist.

I am grateful to the National Science Foundation and Michigan State University for financial support in the form of teaching and research assistantships. I would like to thank the Chemistry departments entire support staff including Dr. Long Lee and Dr. Kermit Johnson in the NMR facility, Paul Reed and Dr. Tom Atkinson for computer help, Scott and Manford in the Glass Shop, Rai for running my Mass Specs.

I owe special thanks to Dr. Ali Zand for continued encouragement and useful discussions, Dr. Kevin McMahon for his laboratory guidance and British humor, and the rest of the Wagner group members, past and present.

I would like to thank my Mother and Father and the rest of my family for their continued support, understanding and encouragement during my graduate studies.

Finally, I am indebted to my fiancée Corey, for her love, patience and endless support of my dream.

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Introduction

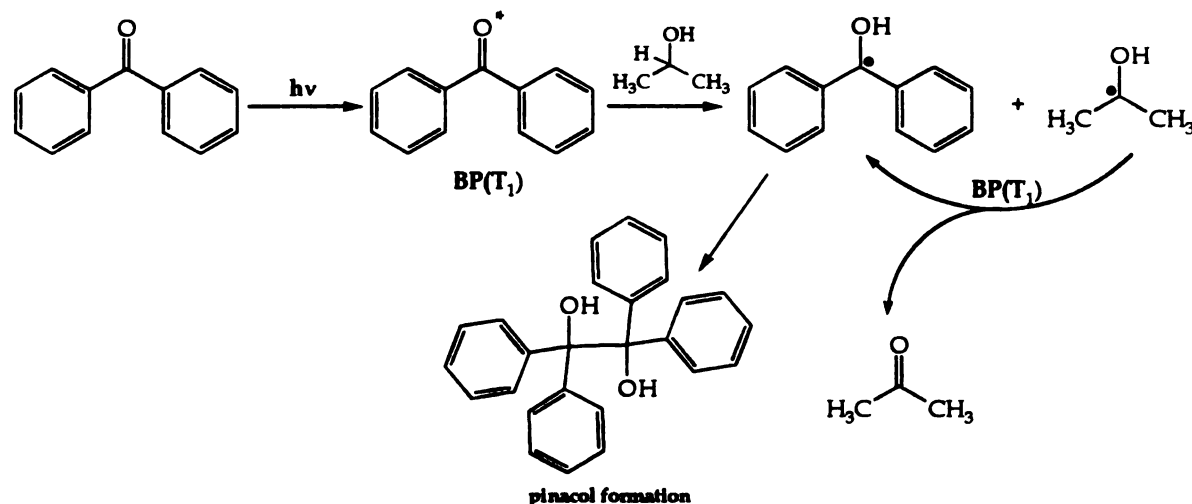
Photochemistry of carbonyl compounds has been a fruitful area of organic photochemistry for the last 40 years. The carbonyl's versatile functionality is evident in lengthy chapters in Organic Chemistry and Biochemistry text books. The importance of photochemistry in nature cannot be understated when considering the significance of photosynthesis, vision and its adverse effects such as skin cancer. The absorption of light provides the energy required for reactions to proceed and affords an alternate reagent for chemists. Target molecules can often be generated by photochemistry that are not possible by ground state reactions. Often, highly strained molecules can be generated by light. Several reactions are highly stereoselective, giving only one diastereomer when several are possible. Although synthetic organic photochemistry has been applied successfully by several groups, it is still in its infancy. Rather than giving a complete history of organic photochemistry, I will only provide a background of the pertinent photochemical processes that relate to my research, which focused primarily on hydrogen abstraction in *o*-alkyl phenyl ketones and reactions of the primary photoproducts.

Typically, photochemical reactions in solution occur from a vibrationally relaxed molecule in either its lowest single S_1 , or triplet state T_1 . Absorption of light promotes a compound from a ground state S_0 to an excited state S_n ; upper singlets rapidly undergo internal conversion to the lowest excited single state S_1 with a rate of 10^{11} - 10^{12} s⁻¹.¹ The lowest singlet state can decay to the ground state by emitting light (fluorescence) with a rate of 10^5 - 10^8 s⁻¹.^{1,2} Photochemical transformations are also possible from the S_1 state including hydrogen abstraction and α -cleavage. Another competing process for the S_1 state is intersystem crossing (ISC) with a rate constant of 10^7 - 10^{11} s⁻¹.¹⁻⁶ The excited triplet can also undergo radiationless decay and a radiative process (phosphorescence) with a rate constant of 10^1 - 10^6 s⁻¹.¹ Chemical reactions (hydrogen abstraction, α -cleavage, etc....) effectively compete with these processes and can be quenched by energy transfer and/or charge transfer with the appropriate quencher. Quenching can occur with a rate constant as high as the rate of diffusion, $\leq 10^{10}$ M⁻¹s⁻¹.⁷

I. Hydrogen Abstraction

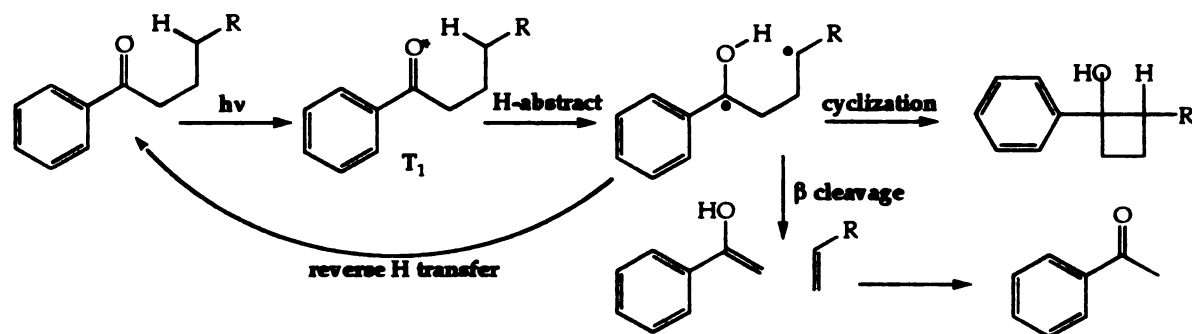
Hydrogen abstraction occurs by both inter and intramolecular processes. Benzophenone is photoreduced in isopropyl alcohol solutions and gives high yields of the pinacol and acetone (see Scheme 1).⁸ Intramolecular hydrogen abstraction presents an alternative pathway for radicals besides intermolecular coupling and disproportionation, in particular cyclization (see Scheme 2).⁹

Collectively, the cyclization and cleavage reactions in Scheme 2 are referred to as the *Norrish Type II* process. The efficiency of hydrogen abstraction depends on a



Scheme 1. Photoreduction of benzophenone in isopropyl alcohol.

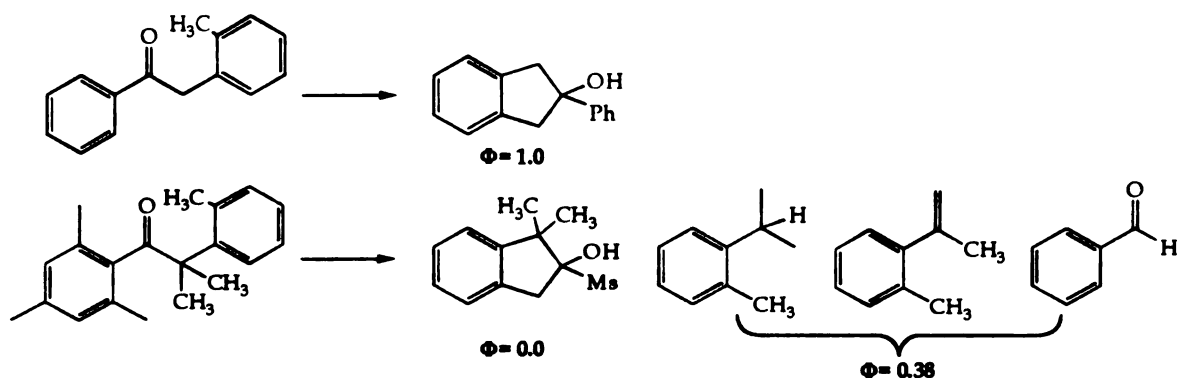
variety of factors including the nature of excited state, multiplicity of the excited state, orientation and the overall thermodynamics of the process. Hydrogen abstraction can occur from both the S_1 and T_1 states. If intersystem crossing to the



Scheme 2. Intramolecular hydrogen abstraction, cyclobutenol formation.

triplet is efficient, as it is for most phenyl ketones, hydrogen abstraction will occur from the triplet state to give a triplet biradical. There are scattered reports of hydrogen abstraction from the singlet state in phenyl ketones which will be

discussed later. The fate of the biradicals depends on their geometry. The geometry is influenced by steric and electronic factors that dictate if the biradical cyclizes, disproportionates (elimination) or hydrogen abstracts (revert or starting ketone, or intermolecular).¹⁰ If the hydrogen abstraction is slowed then α -cleavage can compete see Scheme 3.^{11 12}



Scheme 3. Competition between α -cleavage and hydrogen abstraction.

A. Nature of the excited state; π, π^* versus n, π^* and Singlet versus Triplet

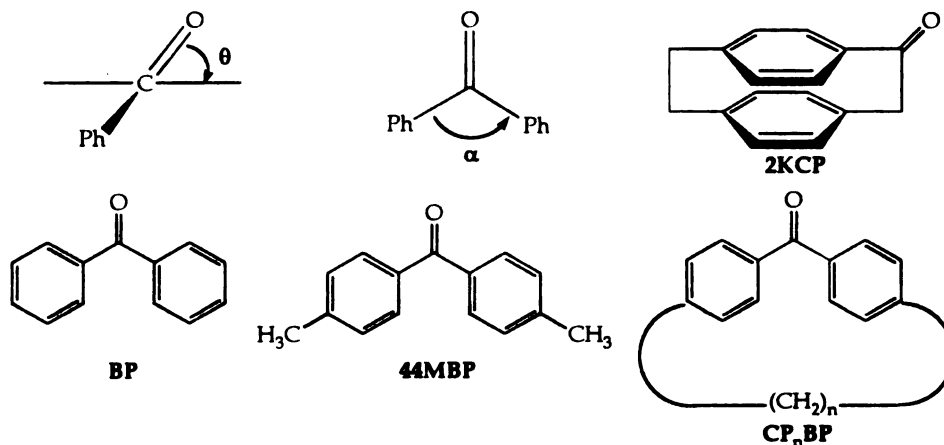
Much of the reactivity of phenyl ketones is due to a particular electronic state. The $^3n, \pi^*$ state is now generally accepted as being equivalent to an electron deficient alkoxy radical whose chemistry parallels thermally generated alkoxy radicals.^{10,13} The $^3\pi, \pi^*$ state is generally only a few kcal/mol above the $^3n, \pi^*$ state in phenyl alkyl ketones. Highly polar solvents, electron donating or π -conjugating electron-withdrawing substituents can invert these states.¹⁴⁻¹⁷ It is well known that ketones with $^3\pi, \pi^*$ lowest triplets are much less reactive than their $^3n, \pi^*$ counterparts in type II reactions but does not necessarily mean that hydrogen abstraction cannot occur from the $^3\pi, \pi^*$ state.^{18,19} Wagner, Kemppainen

and Schott have shown that when the $^3\pi,\pi^*$ and $^3n,\pi^*$ are close enough in energy they can equilibrate and the hydrogen abstraction occurs from the upper $^3n,\pi^*$ state which is only a few percent populated.¹⁹ The effect of ring methyl substituents on the reactivity of butyro- and valerophenones in the type II reaction has been studied by Wagner, Thomas and Harris.²⁰ They found that meta or para methyl groups cause an increase in separation between $^3n,\pi^*$ and $^3\pi,\pi^*$ state. As the energy gap between the $^3\pi,\pi^*$ and $^3n,\pi^*$ states increases, the rate constant for type II decreases proportionally to $-\Delta E_T/RT$. This proves that the reactivity arises from the thermally equilibrated $^3n,\pi^*$ state and not from vibronic mixing of the $^3n,\pi^*$ and $^3\pi,\pi^*$ states.

It is well known that aliphatic ketones undergo type II elimination from both the singlet and triplet n,π^* states.¹⁰ Conjugated dienes, which are efficient triplet quenchers but poor singlet quenchers quench only part of the reaction and give a curved Stern-Volmer plot.¹⁰ In contrast to aliphatic ketones, nearly all aromatic ketones react only from their triplet states, this is attributed to their rapid intersystem crossing. For example, 99.2% of the photoelimination from γ -phenylbutyrylphenone is quenched by 4M pentadiene.^{7a}

Both the Wagner²¹ and Turro^{22,23} groups have studied the effect of twisting the carbonyl group on the excited state of aromatic ketones. Turro compared model compounds benzophenone (BP) and 4,4'-dimethylbenzophenone (44MBP) with a series of cyclophanobenzophenones. Photochemical and photophysical evidence suggested that the n,π^* character of

the lowest triplet state decreased as the cyclophane ring size decreased. The rates of hydrogen abstraction from 1,4-cyclohexadiene in acetonitrile decreased from



1.6×10^8 ($n=12$) to $0.04 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ($n=8$) for the triplet. Wagner, Meador and Scaiano have shown that triplet keto[2.2]paracyclophane (2KPC) is very unreactive towards triplet energy transfer, $\frac{1}{4}$ as reactive as acetophenone in methanol solutions.²¹ From these two studies it is obvious that the reactivity of the triplet phenyl ketones is adversely affected when the benzoyl group is constrained and is no longer conjugated. While Turro suggested inversion of the n,π^* to the π,π^* state with decreased in ring size for CP_nCP, Wagner²⁴ has suggested that there is some undefined lowest triplet state for these "unconjugated" phenyl ketones. These findings may relate to the twisted nature of 2,4,6-trialkylbenzophenones where one of the phenyl rings is twisted nearly perpendicular to the carbonyl plane. The effect of 4'-substituted 2,4,6-triisopropylbenzophenones on benzocyclobutenol formation was studied by Matsuura and coworkers who found odd inductive effects that were introduced

by these substituents. It is not clear what Matsuura's results mean but they will be discussed in detail in the *Discussion*.

B. Geometrical Requirements

Scheffer has studied the orientational requirements for intramolecular hydrogen abstraction of crystalline ketones based on ground state parameters. He determined the most important parameters to be d , θ , Δ and ω . The O-H

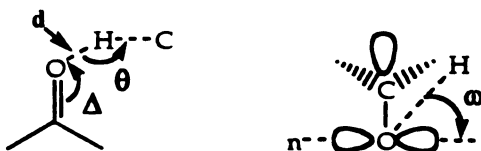


Table 1. Orientational Parameters for Hydrogen abstraction.

parameter	description	theoretical ^c	observed (24 ketones) ^d
d	O-H distance	$\leq 2.7 \text{ \AA}$	2.3-3.1 $\text{\AA}$
θ	O-H-C angle	180°	$85-120^\circ$
Δ	C=O-H angle	$90-120^\circ$	$74-103^\circ$
ω^a	dihedral of C-C=O-H ^b	0°	$0-62^\circ$

^a τ was used by Scheffer but has Wagner suggested ω to lessen the confusion with lifetimes. ^b The dihedral angle that the OH vector makes with respect to the nodal plane of the carbonyl pi system. ^c Taken from several models. ^d A study of 24 ketones in the solid state, 17 γ -hydrogen abstractions with an average of 43° .

distance, d (2.7 $\text{\AA}$), was arrived at by summing the Vander-Waals radii of the O and H; as long as a hydrogen atom is in this vicinity, minimal molecular motion is required for the transfer to occur. A number of models have been suggested and summarized by Wagner.²⁴

C. Photoenolization - formation of *o*-xylylenols*

*The name *o*-xylylenols has been suggested by the Wagner group. Originally these *o*-xylylene derivatives were called "photoenols" but this term is no longer unique because of the several other forms of photoenolization. Another name that commonly appears in the literature for "photoenols" is hydroxy-*ortho*-quinodimethanes.

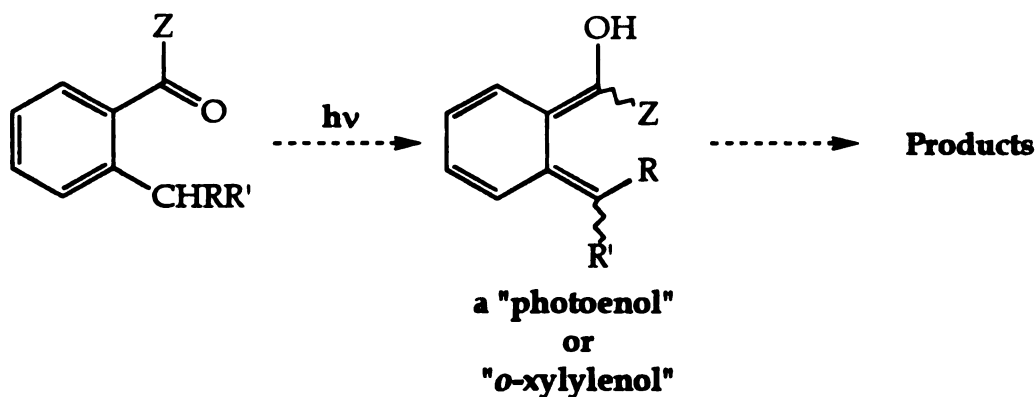
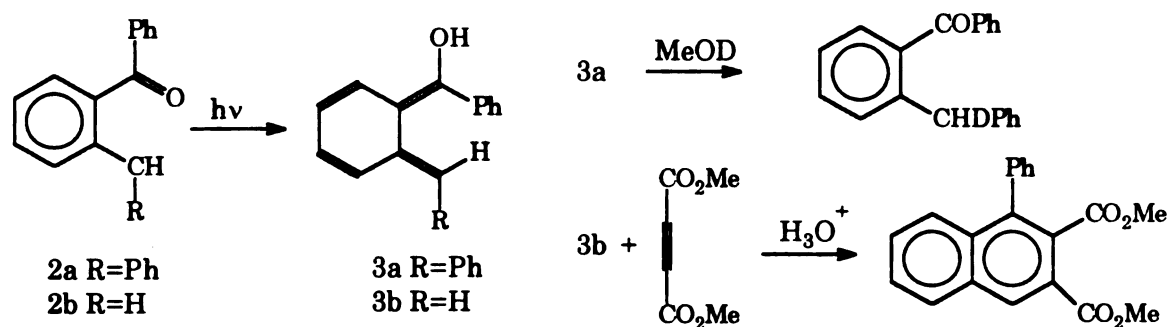


Figure 1. Photoenolization of 2-alkyl phenyl ketones.

The extensive study of the photoreduction of benzophenone to benzopinacol resulted in the discovery of photoenolization of ortho substituted alkyl phenyl ketones. Introduction of an ortho alkyl substituent bearing γ -hydrogen atoms resulted in a large suppression of pinacol formation. 2-Methylbenzophenone has a quantum yield for reduction of only 0.055 in 2-propanol.²⁵ In contrast, 4-methylbenzophenone has a high quantum yield, *ca.* 0.5.²⁵ These experiments suggested that the reduction was not being suppressed by steric or electronic effects; the investigators proposed a photoenol intermediate.²⁶

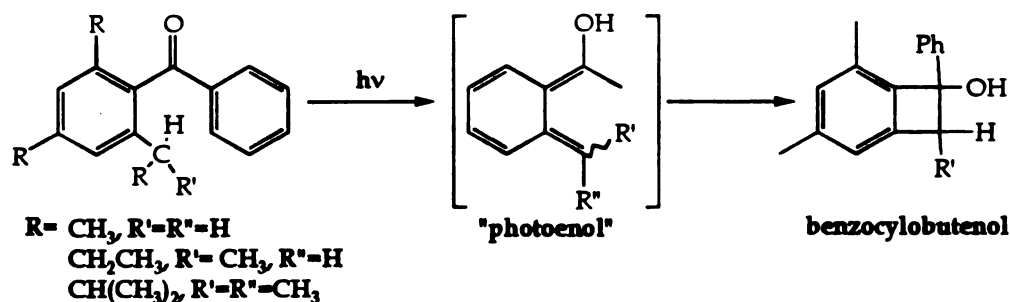
In 1961, Yang and Rivas illustrated that *o*-xylylenol intermediates obtained by the irradiation of 2-methyl and 2-benzylbenzophenones were sufficiently long-lived to allow chemical trapping, by cycloaddition with a dienophile, quenching with oxygen, or by incorporation of deuterium into the ortho alkyl substituent (Scheme 1).²⁶ Because of the importance of such trapping reactions in synthetic work, a better understanding of the mechanism for photoenolization was sought.



Scheme 4. Yang's Photoenolization of 2-Benzyl and 2-Methylbenzophenone.

There are numerous references pertaining to this type of photoenolization that focus on different aspects of the process but it is not possible to mention them all here. After Yang's initial report, two areas in this photoenolization evolved; Diels-Alder trapping of photogenerated xylylenols and flash photolysis studies of transient intermediates often appeared concurrently in the literature. Many investigators confirmed the initial trapping studies by Yang and Rivas, and the mechanism for the formation of *o*-xylylenols captured the attention of numerous research groups.^{25,27} While the chemical trapping was indirect evidence of the *o*-xylylenol, transient absorption spectroscopy provided direct evidence of the enol intermediates. It wasn't until nearly a decade later that

Matsuura reported the subsequent electrocyclic closure of photochemically generated dienols to benzocyclobutenols in 2,4,6-trialkylphenyl ketones (see Scheme 5).²⁷ The cyclization reaction of the *o*-xylylenol to benzocyclobutenol presented another decay pathway but was thought to be limited to congested *o*-xylylenols. More recent activity has focused on the benzocyclobutenol formation from "simple *o*-xylylenols" (derived from ortho alkyl aceto and benzophenones).



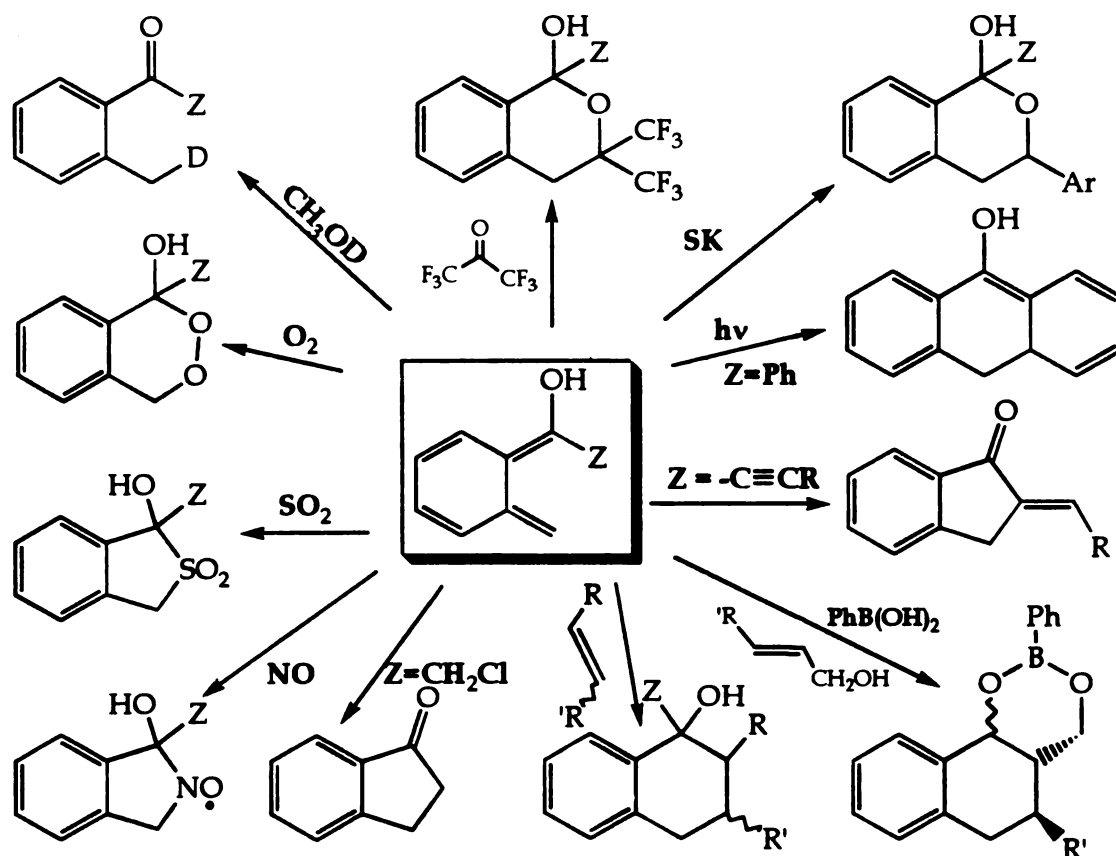
Scheme 5. Benzocyclobutenol formation from 2,4,6-trialkylbenzophenones.

I will first present a brief background of the "fate of photoenols" (trapping and benzocyclobutenol formation) followed by kinetic studies. The understanding of the chemistry of xylylenols is crucial in interpreting the kinetic (spectroscopic) data because of their numerous decay paths. Finally a mechanism will be discussed that incorporates the kinetic data and the competing decay pathways. I will also present recent synthetic applications of *o*-xylylenols as "useful synthetic" intermediates in natural product synthesis.

1. Trapping of xylylenols

Researchers throughout the years have employed numerous trapping reagents for *o*-xylylenols, including acid, base, O_2 , SO_2 , NO , $\text{RB}(\text{OH})_2$, a ground

state aldehyde molecule, perfluoroacetone, and dienophiles that give Diels-Alder products (see Scheme 6). Both intermolecular and intramolecular trapping have been reported. Examples of intramolecular Diels-Alder reactions are given

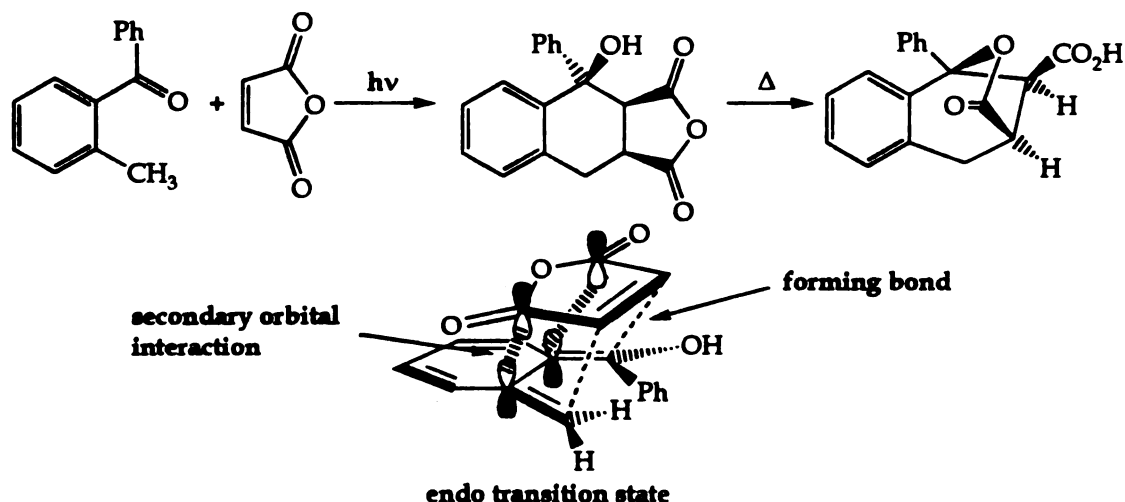


Scheme 6. Trapping of *o*-xylylenonols.

in the *Synthetic Applications* section. If the *o*-xylylenol is formed from a benzophenone, the "Photo-Elbs" reaction can occur and be followed by oxidation to an anthrone or anthracene derivative.

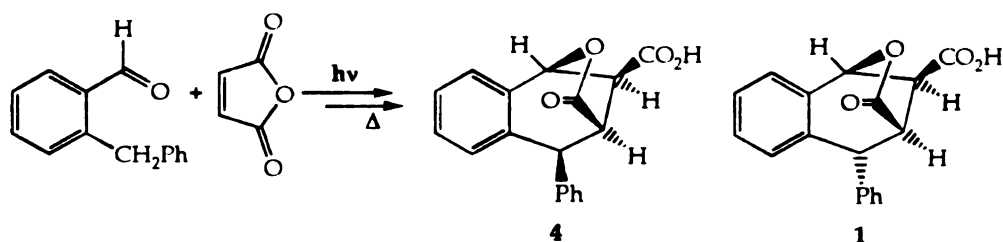
Diels-Alder Trapping. It took nearly seven years after Yang's initial report of photoenols reacting with dienophiles for another example to surface. In 1968, Heindel and Pfau published a paper that examined *o*-xylylenols from substituted *o*-methylbenzophenones being trapped in the presence of dimethyl

acetylenedicarboxylate.²⁸ In the same year, Nerdel and Brodowski reported that the *o*-xylylenol from 2-methylbenzophenone was trapped with maleic anhydride and gave a product which thermally rearranged to a lactone carboxylic acid (see Scheme 7).²⁹ Nerdel and Brodowski also were the first to recognize that the reaction was stereoselective, giving only one Diels-Alder adduct. Presumably the selectivity arises from secondary orbital interactions of maleic anhydride



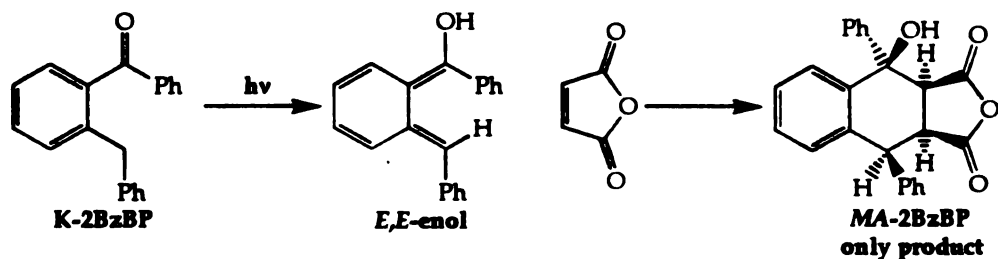
Scheme 7. Trapping of 2-methylbenzophenone with maleic anhydride.

with the E-enol in an endo transition state (see Scheme 7), which are well documented for Diels-Alder reactions. The stereochemistry of the trapped product required the hydroxy and carboxylic acid groups to be *cis*, since warming the sample isomerized the product to a carboxylic acid lactone. In 1971 Sammes and Mellows recognized that Diels-Alder trapping of photogenerated *o*-xylylenols from *o*-alkylbenzaldehydes (and *o*-alkylbenzo-phenones) was also stereoselective.³⁰ In 1974 both Iwata³¹ and Sammes³² published separate accounts



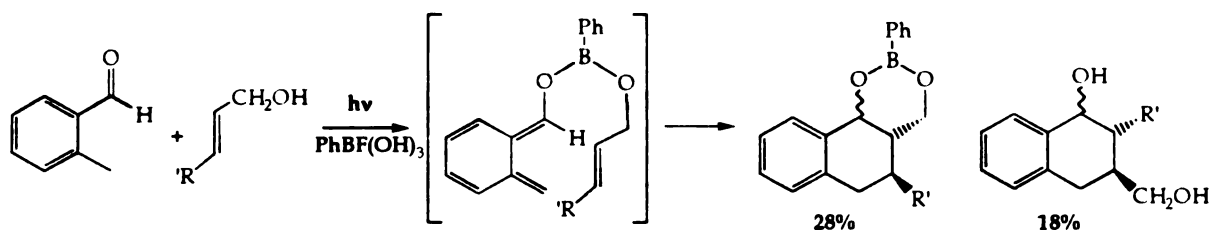
Scheme 8. Sammes trapping of 2-benzylbenzaldehyde with maleic anhydride.

studying the effect of a substituent at the ortho benzylic position. Iwata and coworkers trapped two *o*-xylylenols from 2-benzylbenzaldehyde with dimethyl acetylenedicarboxylate, maleic anhydride and oxygen.³¹ Sammes also obtained two products (in a 4:1 ratio) from irradiation of 2-benzylbenzaldehyde in the presence of maleic anhydride and concluded two *o*-xylylenol intermediates (see Scheme 8).³² Pfau and Heindel were the first to report that the *o*-xylylenol from 2-benzylbenzo-phenone (one of Yang's first ketones) could be trapped by maleic anhydride and other dienophiles.³³ They reported that only one of the possible four diastereomers was formed and was the endo product from the *E,E*-xylylenol (see Scheme 9).



Scheme 9. Pfau and Heindel's first report of Diels-Alder trapping of 2-benzylbenzophenone.

Boron assisted Diels-Alder reaction. Narasaka and coworkers have reported the trapping of the photogenerated *o*-xylylenol intermediates with

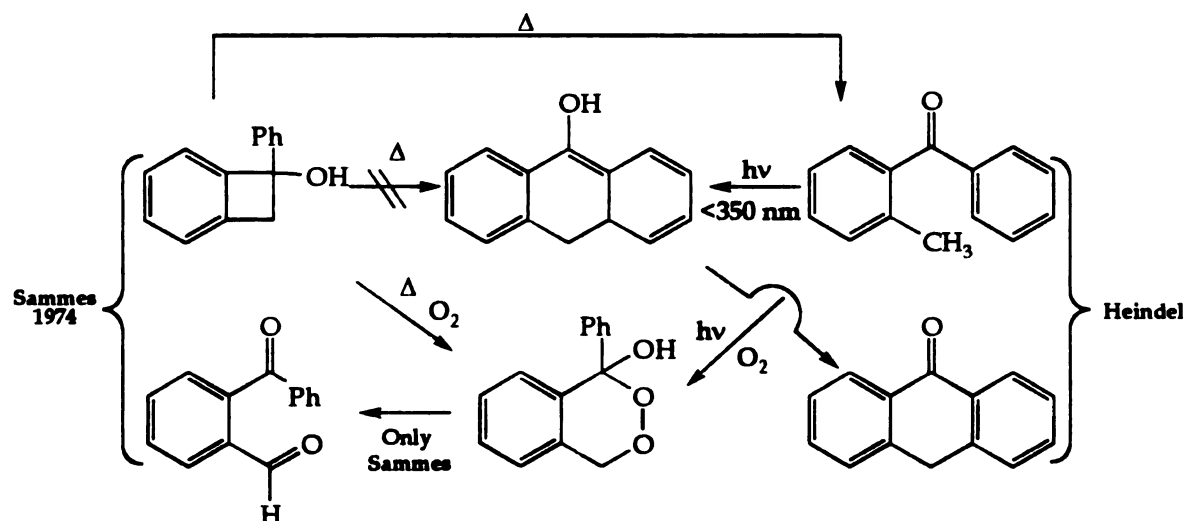


Scheme 10. Narasaka's trapping of *o*-xylylenols with boron compounds.

boron compounds in the presence of dienophiles as useful synthetic intermediates (see Scheme 10).³⁴

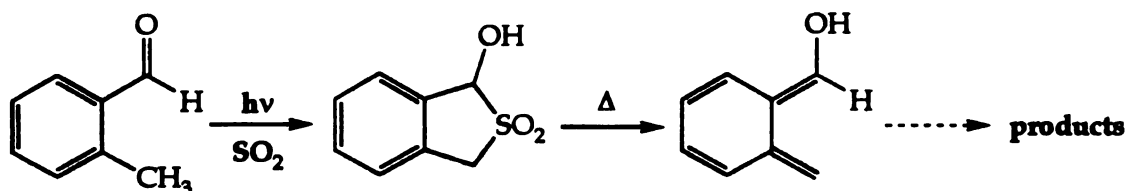
Trapping with oxygen. The first report of trapping with oxygen to give a cyclic peroxide was by Porter and Tchir during flash photolysis of substituted benzophenones, especially 2,4-dimethylbenzophenone.³⁵ Sammes thermally opened 1-phenyl-benzocyclobutenol (prepared by addition of phenyl magnesium bromide to benzocyclobutenone) in oxygenated toluene in the absence of light. While the product solution gave a positive peroxide test, attempted isolation of the peroxide was unsuccessful giving only 2-benzoylbenzaldehyde (see Scheme 11).³² The first report of the photochemical conversion of the *o*-xylylenol from 2-methylbenzophenone into a dihydroanthrone was in 1970 in two different accounts by Porter³⁶ and Heindel³⁷. Heindel and coworkers reported the dihydroanthrone is oxidized in the presence of oxygen to the anthrone; continued irradiation in the presence of oxygen converts the anthrone to the anthroquinone. Interestingly, Sammes found that heating of 1-phenyl-benzocyclobutenol in deaerated toluene smoothly converted it to 2-methylbenzophenone with no sign of the anthracene derivative.³² This demonstrated that a thermal cyclization of the Elbs-type

reaction was not operating and complemented the results from Heindel³⁷ who suggested a second photon was required for cyclization to occur.



Scheme 11. Thermal and photochemical trapping of an enol from 2-methylbenzophenone.

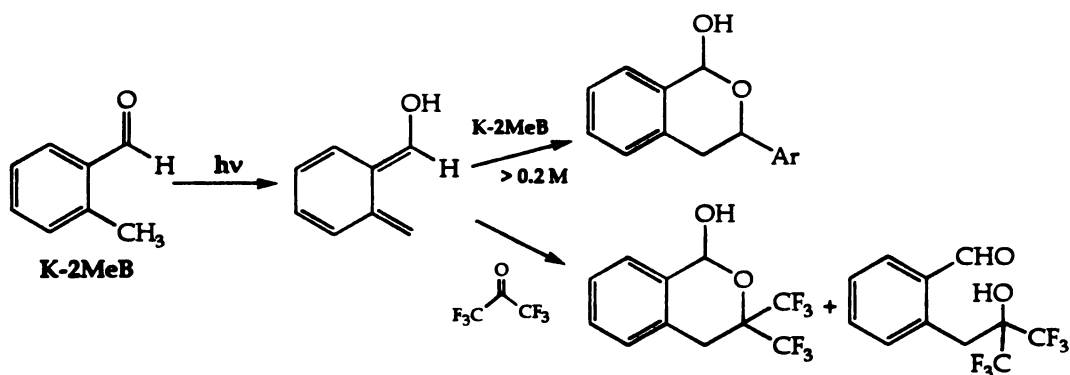
Trapping with SO_2 . Charlton and Durst³⁸ were the first to report that photogenerated enols are readily trapped by SO_2 . The stable sulfones can be subjected to chemical transformations. The enol (or a chemically modified one) can be regenerated by heating the sulfone with subsequent loss of SO_2 .



Scheme 12. Trapping of *o*-xylylenols with SO_2 .

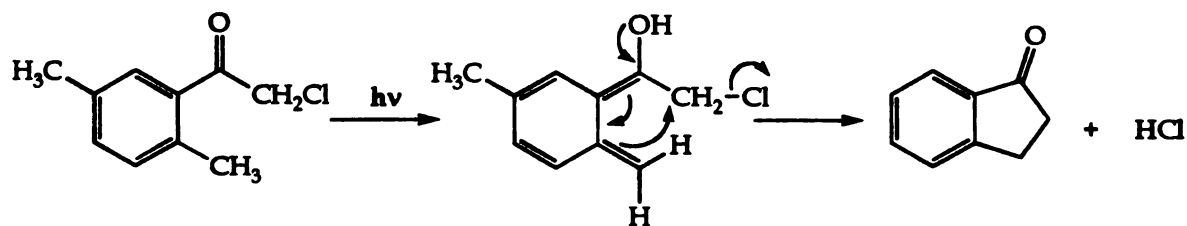
Dimerization. Findlay and Tchir were the first to report the apparent dimerization of 2-methylbenzaldehyde to give a hemiacetal.³⁹ Irradiation of 2-methylbenzaldehyde (K-2MeP) led to Diels-Alder cycloaddition of a ground

state aldehyde molecule with a *o*-xylylenol intermediate, but only at concentrations >0.2 M. Griesbeck and Stadtmüller also found this dimerization and reported that the *o*-xylylenol intermediate reacted with hexafluoroacetone to give a bicyclic hemiacetal and a hydroxy aldehyde (see Scheme 13).⁴⁰ These reports are in contrast to the previous report on 2-methylbenzaldehyde by Sammes.⁴¹ Wilson and Hannemann also reported several dimers from 2-methylbenzophenone.⁵²



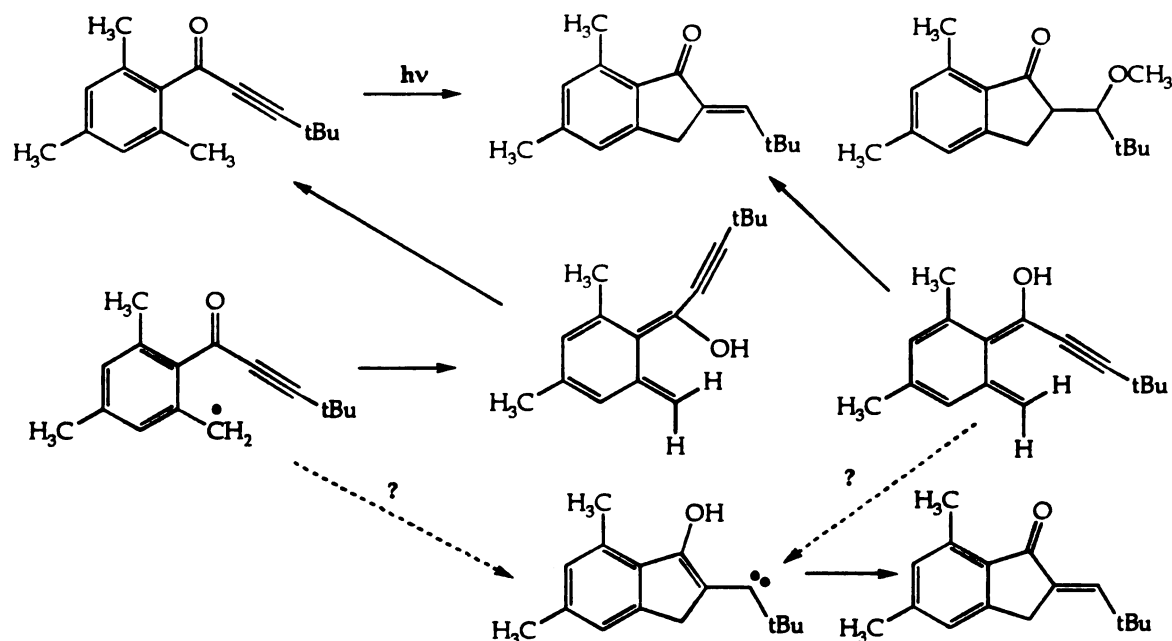
Scheme 13. Dimerization of 2-methylbenzaldehyde.

Intramolecular trapping- formation of indanones. Bergmark has examined how an α -chloro group changes the course of photoenolization.⁴² In non polar solvents 2-indanone is the major product from photolysis of 2-methyl- α -chloroacetophenone (see Scheme 14). Flash photolysis of the same compound was



Scheme 14. Photochemical formation of 2-indanone from α -chloroacetophenones.

conducted by Scaiano. Agosta and coworkers studied intramolecular trapping by a triple bond and proposed biradical addition to yield a carbene that either



Scheme 15. Trapping of a *o*-xylylenol with a triple bond.

rearranges or is trapped by methanol.⁴³ A collaborative effort by of several groups revealed no direct evidence for a carbene and found that *o*-xylylenols are intermediates (see Scheme 15).⁴⁴

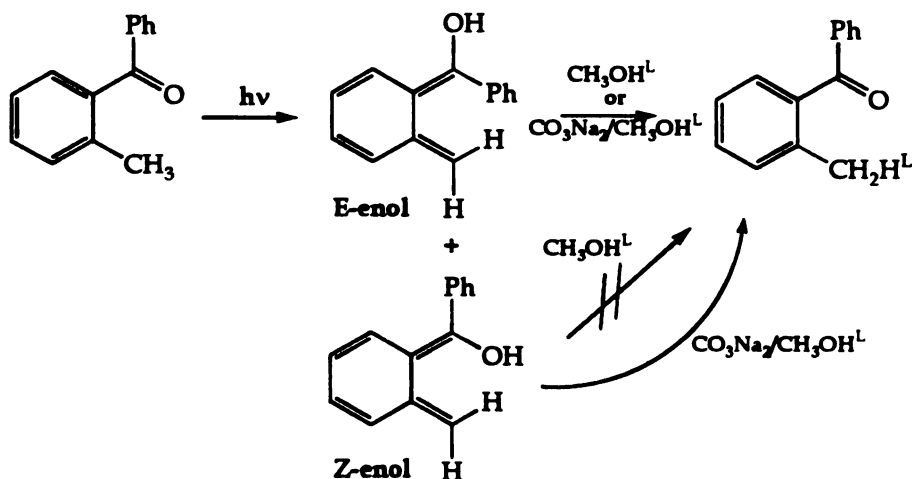
Trapping with acid or base. Wagner and coworkers were the first to report that benzocyclobutenol formation from a variety of aceto and benzophenones could be retarded by added acid.⁴⁵ Sammes had suggested that the reversion of the E-enol from 2-methylbenzophenone (2MeBP) may occur by an intermolecular proton transfer reaction with a second E-enol molecule.²⁵ Scaiano and coworkers have reported a quantitative study of the quenching of

“photoenols” from 2-methylacetophenone (2MeAP), 2MeBP and 2-benzylbenzophenone (2BzBP) by several acids and bases, as summarized

Table 2. Quenching rate constants ($M^{-1}s^{-1}$) for quenching of the E-enols in trifluoroethanol at room temperature.

Acid of Base	2MeAP	2MeBP	2BzBP
NaOH	1.2×10^9	4.0×10^8	4.3×10^8
CH_3ONa	2.6×10^8	2.0×10^8	1.9×10^8
NaN_3	2.3×10^7	1.7×10^7	1.0×10^7
CH_3CO_2Na	5.2×10^6	4.6×10^6	3.1×10^6
Pyridine	7.5×10^5	8.7×10^5	5.9×10^5
$HClO_4$	1.6×10^7	1.0×10^7	2.7×10^5
CF_3CO_2H	1.1×10^6	6.8×10^5	$\sim 2 \times 10^4$
CH_3CO_2H	$\sim 1 \times 10^4$	$\sim 2 \times 10^3$	$< 10^3$

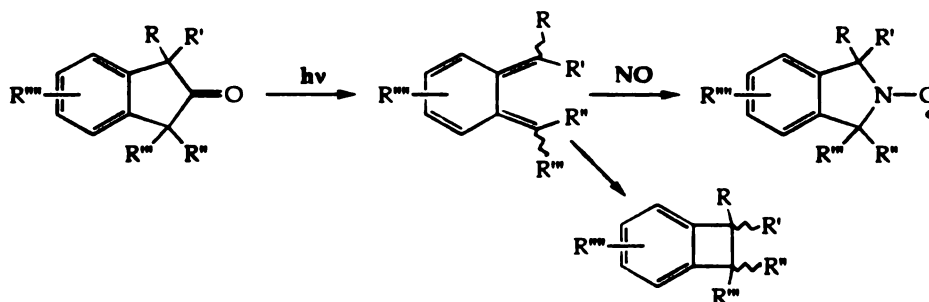
in Table 2.⁴⁶ Gerbicki and coworkers have shown that hydrogen-deuterium and hydrogen-tritium exchange between labeled methanol to be catalyzed by



Scheme 16. Base catalyzed deuterium or tritium exchange in photoenols.

carbonate.⁴⁷ Their findings suggested that both the E and Z-xylylenols participate in the exchange reaction whereas in the absence of catalyst only the E-xylylenol is reactive (see Scheme 16).

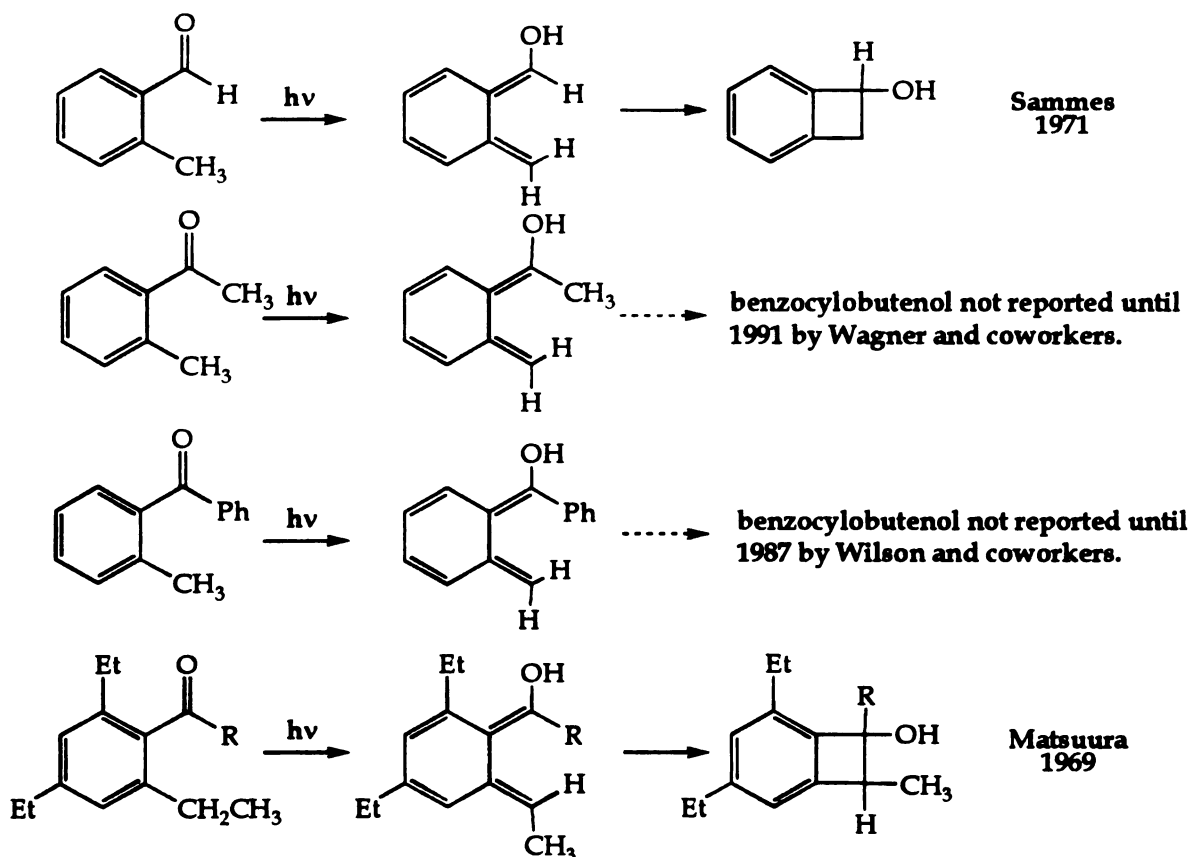
Trapping with nitric oxide. Trapping of photogenerated *o*-xylylenols from ortho alkyl phenyl ketones with nitric oxide has not been reported. However, nitric oxide reacts with tetramethyl-*ortho*-quinodimethane, as previously reported by Korth and Ingold.⁴⁸ Recently Korth has reported the trapping of several substituted *o*-xylylenes generated by photoinduced decarbonylation of substituted 2-indanones with nitric oxide. In addition he showed the *o*-xylylenes close thermally to give substituted benzocyclobutenes (see Scheme 17).⁴⁹



Scheme 17. *o*-Xylylenols generated from photoinduced decarbonylation of 2-indanones.

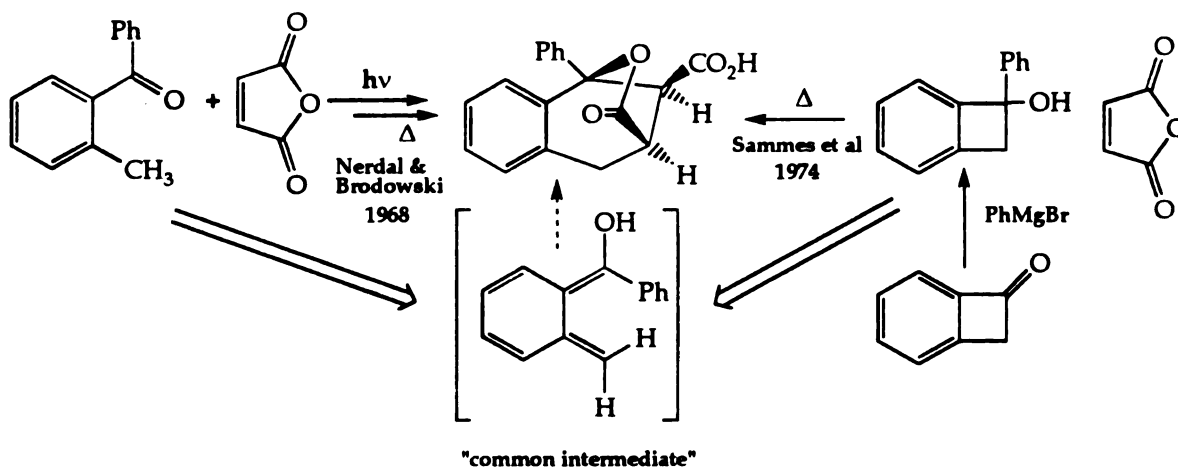
2. Benzocyclobutenols

In 1969 Matsura and Kitaura were the first to report benzocyclobutenols from 2,4,6-trialkyl phenyl ketones.⁵⁰ For over twenty years it was assumed that benzocyclobutenols could be formed only if their corresponding dienols would be too sterically hindered. However, this belief was not consistent with the result from the photolysis of 2-methylbenzaldehyde whose *E*-enol has less steric



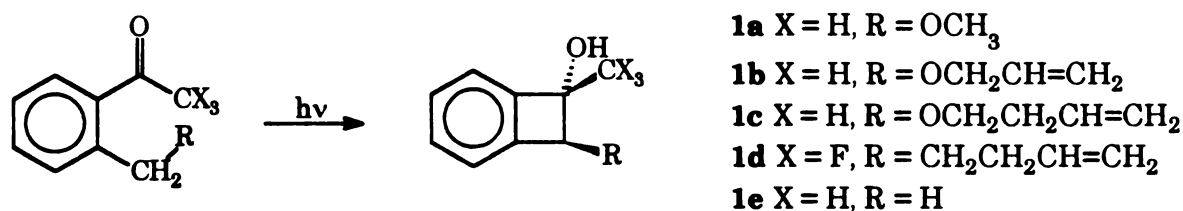
Scheme 18. First reported benzocyclobutenols.

congestion compared to 2-methylacetophenone (whose benzocyclobutenol was not reported until 1991 by Wagner²⁴ and coworkers). In 1974 Sammes and coworkers discovered that irradiation of dilute benzene solutions of 2-methylbenzaldehyde gave a 10% yield of benzocyclobutenol after 35 minutes.⁴¹ Sammes, Arnold and Wallace made the observation that benzocyclobutenol opens on heating to give the same intermediate *o*-xylylenol as obtained by irradiating 2-methylbenzaldehyde; evidence for this common intermediate was that both *thermally or photochemically generated enols gave the same Diels-Alder adduct in the presence of maleic anhydride*.⁵¹ Sammes and coworkers showed that the



Scheme 19. Generation of an E-enol by thermal and photochemical methods.

common *o*-xylylenol intermediate generated thermally or photochemically was not unique to 2-methylbenzaldehyde; 1-Phenylbenzocyclobutenol was synthesized independently, heated in the presence of maleic anhydride giving the identical acid lactone previously reported by Nerdal²⁹ and Brodowski (see Scheme 19).



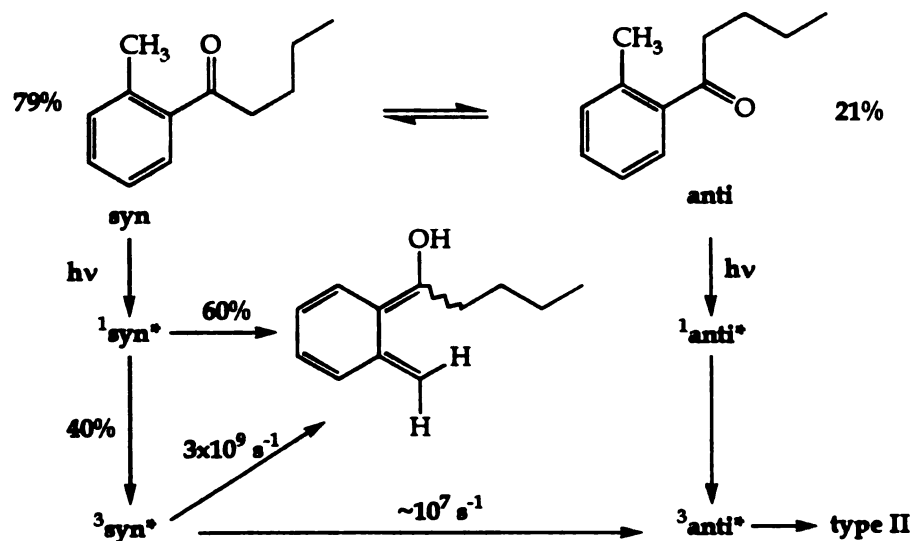
Scheme 20. First report of photochemical formation of benzocyclobutenols from simple aceto-phenones.

It was not until 1987 that Wilson⁵² reported that 1-phenylbenzocyclobutenol was formed in good yield from the irradiation of *o*-methylbenzophenone. This was only the second reported case of a non sterically hindered enol cyclizing. In 1991, Wagner *et al.* reported the diastereoselective

formation of benzocyclobutenols (see Scheme 20) as the major or only product of several *o*-alkyl ketones and proposed a generalized mechanism (see Scheme 25) which I will return to.⁴⁵

3. Kinetics and mechanism.

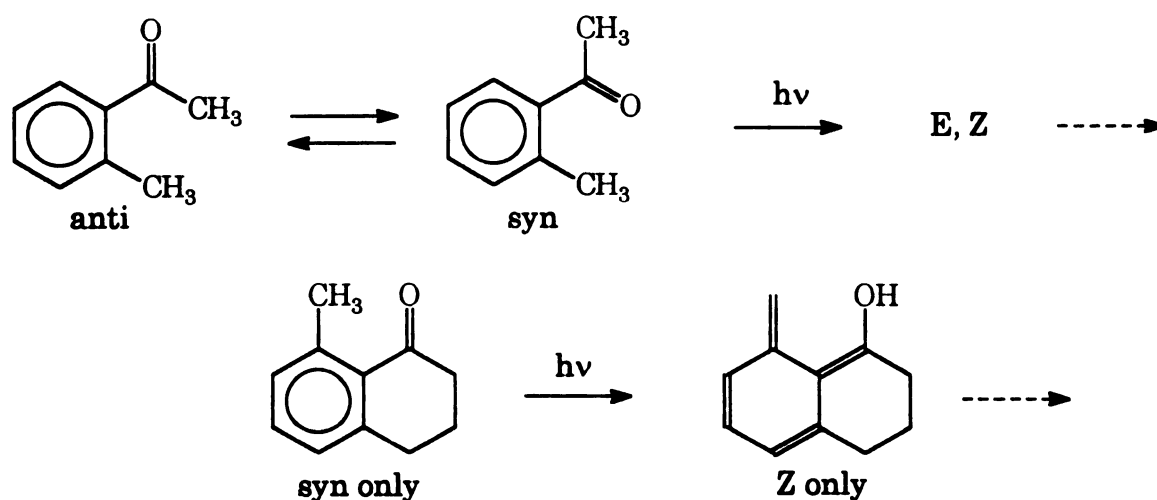
A quantitative quenching and sensitization study of *o*-alkylvalerophenones found that hydrogen abstraction from the ortho carbon competed with γ -hydrogen abstraction.^{53,54} The rate constant for enolization was independent of the ortho-alkyl's CH bond strength (see Scheme 21). The model compounds *o*-methylacetophenone and 8-methyl-1-tetralone in this same study provided pertinent information about the syn rotamer since the tetralone is



Scheme 21. Two kinetically distinct triplets reported by Wagner and Chen.

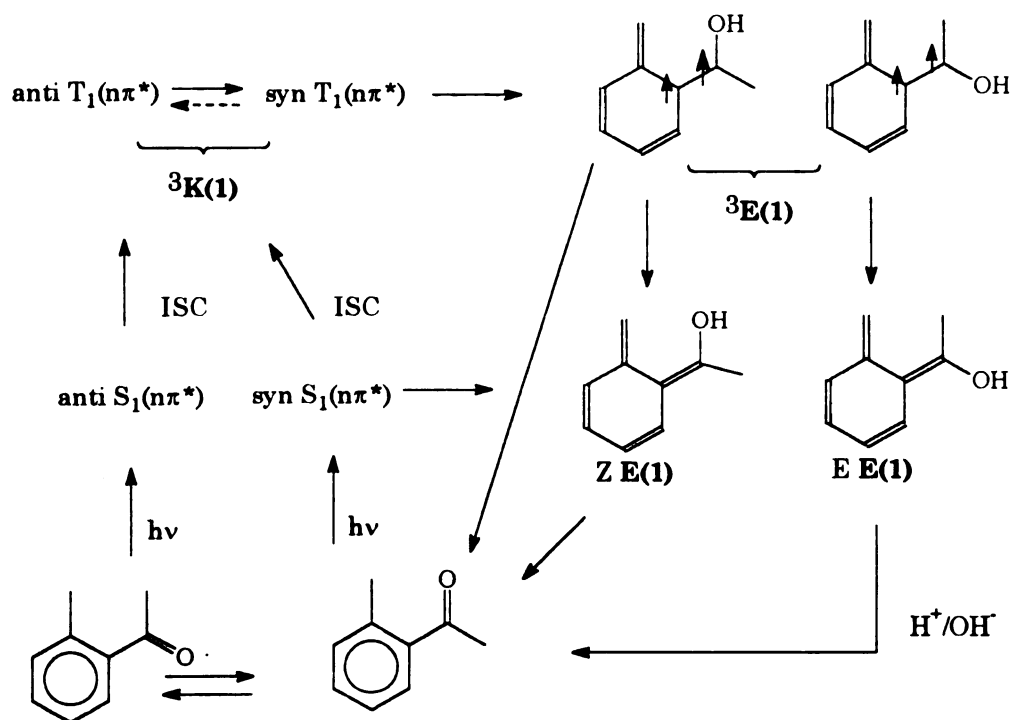
locked in a syn conformation (see Scheme 22). This hydrogen abstraction is a rare case of rotational control of triplet reactivity that arises from two possible ground state rotamers. Controlled rotation about the benzene-carbonyl bond

yields two kinetically distinct anti and syn triplets. The actual geometries of the two rotamers are not known, but the syn is clearly favored for hydrogen abstraction. Several of the *o*-tolylvalerophenones studied had quantum yields for intersystem crossing of only 0.21 which is ~80% less efficient than intersystem crossing of singlet valerophenone. The reaction path was thought to proceed by triplet state γ -Hydrogen abstraction to yield a 1,4-biradical.⁵⁴



Scheme 22. Syn and Anti conformations of 2-methylacetophenone.

Early flash kinetic studies provided bimolecular rate constants for trapping reactions.⁵⁵ A reinvestigation of *o*-methylacetophenone by Haag, Wirz and Wagner in 1977, gave a fairly complete picture for the chemical and physical processes that followed excitation.⁵⁶ As with most other studies, the spectroscopic evidence, except for one new observation, was in agreement with previous data. Although the spectroscopic data was consistent with former researchers, a reassignment of many of the previously assigned transients was

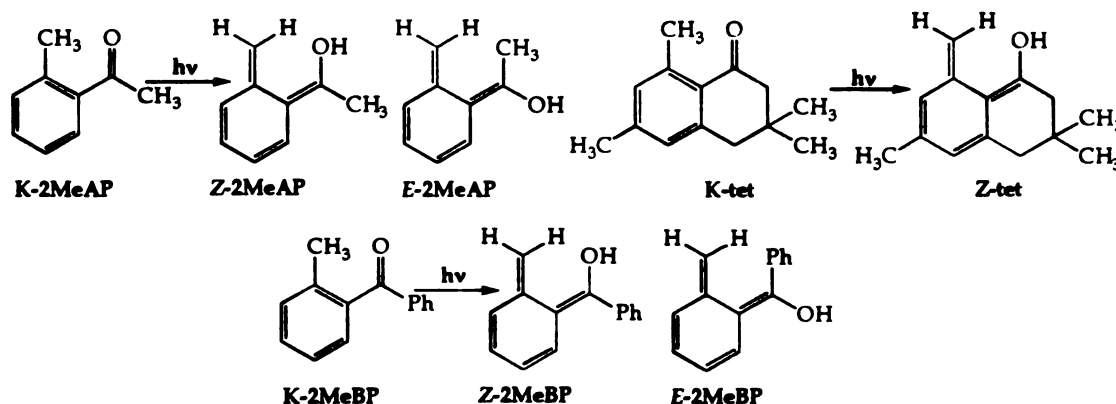


Scheme 23. Kinetic evidence for Syn and Anti conformations of 2-methylacetophenone.

suggested by the authors. The results are summarized in Scheme 23. The elusiveness of the *Z*-dienol in earlier trapping experiments was attributed to a rapid reketonization, *ca.* $10^8 s^{-1}$.⁵⁶ It appeared that the *Z*-dienol would not be of any synthetic utility because of this, but reketonization could be suppressed to $10^4 s^{-1}$ in hydrogen-bond-acceptor solvents such as pyridine, HMPA and DMSO.⁵⁶ The authors also suggested tethering the dienophile to the dienol moiety to force an intramolecular instead of an intermolecular cycloaddition reaction.⁵⁶

The nature of the excited state was determined to be mostly n,π^* triplet character as a result of quenching studies.⁵⁵ It was well established from studies involving benzophenone that excitation of ketones is usually of n,π^* character in

which the first excited singlet state undergoes rapid inter-system-crossing, $\Phi_{isc}=1$ for benzophenone. Early results suggest that hydrogen atom abstraction from the ortho group occurred from the n,π^* triplet. However, in a quenching study of 2-methylacetophenone by *cis*-piperlyene the ketone triplet was effectively quenched but the formation of the corresponding enol was not completely suppressed.⁵⁷ The *o*-xylylenols *E*-2MeBP and *Z*-2MeBP are formed entirely via a triplet pathway since their formation can be completely suppressed at high piperlyene concentrations (see Scheme 24). However, when the triplet of the enols *E*-2MeAP, *Z*-2MeAP and *Z*-tet are quenched by high concentrations (>5M) of piperlyene, only *E*-2MeAP formation is completely quenched but the *Z*



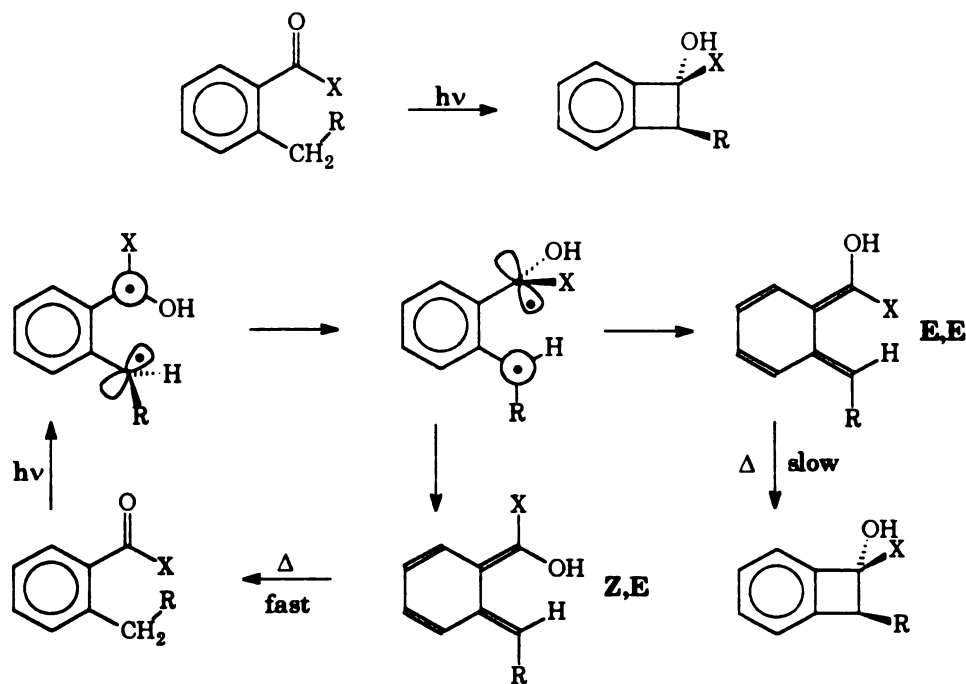
Scheme 24. Inefficient ISC for acetophenones.

enols are not. The authors concluded that 30% of the *Z*-xylylenols must be formed directly from the singlet state. Grellmann and coworkers have studied the kinetics of the photoenolization of 5,8-dimethyl-1-tetralone (DMT) at various temperatures.⁵⁸ It was shown that the hydrogen transfer reaction in the excited triplet states of DMT is largely governed by tunneling effects since nonlinear

Arrhenius plots and large isotope effects were observed. The research group of Garicia-Garibay has also reported deuterium tunneling in triplet 5,8-dimethyl-1-tetraolone by an independent method.⁵⁹ An Arrhenius plot for the triplet decay was constructed by phosphorescence spectroscopy at temperatures between 80 and 15 °K, while evidence for the enol formation was obtained by fluorescence and FTIR spectroscopy. The results obtained by Garicia-Garibay's group are in excellent agreement with Grellmann's laser flash photolysis results. Further information about the photochemical processes was obtained by independent methods. Scaiano detected biradical intermediates by trapping with paraquat dications.^{60,61} The electron transfer experiments using paraquat dications in conjunction with quenching studies led Scaiano to the number and lifetime of the triplet state precursors of photoenols for a variety of ortho substituted aceto- and benzophenones.⁶¹ Scaiano's studies complemented Wagner's^{54,56} previous finding of two kinetically distinct triplets but found evidence for only one biradical intermediate which was the common precursor to the two different enols. Scaiano has also demonstrated that the 1,4-biradical intermediate from *o*-methylacetophenone is quenched efficiently with oxygen and is responsible for formation of singlet oxygen.⁶² Das and coworkers showed that the intermediate biradicals from *o*-methylacetophenone, *o*-methylbenzaldehyde and 2,4,6-trimethylbenzaldehyde are all quenched by triplet energy transfer to β -carotene.⁶³ These researchers were able to measure the growth of β -carotene triplet by its intense transient absorption at 500-550 nm. The three independent

methods (paraquat, oxygen, and β -carotene) by Scaiano and Das show unequivocally that the biradical is a triplet.

The last piece of the mechanistic puzzle involved the formation of 1-methylbenzocyclobutenol from *o*-methylacetophenone reported by Wagner and coworkers.²⁴ This provided an alternative decay pathway for the E-enol which previously was assumed to revert to starting ketone by an intermolecular process.²⁵ The mechanism proposed by Wagner is outlined in Scheme 25. The triplet of the enol is assumed to resemble that of a twisted biradical,⁶¹ and decay to the ground state enol proceeds through this intermediate. The biradicals are

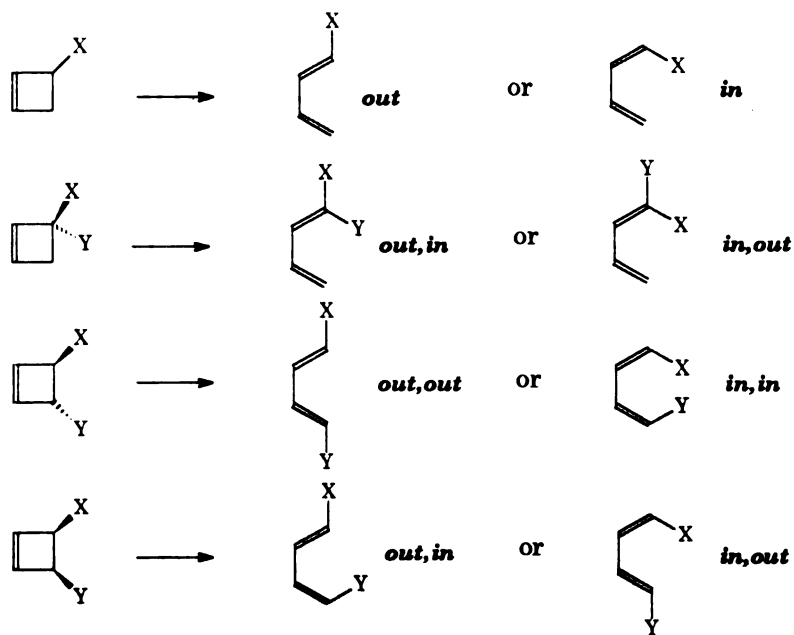


Scheme 25. Proposed mechanism for benzocyclobutenol formation proposed by Wagner and coworkers.

required to live long enough to undergo facile coupled rotation around both benzylic carbon atoms. This must be the case since two possible enols are

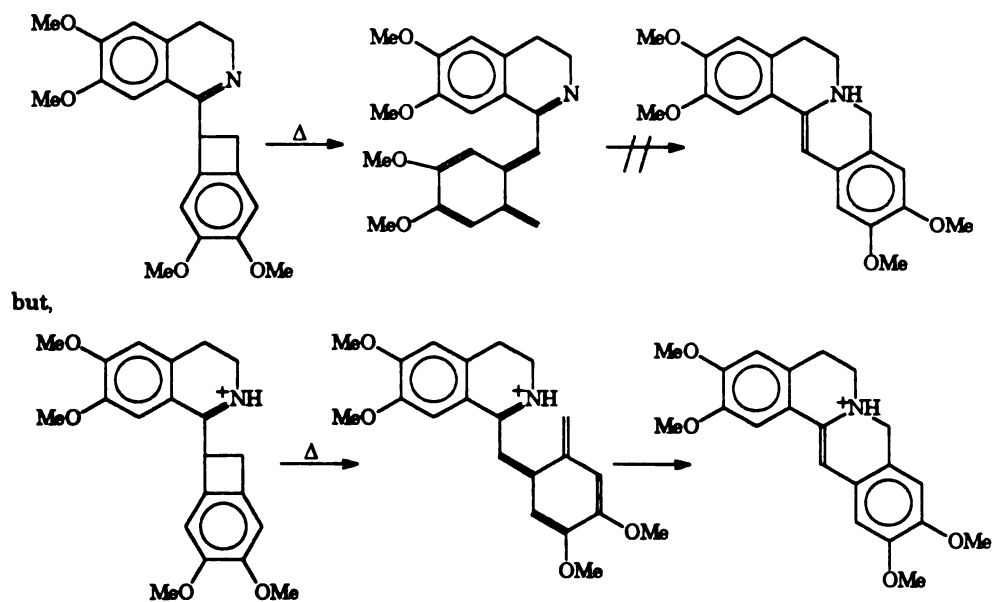
formed, E and Z.⁵⁶ The Z-enol undergoes a facile 1,5-sigmatropic hydrogen shift to regenerate starting ketone. Only the E-enol lives long enough to be trapped. The authors also reported that only the E-1-phenyl-2-benzocyclobutenol was formed from irradiation of 2-ethylbenzophenone and suggested a conrotatory cyclization of the E,E-enol to explain the diastereoselectivity.²⁴ For the E,E-enol to form, a 180° twist is required around the benzene-carbonyl bond, so both benzylic sites must be able to freely rotate.⁶¹ Direct cyclization of the 1,4-biradical appears not to be the case for two reasons: a) The stereochemical outcome of benzocyclobutenol formation gives the opposite stereoselectivity from most other biradical cyclizations. b) Stereoselective formation of the less stable product suggested a concerted pathway. Also, irradiation of *o*-ethylbenzophenone in the presence of *p*-toluenesulfonic acid inhibits benzocyclobutenol formation.⁴⁵ Valerophenone in benzene containing acid reacts completely after irradiation for 15 minutes, thus acid *does not* destroy the ketones' photoreactivity.⁴⁵ This information suggests that the biradicals are not responsible for benzocyclobutenol formation since biradical reactivity should not be destroyed by acid. .

An area that has recently been addressed by Houk⁶⁴ and is directly related to the thermal opening of benzocyclobutenols is torquoselectivity (Scheme 26). Torquoselectivity is the selectivity for outward or inward twisting during the breaking of the C-C bond. It is due to an electronic effect arising from the interaction of nonbonding molecular orbitals of the substituent and the



Scheme 26. Outward and/or inward conrotatory processes for mono- and disubstituted cyclobutenes.

breaking bond in the transition state. In general, electron donating groups (hydroxy, methoxy, etc.) tend to rotate outward while electron withdrawing



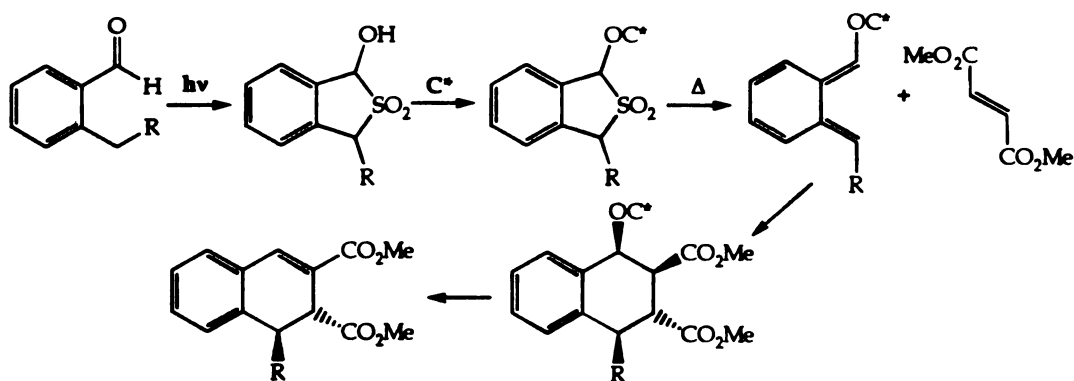
Scheme 27. An example of Alkoloid synthesis.

groups (formyl, trifluoro, etc.) rotate inward. The selectivity seems to be independent of sterics and its origin appears to be electronic in nature. One interesting example of this selectivity appears in the synthesis of alkaloids (see Scheme 27).⁶⁵ The major difference in the reactivity of the cyclic imine and the iminium ion is attributed to the conjugated imine being a weak acceptor like a cyano or ester functionality, thus preferring to rotate outward to form the E-xylylene. The iminium species is a strong π -acceptor and turns inwards like the formyl group, thus creating the Z-xylylene which further cyclizes to form the desired product.⁶⁴

4. Synthetic Applications

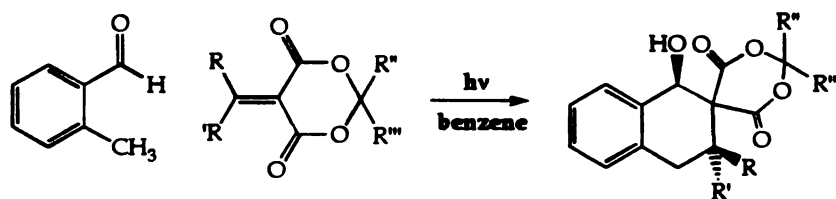
In the last 10 years there has been a significant amount of activity in the utilization of photogenerated xylylenols towards synthetic targets. Several reviews have appeared which focus on the application of *o*-quinodimethanes.^{25,66-}

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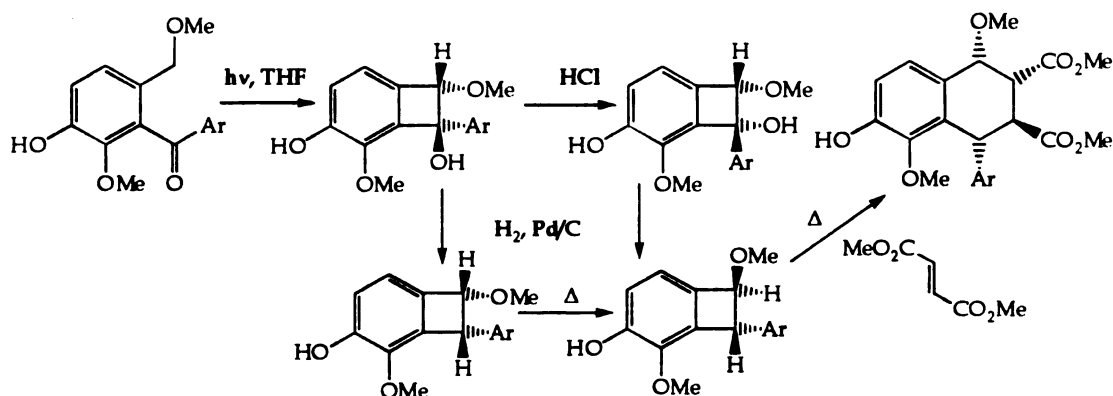
Scheme 28. Asymmetric induction using photogenerated hydroxybenzenesulfoxes

Several groups have trapped photogenerated xylylenols with sulfur dioxide followed by thermal opening in the presence of dienophiles to give Diels-Alder adducts including Charlton⁷², Durst⁷³⁻⁷⁵ and Scheffer⁷⁶. Both Charlton and Durst have induced enantioselectivity with chiral auxiliaries. Charlton prepared 1-alkoxy-1,3-dihydrobeno[c]thiophene-2,2-dioxides and 1-alkoxy-3-phenyl-1,3-dihydrobeno[c]thiophene-2,2-dioxides from hydroxybenzenesulfones (see Scheme 28).^{77,78} Other groups have trapped the photo-generated *o*-xylylenols directly with dienophiles to give both regio- and diastereoselective Diels-Alder adducts as the primary product. Spiro- and polyspirocyclic compounds containing the 1,2,3,4-tetrahydro-1-naphthol structure were obtained by the Diels-Alder reaction of the photoenol of 2-methylbenzaldehyde with 5-alkylidene-1,3-dioxane-4-dione derivatives by Sugiyama (see Scheme 29).^{79,80}



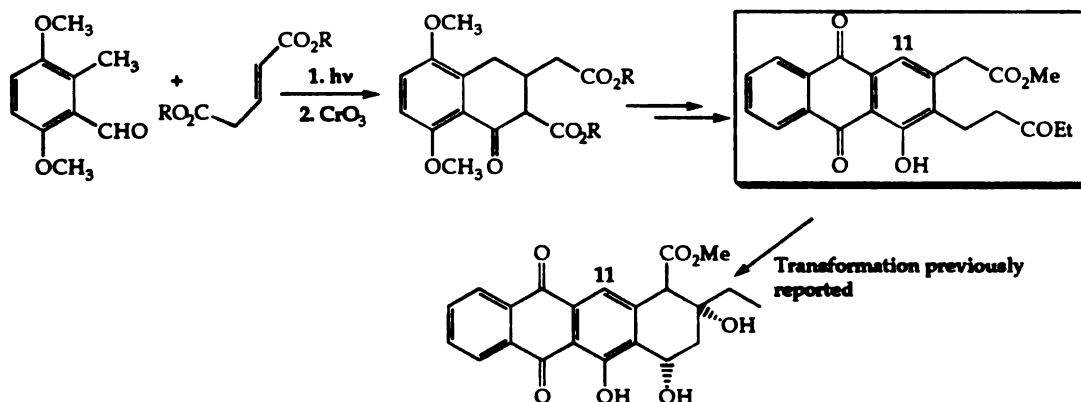
Scheme 29. Photochemistry of 2-methylbenzaldehyde with 5-alkylidene-1,3-dioxane-4-dione

Stereoselective photocyclization of highly congested benzophenones and benzaldehydes gave benzocyclobutenol methyl ether intermediates which were used enroute to the synthesis of naturally occurring lignan podophyllotoxin and related drugs (see Scheme 30).^{81,82}



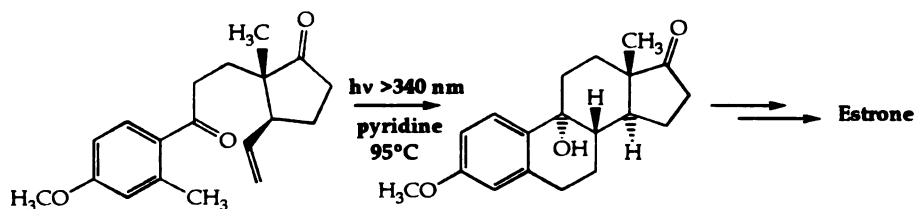
Scheme 30. Synthesis of Naturally occurring Lignan Podophyllotoxin .

Kraus and Chen have reported a short synthesis of 4-deoxyaklavinone via photoenolization of an ortho substituted benzaldehyde.⁸³ The 11-deoxyanthracycline skeleton of 4-deoxyaklavinone was constructed starting from 3,6-dimethoxy-2-methyl-benzaldehyde and diallyl 2-pentenedioate by a regioselective intermolecular Diels-Alder reaction following photoenolization (see Scheme 31). The 11-deoxyanthracycline are of particular medicinal interest because they exhibit dramatically lower cardiac toxicities than their 11-hydroxy counterparts.



Scheme 31. Kraus synthesis of 4-deoxyaklavinone via photoenolization.

Quinkert and Stark employed a photogenerated benzocyclobutenol and took advantage of its reactivity in the complete synthesis of Estrone (see Scheme 32).⁸⁴

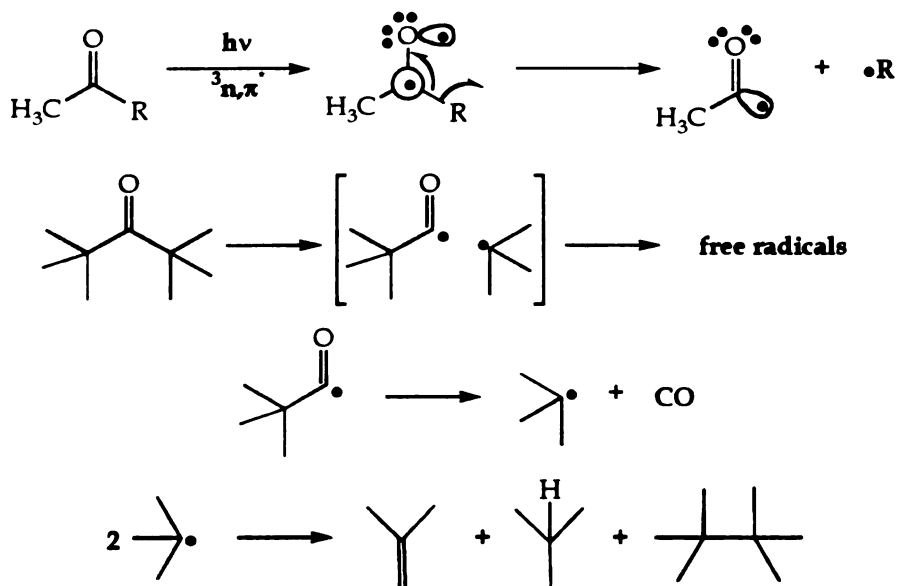


Scheme 32. Quinkert and Stark's photochemical synthesis of Estrone.

II. Photofragmentation

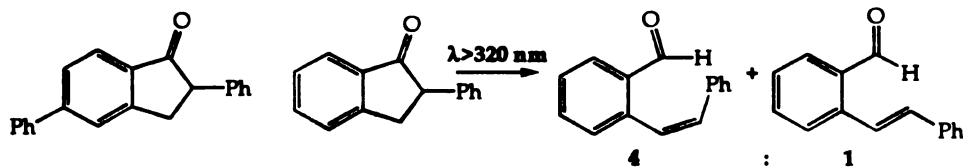
A. α -cleavage

The *Norrish Type I* reaction or α -cleavage depends on the nature of the excited state, the stability of the resulting radical and the amount of steric congestion in the reacting ketone. The homolytic cleavage is usually followed by disproportionation, coupling or trapping by hydrogen donors. The fragmentation results from an overlap of the nonbonding n-orbital of the carbonyl oxygen with the σ bond between the carbonyl carbon and the α -carbon atom in the excited state (see Scheme 33).⁸⁵ If the carbonyl is part of a cyclic system then the rate of cleavage also depends on the ring size due to the difference in strain energy and stereoelectronic factors. Most α -cleavage reactions occur from the n, π^* triplet state since cleavage from the singlet state is approximately 100 times slower.



Scheme 33. α -Cleavage of carbonyl compounds.

Baum has reported that 2-phenyl-1-indanone undergoes α -cleavage followed by an internal disproportionation to give the cis and trans enals in a 1:4 ratio (see Scheme 34).⁸⁶ The study concluded the reaction cleavage process was occurring from the $^3n,\pi^*$ state and not the $^3\pi,\pi^*$ state since the 2-phenyl-1-indanone reacted while 2,6-diphenyl-1-indanone did not undergo the Norrish type 1 reaction. The difference between the two is that 2-phenyl-1-indanone has a lowest $^3n,\pi^*$ state while 2,6-diphenyl-1-indanone has a lowest $^3\pi,\pi^*$ state. The authors reported that the phenyl group at the 2-position was required since

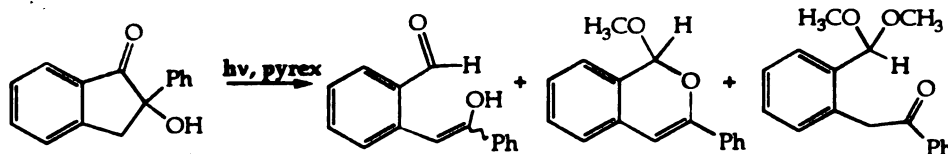


Scheme 34. Photochemistry of 2-Phenyl-1-indanone.

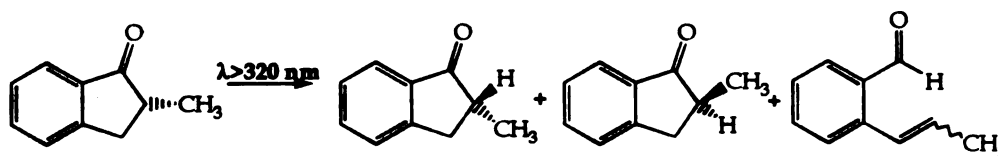
1-indanone and 2-methylindanone did not under α -cleavage in benzene.

Padwa⁸⁷ and Hamer^{88,89} have both reported the α -cleavage of substituted 2-hydroxy-indanones (see Scheme 35). Padwa has found that 2-hydroxy-2-phenyl-1-indanone in methanol solutions disproportionates to give an enolaldehyde which cyclizes to form the hemiacetal.

Henin, Muzart and coworkers have shown that irradiation of optically active (R)-2-methylindan-1-one causes racemization (see Scheme 35), after α -cleavage in acetonitrile solutions, although quantum yields were not reported.⁹⁰ Apparently biradical recombination is operative since racemization occurred.



Scheme 35. Photochemistry of 2-Hydroxy-2-phenyl-1-indanone.



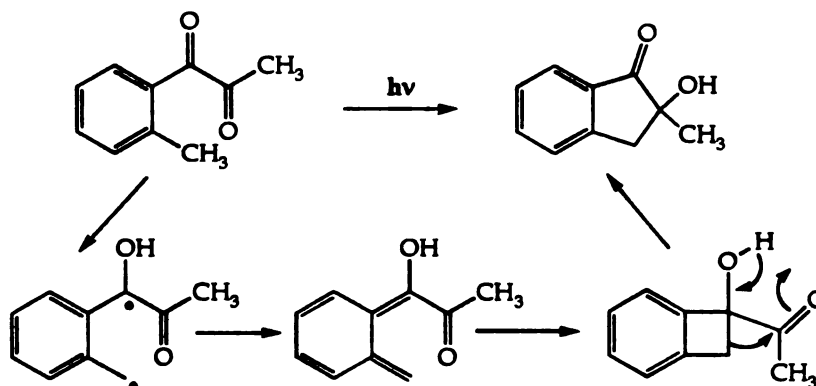
Scheme 36. Photochemistry of (R)-2-Methylindan-1-one.

Lewis has investigated the α -cleavage of deoxybenzoin^{91,92}, benzoin and benzoin ethers and concluded α -cleavage arises from the lowest $^3n,\pi^*$ state⁹³. Deoxybenzoin with α -methyl and α -phenyl substituents undergo only α -cleavage in benzene but photoreduction competes with α -cleavage in 2-propanol-benzene solutions. The effect of the α -substituents upon triplet lifetimes indicated that the rate constants for cleavage do not depend on the

stability of the resulting radicals. For benzoin and benzoin ethers Lewis and coworkers found that α -cleavage was the primary process in benzene solutions and the substituents at the α -position had little effect on the efficiency of cleavage. However, they had a pronounced effect on the rate constant for α -cleavage. Benzoin alkyl ethers were $\sim 10^5$ more reactive toward α -cleavage than deoxybenzoin.

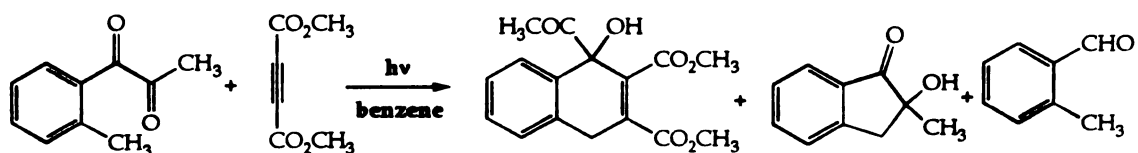
1. Photochemistry of benzils and their photoproducts.

The formation of α -hydroxyindanones from 1,2-diketones has presented a mechanistic dilemma for the last twenty years. Benzil and other aryl diketones (not bearing γ -hydrogens) are known to be inert to conventional photolysis.^{94,95} Scaiano reported that cleavage occurs with biphotonic laser light and argued that a second photon was required since the triplet energy of benzil (60 kcal/mole) is not sufficient to break the carbon-carbon bond.⁹⁶ However, the benzoyl radicals mainly recoupled to give starting ketone.



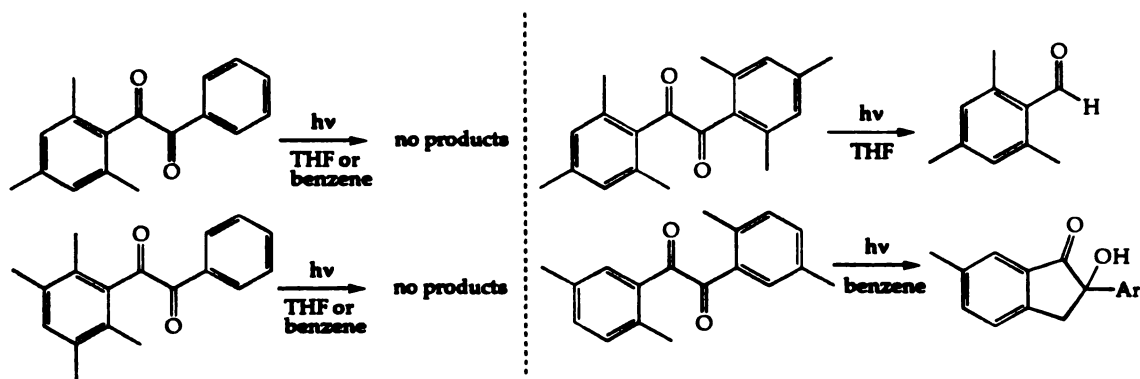
Scheme 37. Photochemistry of 1-(2-tolyl)-1,2-propanedione as reported by Hamer and Bishop.

Hamer and Bishop were the first to report that irradiation of 1-(2-tolyl)-1,2-propanedione formed 2-hydroxy-2-methyl-1-indanone and proposed an α -xylylenol intermediate (see Scheme 37).⁹⁷ Ogata and Takagi contributed two reports of the irradiation of 1-(2-tolyl)-1,2-propanedione.^{98,99} In one account irradiation in the presence of dimethyl acetylenedicarboxylate in benzene gave a trapped Diels-Alder product apparently from a photoenol formed by γ -hydrogen abstraction (see Scheme 38).⁹⁸



Scheme 38. Photochemistry of 1-(2-tolyl)-1,2-propanedione as reported by Ogata and Takagi.

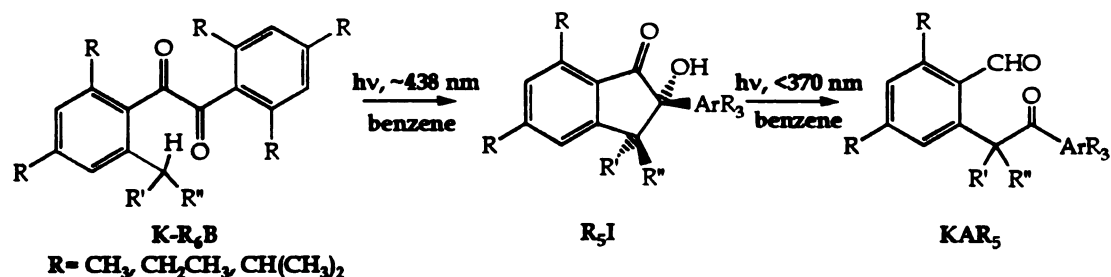
Maruyama and coworkers irradiated several 1,2-diketones including 2,4,6-trimethylbenzil, 2,3,5,6-tetramethylbenzil, 2,4,2',4'-tetramethylbenzil and 2,4,6,2',4',6'-hexamethylbenzil (see Scheme 39).¹⁰⁰ However only 2,4,2',4'-tetramethylbenzil gave an α -hydroxyindanone product while 2,4,6,2',4',6'-



Scheme 39. Results from photochemistry of 1,2-diketones by Maruyama.

hexamethylbenzil formed 2,4,6-trimethylbenzaldehyde from type I cleavage. Maruyama suggested the α -hydroxyindanone was formed from δ -hydrogen abstraction followed by biradical coupling.

Recently we reported that structurally symmetric hexaalkylbenzils undergo δ -hydrogen abstraction and give substituted α -hydroxyindanones in high yield (see Scheme 40).¹⁰¹ A comparison of their solution and solid state reactions indicated that the three compounds hexamethyl-, hexaethyl-, and hexaisopropylbenzil all photocyclize both in solution and as solids to 5,7-dialkyl-2-(2',4',6'-trialkylphenyl)-2-hydroxy-1-indanones. At wavelengths <370 nm these



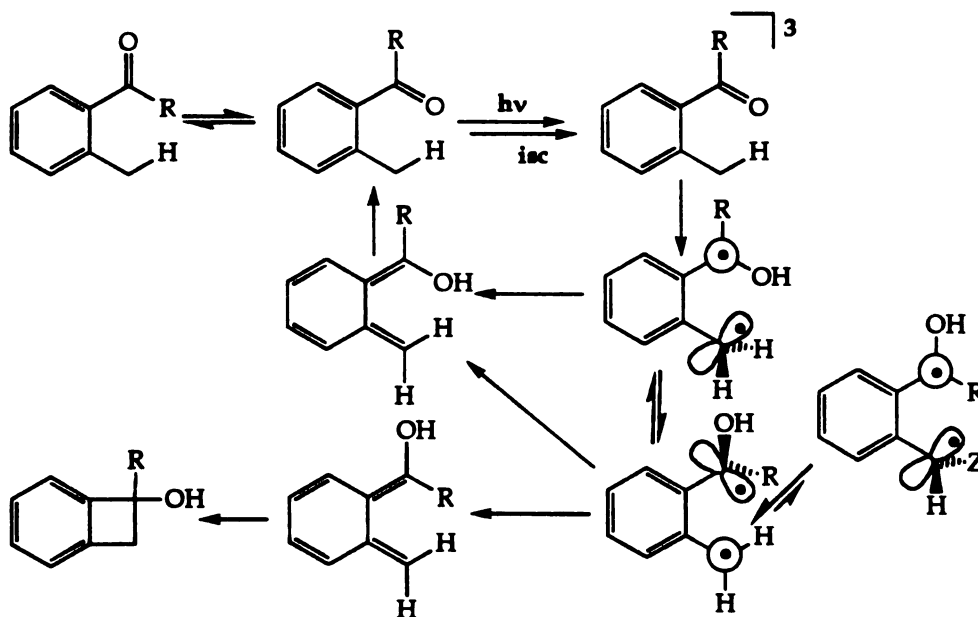
Scheme 40. α -Hydroxyindanone formation from hexalkylbenzils.

primary photoproducts undergo a secondary photocleavage to ketoaldehydes. The hexaethylbenzil gave only the Z isomer in the solid but gave a 2:1 (Z:E) ratio at low conversion in benzene. We suggested that much of the reaction involved δ -hydrogen abstraction followed by coupling of the 1,5-biradical. This conclusion was based on the solid state reactivity and the preference for the formation of the Z-hydroxyindanone from the hexaethylbenzil in solution. The α -cleavage to a ketoaldehyde was not reported by previous researchers who

studied other 1,2-diketones that formed α -hydroxyindanones⁹⁷⁻¹⁰⁰, but was mentioned in a separate account by Hamer^{88,89}.

III. Goals of Research

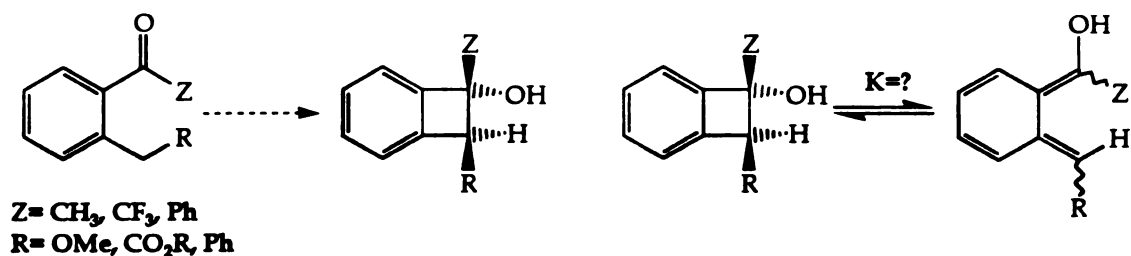
The chronology of benzocyclobutenol formation from the parent ketone is of current interest. Factors that affect this chronology are: 1) initial geometry for hydrogen abstraction; 2) nature of the excited state-(it is generally assumed that the *o*-xylylenol intermediates occur from the $^3n,\pi^*$ state, early evidence for singlet reaction in 2-methylacetophenone has not been addressed); 3) the lifetime of the biradical, what factors need be considered for the biradical $\rightarrow$ *o*-xylylenol transformation; 4) once formed what is the fate of *o*-xylylenols; 5) the stability (or instability) of the benzocyclobutenol.



Scheme 41. Ketone to benzocyclobutenol chronology.

A. Photoenolization of ortho substituted phenyl ketones

Several questions have been stimulated by the initial study by on the formation of benzocyclobutenols from aceto- and benzophenones.⁴⁵ Why is the E,E but not the E,Z enol formed, which is evident by the fact that only the E-benzocyclobutenol is formed from 2-ethylbenzophenone? One of my goals

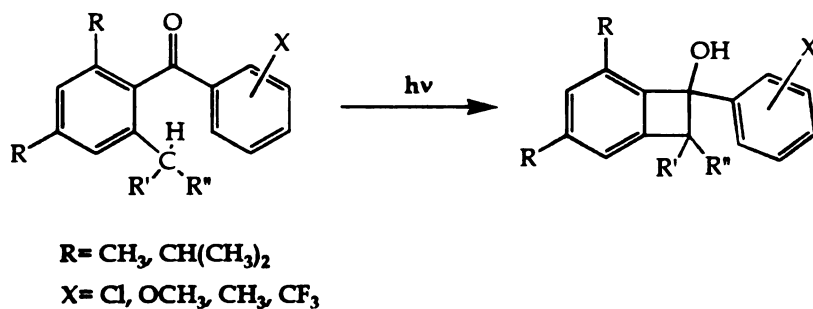


was to gain a better understanding of the diastereoselectivity and investigate how substituents (Z and R) affect this selectivity. Another goal was to study the benzocyclobutenol stability as affected by the substituents R and Z and to examine the xylylenol/benzocyclobutenol equilibrium. All these issues are important considering the synthetic usefulness of these intermediates, thus a comprehensive study of the substituent effects on the photocyclization of ortho alkyl acetophenones, benzophenones and α,α,α -trifluoroacetophenones to benzocyclobutenols was undertaken.

B. Photoenolization of 2' substituted 2,4,6-trialkylbenzophenones.

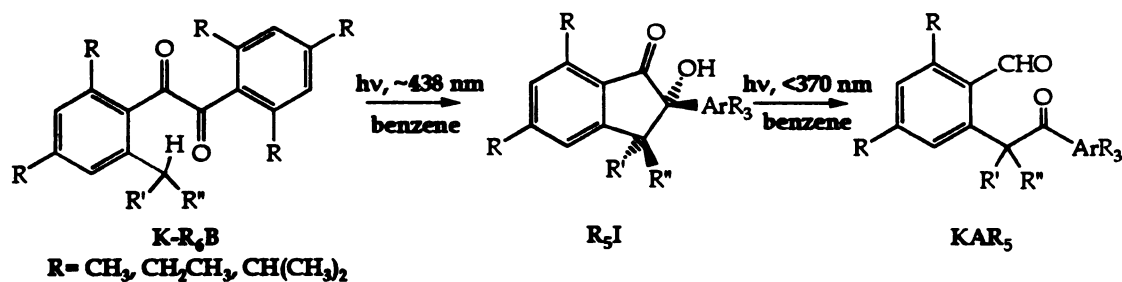
The goal of this study was to examine the effect of 2' substituents on benzocyclobutenol formation. In particular, the effect of having one (or both) of the phenyl rings twisted relative to the carbonyl group. I thought this

noncoplanarity would influence both hydrogen abstraction and cyclization of the *o*-xylenols. Several 4'-substituents were examined to confirm Ito's and Matsuura's results.¹⁰²



C. α -Cleavage of substituted α -hydroxyindanones

The goal of this study was to examine the effects of steric congestion on the efficiency for α -cleavage. The study was prompted by Park's results for the photocyclization of 2,4,6,2',4',6'-trialkylbenzils that the α -hydroxyindanone products were photolabile.¹⁰³



Results and Discussion

I. General procedures

The common protocol for the photochemical studies was to first conduct NMR screening experiments. The experiments provided several advantages over conventional analysis (gas chromatography and HPLC) especially if the resulting photoproducts were thermally labile or readily air oxidized. A ^1H -NMR spectrum was acquired prior to irradiation. The sample was then irradiated at the appropriate wavelength and a second ^1H -NMR spectrum is acquired at low conversion, usually after 20 or 30 minutes. The reaction was monitored periodically depending on the efficiency of the reaction. If the photochemical reaction was successful then a large scale (50-500mg) reaction was conducted in the equivalent non-deuterated NMR solvent and monitored by NMR, GC, or HPLC. Comparing the NMR screening results with the large scale results provided information about the stability of the resulting photoproducts. This information was necessary in order to distinguish the excited state chemistry from the thermal chemistry. When possible the products of the photoreaction were isolated by silica gel column chromatography followed by PTLC. However it was not always possible to isolate the benzocyclobutenols

due to their thermal lability and acid sensitivity. In such cases, the benzocyclobutenols were identified by their crude ^1H -NMR spectrum.

A modified Karplus-equation¹⁰⁴ implemented by Bother-By¹⁰⁵ given in Equation 1 was used in conjunction with molecular mechanics calculations (MM2 force field) to predict ^1H - ^1H vicinal coupling constants ($^3J_{\text{H-H}}$).

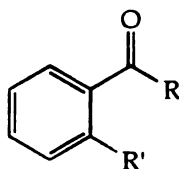
$$\text{Equation 1.} \quad J_{\text{vic}} = 7 - \cos(\phi) + 5 \cos(2\phi)$$

Quantum yields were measured by irradiation of degassed solutions of ketones in tubes containing a fixed amount of internal standard parallel to valerophenone actinometer. The product concentrations were determined by GC, HPLC or ^1H NMR. The quenching studies were conduct in the same manner as the quantum yields but with various concentrations of 2,5-dimethyl-2,4-hexadiene or pyrene as a quencher.

II. Results for *o*-alkyl acetophenones and benzophenones

A. General preparation of ketones

Although the *o*-alkyl acetophenones and benzophenones are structurally similar, a general syntheses of the target compounds was not attempted. The aceto- and benzophenone derivatives with electron withdrawing groups substituted at the ortho benzylic position presented a synthetic challenge. Ideally, coupling of the appropriately substituted Grignard with acetyl or

Table 3. *o*-Alkyl phenyl ketones studied.

Ketone	R	R'	Abbreviation
<i>2-benzylacetophenone</i>	CH ₃	CH ₂ Ph	2BzAP
<i>(2-acetylphenyl)acetic acid</i>	CH ₃	CH ₂ COOH	2AcMAP
<i>(2-acetylphenyl)acetic acid-d₁</i>	CH ₃	CH ₂ COOD	2AcMAPd₁
<i>ethyl (2-acetylphenyl)acetate</i>	CH ₃	CH ₂ COOEt	2EsMBP
<i>N,N-diethyl ('-acetyl)phenyl acetamide</i>	CH ₃	CH ₂ CONEt ₂	2AmMAP
<i>2'-methyl-2,2,2-trifluoroacetophenone</i>	CF ₃	CH ₃	2MeTFA
<i>2'-ethyl-2,2,2-trifluoroacetophenone</i>	CF ₃	CH ₂ CH ₃	2EtTFA
<i>2'-(methoxymethyl)-2,2,2-trifluoroacetophenone</i>	CF ₃	CH ₂ OCH ₃	2MOMTFA
<i>2-ethylbenzophenone</i>	Ph	CH ₂ CH ₃	2EtBP
<i>2-benzylbenzophenone</i>	Ph	CH ₂ Ph	2BzBP
<i>(2-benzoyl)-1,1-dideutero-diphenylmethane</i>	Ph	CD ₂ Ph	2BzBPd₂
<i>(2-benzoylphenyl)acetic acid</i>	Ph	CH ₂ COOH	2AcMBP
<i>(2-benzoylphenyl)acetic acid-d₁</i>	Ph	CH ₂ COOD	2AcMBPd₁
<i>ethyl (2-benzoylphenyl)acetate</i>	Ph	CH ₂ COOEt	2EsMBP
<i>N,N-diethyl (2-benzoylphenyl)acetamide</i>	Ph	CH ₂ CONEt ₂	2AmMBP
<i>2,2'-dimethylbenzophenone</i>	2'-MePh	CH ₃	M₂BP

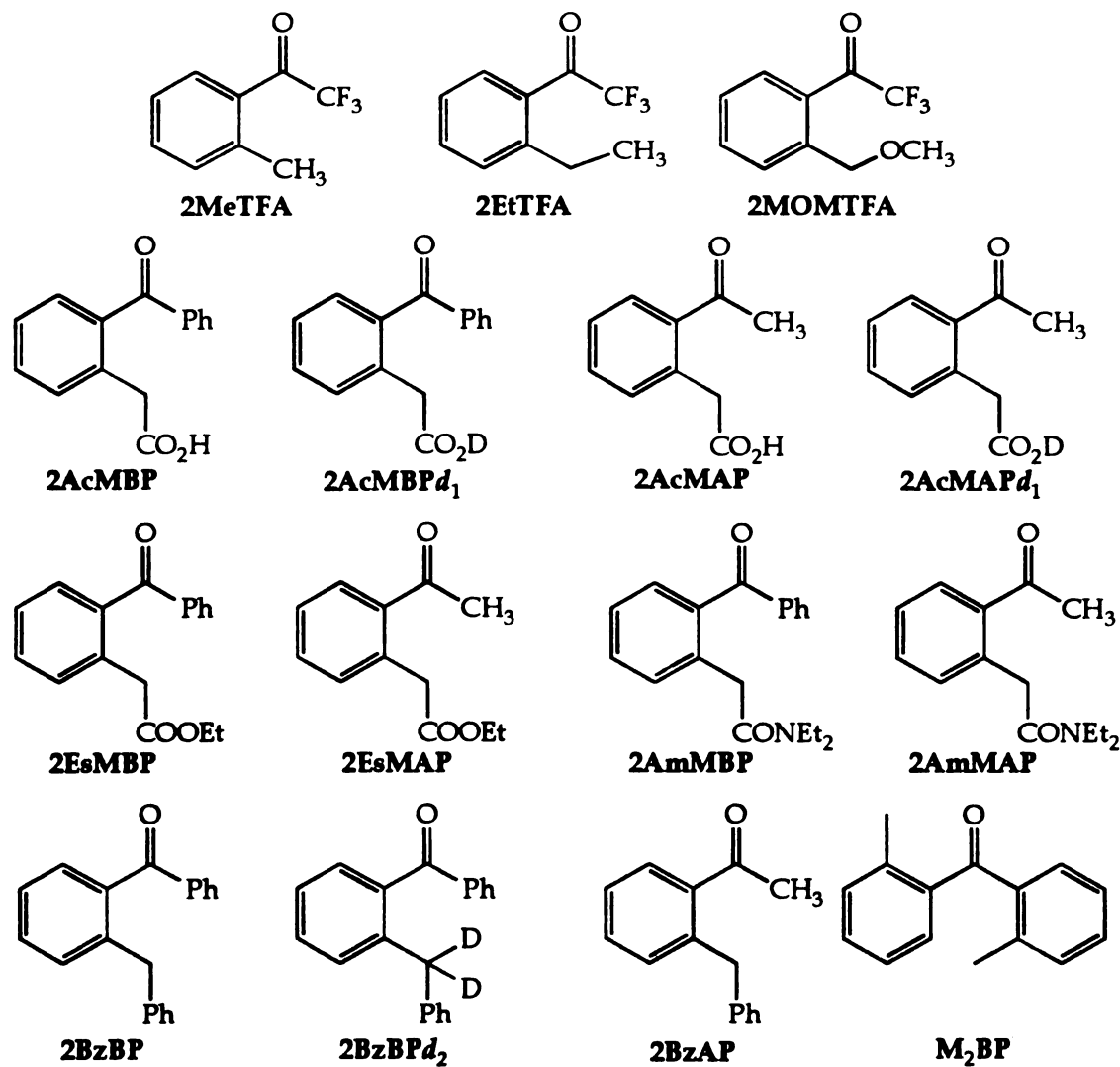


Figure 2. *o*-Alkyl phenyl ketones studied.

benzoyl chloride would give the target ketones. However, deprotonation of the benzylic position should compete with nucleophilic addition of the Grignard reagent. The ortho acetyl and benzoyl phenylacetic acid derivatives were synthesized by nucleophilic addition of either methyl or phenyl Grignard reagent with 1-indanone. The alcohol was dehydrated to a 1-substituted indene

which was subjected to oxidative cleavage with CrO_3 . The esters and amides were synthesized from the phenylacetic acids by standard methods.

The α,α,α -trifluoroacetophenones and ketones **2BzBP** and **M₂BP** were synthesized by bromine-lithium exchange. The corresponding aryl bromide was allowed to react with *n*-butyl lithium. The aryl lithium species was then reacted with ethyl α,α,α -trifluoroacetate in diethyl ether to yield the desired α,α,α -trifluoroacetophenones.

Table 3 and Figure 2 provides the structures of the ketones studied.

B. Identification of Benzocyclobutenols

Table 4 lists relevant chemical shifts of benzocyclobutenols. Most of the chemical shifts for the benzylic hydrogens of the benzocyclobutenol appear between 3.0 and 4.0 ppm with the exception of **2MeTFA-CB**. The appearance of this resonance was used to gauge the progress of the photochemical reaction. The ^{13}C -NMR spectra of the benzocyclobutenols contained 2 characteristic resonances, one at 42.0–66.0 ppm, the other at 78.0–87.0 ppm. These chemical shifts are consistent with literature data for benzocyclobutenes generated by the decarbonylation of 2-indanones.¹⁰⁶

Structural assignments for benzocyclobutenols were based on the relative chemical shifts of the two possible isomers. It is generally accepted that a methyl substituent *cis* to a phenyl group is shifted upfield relative to the *trans* isomer.¹⁰⁷⁻

¹⁰⁸ This shielding effect has been observed for substituted indanols and

benzocyclobutenols by Zand¹⁰⁹ and Park¹⁰³ in our group. For example, Park showed that the irradiation of 2-ethylbenzophenone yields only one diastereomer, 2EtBP-ECB. However, treatment of the benzocyclobutenol with acid leads to a mixture of 2EtBP-ECB and 2EtBP-ZCB. The only methyl resonance prior to isomerization was at 0.80 ppm; after treatment with acid a second methyl doublet appeared with a chemical shift of 1.20 ppm. This new resonance at 1.21 ppm was assigned to to the *Z* isomer, 2EtBP-ZCB.

Zand has shown that the hydroxy group in *E*-1-methyl-2-phenyl-2-indanol (*E*-ind) shields the adjacent *cis* hydrogen (3.23 ppm, **a**) relative to the *Z* isomer (*Z*-ind) whose equivalent hydrogen atom is at 3.46 ppm (**a'**). The methyl group (0.73 ppm, **b**) for *E*-ind is shielded relative to *Z*-ind whose equivalent methyl group **b'** has a chemical shift of 1.16 ppm.

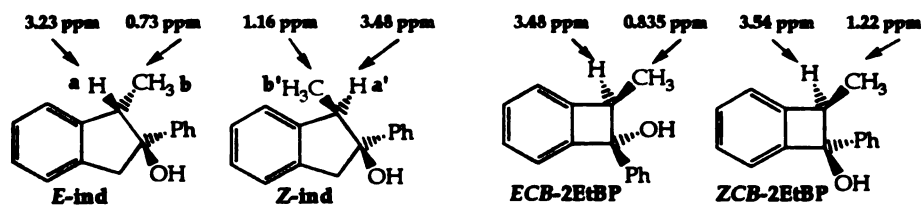


Figure 3. Chemical shifts for indanols (CDCl₃) and benzocyclobutenols (toluene-*d*₈).

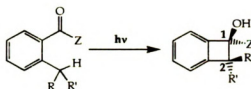


Table 4. Chemical shifts of benzocyclobutenols from o-alkylphenyl ketones

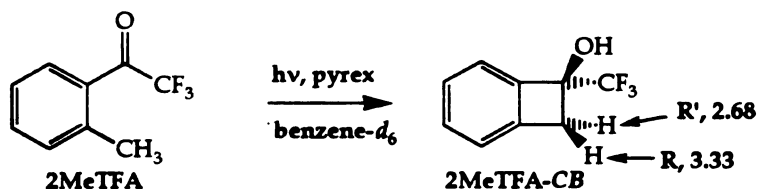
Product	solvent	R, σ (ppm)	R', δ (ppm)	OH, δ (ppm)	C1	C2
2MeTFA- CB	benzene- d_6	H, 3.33	H, 2.68	2.04	—	—
2MeTFA-CB	chloroform- d_1	H, 3.71	H, 3.27	2.84	—	—
2MeTFA-CB	acetonitrile- d_3	H, 3.64	H, 3.23	5.01	78.54	42.18
2EtTFA-ECB	benzene- d_6	H, 3.08	CH ₃ , 1.24	—	—	—
2EtTFA-ECB	chloroform- d_1	H, 3.73	CH ₃ , 1.49	—	80.89	52.34
2MOMTFA- ECB	chloroform- d_1	H, 4.88	OCH ₃ , 3.65	—	—	—
2MOMTFA- ZCB	chloroform- d_1	H, 5.09	OCH ₃ , 3.59	—	—	—
2EtBP- ECB	acetonitrile- d_3	H, 0.813	CH ₃ , 0.813	4.18	84.67 ^b	54.86 ^b
2EtBP- ECB	benzene- d_6	H, 3.49	CH ₃ , 0.800	1.96	—	—
2EtBP-ECB	toluene- d_8	H, 3.48	CH ₃ , 0.835	—	—	—
2EtBP- ECB	acetone- d_6	H, 3.70	CH ₃ , 0.821	5.19	—	—
2EtBP- ZCB	toluene- d_8	CH ₃ , 1.22	H, 3.54	—	—	—
2BzBP ^a - ECB	benzene- d_6	H, 4.75	Ph, —	2.20	—	—
2BzBP ^a - ECB	acetonitrile- d_3	H, 4.92 ^b	Ph, —	4.81 ^b	87.17 ^b	66.40 ^b
2BzBP ^a - ECB	toluene- d_8	H, 4.65	Ph, —	2.27	—	—

^a from crude ¹H-NMR. ^b -30°C.

C. Individual Ketones.

1. *2'-methyl-2,2,2-trifluoroacetophenone* (2MeTFA) and *2'-ethyl-2,2,2-trifluoroacetophenone* (2EtTFA).

2'-methyl-2,2,2-trifluoroacetophenone



Scheme 42. Photochemistry of 2'-methyl-2,2,2-trifluoroacetophenone, ^1H -NMR values in benzene- d_6

Irradiation of a 0.10 M 2MeTFA benzene- d_6 solution gave only one product, 2MeTFA-CB, in quantitative yield. The reaction was complete (100% conversion) after 13 hours of irradiation. The formation of 2MeTFA-CB was independent of light source and was formed by irradiation with either a medium pressure mercury arc lamp (Pyrex filtered, 17-20°C) or in a Rayonet reactor (300 nm lamps). The quantum yield for 2MeTFA-CB formation was measured at 313 nm by ^1H -NMR and found to be 0.074 (10% conversion). The singlet at 2.22 ppm for the ortho methyl group disappeared at the same rate as the growth of an AB quartet at 2.68 ppm ($J = 14.9$ Hz) and 3.33 ($J = 14.1$ Hz) ppm in benzene- d_6 . A second quartet coupling of $\sim 1\text{H}$ was apparent for the doublet at 2.68 ppm, which is likely due to ^1H - ^{19}F and ^{13}C - ^{19}F through space coupling which will be discussed in detail for 2EtTFA-ECB. The most important fact though is the chemical shift of the hydrogen cis to the hydroxy group. If we compare

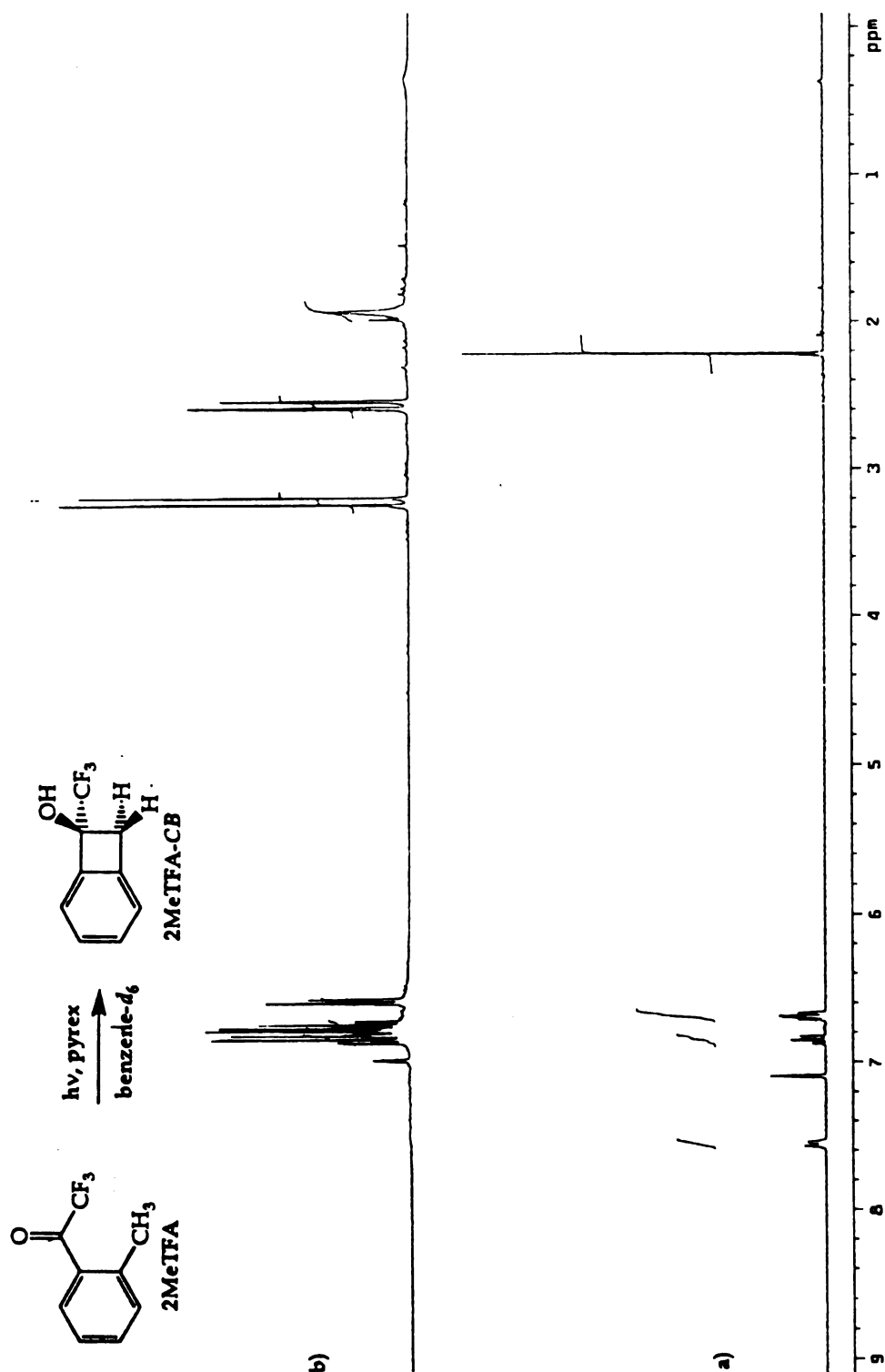
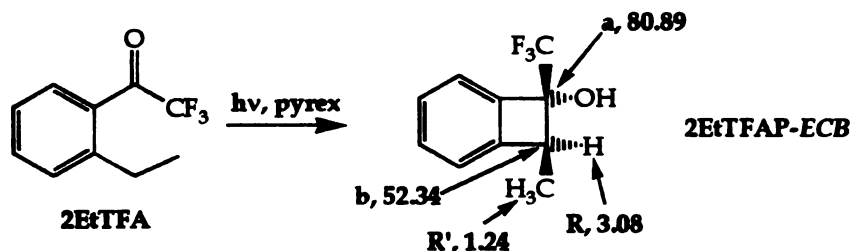


Figure 4. ¹H-NMR Spectra of 2MeTFA in benzene-*d*₆ a) before irradiation b) 13 hours after irradiation.

the chemical shifts for R and R' for 2EtBP-ECB, 2EtBP-ZCB and 2EtTFA-ECB in Table 4 and M₃BP-CB in Table 17 the methyl substituent does not significantly change the chemical shift of the benzylic methine hydrogen but the adjacent phenyl ring and OH group do affect the chemical shift. For 2EtBP-ECB the chemical shift of R is 3.66 ppm in benzene-*d*₆, in agreement with the 3.33 ppm chemical shift for 2EtTFA-CB. Thus, for 2MeTFA-CB the resonance at 2.68 ppm is assigned to hydrogen R' which is cis to the trifluoromethyl group while the resonance at 3.33 ppm is assigned to hydrogen R which is cis to the hydroxy group.

The ¹³CNMR in acetonitrile-*d*₃ has nine resonances, three of which showed ¹³C-¹⁹F couplings; one at 42.18 which is assigned to benzylic methylene; a quartet at 78.54 (*J*_{CF} = 32.22 Hz) assigned to the benzylic carbon with the CF₃ and OH groups attached, six aromatic carbons at 122.9, 124.6, 128.9, 131.9, 143.0 (*J*_{CF} = 2.38 Hz) and 143.2 ppm, and the trifluoromethyl carbon at 126.3 (*J*_{CF} = 278.9 Hz). For ¹H-NMR spectral data see Figure 4.

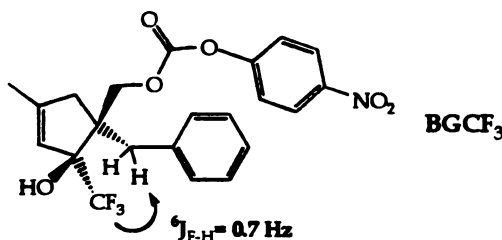
2'-ethyl-2,2,2-trifluoroacetophenone



Scheme 43. Photochemistry of 2'-ethyl-2,2,2-trifluoroacetophenone, ¹³C-NMR values in CDCl₃, ¹H-NMR values in benzene-*d*₆.

Irradiation of a 0.01 M 2EtTFA benzene- d_6 solution gave only one product, identified as 2EtTFA-ECB, in quantitative yield with no trace of the second isomer (2EtTFA-ZCB). The reaction was complete (100% conversion) after 12 hours of irradiation with Pyrex filtered light from a medium pressure mercury arc lamp. The triplet at 0.979 ppm and the quartet at 2.61 ppm for the α -ethyl group disappeared at the same rate as the growth of a quartet at 3.08 ppm ($J = 7.4$ Hz) and a doublet of quartets at 1.24 ($J = 7.4, 1.8$ Hz) ppm in benzene- d_6 . The 1.8 Hz coupling to the doublet at 1.24 ppm is assigned to ^1H - ^{19}F through space coupling.

^{19}F - ^1H and ^{19}F - ^{13}C through space coupling is well documented¹¹⁰. One unambiguous example has been reported by the Bégué group which identified a $^6J_{\text{H-F}} = 0.7$ Hz coupling from NMR data which was correlated to the crystal structure for a trifluoromethylcyclopentenol (BGCF₃).¹¹¹ The identification of the trifluoroethylbenzocyclobutenols at times was difficult because they are extremely volatile like their parent ketone and their spectral data must be



acquired immediately. On several occasions, the solid product had evaporated while being stored in a vial or round bottom flask. The ^{13}C NMR spectrum shows three ^{19}F -coupled resonances with chemical shifts at 13.47 (q, $J_{^{13}\text{C}-^{19}\text{F}} = 2.12$ Hz, R'), 80.89 (q, $J_{^{13}\text{C}-^{19}\text{F}} = 30.7$ Hz, a) and 125.5 ppm (q, $J_{^{13}\text{C}-^{19}\text{F}} = 282$ Hz, R). The

methyl carbon which is the farthest atom via bonds, shows ^{13}C - ^{19}F coupling, whereas carbon atom **b**, which is closer via bonds, does not show ^{13}C - ^{19}F coupling. The same is true for the ^1H -NMR spectrum. The benzylic methine hydrogen is one atom closer to the trifluoromethyl group than the methyl protons but does not show ^1H - ^{19}F coupling, whereas the methyl protons do. The expected doublet for the benzylic methyl group appears as a doublet of quartets with $^2J = 7.14$ Hz and $^6J_{\text{H-}^{19}\text{F}} = 1.75$ Hz. Also, only one (at 2.68 ppm) of the two resonances for the benzylic methylene of 2MeTFA-CB showed a ^1H - ^{19}F coupling of 0.8 Hz. This smaller coupling observed for 2MeTFA-CB may reflect a larger ^1H - ^{19}F distance as compared to a shorter C^{19}F_3 - $^1\text{H}_3\text{C}$ distance for 2EtTFA-ECB. ^1H - ^1H nOe provided no useful structural information because of the limited number of hydrogens. A ^{19}F - ^{13}C nOe experiment was attempted but no nOe was observed. However, this may be due the different type of spectrometer I used compared to the reference literature.¹¹² Thus, the stereochemical assignment of 2EtTFA-ECB is based on the ^{19}F through space coupling and the chemical shifts from previously characterized benzocyclobutenols. The expected chemical shift for the benzylic methine of the 2EtTFA-ZCB should be substantially shielded (i.e. ~ 2.7 ppm) based on the ^1H -NMR assignment of 2MeTFA-CB. For ^1H -NMR spectral data see Figure 5. The IR spectrum showed no carbonyl stretch but showed a broad stretch at 3610 cm^{-1} indicating the presence of a hydroxy group. In contrast to E-2-methylbenzocyclobutenol, the acid catalyzed isomerization

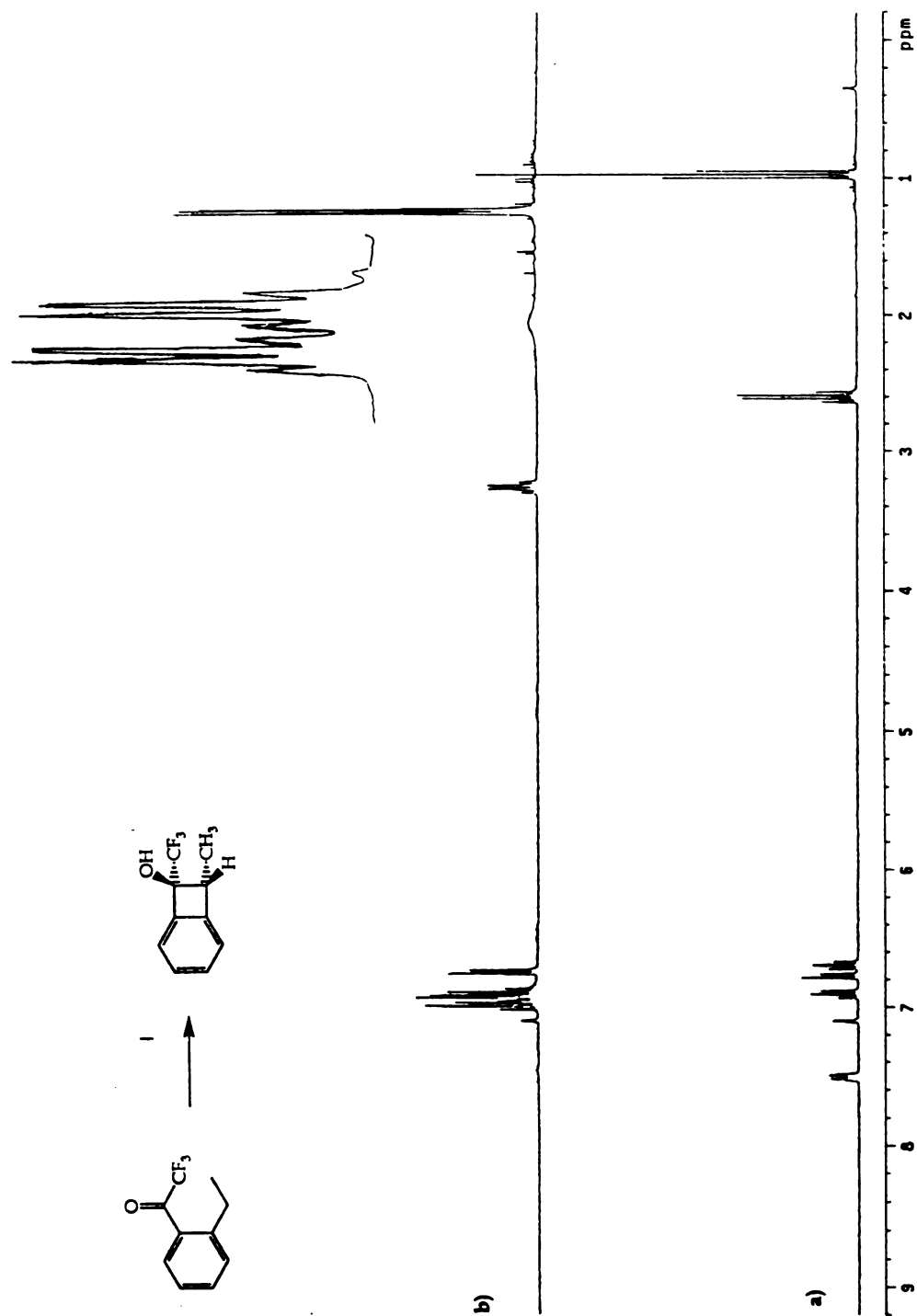
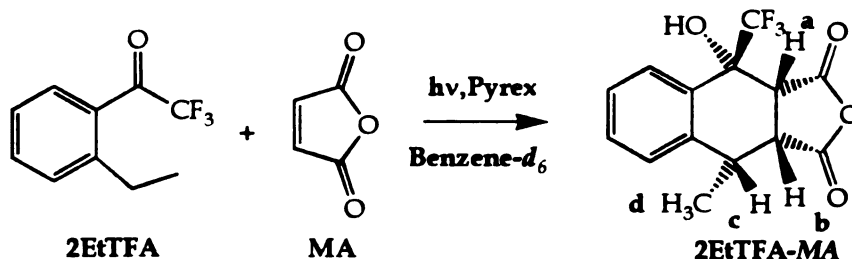


Figure 5. ¹H-NMR Spectra of 2EtTFA in benzene-*d*₆, a) before irradiation b) 12 hours after irradiation.

of 2EtTFA *ECB* to 2EtTFA-*ZCB* did not occur with *p*-toluenesulfonic acid. This is probably due to the slow loss of water by a S_N1 mechanism which would put a positive charge next to the already electron deficient trifluoromethyl group.



Scheme 44. Photochemistry of 2EtTFA in the presence of MA.

Irradiation of 0.01M 2EtTFA benzene solution in the presence of excess maleic anhydride (MA) gave one major product. The reaction was complete (100% conversion) after 9 hours of irradiation with Pyrex filtered light from a medium pressure mercury arc lamp. If equimolar amounts of 2EtTFA and MA were used a mixture of 2EtTFA-*CB* and 2EtTFA-*MA* was observed. The ^1H -NMR spectrum of the Diels-Alder adduct showed four aliphatic resonances. ^1H -nOe of the four hydrogens gave the following enhancements (see Figure 6); 4% for $\text{H}(\text{d}) \rightarrow \text{H}_{26}(\text{c})$, 6% for $\text{H}_{26}(\text{c}) \rightarrow \text{H}_{27}(\text{b})$ (MM2 distance = 2.3 Å), 2% for $\text{H}_{26}(\text{c}) \rightarrow \text{H}_{28}(\text{a})$ (MM2 distance = 3.8 Å), 4% for $\text{H}_{27}(\text{b}) \rightarrow \text{H}_{28}(\text{a})$ (MM2 distance = 2.4 Å). The structural assignment is based on the ^1H -nOe data and experimental vicinal coupling constants: 9.5 Hz for the dihedral angle $\text{H}_{26}(\text{c})\text{-C}_7\text{-C}_8\text{-H}_{27}(\text{b})$ and 9.2 Hz for $\text{H}_{27}(\text{b})\text{-C}(8)\text{-C}(9)\text{-H}_{28}(\text{a})$. The stereochemical assignment of 2EtTFA-*MA* is consistent with 2EtTFA-*exoMAEE* even though the experimental and

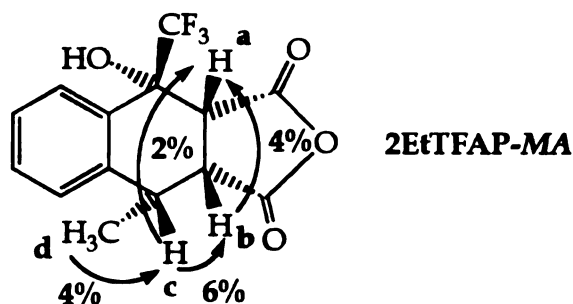
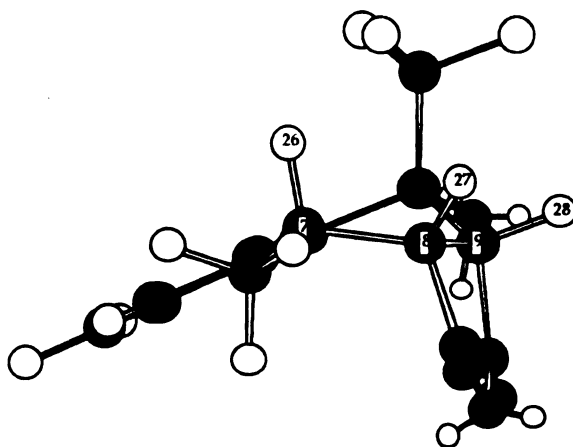


Figure 6. nOe enhancements of 2EtTFA-MA in CDCl₃.

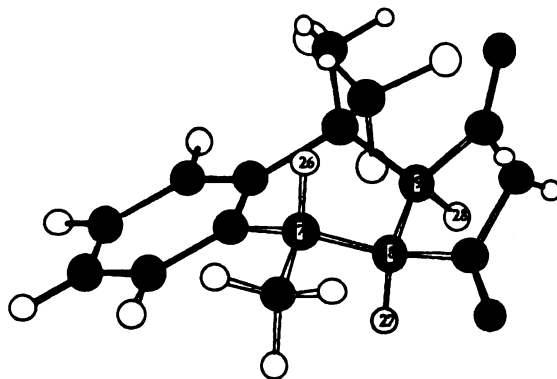
predicted $^3J_{\text{H-H}}$ values differ by 1.4 Hz for the $\text{H}_{26}(\text{c})\text{-C}_7\text{-C}_8\text{-H}_{27}(\text{b})$ dihedral angle. The diastereomers *2EtTFA-exoMAEZ* and *2EtTFA-endoMAEE* were ruled out from the nOe experiment because of their trans configuration of the benzylic methine (H_{26}) and bridgehead methine (H_{27}) which would not be expected to give a large enhancement. The discrepancy in the theoretical and experimental $^3J_{\text{H-H}}$ values may be due to the differences in electronegativity of the substituent attached to the hydrogen that has vicinal coupling.¹¹³ *2EtTFA-endoMAEZ* cannot be ruled out completely based on the nOe and the experimental $^3J_{\text{H-H}}$ values. It is unlikely that both of the theoretical $^3J_{\text{H-H}}$ values would differ from experiment for the dihedral angles $\text{H}_{26}(\text{c})\text{-C}_7\text{-C}_8\text{-H}_{27}(\text{b})$ and $\text{H}_{27}(\text{b})\text{-C}_8\text{-C}_9\text{-H}_{28}(\text{a})$ since the coupled hydrogens have attached groups with nearly identical electronegativities.



MM2 steric energy of 2EtTFA-*exo*MAEE
27.68 kcal/mole

Table 5. MM2 DH angles of *E*-2EtTFA-*exo*MAE

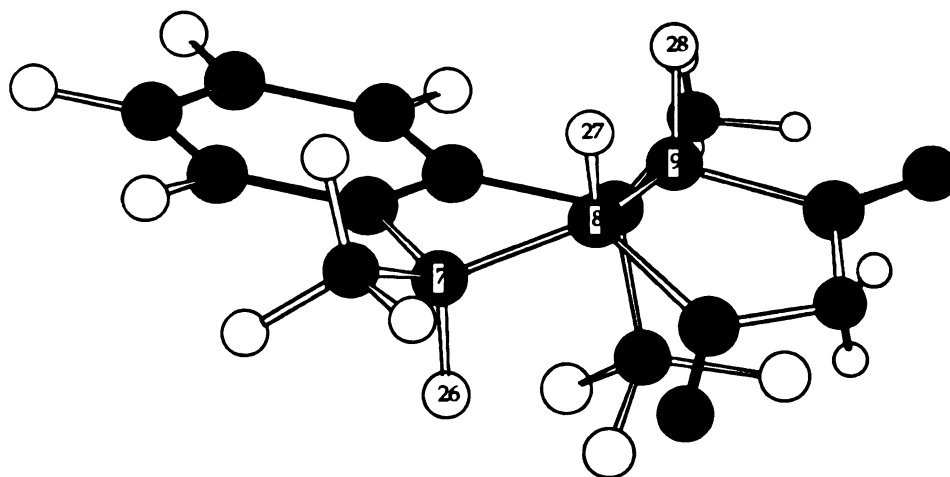
Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{\text{H-H}}$, Hz
H(26)	C(7)	C(8)	H(27)	33.8	8.08
H(27)	C(8)	C(9)	H(28)	26.0	9.18



MM2 steric energy of 2EtTFA-*exo*MAEZ
31.85 kcal/mole

Table 6. MM2 DH angles of 2EtTFA-*exo*MAEZ

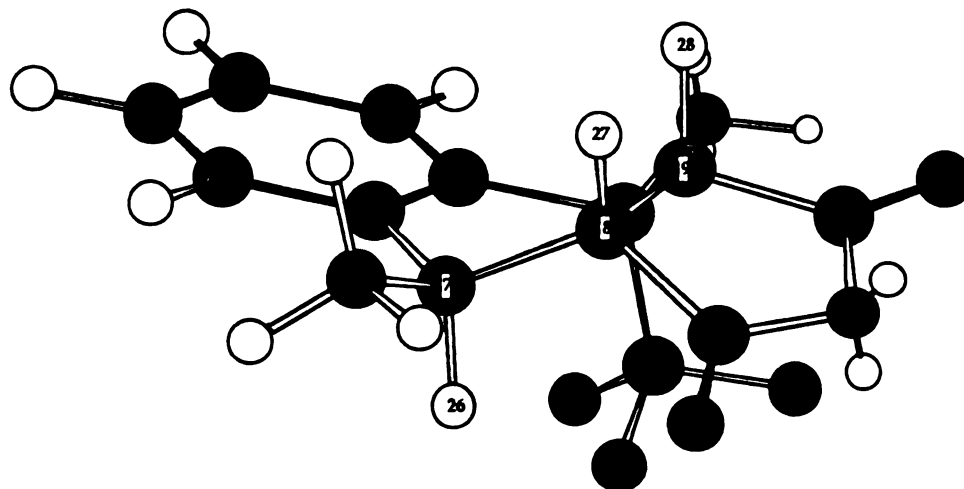
Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{\text{H-H}}$, Hz
H(26)	C(7)	C(8)	H(27)	-177.5	13.0
H(27)	C(8)	C(9)	H(28)	-29.0	10.2



MM2 steric energy of 2EtTFA-endoMAEE
33.39 kcal/mole

Table 7. MM2 DH angles of 2EtTFA-endoMA

Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{\text{H-H}}$, Hz
H(26)	C(7)	C(8)	H(27)	-150.2	10.2
H(27)	C(8)	C(9)	H(28)	-16.4	10.9

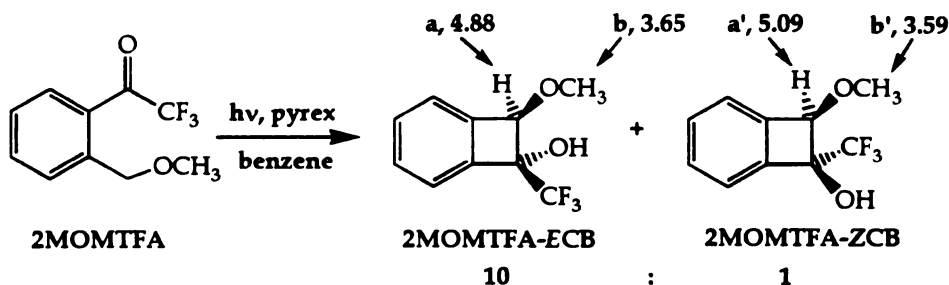


MM2 steric energy of 2EtTFA-endoMAEZ
Steric energy: 36.23 kcal/mole

Table 8. MM2 DH angles of 2EtTFA-endoMAEZ.

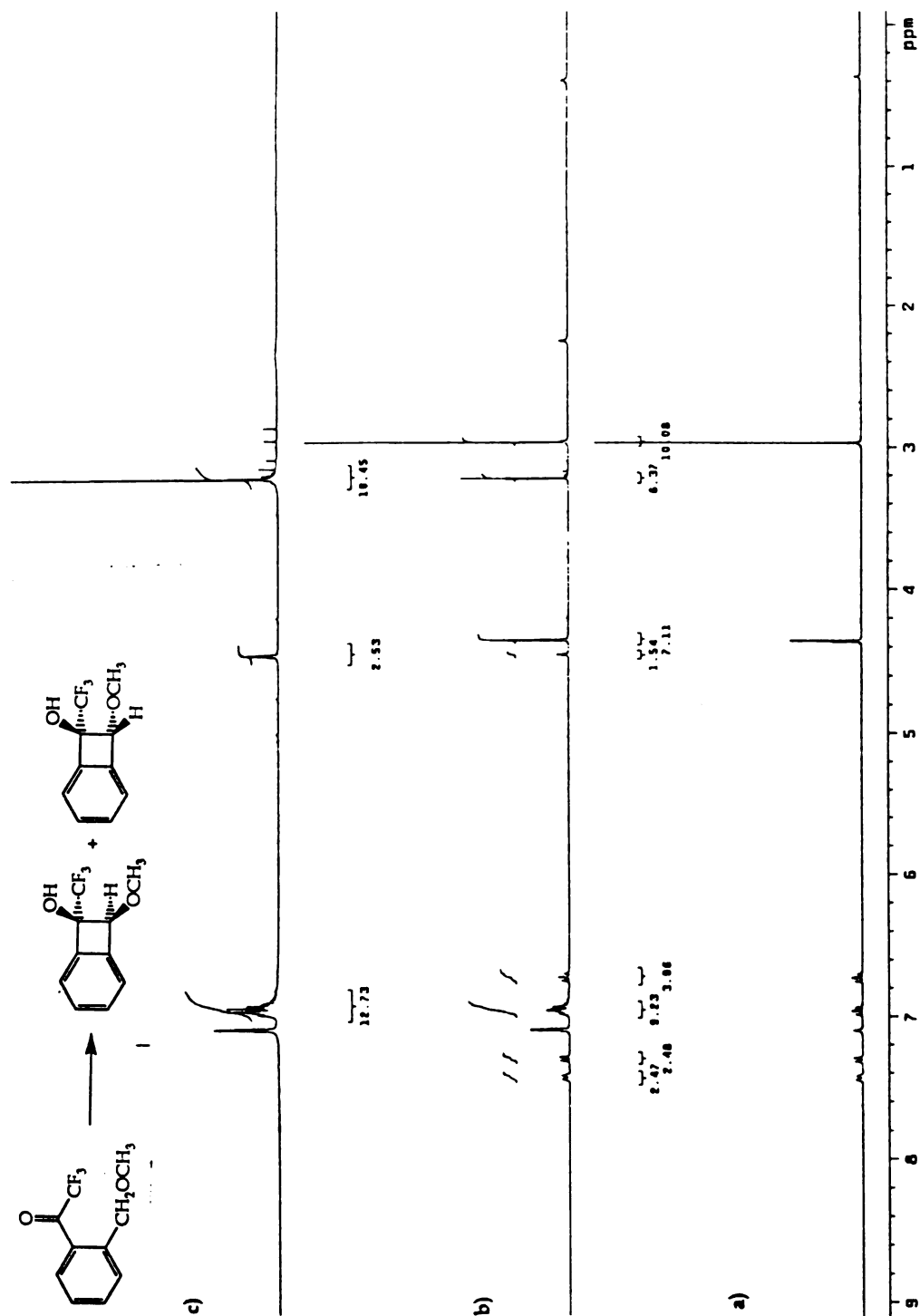
Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{\text{H-H}}$, Hz
H(26)	C(7)	C(8)	H(27)	0.300	11.0
H(27)	C(8)	C(9)	H(28)	-28.5	8.85

2. 2'-methoxymethyl-2,2,2-trifluoroacetophenone (2MOMTFA).



Scheme 45. Photochemistry of 2'-methoxymethyl-2,2,2-trifluoroacetophenone, chemical shift values in CDCl_3

Irradiation of 2MOMTFA in benzene gave two major products 2MOMTFA-ECB and 2MOMTFA-ZCB in a 10/1 ratio. It appeared that only one diastereomer was formed in the NMR scale photoreaction in benzene- d_6 (see Figure 7). However, the preparative scale reaction in benzene was analyzed by ^1H -NMR in chloroform- d_1 and a second product was identified as 2OMTFAP-ZCB, which had a ^1H -NMR spectral pattern similar to that of 2MOMTFA-ECB with only small changes in chemical shifts. The chemical shift for the benzylic methine hydrogen of 2OMTFAP-ECB is at 4.88 ppm slightly up-field relative to that of 2MOMTFA-ZCB at 5.09 ppm (see Figure 8). The reaction solution had turned orange-brown and persisted after the irradiation was complete. A minor product was evident in the crude ^1H -NMR from the photoreaction in benzene- d_6 but was not isolated.



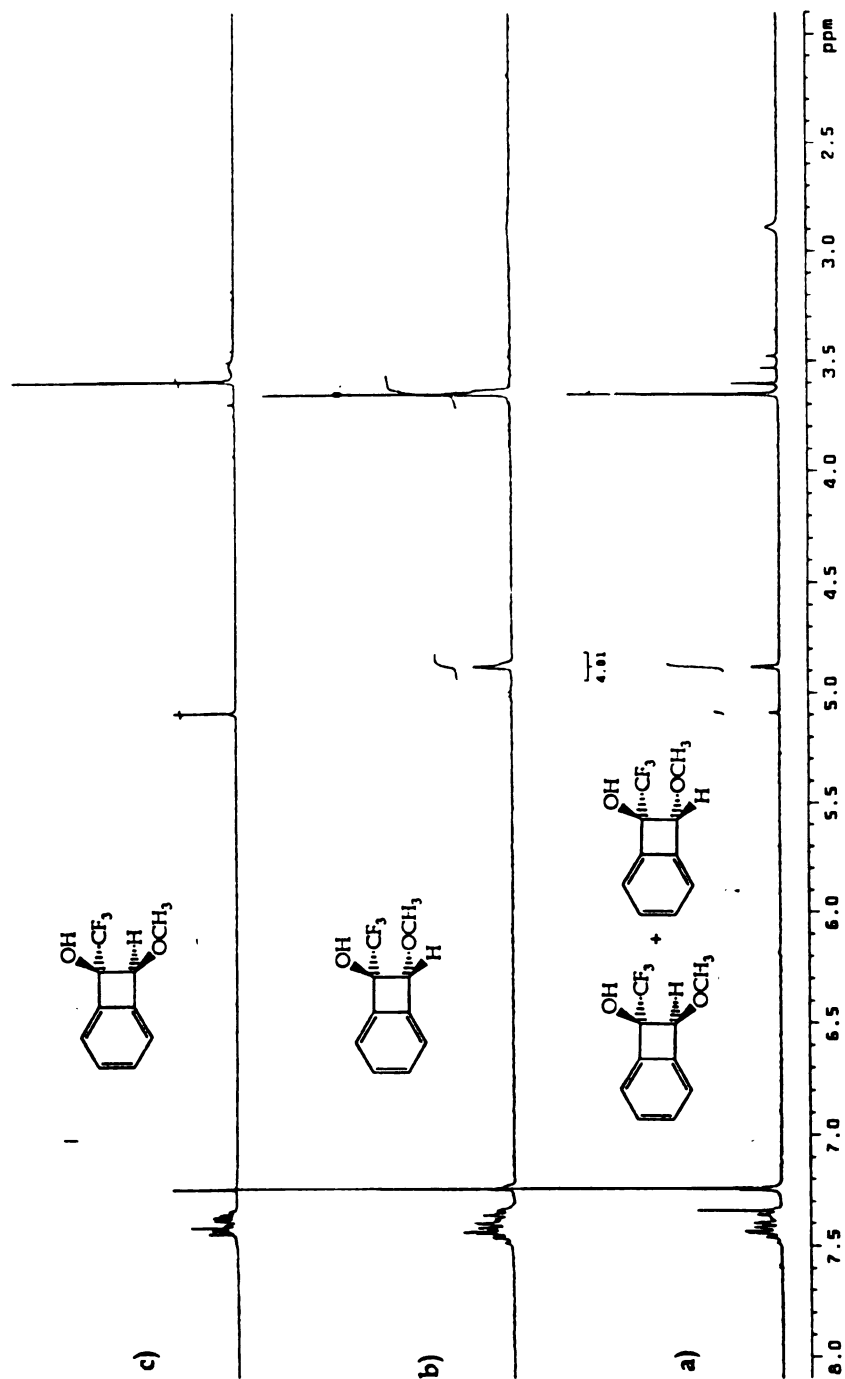
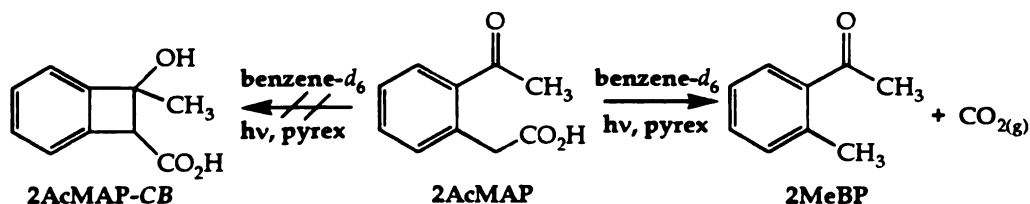


Figure 8. ^1H -NMR Spectra in CDCl_3 a) of 2MOMTFA after 16 hours irradiation in benzene b) isolated 2MOMTFA-ECB c) isolated 2MOMTFA-ZCB.

3. (2-acetylphenyl)acetic acid (2AcMAP) and (2-benzoylphenyl)acetic acid (2AcMBP)

(2-acetylphenyl)acetic acid (2AcMAP)



Scheme 46. Photochemistry of o-acetylphenylacetic acid

Irradiation of a ~0.01 M benzene- d_6 solution of 2AcMAP gave quantitatively 2-methylacetophenone (2MeAP). The reaction was complete (100% conversion) after 20 minutes of irradiation in a Rayonet reactor with 300 nm lamps; the temperature of the reactor was ~40°C throughout the course of the reaction. This short irradiation is in sharp contrast to the typically long irradiation times for simple ortho substituted acetophenones. During the course of the reaction the methylene signal at 3.53 ppm disappeared with the simultaneous formation of two new signals at 2.05 and 2.47 ppm. The characteristic AB quartet (with a chemical shift δ 3.4 ppm) for the expected 2AcMAP-CB was not observed. The product was identified and confirmed by comparing the ^1H -NMR spectrum of an authentic sample of 2-methylacetophenone with the crude photochemical reaction mixture from 2AcMAP (see Figure 9). Gas chromatography revealed that the photochemical reaction mixture from 2AcMAP contained a compound with an identical retention time as the authentic 2MeAP. Gas chromatographic analysis of the

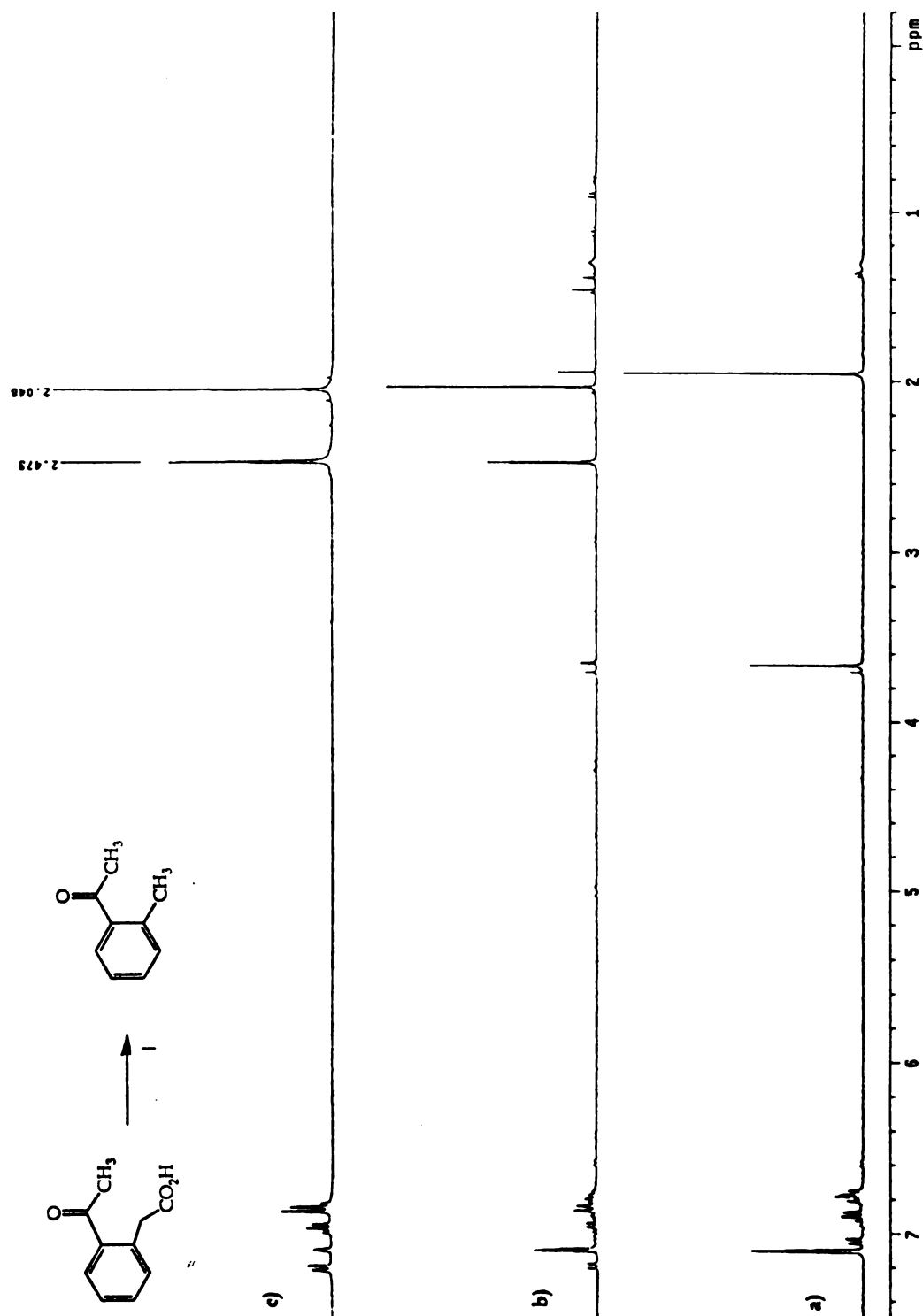
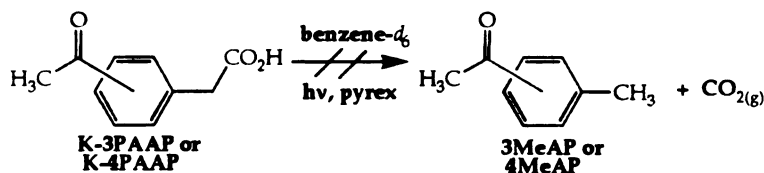


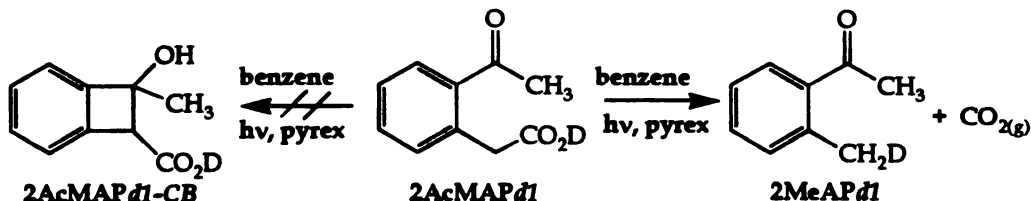
Figure 9. ^1H -NMR Spectra of K-2AcMAP in benzene- d_6 a) before irradiation b) after 20 minutes irradiation c) standard 2-methylacetophenone.

reaction solution with added 2MeAP showed only one peak in the chromatogram confirming the photoproducts identity.



Scheme 47. Photochemistry of meta and para methylphenylacetic acid

A mixture of m- and p-acetylphenyl acetic acid was irradiated under similar conditions as the ortho counterpart. A 0.01 M degassed benene- d_6 solution was irradiated with Pyrex filtered light from a medium pressure Mercury arc lamp. The reaction was monitored by ^1H -NMR by periodically acquiring spectrums; after 30 minutes the ^1H -NMR spectrum was unchanged. After 30 hours the sample had turned green-yellow in color and a precipitate had formed on the bottom of the NMR reaction tube which was consistent with previous reports.¹¹⁴ Mainly starting ketone remained. However, two small singlets were visible at 1.82 and 2.08 ppm but no attempt was made to isolate these products. The meta and para phenylacetic acid were irradiated as a mixture because the separation from the synthesis proved difficult but not necessary.



Scheme 48. Photochemistry of deuterio o-acetylphenylacetic acid

The deuterio acid **2AcMAP d_1** was synthesized in order to elucidate the fate of deuterium atom when photolyzed. A benzene solution of **2AcMAP d_1** was degassed and irradiated. The progress of the reaction was monitored by ^2H -NMR and was complete after 110 minutes. ^2H -NMR analysis showed the disappearance of the broad RCOOD peak at 0.60 ppm (the identity of this peak is not certain, it may be a species involving hydrogen bonding between the carboxylic acid and residual H_2O or D_2O) with the simultaneous growth of a sharp singlet at 2.50 ppm. Also a new peak grows in at ~ 0.35 ppm which is the same as standard D_2O in benzene, it is likely that the hydrogen-bond complex is destroyed when irradiated (see Figure 10) The new singlet at 2.50 ppm is consistent with the formation of **2MeAP d_1** (it is possible that more than one deuterium has been incorporated and will be examined more closely for **2AcMBP d_1**) with the deuterium being incorporated at the benzylic position and complement the previously described experiment for **2AcMAP** in benzene- d_6 .

A benzene- d_6 solution of phenylacetic acid (0.20 M) and acetophenone(0.13 M) was irradiated in order to sensitize the decarboxylation.



The reaction was monitored by ^1H -NMR analysis; after 30 minutes the ^1H -NMR spectrum was unchanged. The spectrum of the mixture did not change significantly after 30 hours of irradiation but several minor peaks were evident with chemical shifts between 2.3-2.5 ppm and 1.6-1.8 ppm.

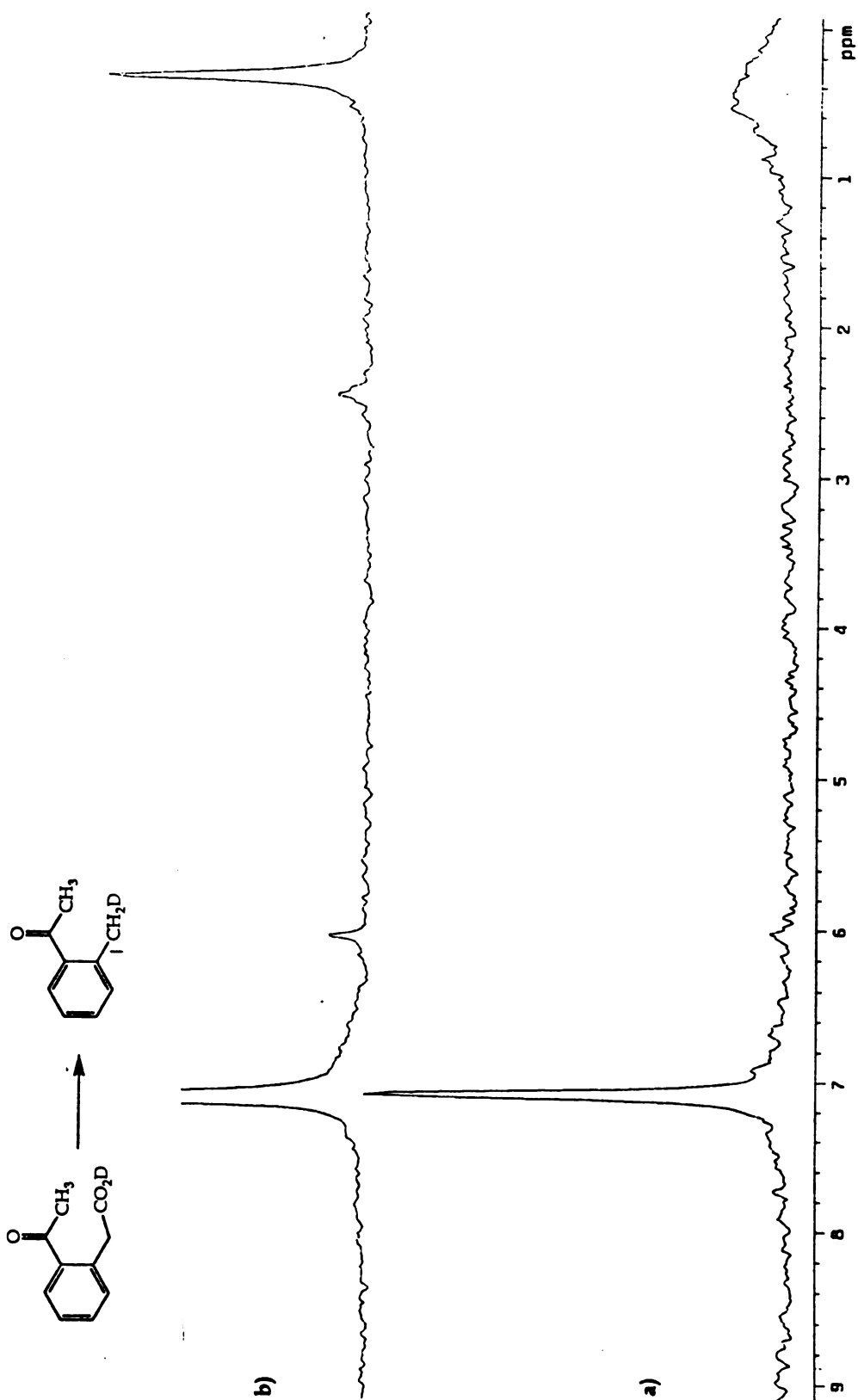
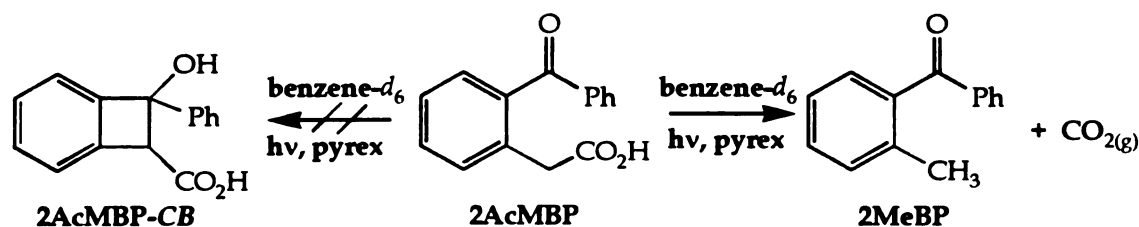


Figure 10. ^1H -NMR Spectra of 2AcMAPd1 in benzene a) before irradiation b) after 110 minutes irradiation.

(2-benzoylphenyl)acetic acid (2AcMBP)

Scheme 49. Photochemistry of (2-benzoylphenyl)acetic acid.

Irradiation of a ~0.01 M benzene-*d*₆ solution of 2AcMBP gave quantitatively 2-methylbenzophenone (2MeBP). The reaction was complete (100% conversion) after 20 minutes of irradiation in a Rayonet reactor with 300 nm lamps; the temperature of the reactor was ~40°C throughout the course of the reaction. During the course of the reaction the methylene signal (at 3.80 ppm) of 2AcMBP disappeared with the simultaneous formation of a new singlet at 2.19 ppm. The characteristic AB quartet (with a chemical shift σ 3.4 ppm) for the expected 2AcMBP-CB was not observed. The product was identified as 2MeBP and confirmed by comparing the ¹H-NMR spectrum of an authentic sample with the crude photochemical reaction mixture from 2AcMBP (see Figure 11) Gas chromatography revealed that the photochemical reaction mixture from 2AcMBP contained a compound with an identical retention time as authentic 2-methylbenzophenone. GC analysis of the reaction solution with added 2MeBP showed only one peak in the chromatogram confirming the photoproduct's identity.

The photochemical decarboxylation was confirmed by measuring CO_{2(g)} formation directly by FTIR analysis. The irradiation was carried

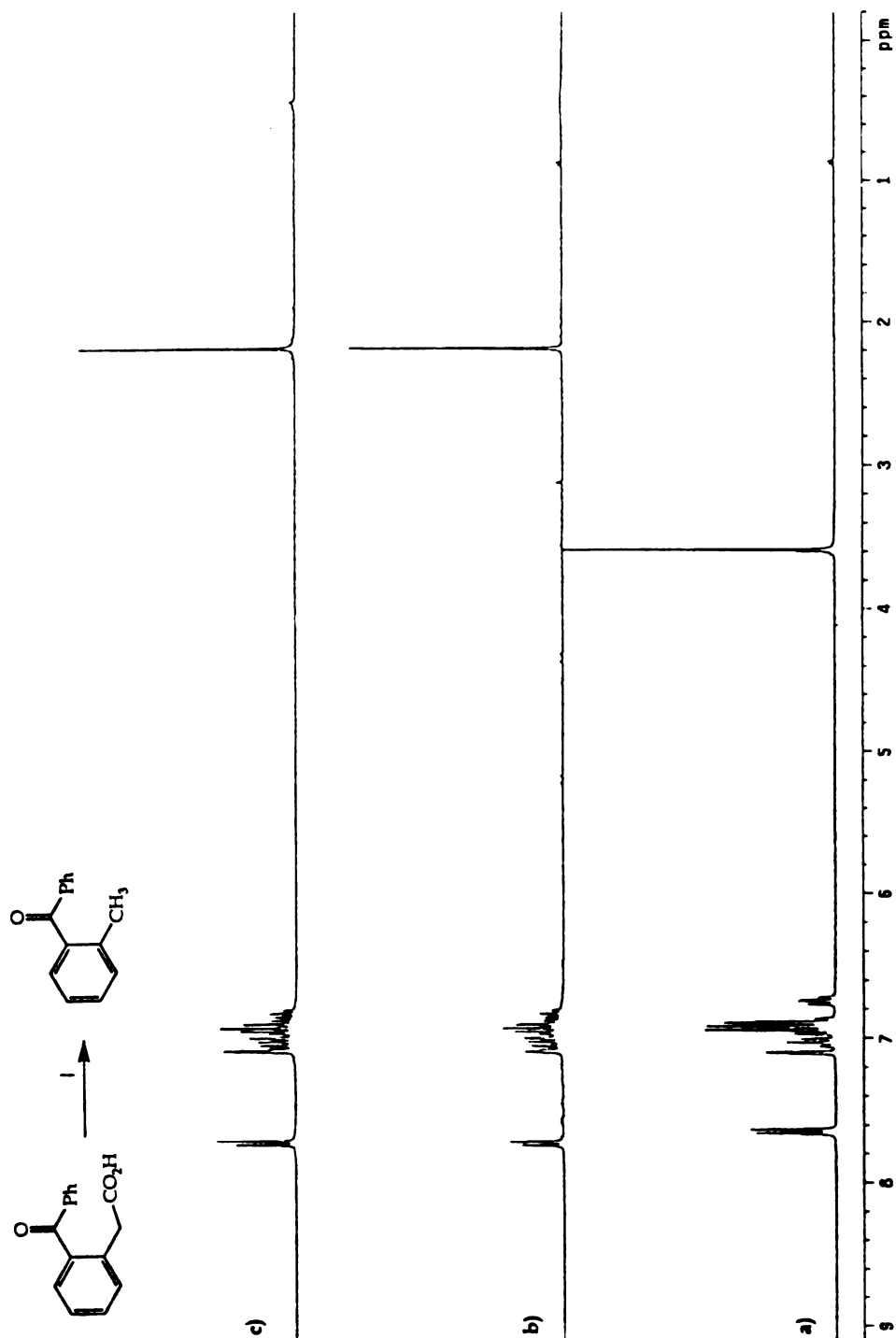
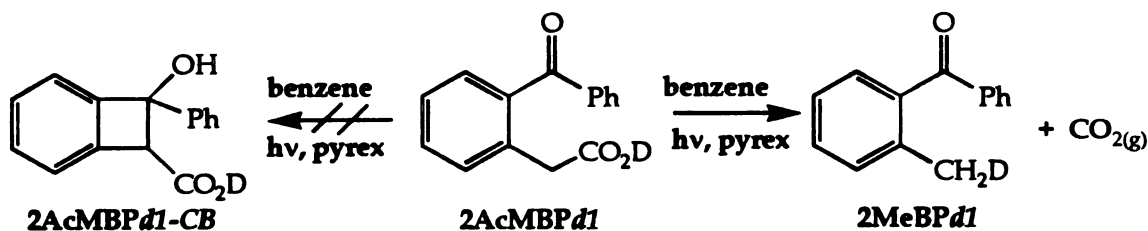


Figure 11. ^1H -NMR Spectra of 2AcMBP a) before irradiation b) after 10 minutes irradiation c) standard 2-methylbenzophenone.

out in benzene in an IR solution cell and after 10 minutes of irradiation a bubble had formed in the cell. The FTIR spectrum showed the formation of new stretches at 2240.0 and 1662.9 cm^{-1} (see Figure 12). The stretch at 2240.0 cm^{-1} corresponds to the evolved $\text{CO}_2(\text{g})$, while the stretch at 1662.9 cm^{-1} is the carbonyl stretch for 2-methylbenzophenone (see Figure 12). Also a saturated solution of $\text{CO}_2(\text{g})$ dissolved in benzene was prepared and showed a maximum transmittance of 53% in the same solution cell which is similar to the value obtained during the irradiation of 2-PABP which had a maximum transmittance of 60%.



Scheme 50. Photochemistry of deuterio (2-benzoylphenyl)acetic acid.

The deuterio acid 2AcMBPd1 was synthesized in order to elucidate the fate of deuterium atom when photolyzed. A 0.01M benzene solution of 2AcMBPd1 was degassed and irradiated in a Rayonet reactor (300 nm, $\sim 40^\circ\text{C}$). The progress of the reaction was monitored by ^2H -NMR and was complete after 20 minutes (see Figure 13). ^2H -NMR analysis showed the disappearance of the broad RCOOD peak at 2.5 ppm with the simultaneous growth of a sharp singlet at 2.25 ppm. This new singlet is consistent with the formation of 2MeBP-d₁.

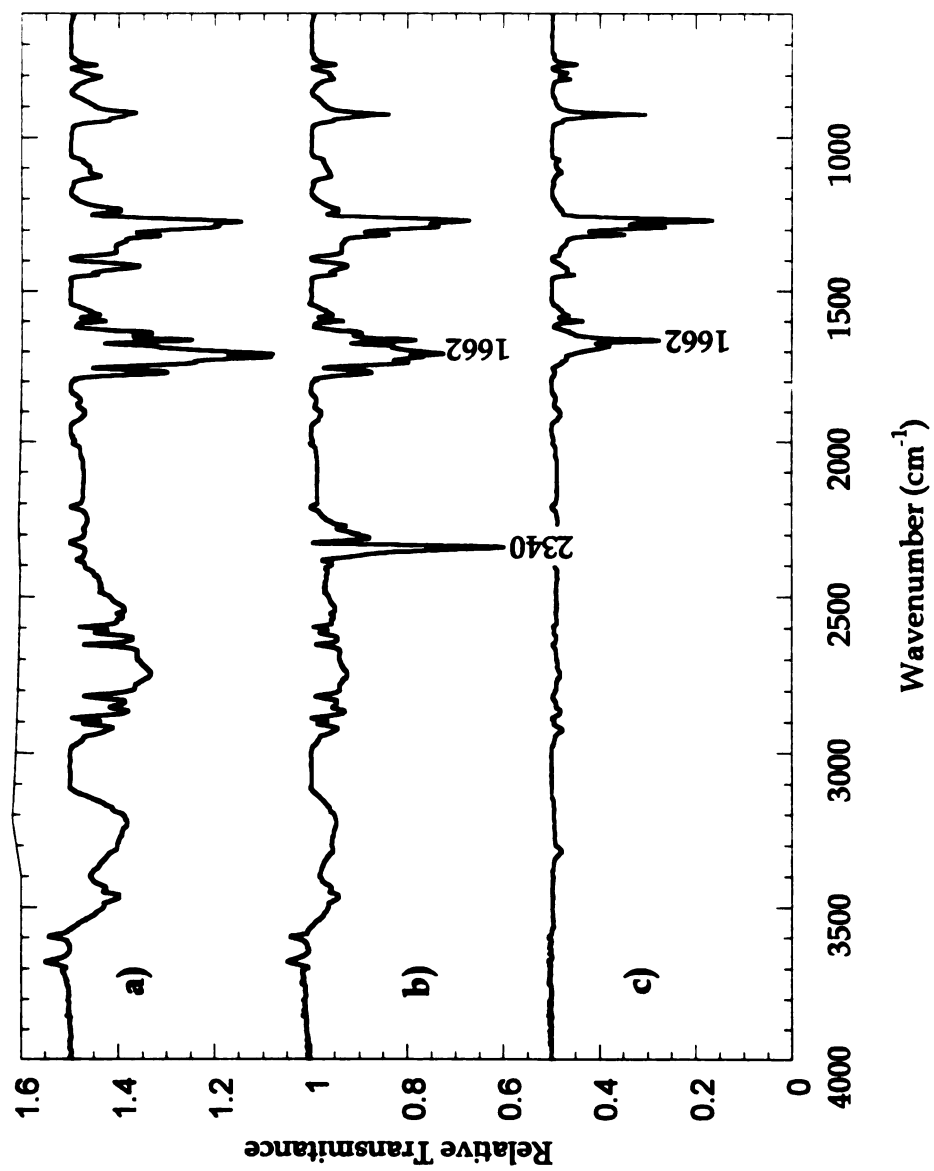


Figure 12. Infrared transmittance spectra of (a) 2AcMBP before irradiation (b) 2AcMBP after 10 minute irradiation (c) authentic 2MeBP. All spectra acquired in benzene.

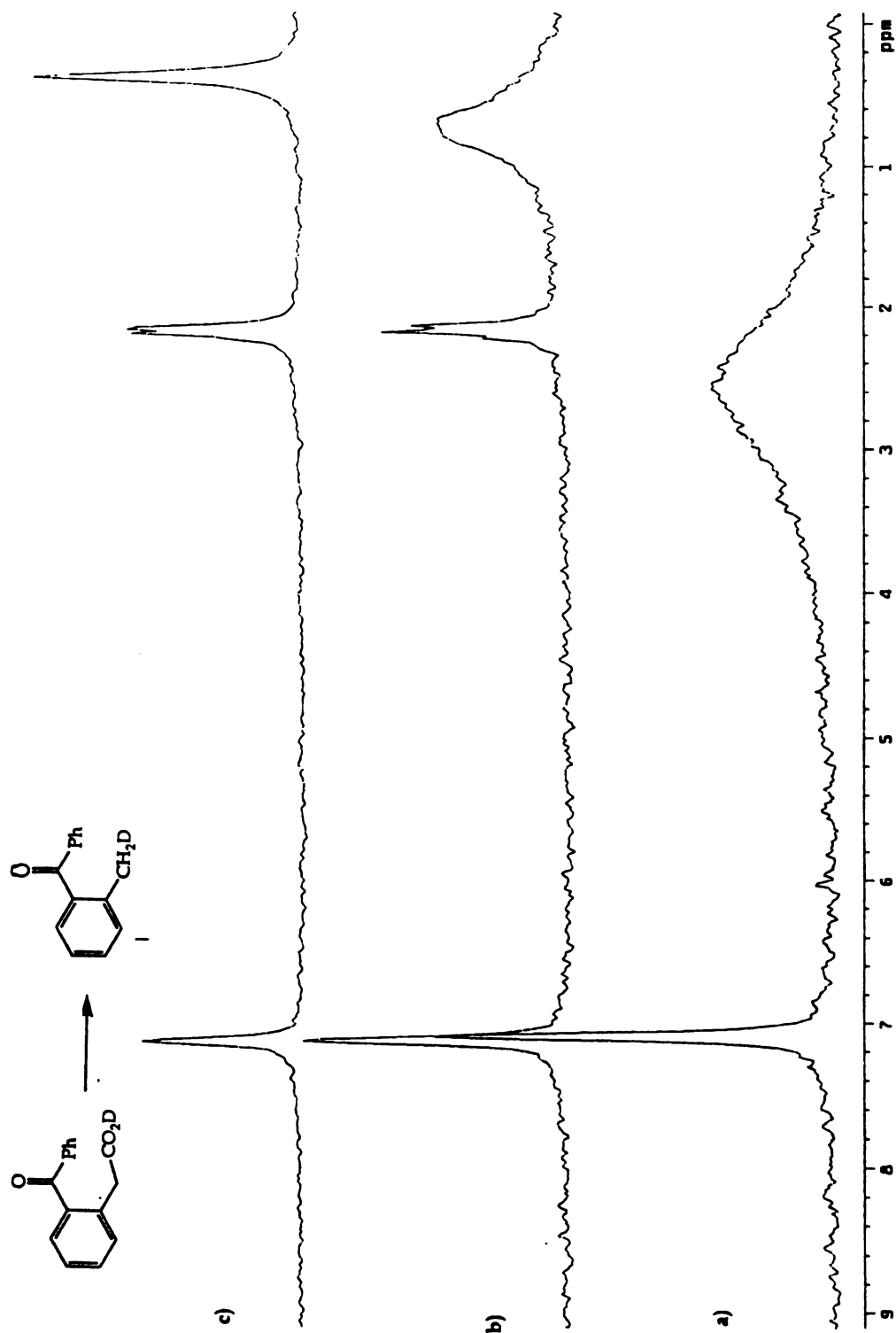
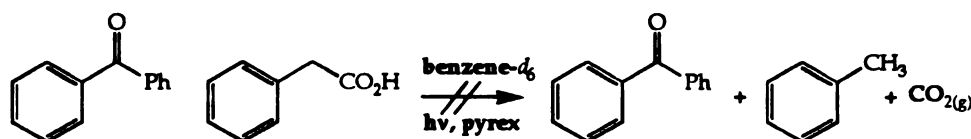


Figure 13. ²H-NMR Spectra of 2AcMBPd1 in benzene a) before irradiation b) after 20 minutes irradiation c) after 110 minutes irradiation..

A 0.01M benzene- d_6 solution of 2AcMAP d_1 was degassed and irradiated in a Rayonet reactor (300 nm, $\sim 40^\circ\text{C}$). The progress of the reaction was monitored by ^1H -NMR and was complete after 32 minutes. ^1H -NMR analysis (see Figure 14) showed the disappearance of the benzylic methylene singlet of 2AcMAP d_1 at 3.60 ppm with the simultaneous growth of a sharp singlet at 2.21 ppm and a deuterium coupled peak at 2.15 ppm (t, 1:1:1, $J = 2.1$ Hz). The combined integration of these two new peaks correlated to $\sim 50\%$ conversion after 5 minutes of irradiation. Mass spectral analysis was conducted on the reaction mixture (after the 32 minutes of irradiation, see Figure 15). The mass spectrum was compared to the fragmentation pattern of authentic 2MBP (see Figure 16) and shows a 1:1 ratio of mono:di deuterated (benzylic position) 2MBP judged from the intensity of the fragments at $m/e = 120$ and 121.



A benzene- d_6 solution of phenylacetic acid (0.15 M) and benzophenone (0.12 M) was irradiated in order to sensitize the decarboxylation. The reaction was monitored by ^1H -NMR analysis. The spectrum of the mixture did not change significantly after 30 hours of irradiation but several small peaks were visible with chemical shifts in the ranges of 2.4-2.7, and 4.0-5.1 ppm, there was also a small peak at ~ 2.05 ppm. No attempts were made to isolate these products since their chemical yields were so low.

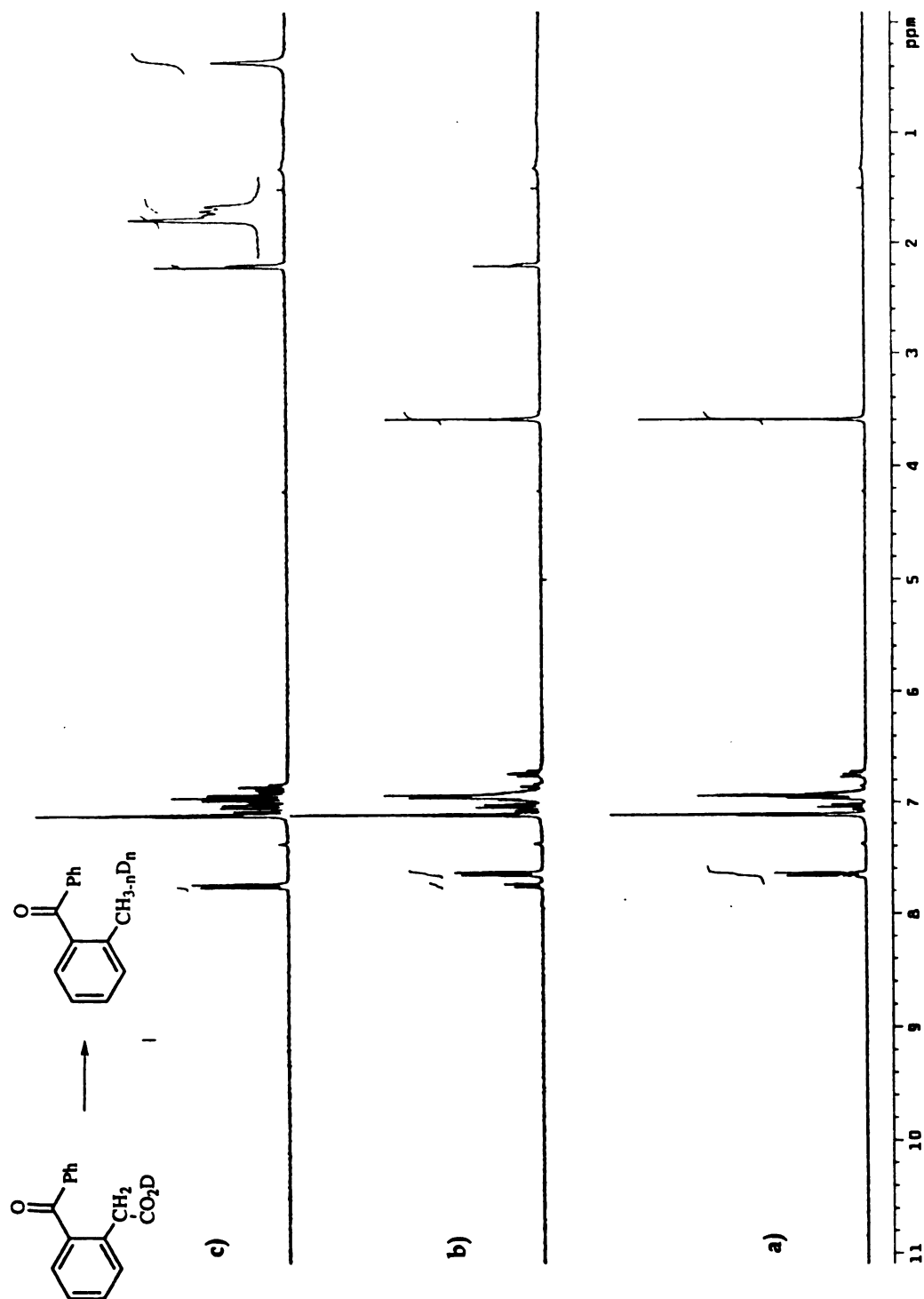
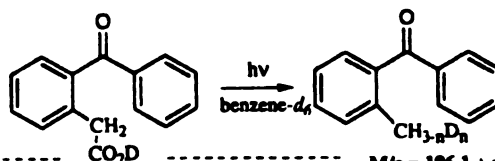
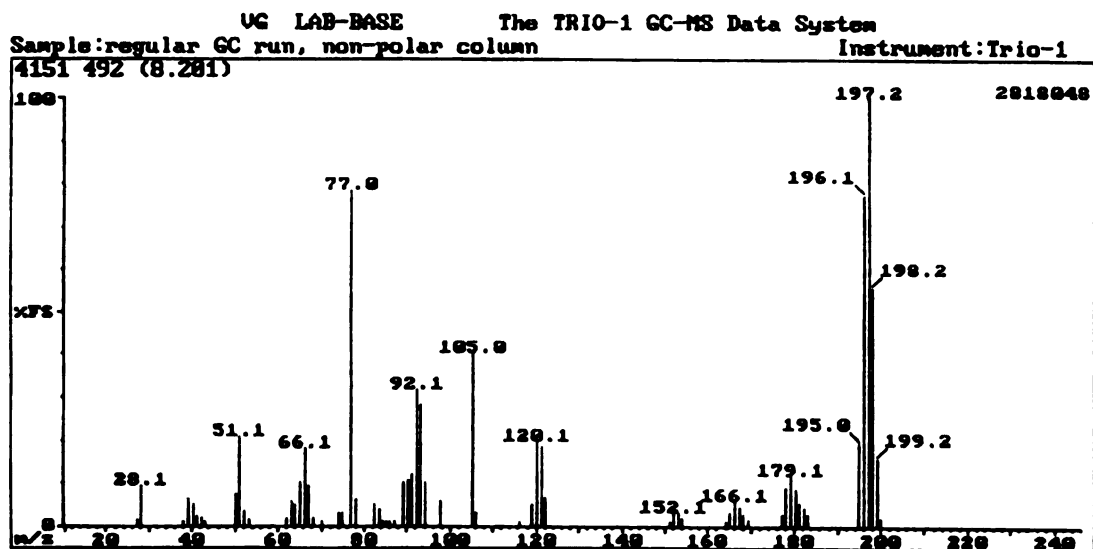
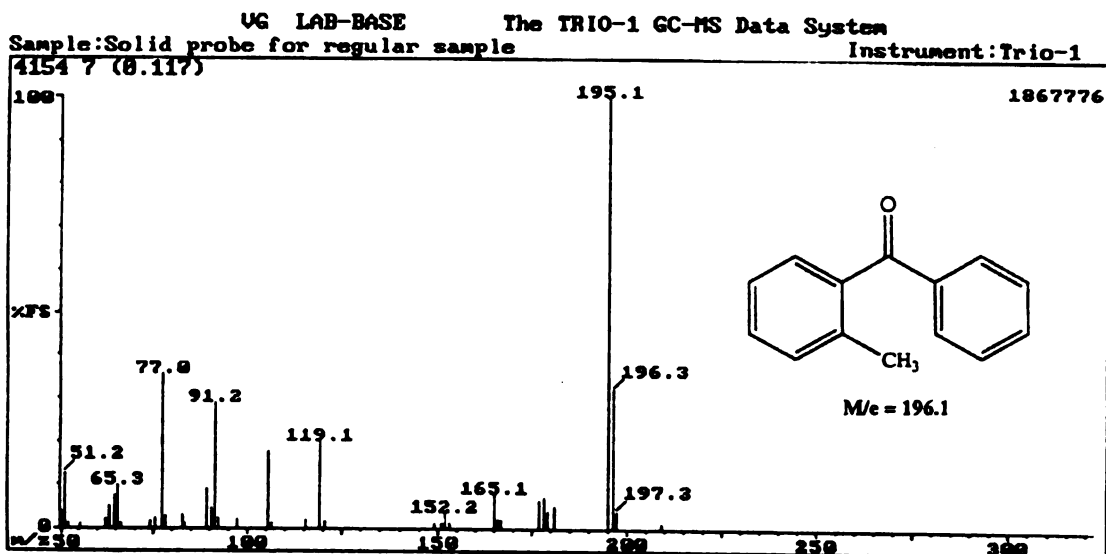


Figure 15 a) 2AcMBPd1 before irradiation in benzene- d_6 b) after 5 min. irradiation c) after 32 min. irradiation.



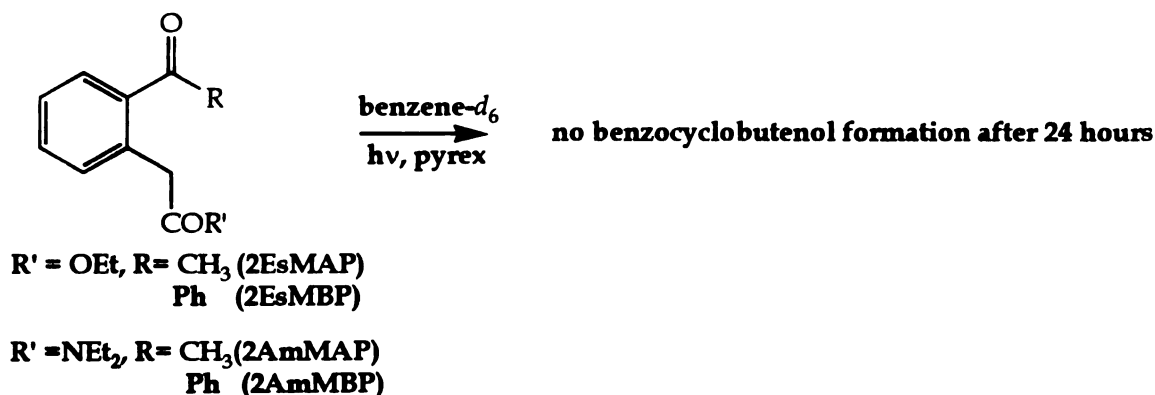
4151 492 (8.201)				M/e = 196.1 + n				2818048			
Pk#	Mass	Abs Int	Rel Int	Pk#	Mass	Abs Int	Rel Int	Pk#	Mass	Abs Int	Rel Int
1	27.1	47360	1.68	35	93.1	790528	28.05				
2	28.1	262144	9.30	36	94.1	282624	10.03				
3	38.1	30464	1.08	37	97.7	162816	5.78				
4	39.1	177152	6.29	38	105.0	1130496	40.12				
5	40.1	144384	5.12	39	106.1	86016	3.05				
6	41.1	66560	2.36	40	116.1	32000	1.14				
7	42.1	50432	1.79	41	119.0	141312	5.01				
8	43.1	29184	1.04	42	120.1	544768	19.33				
9	50.0	204800	7.27	43	121.2	512000	18.17				
10	51.1	585728	20.78	44	122.2	187392	6.65				
11	52.1	96256	3.42	45	151.1	34048	1.21				
12	53.1	42752	1.52	46	152.1	89088	3.16				
13	62.0	56320	2.00	47	153.1	92160	3.27				
14	63.1	168960	6.00	48	154.1	51456	1.83				
15	64.1	139264	4.94	49	164.1	28928	1.03				
16	65.1	286720	10.17	50	165.1	84992	3.02				
17	66.1	499712	17.73	51	166.1	159744	5.67				
18	67.1	266240	9.45	52	167.1	119808	4.25				
19	68.1	51712	1.84	53	168.1	73728	2.62				
20	70.0	28928	1.03	54	169.1	42752	1.52				
21	74.0	92160	3.27	55	177.1	75776	2.69				
22	75.1	88064	3.13	56	178.1	257024	9.12				
23	77.0	221840	78.49	57	179.1	331776	11.77				
24	78.1	171008	6.07	58	180.1	243712	8.65				
25	82.3	144384	5.12	59	181.1	152576	5.41				
26	83.5	111616	3.96	60	182.1	125952	4.47				
27	84.3	35072	1.24	61	183.1	75776	2.69				
28	85.0	32768	1.16	62	195.0	540672	19.19				
29	86.0	28416	1.01	63	196.1	2179072	77.33				
30	87.1	34816	1.24	64	197.2	2818048	100.00				
31	89.0	286720	10.17	65	198.2	1572864	55.81				
32	90.1	299008	10.61	66	199.2	434176	15.41				
33	91.1	339968	12.06	67	200.2	50688	1.80				
34	92.1	884736	31.40								

Figure 15 Mass spectrum of 2AcMBPd₁ after 32 min. irradiation in benzene-d₆.



4154 7 (0.117)				1867776			
Pk#	Mass	Abs Int	Rel Int	Pk#	Mass	Abs Int	Rel Int
1	50.3	70656	3.78	21	105.1	327680	17.54
2	51.2	234496	12.55	22	106.3	19968	1.07
3	52.2	24320	1.30	23	115.1	39168	2.10
4	55.3	24320	1.30	24	119.1	368640	19.74
5	62.2	38400	2.06	25	120.3	28672	1.54
6	63.2	92160	4.93	26	149.1	20224	1.08
7	64.7	138240	7.40	27	151.2	20224	1.08
8	65.3	181248	9.70	28	152.2	65024	3.48
9	66.2	18944	1.01	29	153.2	22784	1.22
10	74.1	30720	1.64	30	165.1	148480	7.95
11	75.2	40448	2.17	31	166.2	34560	1.85
12	77.0	659456	35.31	32	167.2	37632	2.01
13	78.2	49152	2.63	33	177.1	115712	6.20
14	82.4	58624	3.14	34	178.2	133120	7.13
15	83.3	23040	1.23	35	179.2	75776	4.06
16	89.1	167936	8.99	36	181.1	93184	4.99
17	90.2	88064	4.71	37	195.1	1867776	100.00
18	91.2	540672	28.95	38	196.3	593920	31.80
19	92.3	44800	2.40	39	197.3	69632	3.73
20	97.2	39936	2.14	40	209.2	19968	1.07

Figure 16 Mass spectrum of authentic 2-methylbenzophenone.

2-Acetyl and Benzoylphenylacetic acid derivatives**Scheme 51. Photochemistry of *o*-Acetyl and Benzoylphenylacetic acid derivatives**

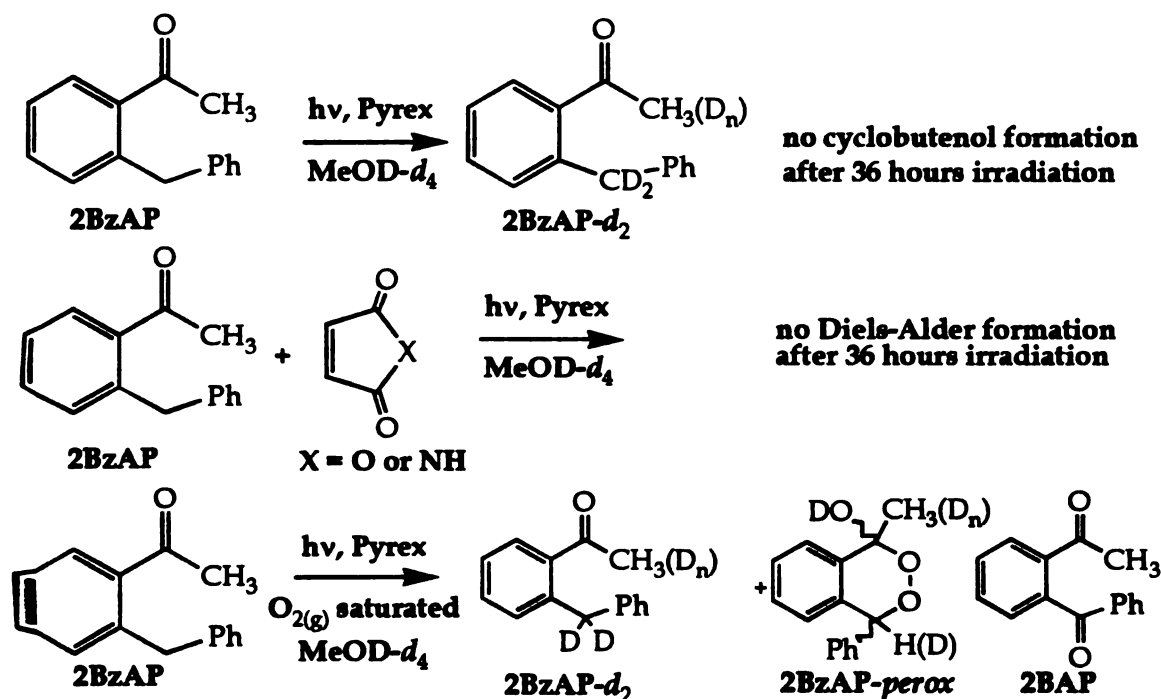
The ketones 2AmMAP, 2AmMBP, 2EsABP and 2EsMBP were irradiated as 0.01 M benzene- d_6 solutions through Pyrex filtered light from a medium pressure Mercury arc lamp. 2AmMAP and 2AmMBP did not give any appreciable photoproducts after 24 hours of irradiation. This is an especially long time to irradiate *o*-alkyl benzophenones which normally have quantum efficiencies from 0.10 to 1.0 and show significant product formation within 10-20 minutes.

Irradiation of 2EsABP gave no products after 24 hours of irradiation in benzene- d_6 . No products were visible by ^1H -NMR analysis after 30 minutes of irradiation of 2EsMBP in benzene- d_6 . After 5 hours of irradiation, the reactor setup had warmed to 55°C and two products had formed in approximately a 2:1 ratio. The ^1H -NMR spectrum showed two new triplets in a 2:1 ratio at 0.502 and 0.875 ppm, two new quartets in a 2:1 ratio 3.24 and 3.54 ppm, and two new doublets at 7.20 and 8.50 ppm. The solution consisted of mainly starting ketone

(~90%). The irradiation was continued for 48 hours and the two product peak intensities grew and at least two more additional products had formed. The spectrum had become very complicated with at least four triplets in the range of 0.50-0.95, four quartets in the range of 3.20-4.10, an AB quartet at 3.12 ppm, three singlets between 4.60 and 4.90 ppm, a singlet at 5.7 ppm, and three sets of doublets between 6.3 and 6.6 ppm and a complicated aromatic region. No attempts were made to isolate the products.

4. 2-benzylacetophenone (2BzAP) and 2-benzylbenzophenone (2BzBP)

2-benzylacetophenone (BzAP)



Scheme 52. Photochemistry of o-benzylacetophenone

Several crystals (~25 mg) of 2-Benzylacetophenone (2-BzAP) were packed into a capillary tube which was placed in an NMR tube and deaerated by the usual procedure. The tube was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp for 24 hours and then the capillary broken and the solid dissolved in chloroform- d_1 . ^1H -NMR analysis showed only starting ketone and no trace of any new products. However, the appearance of the crystals changed dramatically as a result of irradiation. Before irradiation the crystals were ~0.5 mm x ~1 mm but became powder-like after irradiation.

Irradiation in degassed methanol- d_4 gave primarily deuterium incorporated products. Deuterium was incorporated in both the acetyl and benzylic positions during irradiation. The methylene singlet of 2BzBP at 4.22 ppm disappeared at a faster rate than the acetyl singlet at 2.40 ppm. Four hours of irradiation in a Rayonet reactor (300 nm) produced a new broad singlet at 4.20 ppm which is attributed to deuterium incorporation. The incorporation in the benzylic position arises from photochemistry since 2BzAP left standing in the dark in methanol- d_4 after 7 days shows no incorporation in this position. Incorporation of deuterium in the acetyl position proceeds in the dark on the same time scale that the photochemistry was conducted and is most likely catalyzed by acid impurities in the methanol and is ~30% complete after 3 days.

During the irradiation in methanol- d_4 in a Rayonet reactor (300 nm, 45°C) ^1H -NMR showed the formation of a singlet at 1.06 ppm but lacked a singlet between 4.0 and 5.0 ppm (which would be expected for the 2BzAP-CB).

Irradiation in methanol or methanol- d_4 of 2BzAP with Pyrex filtered light from a mercury arc lamp at 25°C did not show this resonance. It was not clear if the product had formed in methanol (since I could not monitor by NMR without removing the protic solvent), it was possible that the product formed but thermally decomposed when the solvent was removed by rotoevaporation. To remedy this potential problem of thermal lability the solvent was removed with a stream of air instead of heating, again no product was observed after 48 hours of irradiation.

In order to elucidate if the photoenol was generated, attempts were made to trap the intermediate in a Diels Alder reaction. Maleic anhydride and oxygen were employed as dienophiles. The trapping of 2BzAP with oxygen led to a mixture of products, mainly two different cyclic peroxides (2BzAP-*perox*) and 2-benzoylacetophenone (2BAP). The peroxides were formed in methanol, methanol- d_4 , benzene- d_6 and acetonitrile- d_4 by purging the sample with a continuous stream of oxygen for twenty minutes followed by irradiation. The formation of 2BzAP-*perox* was independent of light source and could be formed by irradiation with either a medium pressure mercury arc lamp (Pyrex filtered, 17-20°C) or in a Rayonet reactor (300 nm lamps). To get complete conversion of 2BzAP to the peroxides, it was necessary to have the 2BzAP concentration more dilute than usual (0.001 M) since a ketone concentration of 0.01 M exceeded the concentration of dissolved oxygen. The formation of the peroxides was observed by ^1H -NMR analysis which showed two singlets at 6.06 (1H) and 6.02 ppm (1H),

two doublets at 6.69 ($J = 8.1$ Hz, 1H) and 6.99 ppm (7.8 Hz, 1H), and one methyl singlet at 1.65 ppm (6H) in methanol- d_4 . The integration of these peaks in methanol- d_4 was not accurate since some of the peroxide was generated from a deuterated ketone (resulting from incorporation of deuterium into the enol intermediate). This was shown by ^2H -NMR analysis of the same sample in CH_3OH . The CH_3OH was removed after the ^2H -NMR was acquired and the sample dissolved in chloroform- d_1 . The ^1H -NMR spectrum showed *two* methyl signals at 1.70 and 1.74 ppm, accompanied by two broad singlets at 3.56 and 3.69 ppm which are assigned to the hydroxy groups of the peroxide. For details of the ^1H -NMR and ^2H -NMR analysis see Figure 17. To remedy the problem of having products with incorporated deuterium, photolysis was conducted in CH_3OH under aerobic conditions. Integration of the benzylic methine hydrogens of the peroxide generated in CH_3OH gave a ratio of 1:1 (δ 6.29 ppm : δ 5.98 ppm). Another product was detected when 2BzAP was irradiated in oxygen saturated methanol- d_4 which had a singlet at 2.50 ppm in the ^1H -NMR spectrum. This product was identified as 2-Benzoylacetophenone (2BAP) and was isolated by PTLC. Its spectrum was consistent with previous reports of 2BAP being generated from 2-benzyloxyacetophenone.¹¹⁵

Irradiation of 2BzAP in degassed benzene- d_6 , acetonitrile- d_4 or acetone- d_6 solutions gave no significant product formation after 48 hours irradiation. However, several small peaks formed at ~ 1 ppm but no attempt was made to isolate these minor components. A benzene- d_6 solution with excess maleic

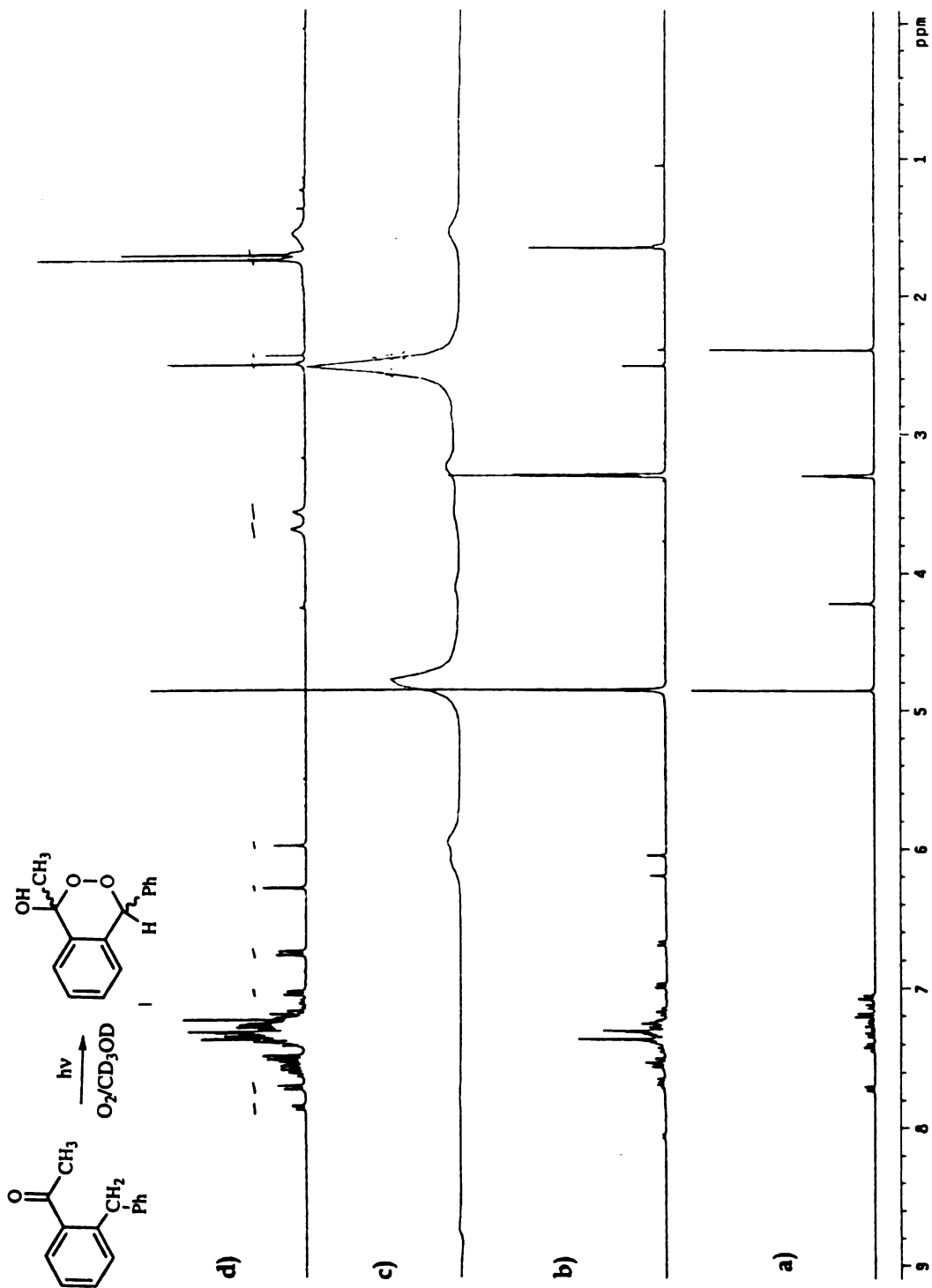
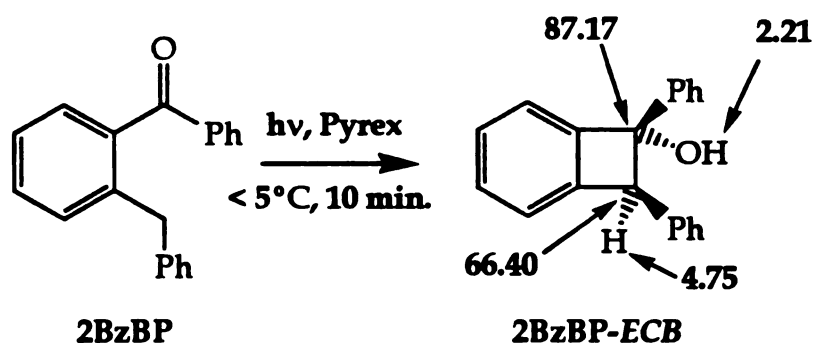


Figure 17 a) 2BzAP before irradiation in O_2 sat. methanol- d_4 , b) after 24 h. irradiation c) 2H -NMR of sample (b) in methanol d) 1H -NMR of sample (c) in chloroform- d_1 .

anhydride gave no products after 48 hours under identical reaction conditions. A methanol- d_4 solution of 2BzAP with excess maleic anhydride present gave no products after 36 hours of irradiation. A methanol- d_4 solution of 2BzAP with excess maleimide present gave no products after 36 hours of irradiation. However, the maleimide had disappeared but the ketone remained. The solution had turned a faint dingy-yellow color accompanied by the formation of a precipitate after the irradiation.

2-benzylbenzophenone (2BzBP)



Scheme 53. Photochemistry of 2BzBP, Chemical shifts (ppm) for ^1H in benzene- d_6 , for ^{13}C in CD_3CN .

Irradiation of 0.01-0.10 M 2BzBP in acetonitrile- d_4 , benzene- d_6 , methanol- d_4 and toluene- d_8 at temperatures of 0°C and -72°C gave 2BzBP-ECB quantitatively within 10 minutes. The formation of 2BzBP-ECB was independent of light source and could be formed by irradiation with either a medium pressure mercury arc lamp (Pyrex filtered) or in a Rayonet reactor (300 nm lamps), but the temperature had to be carefully maintained ($<5^{\circ}\text{C}$). The quantum

yield for 2BzBP-ECB formation was measured with Pyrex filtered light in a immersion well setup (not corrected for different Hg line intensities) by ^1H -NMR and found to be 0.095 (13% conversion). The benzylic methylene singlet at 4.02 ppm (of 2BzBP) disappeared at the same rate as the growth of a two singlets at 2.21 (broad) and 4.75 ppm in benzene- d_6 . For details of the equivalent reaction conducted in acetonitrile- d_4 , see Figure 18. The broad peak at 1.21 ppm disappeared when washed with deuterium oxide, indicating that it was a hydroxy group. The ^{13}C -NMR spectrum of 2BzBP-ECB had 16 unique carbon resonances, 14 aromatics and two aliphatics (66.40 and 87.17 ppm); for details see Figure 19. These aliphatic resonances are consistent with a benzocyclobutenol structure. The ^{13}C -NMR spectrum of *E*-1-phenyl-2-methyldihydrobenzocyclobutenol (2EtBP-ECB) was acquired at -30°C in acetonitrile- d_4 and used as a model structure since it had been previously characterized by Park. The two analogous aliphatic carbon atoms of 2EtBP-ECB have resonances at 54.86 and 84.67 ppm.

The reaction was sensitive to oxygen, temperature and irradiation time. Also, how the sample was handled after irradiation was complete was extremely important. The 2BzBP-ECB was stable at -72°C (a sample was stored for one week in a mixture of EtOH/ $\text{CO}_2(\text{s})$ in a dewar) but decomposed rapidly at room temperature to give the starting ketone.

When the photochemistry was conducted at room temperature (in acetonitrile- d_4 , benzene- d_6 or toluene- d_8) it was not possible to push the reaction

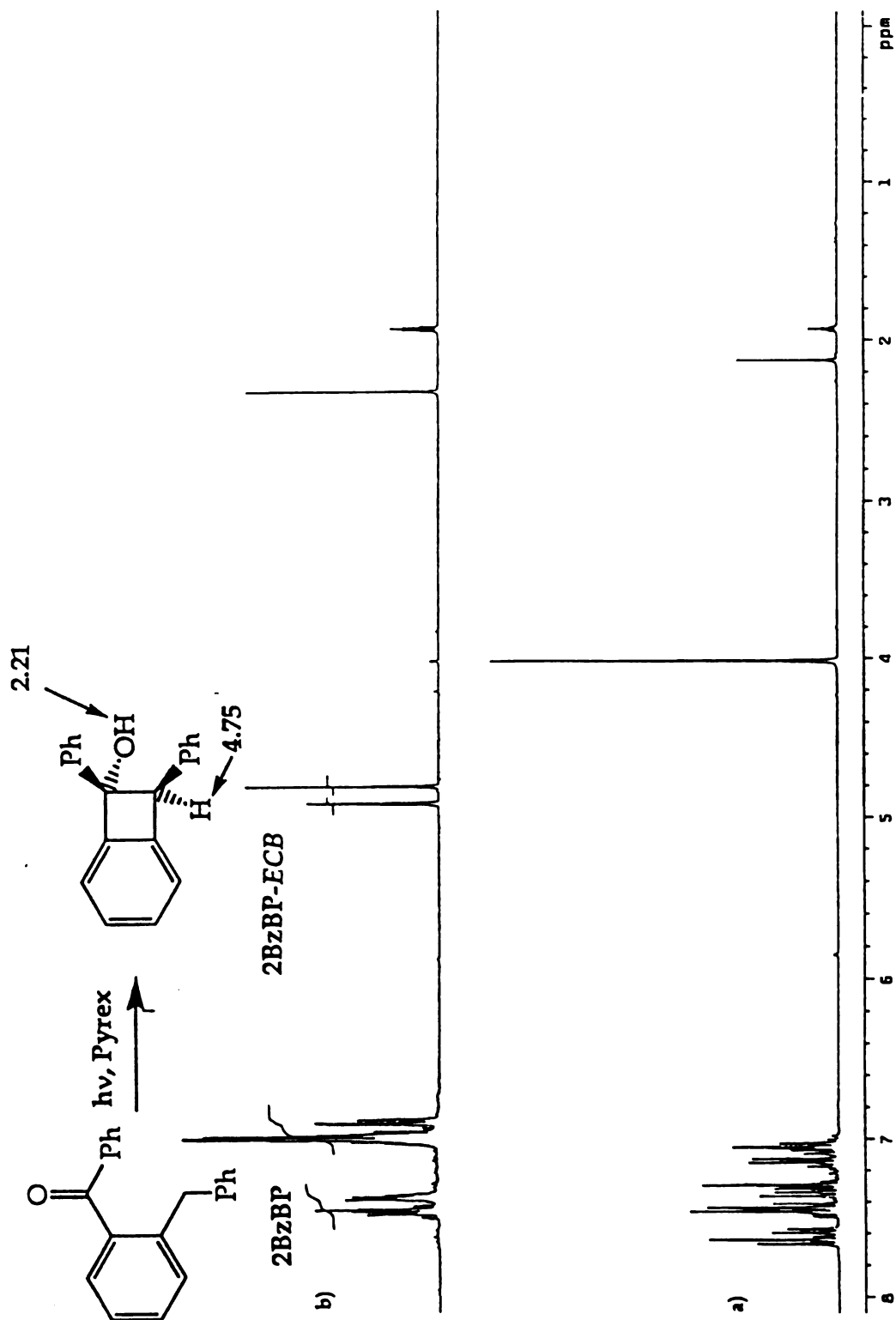


Figure 18. $^1\text{H-NMR}$ Spectra of 2BzBP at -30°C in CD_3CN a) before irradiation b) after 20 minutes irradiation.

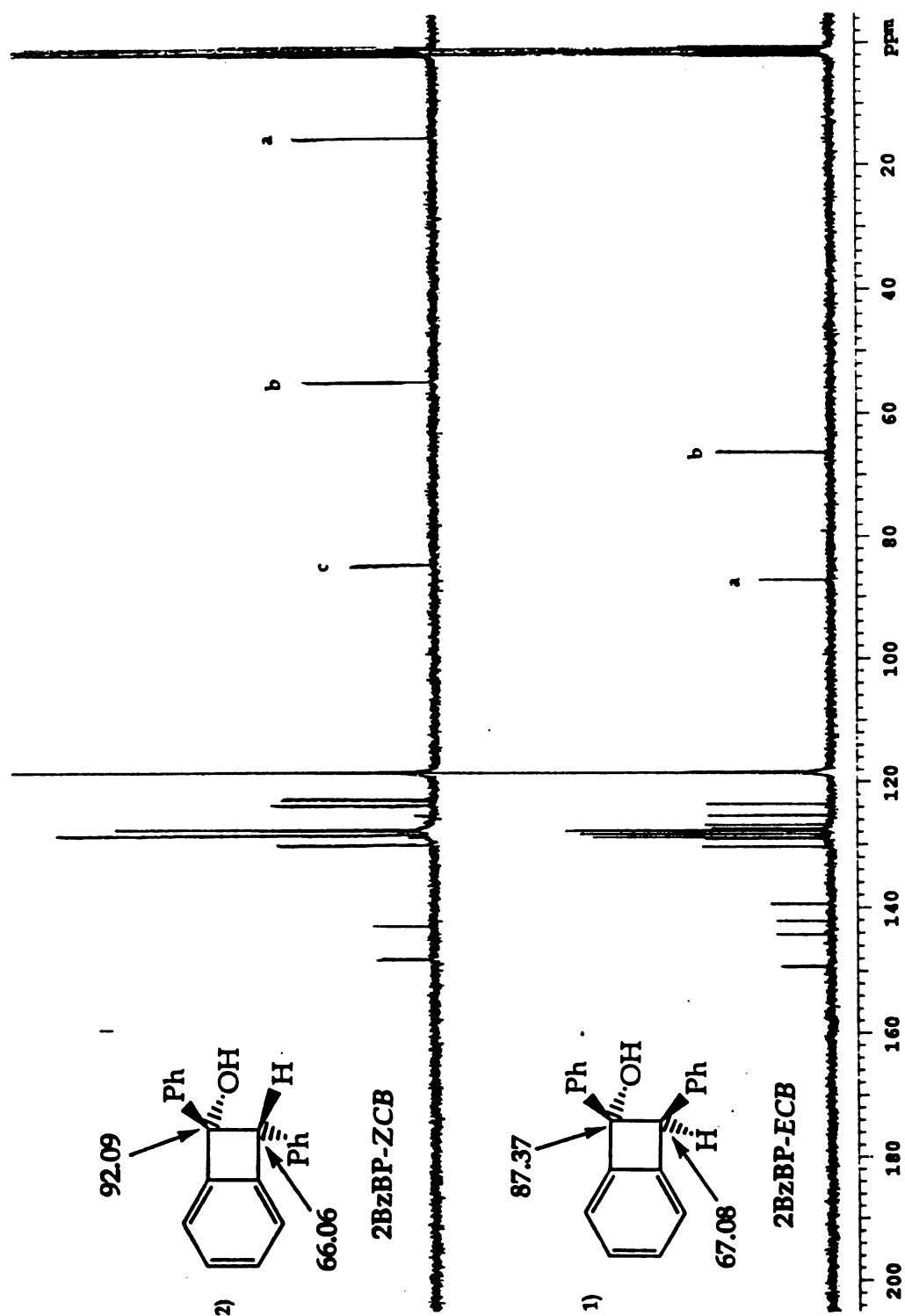
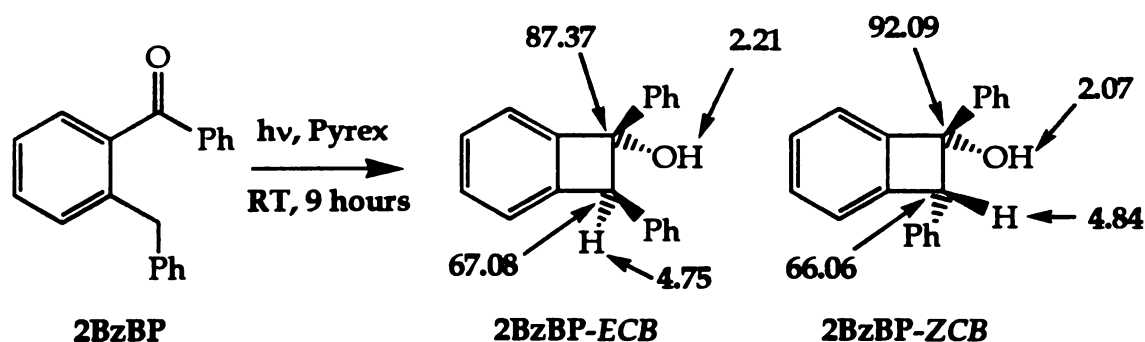


Figure 19. ^{13}C -NMR Spectra at -30°C in CD_3CN 1) 2BzBP-ECB 2) 2EtBP-ECB.

to completion (i.e. complete conversion to 2BzBP-ECB) After 9 hours of irradiation (Pyrex filtered light in immersion well setup, 17-20°C) of a 2BzBP benzene- d_6 solution, ^1H -NMR analysis indicated the reaction mixture contained 2BzBP, 2BzBP-ECB and a third product. The unidentified product had two



Scheme 54. Prolonged irradiation of 2BzBP at RT, chemical shifts (ppm) in benzene- d_6 .

significant resonances at 2.07 (broad) and 4.84 ppm. The broad peak at 2.07 disappeared when washed with deuterium oxide. The ^{13}C -NMR of the mixture in benzene- d_6 showed two new aliphatic resonances at 67.08 and 92.09 ppm indicating a benzocyclobutenol structure (for 2BzBP-ECB in benzene- d_6 the chemical shifts are 67.08 and 87.37 ppm). This third product is assigned to 2BzBP-ZCB based on these spectral properties. Prolonged irradiation of the same sample (~48 hours) gave a mixture of products with no aliphatic peaks and complex vinyl and aromatic regions.

When 2BzBP is irradiated with Pyrex filtered light in a ethanol glass at 77°K a dark orange-amber matrix is formed. This color persists until the sample is warmed; it disappears at -72°C and a light yellow color remains. Irradiation in a toluene glass gives the same color, but it is not as intense. For every experiment

that was conducted a fluorescent green color persisted after irradiation. The intensity always (reaction was done >25 times) increased with time and warming of the sample (even warming from 0→25°C). ¹H-NMR analysis of the fluorescence showed only starting ketone (on occasion there were very small vinyl peaks but were not required for the color). A UV and fluorescence spectrum (see Figure 20) were acquired but the structure is still not known.

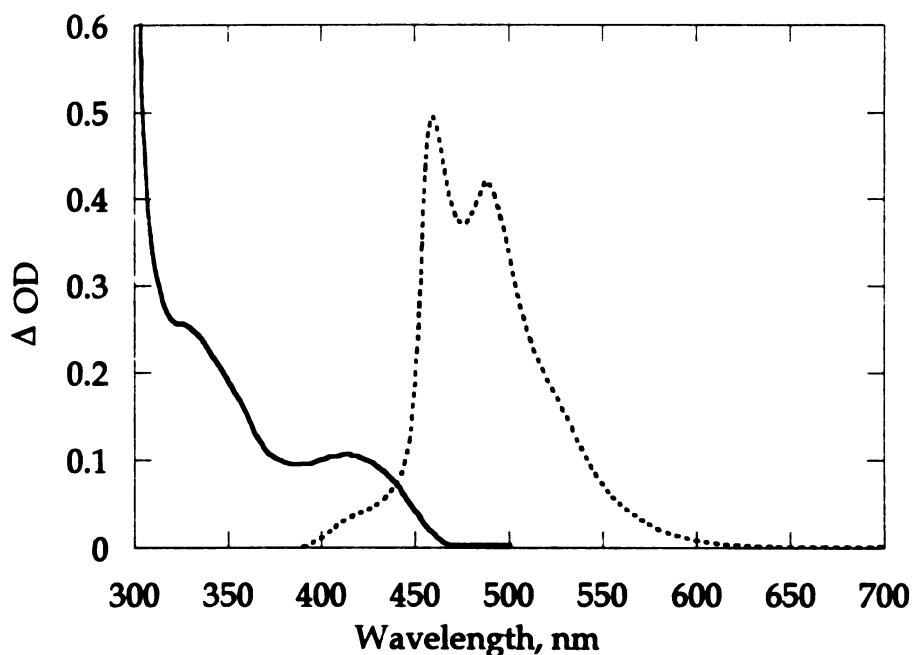


Figure 20. Fluorescence and absorption spectrums of fluorescent green sample in benzene. Sample irradiated in Pyrex UV cuvet for 2 hours in Rayonet reactor (45°C, 300nm), fluorescenc and absorption spectra obtained at room temperature.

Irradiation of an oxygen purged 0.03 M 2BzBP benzene-*d*₆ solution in a Rayonet reactor setup (300 nm lamps) gave 2-benzoylbenzphenone (Bz2BP). After 8 hours of irradiation the benzylic hydrogens at 4.02 ppm had disappeared

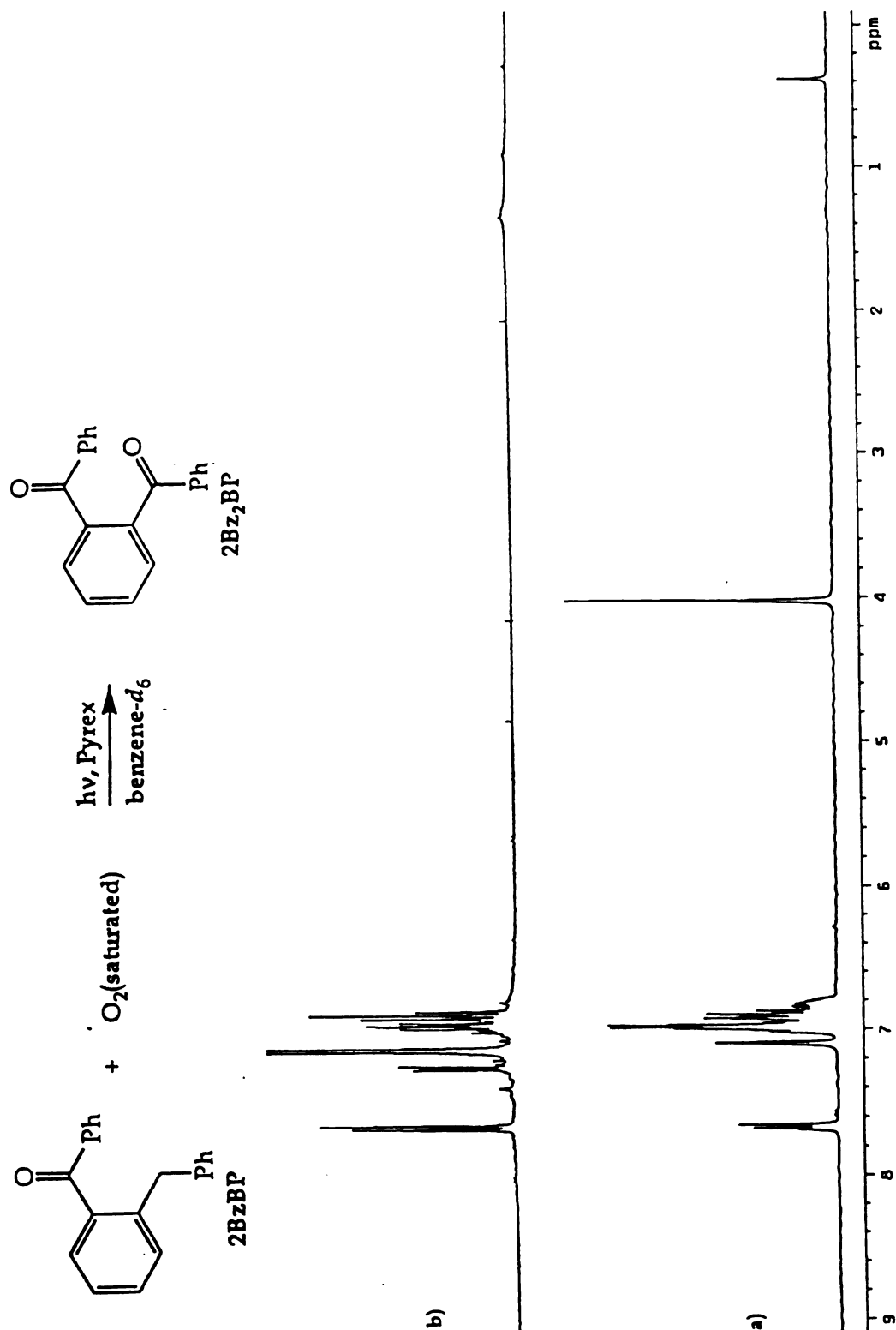
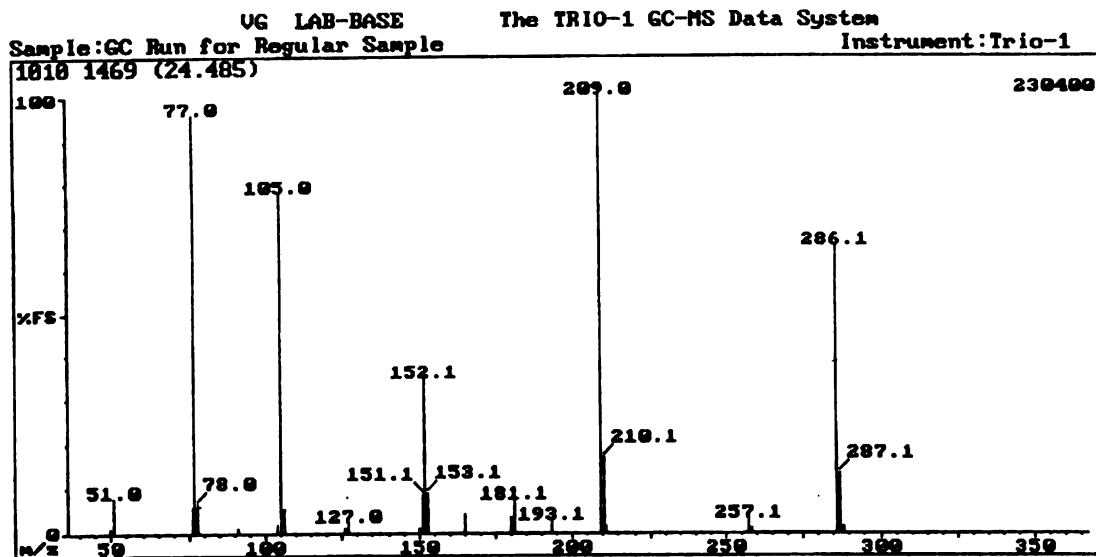
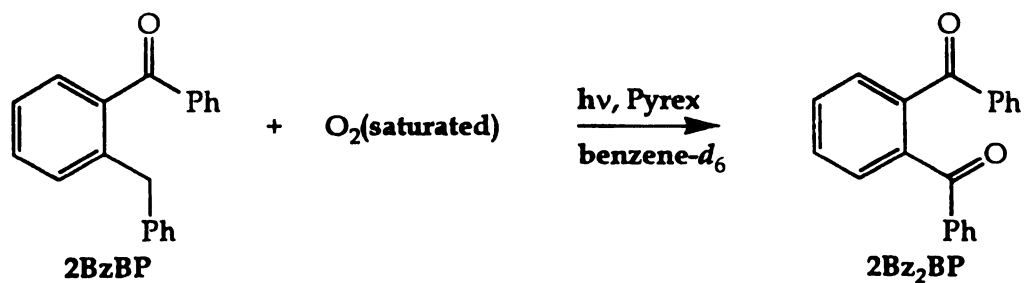


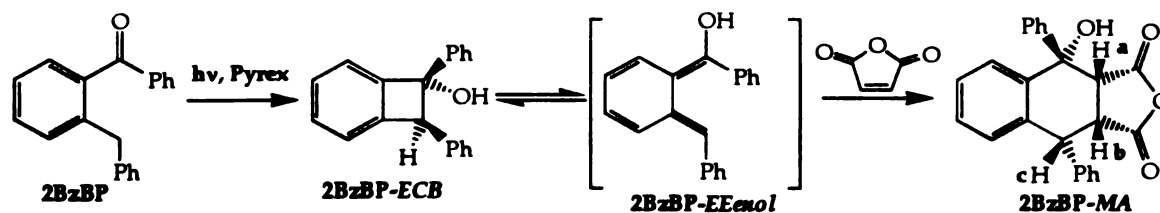
Figure 21. ¹H-NMR spectrum of 2BzBP in O₂ saturated benzene-d₆ a) before irradiation b) after 8 hours irradiation.



1010 1469 (24.485)						230400		
Mass	Abs Int	Rel Int	Mass	Abs Int	Rel Int	Mass	Abs Int	Rel Int
50.0	2304	1.00	126.1	3072	1.33	193.1	6208	2.69
51.0	18176	7.89	127.0	5248	2.28	209.0	230400	100.00
76.0	13056	5.67	150.1	2992	1.30	210.1	38144	16.56
77.0	220160	95.56	151.1	19968	8.67	211.1	3584	1.56
78.0	15552	6.75	152.1	79872	34.67	257.1	7360	3.19
91.0	3056	1.33	153.1	20480	8.89	258.1	2416	1.05
103.9	4864	2.11	165.1	9600	4.17	286.1	150528	65.33
105.0	179200	77.78	180.1	8000	3.47	287.1	30208	13.11
106.1	12992	5.64	181.1	16896	7.33	288.1	3968	1.72

Figure 22. Mass spectrum of 2BzBP in O_2 saturated benzene- d_6 after 8 hours irradiation.

and the solution remained clear. The NMR sample solution was submitted for mass spectral analysis and the chromatograph indicated only one product and no starting ketone. There were only aromatic hydrogens evident in the ^1H -NMR spectrum. Mass spectral analysis gave an m/z peak at 286.1 which is consistent with Bz_2BP . For details of the ^1H -NMR reaction and the mass spectrum of the product, see Figure 21.



Scheme 55. Thermal chemistry of 2BzBP-CB

When the irradiation of 2BzBP was conducted at -72°C the sample color was less intense than irradiations conducted at 0°C . Introduction of a degassed maleic anhydride solution via syringe (at room temperature) to the fluorescent sample gave a Diels-Alder BzBP-MA product within minutes and was accompanied by a loss of color. The ^1H -NMR spectrum was acquired immediately (< 2 minutes, see Figure 23) after the introduction of the dienophile. The spectrum showed three new sets of peaks in the aliphatic region, a doublet of doublets at 2.77 ppm ($J = 9.3, 9.0$ Hz, 1H, b) and two doublets at 3.14 ($J = 9.3$ Hz, 1H, a) and 3.72 ppm ($J = 9.0$ Hz, 1H, c). If the reaction tube contained both 2BzBP-ECB and 2BzBP-ZCB and maleic anhydride was added via syringe, only the E isomer reacted with to give a product, the Z isomer was stable under these conditions (room temperature).

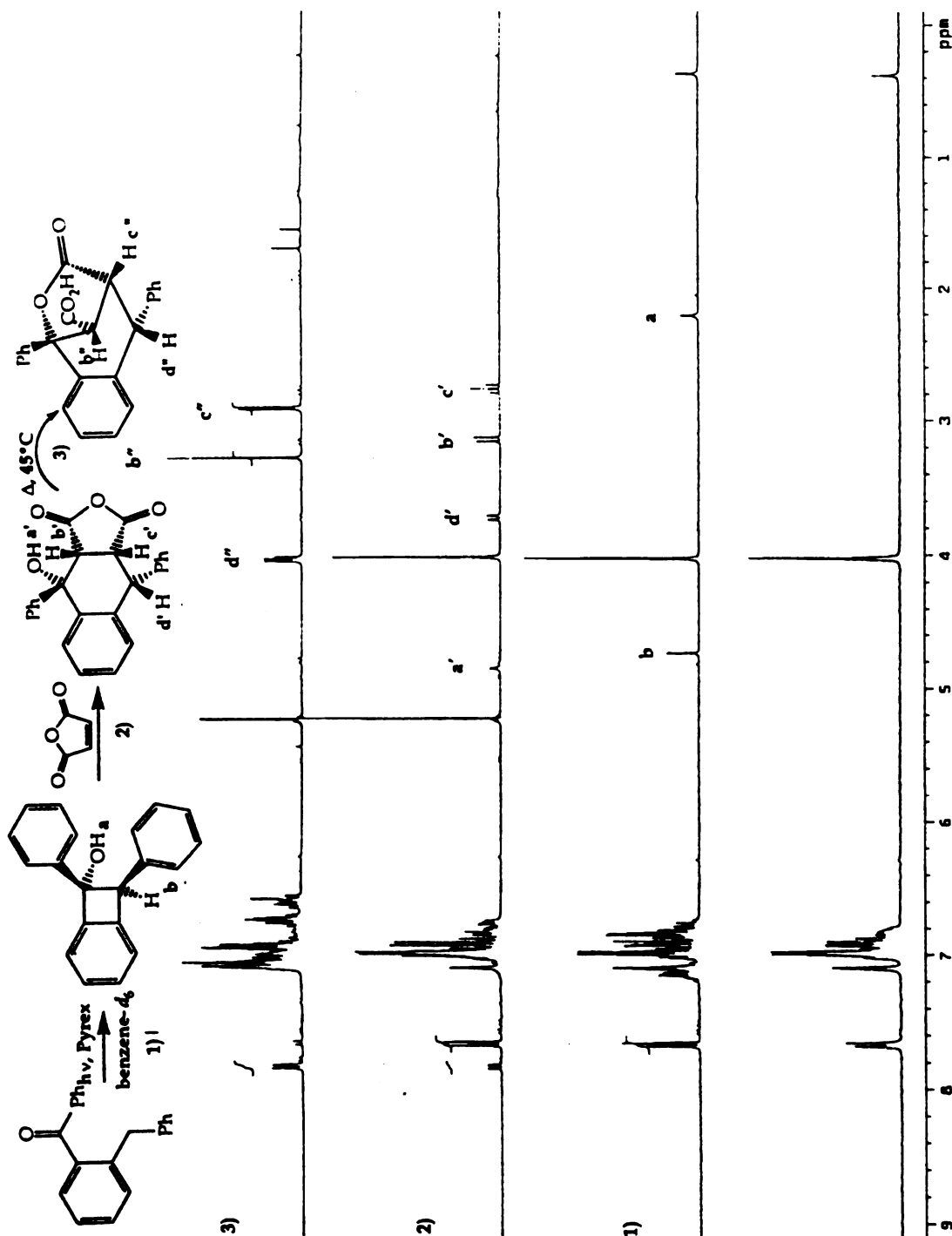
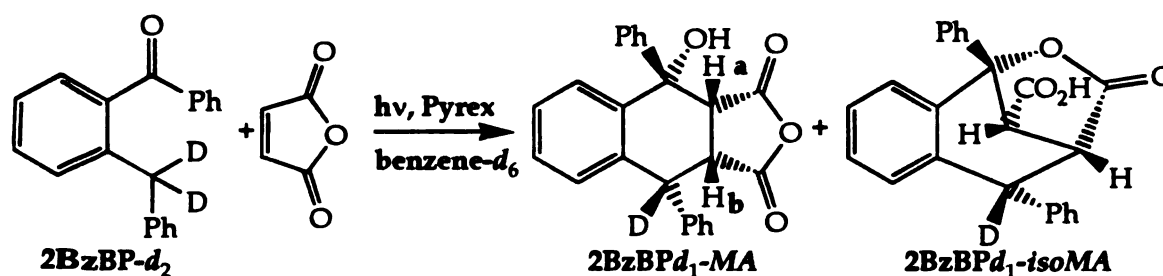


Figure 23. ^1H -NMR Spectra of 2BzBP before irradiation. in benzene- d_6 1) after 1 hour irradiation at 45°C . 2) 2 minutes after maleic anhydride added via syringe to (1). 3) heated (2) 3 hours at 75°C .

The Diels-Alder adduct could be formed by either irradiating the ketone in the presence of maleic anhydride (see Figure 24) or addition of maleic anhydride to the 2BzBP-ECB solution. The 2BzBP-MA decomposed to 2BzBP-isoMA at temperatures $>45^{\circ}\text{C}$ and if care was not taken to maintain the reaction solution's temperature, decomposition occurred during photolysis. The deuterio species 2BzBPd₂ was prepared in order to accurately assign the resonances of 2BzBP-MA. 2BzBPd₂ was irradiated in benzene-d₆ with maleic anhydride present and was completely converted to a 1:1 mixture of 2BzBPd₁-MA and 2BzBPd₁-isoMA after 7 hours of irradiation (see Figure 25). The irradiation was



conducted in a Rayonet reactor with 300nm lamps. The ¹H-NMR spectrum showed two new aliphatic doublets at 2.74 (J = 9.3 Hz, 1H, b) and 3.12 (J = 10.2 Hz, 1H, a) after 90 minutes. The spectrum lacked both the coupling of the benzylic methine to the bridgehead which formerly was a doublet of doublets at 2.77 ppm and the doublet at 3.77 ppm. Thus, the resonance at 3.77 ppm in 2BzBP-MA is assigned to benzylic methine (c) and is in agreement with the previous literature reports for this Diels-Alder adduct.¹¹⁶ The crude mixture of 2BzBPd₁-MA and 2BzBPd₁-isoMA from the irradiation of 2BzBPd₂ was

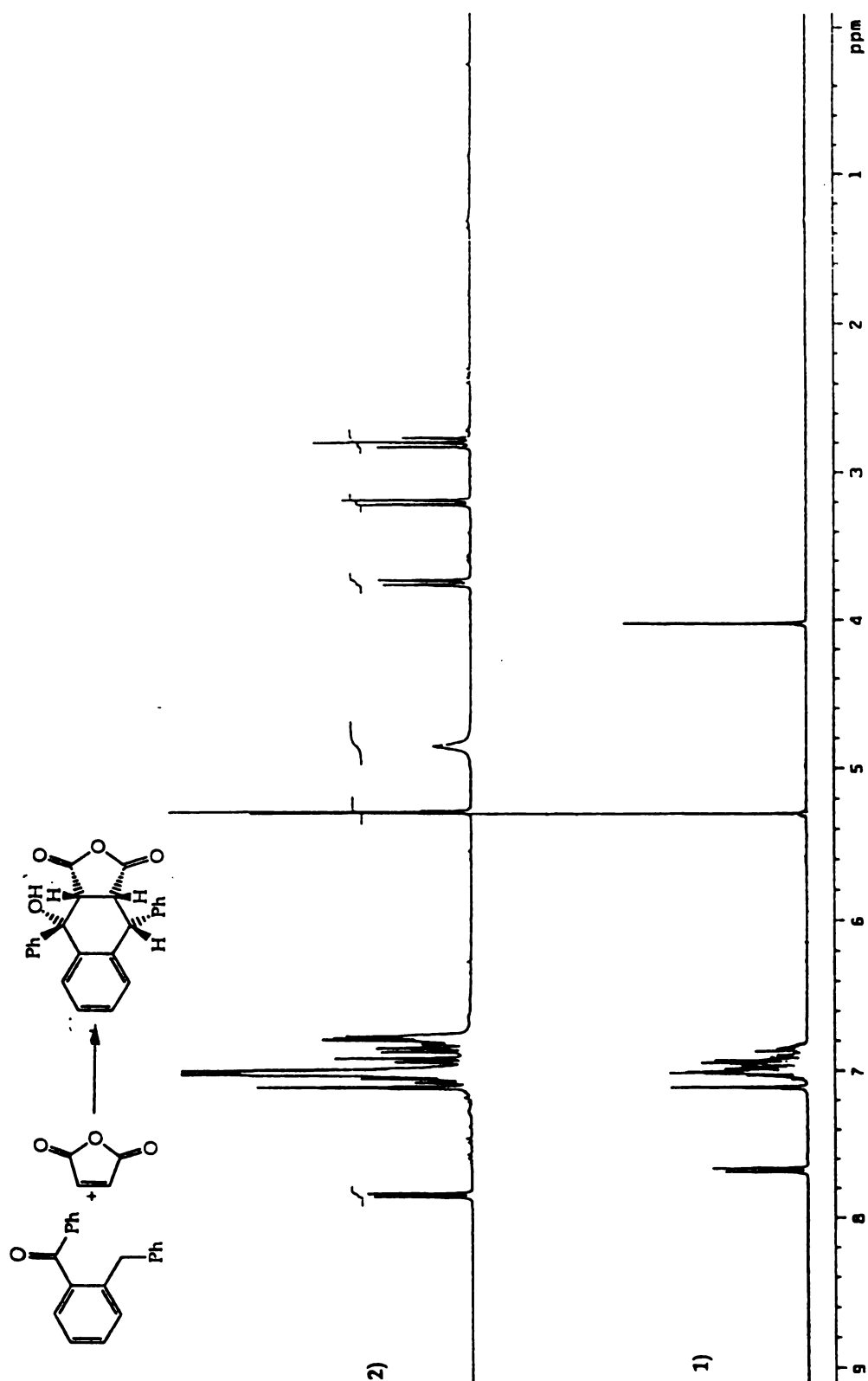


Figure 24. $^1\text{H-NMR}$ Spectra of 2BzBP in presence of maleic anhydride in benzene- d_6 1) before irradiation 2) after 1 hour irradiation at 0°C .

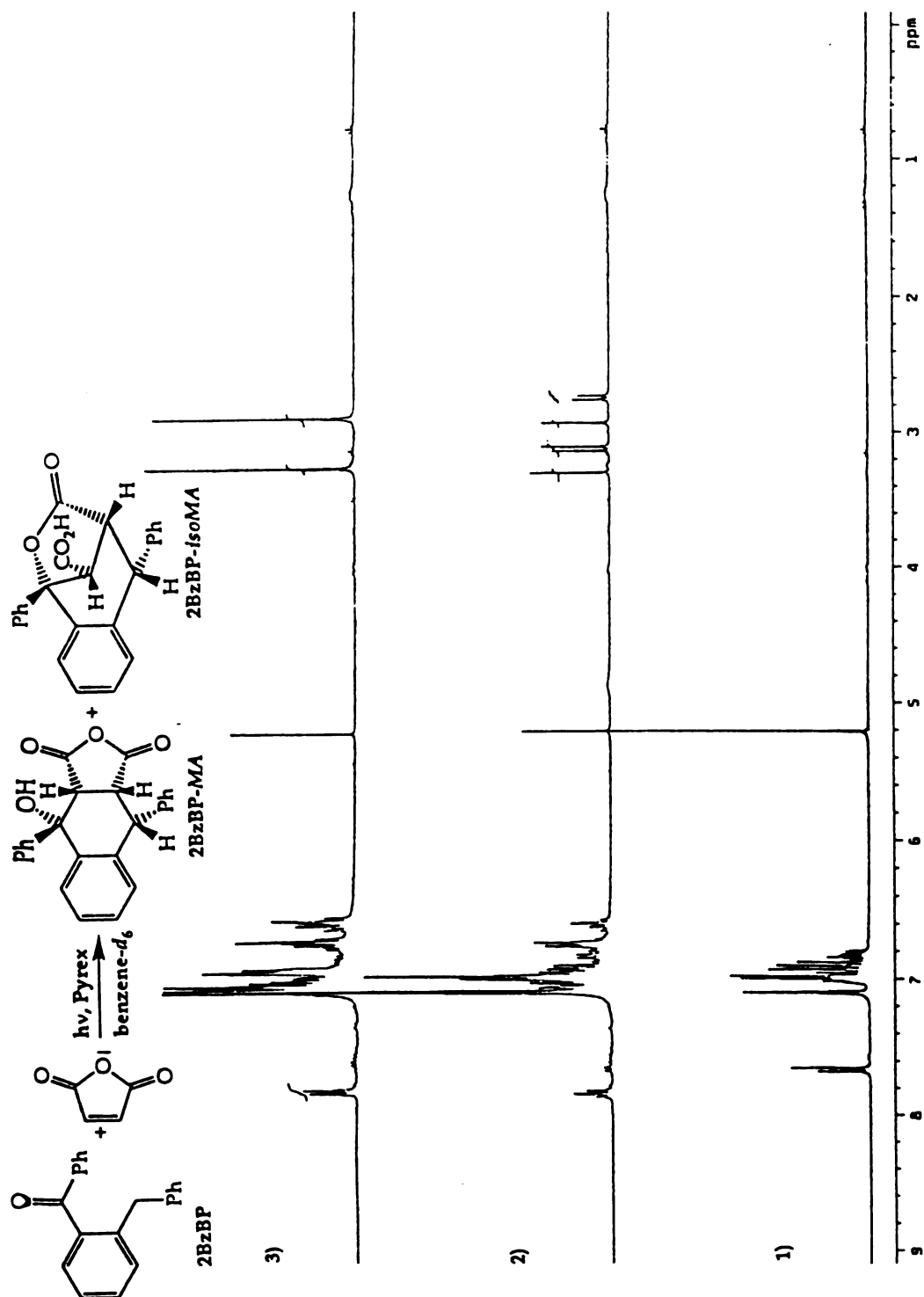
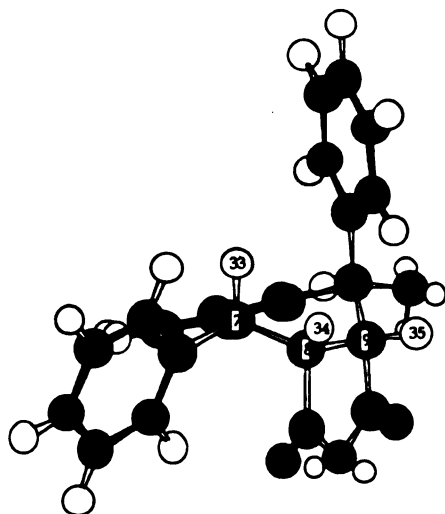


Figure 25. ¹H-NMR Spectra of 2BzBPd₂ in the presence of maleic anhydride 1) before irradiation 2) after 5 hours irradiation at 45°C 3) heating (2) for 10 hours at 50°C.

completely converted to **2BzBP_{d1}-isoMA** after heating at 20 hours at 50°C. The ¹H-NMR spectra showed the formation of the two singlets at 2.91(1H) and 3.28(1H) at the expense of the two doublets at 2.74 and 3.12 ppm

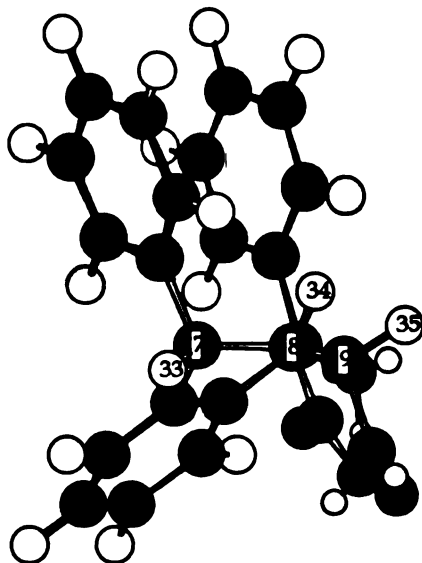
Only one of the four possible Diels-Alder adducts is formed. The structural assignment is based on the experimental vicinal coupling constants: 9.3 Hz for the dihedral angle H(35)-C(7)-C(8)-H(38) and 9.0Hz for the dihedral angle H(38)-C(8)-C(9)-H(39). The four possible Diels-Alder adducts were minimized by molecular mechanics (MM2) and the theoretical dihedral angles were calculated using Equation 1 and are given in Table 9-Table 12. The stereochemical assignment of **2BzBP-MA** is consistent with **2BzBP-*exo*MAEE**. The three other isomers **2BzBP-*exo*MAEZ**, **2BzBP-*endo*MAZZ** and **2BzBP-*endo*MAZE** were excluded since one of the theoretical values was much too low as compared to the experimental values.



MM2 steric energy of 2BzBP-*exo*MAEE
18.22 kcal/mole

Table 9. MM2 DH angles of 2BzBP-*exo*MAEE.

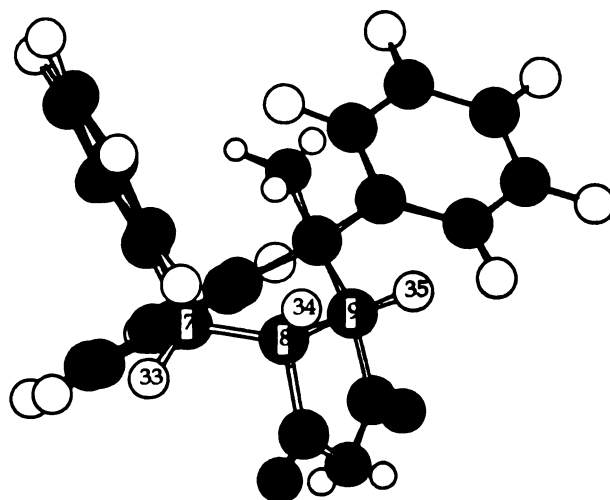
Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{H-H}$, Hz	Obs $^3J_{H-H}$, Hz
H(35)	C(7)	C(8)	H(38)	41.30	6.90	9.3
H(38)-	C(8)	C(9)	H(39)	24.15	9.42	9.0



MM2 steric energy of 2BzBP-*exo*MAEZ
15.87 kcal/mole

Table 10. MM2 DH angles of 2BzBP-*endo*MAEZ.

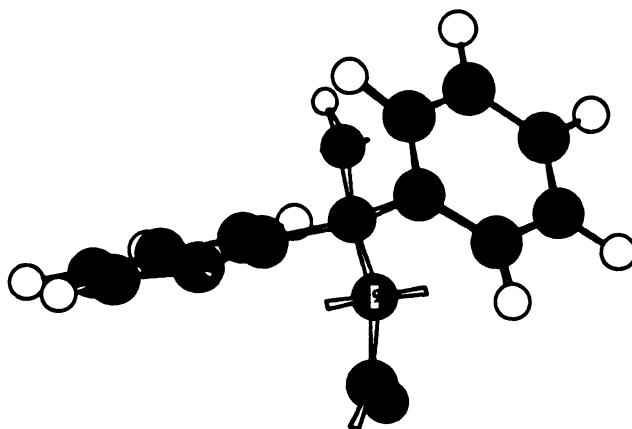
Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{H-H}$, Hz	Obs $^3J_{H-H}$, Hz
H(33)	C(7)	C(8)	H(34)	-81.19	2.08	9.3
H(34)-	C(8)	C(9)	H(35)	17.56	10.6	9.0



MM2 steric energy of 2BzBP-*endo*MAZZ
21.36 kcal/mole

Table 11. MM2 DH angles of 2BzBP-*exo*MAZZ.

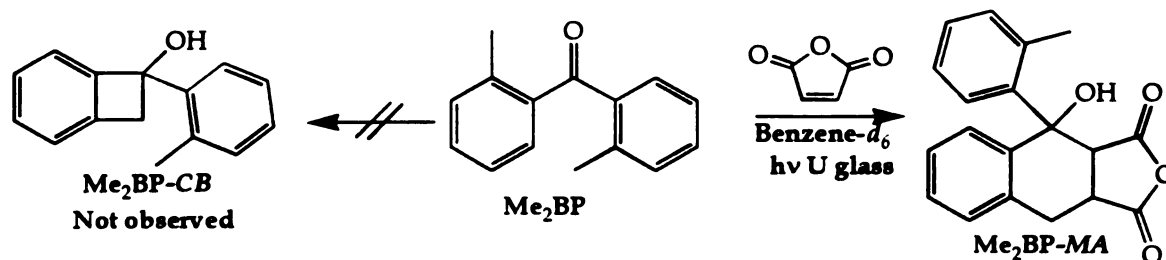
Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{\text{H-H}}$ Hz	Obs $^3J_{\text{H-H}}$ Hz
H(33)	C(7)	C(8)	H(34)	-90.64	2.01	9.3
H(34)-	C(8)	C(9)	H(35)	20.89	9.80	9.0



MM2 steric energy of 2BzBP-*endo*MAZE
23.34 kcal/mole

Table 12. MM2 DH angles of 2BzBP-*exo*MAZE.

Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{\text{H-H}}$ Hz	Obs $^3J_{\text{H-H}}$ Hz
H(33)	C(7)	C(8)	H(34)	28.69	2.01	9.3
H(34)-	C(8)	C(9)	H(35)	28.71	9.80	9.0

5. 2,2'-dimethylbenzophenone (M_2BP)Scheme 56. Photochemistry of 2,2'-dimethylbenzophenone (M_2BP)

Irradiation of M_2BP in benzene- d_6 did not give $M_2BP\text{-CB}$, as concluded by the absence of the characteristic AB quartet near 3.5 ppm observed for other benzocyclobutenols. The ketone reacted with maleic anhydride efficiently to give one major Diels-Alder product (see Figure 26). The photostable product possessed a $^1\text{H-NMR}$ spectrum consistent with $M_2BP\text{-MA}$. The two possible Diels-Alder adducts were minimized by molecular mechanics (MM2) and the theoretical dihedral angles were calculated using Equation 1 and are given in Table 13 and Table 14. The stereochemical assignment of $M_2BP\text{-MA}$ is based on these theoretical predictions and are consistent with $M_2BP\text{-exoMA}$. The bridgehead methine at 3.55 ppm appears as a ddd and has vicinal coupling constants of $^3J = 9.9, 9.6$ and 4.8 Hz, in agreement for the calculated values of $M_2BP\text{-exoMA}$ which are 12.7 Hz ($J_{\text{exp}} = 9.6$ Hz) for the dihedral angle $\text{H}(35)\text{-C}(7)\text{-C}(8)\text{-H}(38)$, 9.56 Hz ($J_{\text{exp}} = 9.9$ Hz) for the dihedral angle $\text{H}(38)\text{-C}(8)\text{-C}(9)\text{-H}(39)$, and 5.20 Hz ($J_{\text{exp}} = 4.8$ Hz) for the dihedral angle $\text{H}(34)\text{-C}(7)\text{-C}(8)\text{-H}(38)$. These

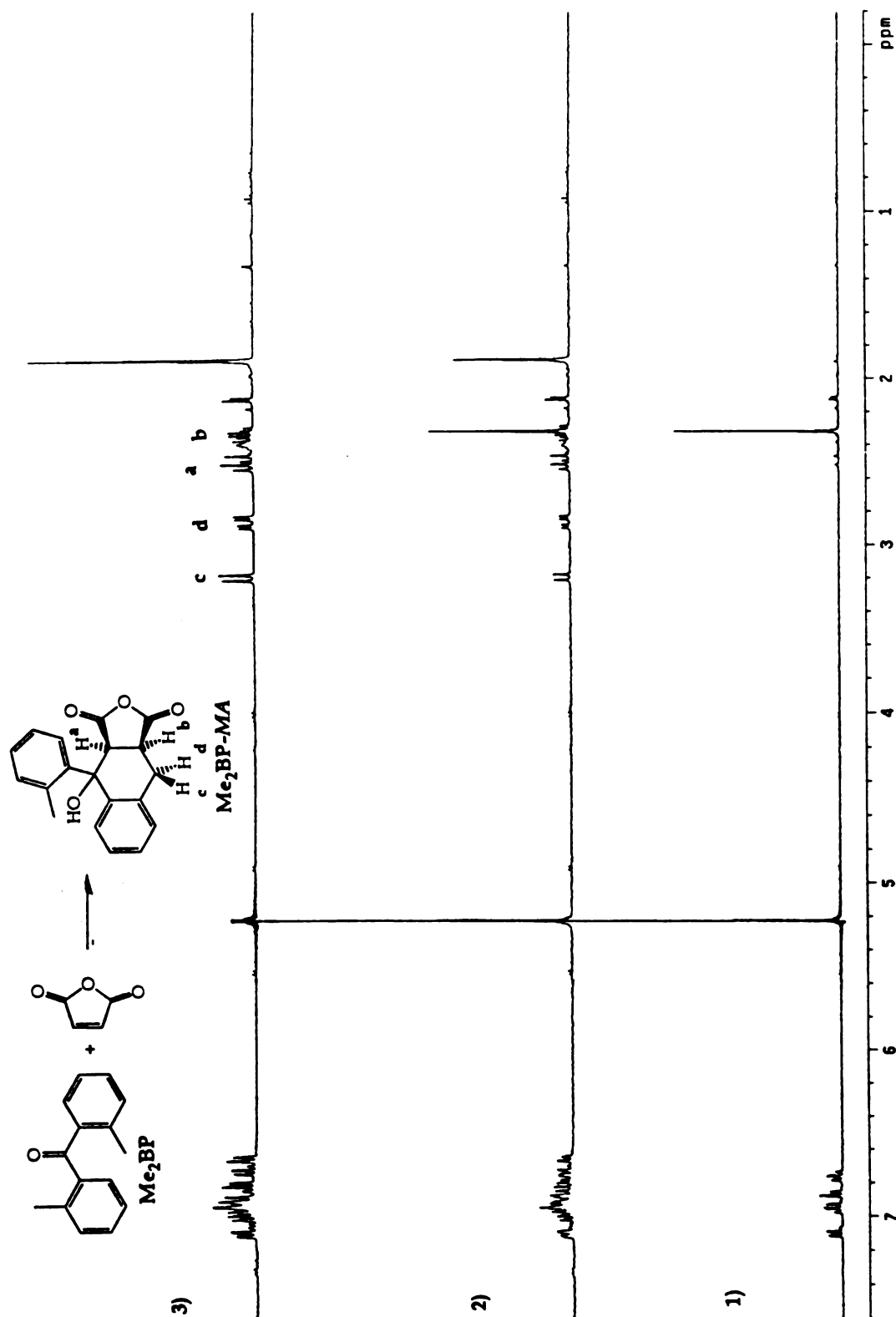
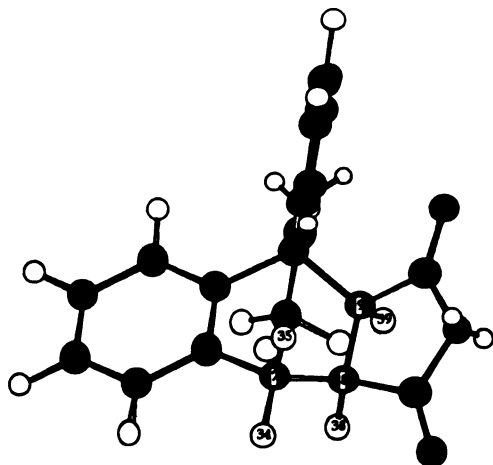


Figure 26. ^1H -NMR Spectra of M_2BP in the presence of maleic anhydride 1) before irradiation 2) after 30 minutes irradiation 3) after 4 hours irradiation.

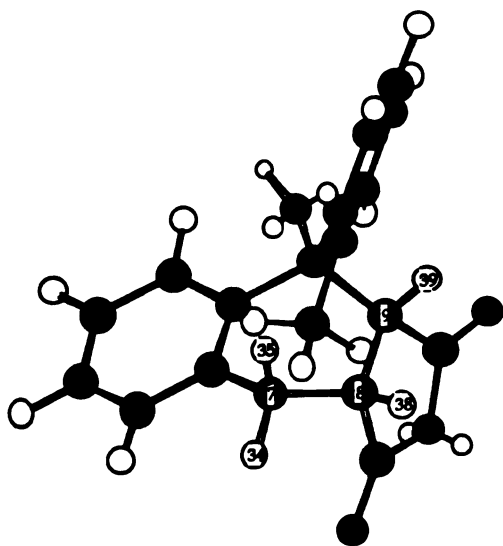
experimental and theoretical values differ slightly but the predicted values for the M_2BP -*endoMA* isomer demand two of the vicinal couplings to be <5 Hz



MM2 steric energy of M_2BP -*exoMA*
18.842 kcal/mole

Table 13. MM2 DH angles M_2BP -*exoMA*

Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{H-H}$, Hz
H(35)	C(7)	C(8)	H(38)	169.9	12.7
H(34)	C(7)	C(8)	H(38)	51.85	5.20
H(38)	C(8)	C(9)	H(39)	-22.93	9.56



MM2 steric energy of M_2BP -*endoMA*
22.98 kcal/mole

Table 14. MM2 DH angles M_2BP -*endoMA*

Atom 1	Atom 2	Atom 3	Atom 4	DH <	Calc $^3J_{H-H}$, Hz
H(35)	C(7)	C(8)	H(38)	54.27	4.83
H(34)	C(7)	C(8)	H(38)	62.82	3.63
H(38)	C(8)	C(9)	H(39)	16.83	10.21

III. Discussion for Photoenolization of o-alkyl phenyl ketones

A.Simple o-Xylylenols

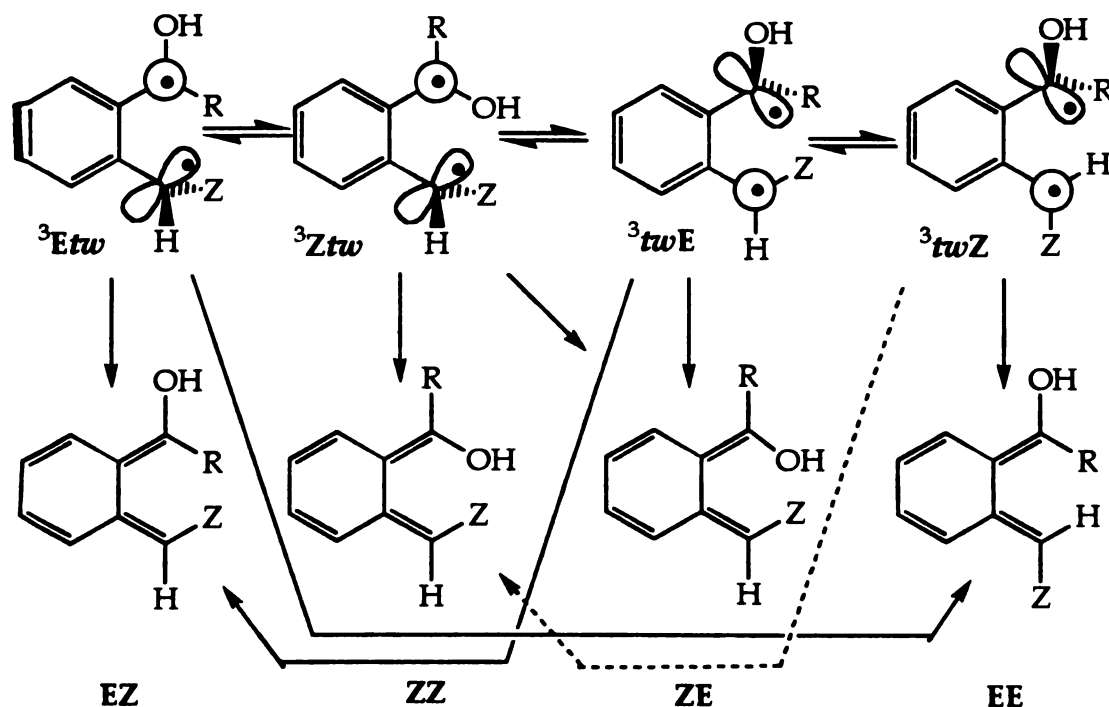
The high diastereoselectivity that was reported by the Wagner⁴⁵ group prompted my study of substituent effects on photoenolization of o-alkyl phenyl ketones including acetophenones, trifluoroacetophenones, benzophenones and trialkylbenzophenones.

Other than an early a report by Matsuura in 1969 for 2,4,6-triethylbenzophenone, no ketones that could form a diastereomeric mixture of benzocyclobutenols (i.e. $Z \neq H$) have been investigated.⁵⁰ For ketones without a substituent ($Z=H$) at the ortho benzylic position, only two o-xylylenols are possible, Z and E. Pfau was the first to point out that 2-ethyl- and 2-benzylbenzophenone form only one diastereomer when irradiated in the presence of maleic anhydride and concluded that only E,E-xylylenol could explain the high diastereoselectivity.³³

Wagner and coworkers a few years ago suggested a mechanism that considered possibility of forming four different enols and how the triplet xylylenol geometry determines which of the four possible ground state xylylenols are formed.⁴⁵ The mechanism was based on four premises: 1) the biradical triplet resembles a triplet diene with one end of the biradical twisted 90° out of conjugation with the benzene ring while the other one remains coplanar; 2) the radical site that benefits the most from the conjugation with the

benzene ring will remain so while the other radical site must assume a twisted geometry (see Scheme 57; *Etw*, *Ztw*, *twE*, *twZ*); 3) the end conjugated with the central ring has a preferred geometry with its larger substituent pointed out; 4) the twisted end rotates about equally in both directions when collapsing to the ground state, like most triplet alkenes.¹¹⁷

The variations in the photochemistry of several ketones that I studied along with previously published results seem to support the mechanism in Scheme 41 and Scheme 57.



Scheme 57. Triplet 1,4-biradicals, precursors to o-xylenols.

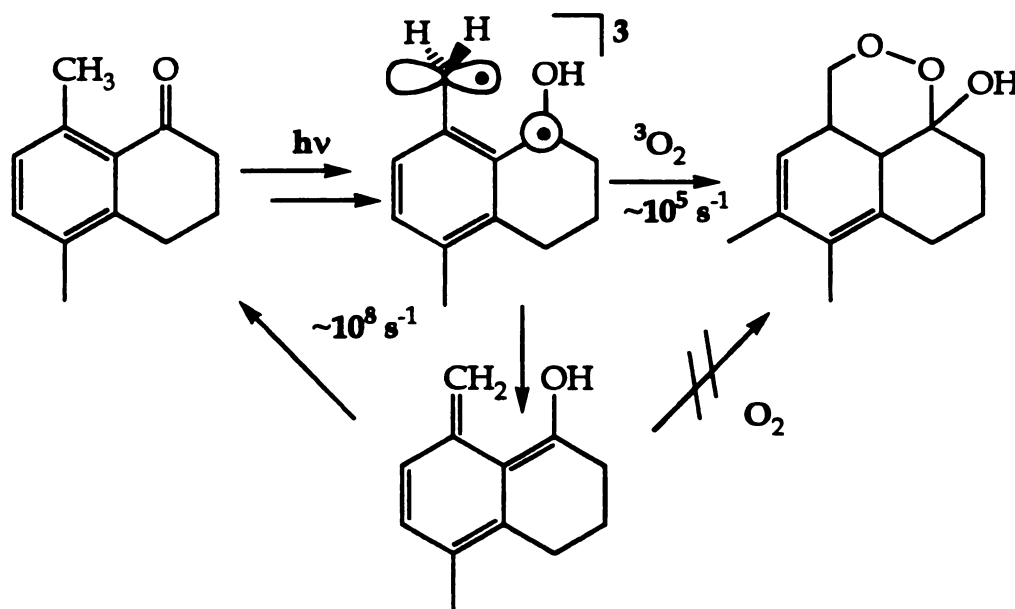
The ketones which provided the most insightful information were 2-ethylbenzophenone, 2-benzylacetophenone and 2-benzylbenzophenone. The photochemistry of 2-ethylbenzophenone has been reported previously but its

interpretation is crucial in construction of a complete picture for this photoenolization.⁴⁵ 2-Ethylbenzophenone gives only the E-2-methyl-1-phenylbenzocyclobutenol when irradiated in benzene. Explanation of this high diastereoselectivity is as follows 1) the second benzene ring attached to the newly formed hydroxy radical site can stabilize this site as has been observed for other biradicals, so its end of the triplet xylylenol is twisted and the methyl substituent on the ortho benzylic position prefers to be pointed away to minimize steric problems. Thus, the biradical conformation *twE* is the predominant geometry and decays to the EE and ZE xylylenols. The ZE is assumed to revert rapidly to starting ketone by an allowed 1,5-sigmatropic hydrogen shift as previously reported for similar ketones. The *twZ* geometry is calculated (AM1/3-21G*) to be 4 kcal/mole less stable than *twE*, a difference which is comparable to that calculated for the stereoselectivity-defining α -methylbenzyl site in the 1,5-biradical from α -(*o*-ethylphenyl)acetophenone. Thus, the EE *o*-xylylenol is the only tetraene that is populated enough that can lead to benzocyclobutenol formation. It should be noted that the biradicals must live long enough for concerted bond rotations to occur around both bonds between the benzene ring and the benzylic radical sites, otherwise both the EE and ZE enols could not be formed. Also the barrier for this concerted rotation must be kinetically attainable. The *Ztw* closely resembles the biradical geometry immediately after hydrogen abstraction has occurred; if the barrier is too high the geometries *Etw*, *twE* and *twZ* will not be achieved. Previous notions that the

biradical was cyclizing directly were disproved since added acid quenched benzocyclobutenol formation, thus benzocyclobutenol formation demands the xylylenol $\rightarrow$ benzocyclobutenol chronology.

Previous reports found 2-benzylacetophenone (2BzAP) to be unreactive when irradiated in the presence of several dienophiles including maleic anhydride.¹¹⁸ I also found that 2BzAP is photoinert in benzene with and without added dienophiles. However, in methanol- d_4 it undergoes rapid deuterium exchange at the benzylic position and slower deuterium incorporation at the acetyl methyl. When irradiated in oxygen saturated methanol, benzene or acetonitrile it forms three products, two cyclic peroxides and 2-acetylbenzophenone. Thus, γ -hydrogen abstraction is occurring but for some reason does not lead to benzocyclobutenol formation. The best geometry of the 1,4-biradical from 2BzAP is *Ztw* since sterically the OH would prefer to be pointed in while the methyl group prefers to be pointed outward. The other end of the biradical with the phenyl substituent is capable of twisting thus having this benzylic radical site perpendicular to the central ring. Decay of the *Ztw* biradical geometry would lead to formation of ZZ and ZE xylylenols, both of which revert rapidly to starting ketone before cyclizing or reacting with dienophiles. The fact that two peroxides are formed suggests that either; 1) oxygen is reacting by a stepwise addition to any of the four xylylenols 2) all four enols are formed, the two pairs ZE-EZ and EE-ZZ would both give the two different peroxides if oxygen addition was diastereoselective 3) the oxygen is not

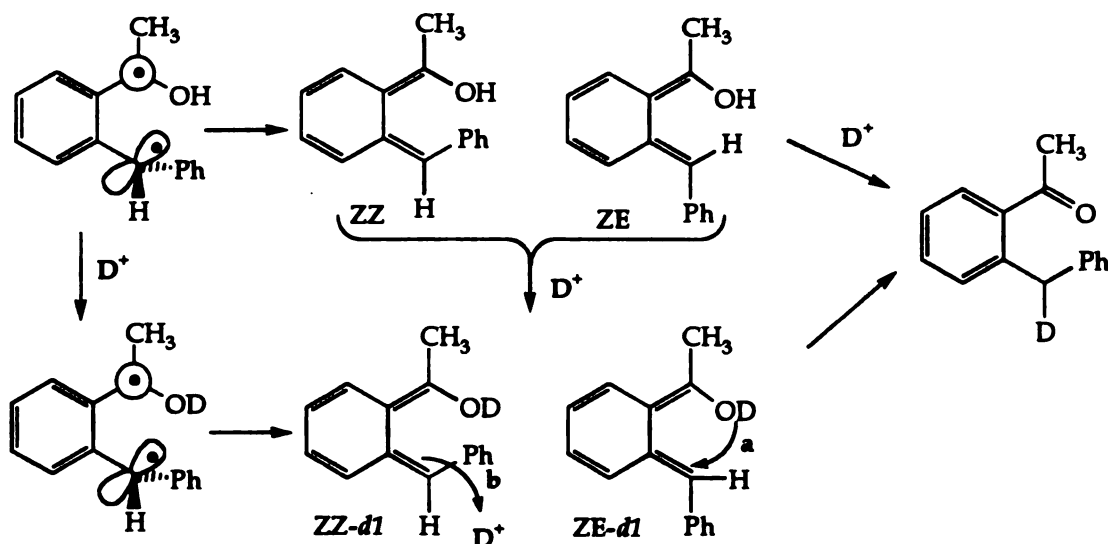
reacting with the xylylenol but with the biradical instead. That no benzocyclobutenols are formed suggests that the EE and EZ xylylenols are not formed. In fact the *Etw* biradical is calculated to be 4 kcal/mole higher in energy than *Ztw*. The possibility of oxygen adding to the triplet biradical before decay to the xylylenol has been suggested previously.¹¹⁹ Irradiation of 2,8-dimethyltetralone in the presence of oxygen gives a cyclic peroxide which can only arise from the Z xylylenol because of geometrical constraints.¹¹⁹ However, the authors suggested that the peroxide is derived from the triplet of the *o*-xylylenol since the reaction rate of oxygen with ground state dienols (ca. $2 \times 10^5 \text{M}^{-1}\text{s}^{-1}$)⁵⁷ is far too slow to compete with the intramolecular reketonization



Scheme 58. Trapping of xylylenol triplet by oxygen.

(see Scheme 58).⁵⁶ Presumably, an energy transfer mechanism from the triplet dienol to triplet oxygen predominates but some chemical trapping is also occurring.

One question that arises is whether the deuterium is incorporated by an intermolecular or intramolecular mechanism (see path **a** and **b** in Scheme 59). Path **a** demands the exchange of the hydroxy proton with a deuterium atom from the solvent. It is likely that the methanol solvates the biradical, during solvation the proton is exchanged for a deuterium atom and decay to the ZE xylylenol follows. Scaiano has shown that the E o-xylylenols react with acid with rate constants of $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$,⁴⁶ but the rate constant for 1,5-intramolecular hydrogen transfer is 10^8 s^{-1} , thus the intramolecular path should predominate.

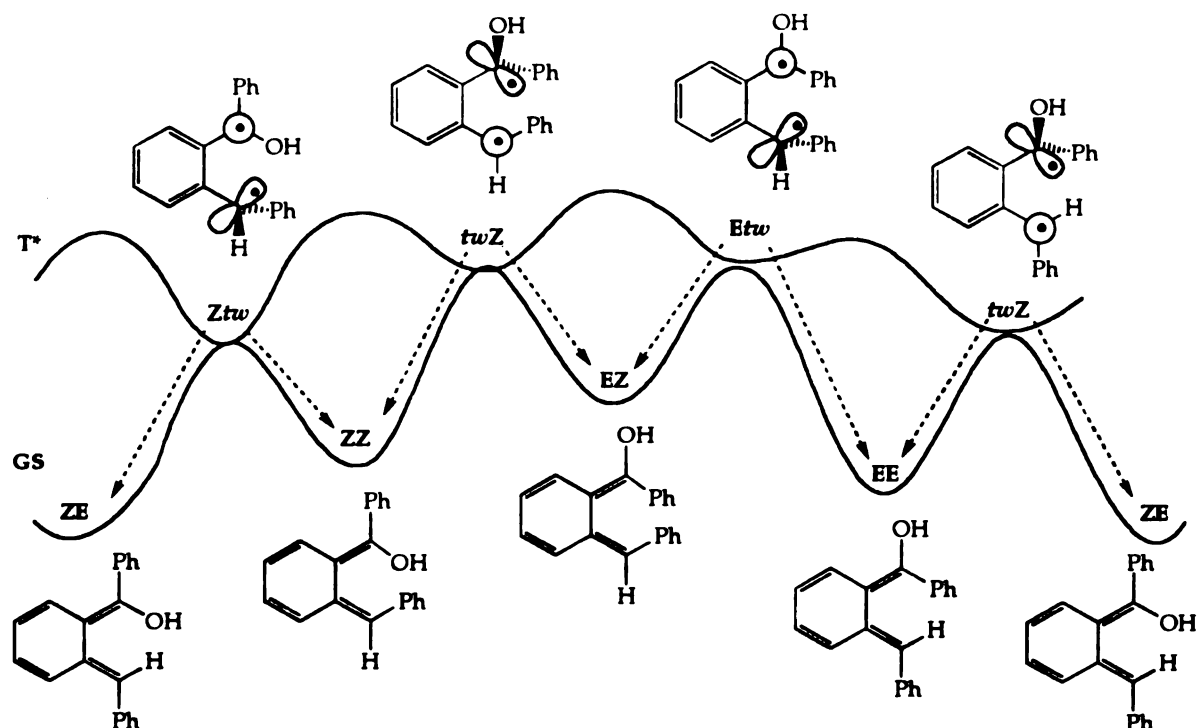


Scheme 59. Photochemical deuteration of 2-benzylacetophenone.

The photochemistry of 2-benzylbenzophenone (2BzBP) was previously reported to involve H/D exchange at the benzylic position. Pfau's finding that irradiation in the presence of maleic anhydride produced a single diastereomer and our contribution that only E-benzocyclobutenol is formed suggests that only one xylylenol is responsible for product formation. With the phenyl ring as a substituent at the ortho benzylic position, the biradical that is formed can easily

twist at each site. The facile twisting at *both* ends could not be achieved in the triplet biradicals of 2-ethylbenzophenone or 2-benzylacetophenone. The two geometries *Ztw* and *twE* are expected to be the most populated since the steric energy is smallest with the OH pointed inward for *Ztw* and the H pointed inward for *twE*. The decay of *Ztw* would lead to the formation of ZZ and ZE enols, both of which should lead to reketonization. It is likely that the enolic OH of the ZZ isomer can hydrogen bond to the opposite phenyl group slowing down the 1,5-sigmatropic reversion to ketone and could possibly cyclize to the E-benzocyclobutenol. The decay of *twE* would lead to EE and ZE enols but only the EE enols live long enough to cyclize. There is evidence that EE, ZE, and ZZ enols have been detected by flash photolysis, however the absence of the EZ is blamed on sterics. Moreover, the other two geometries *Etw* and *twZ* would require a phenyl group to be pointed in which seems unlikely. Scheme 60 shows a relative energy diagram of the four possible triplet and ground state enols of which only the EE xylylenol can lead to product formation.

The flash photolysis of 2-benzylbenzophenone has been carried out by Yang,¹²⁰ Porter³⁵ and Scaiano¹²¹. However, a consensus has not been reached to this day. (see Table 15). Yang observed two transients with lifetimes 526 μ s and 10 s in cyclohexane. The former was assigned to the triplet-triplet absorption and the latter was assigned to an enol (but with no stereochemistry). Porter also found the same transients as Yang with lifetimes of 520 μ s and 7 s in cyclohexane which were assigned to a Z-enol and an E-enol respectively. A third transient



Scheme 60. Triplet biradical surface for 2-benzylbenzophenone.

was also observed with a lifetime of 50 ns, however no assignment was made. Scaiano found a transient (330 nm) not observed by Yang or Porter with a lifetime of 20 ns in acetonitrile which was quenched by oxygen but not by 1,3-hexadiene, assigned to the triplet biradical transient at 440 nm (the photoenol region) which grew in at the same rate the 330 nm transient disappeared. Two other transients were observed in acetonitrile with lifetimes at 280 ns and 190 μ s which were assigned to the ZE and EE enols respectively. In benzene only two transients were observed with lifetimes of <30ns and 470 μ s, which are consistent with Porter's measurements but were assigned the ZE and EE enols respectively. The long lived species (>1 s) was observed but not analyzed by Scaiano, probably due to his flash setup. The combined results of these three

studies provides a fairly complete picture of the number of xylylenols that can be formed from 2-benzylbenzophenone (see Table 15). Not surprisingly, the most sterically hindered EZ enol is not detected by any of the three groups and is probably never formed.

Table 15. Summary of flash photolysis of 2BzBP by several groups.

Transient	Yang ^a (τ , assigned)	Porter ^a (τ , assigned)	Scaiano (τ , assigned)
³ BR	—	—	(20 ns, ³ BR) ^b
ZE-enol	—	50 ns (not assigned)	(280 ns, ZE) ^b ,(<30 ns, ZE) ^c
ZZ-enol	526 μ s ('T-'T)	520 μ s (a Z enol)	(190 μ s, EE) ^b ,(470 μ s, EE) ^c
EE-enol	10 s (an enol)	7 s (an E enol)	—

^a cyclohexane. ^b acetonitrile. ^c benzene.

The elegant study by Haag, Wirz and Wagner⁵⁶ for 3,3,6,8-tetramethyl-1-tetralone convincingly demonstrated that the Z enol had a lifetime of 30 ns in benzene and 270 ns in acetonitrile in agreement with the ZZ enol of 2-benzylbenzophenone from Scaiano's work (<30 ns in benzene and 280 ns in acetonitrile). The fate of the ZZ enol has been firmly established as a 1,5-sigmatropic shift to regenerate starting material. The ~500 μ s transient which absorbs in the range 380-550 nm and was reported by all three groups and demands a xylylenol assignment. Scaiano assigned this transient to the EE-enol but is most likely incorrect based on the following: 1) the EE enol readily reacts with maleic anhydride as reported by Pfau and confirmed in our laboratory

which is contrary to Scaiano's finding. Also Porter's 7 second transient reacted with dimethyl acetylenedicarboxylate with a rate constant of $1 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$; 2) the transient absorption spectrum of this species ranges from ~350-600 nm compared to Porter's report of Z-enol which absorbed between 380-550 nm, Porter claimed the E-enol should absorb at shorter wavelengths (assigned to 7 second transient, 360-450 nm) owing to non-planarity of the phenyl ring and the tetraene system; 3) approximately 25% of the Scaiano's decay profile remained after 1000 μs but was not assigned. It is clear the E-enol is the only xylylenol that lives long enough to cyclize but the E-benzocyclobutenol formation was missed by all previous studies. *These flash studies support the product studies reported in this thesis and the finding that only the E-benzocyclobutenol is formed from 2-benzylbenzophenone.*

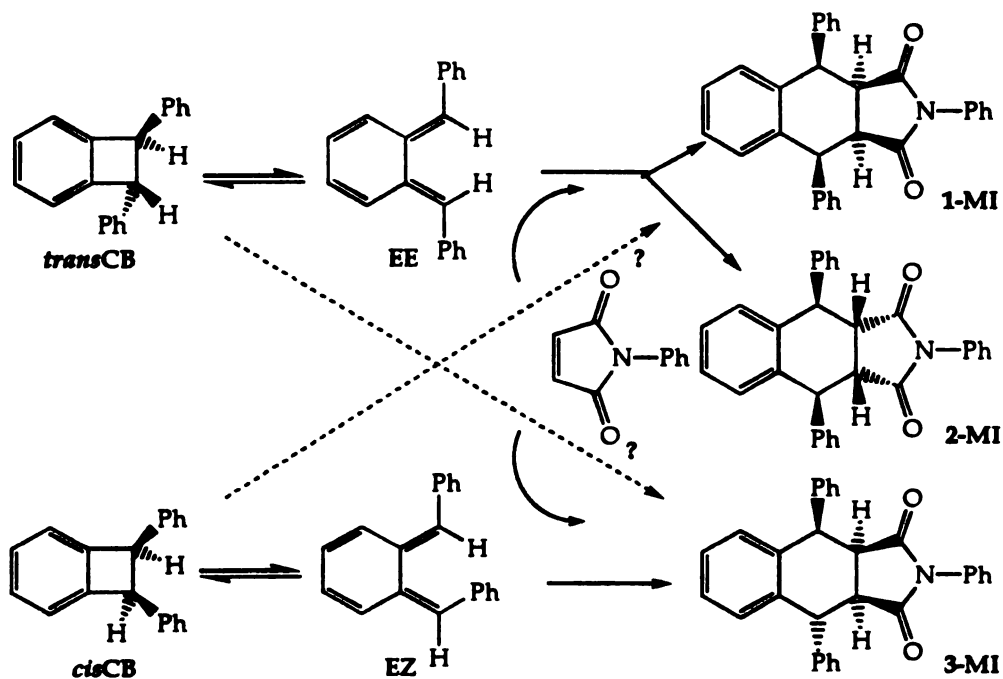
The thermal lability of E-1,2-diphenylbenzocyclobutenol (2BzBP-ECB) is likely the reason it has eluded researchers for over three decades.^{26,121} Superficially it appears that there is an equilibrium between 2BzBP and 2BzBP-ECB but it is difficult to imagine how this conversion could take place without some other intermediate. Addition of maleic anhydride to a 2BzBP-ECB solution shifts this equilibrium such that 2BzBP-ECB is consumed within minutes giving a Diels-Alder like product. The most likely candidate for this intermediate is an *o*-xylylenol because it reacts with dienophiles. Moreover, the Diels-Alder product that is formed by adding maleic anhydride to benzocyclobutenol solution is identical to the one formed by irradiation of 2-benzylbenzophenone in the presence of maleic anhydride. *It is concluded that photochemical and thermally*

generated xylylenol is the same species. Other researchers have seen similar equilibria between benzocyclobutenes and xylylenes.^{122,123} Huisgen and Seidel studied the thermal opening of *cis* and *trans* 1,2-diphenylbenzocyclobutene (**Ph₂CB**) in the presence of a variety of dienophiles.¹²⁴ Two important facts from his study are: 1) The *cis* isomer opens to the xylylene ~10 times faster than the *trans* isomer; the measured rate constants were 260 and $3.70 \times 10^{-5} \text{ s}^{-1}$ for the *cis* and *trans* respectively at 50°C; 2) when tetracyanoethylene (TCE) is employed as a dienophile the rate determining step is the opening of the **Ph₂CB** and not the addition to the dienophile but when maleic anhydride is used as the trapping species then its consumption is rate determining.

A possibility is that the maleic anhydride can react directly with the benzocyclobutenol. Quinkert addressed this same question for *cis* and *trans* 3,4-diphenylbenzocyclobutene (see Scheme 61).¹²⁵ The *transCB* reacts quantitatively and smoothly at room temperature with N-phenylmaleimide to form two products 1-MI and 2-MI in a 15:1 ratio (the major product was not identified, presumably it would be 1-MI from *endo* addition). The *cis* isomer is less reactive, in two weeks at room temperature it formed an adduct with the same dienophile to form 3-MI. The Diels-Alder adducts 1-MI and 2-MI were not formed from *cisCB* nor was 3-MI formed from *transCB* ruling out direct reaction of the dienophile with the benzocyclobutene. Quinkert's finding that *cisCB* is less reactive (i.e. higher activation energy for opening) than the isomeric *transCB* is interesting from a thermodynamic view. My finding that the **2BzBP-ECB** is

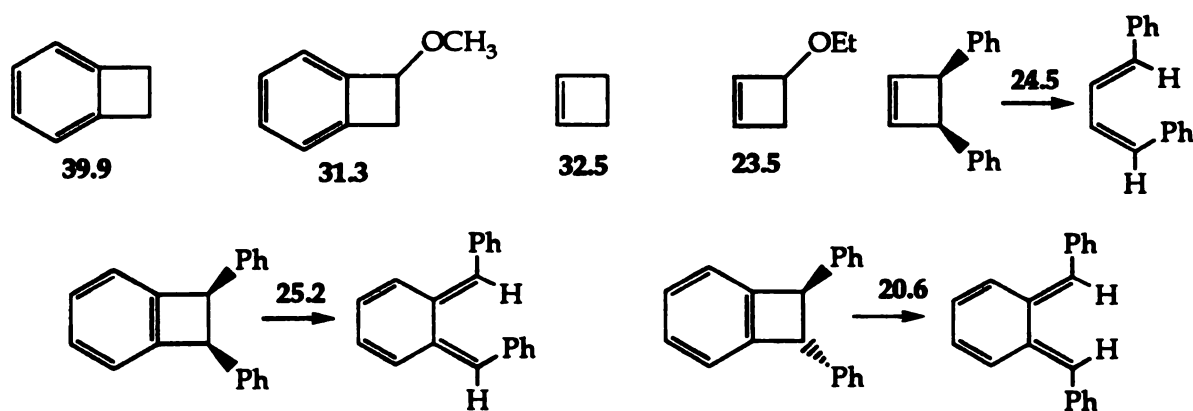
thermally labile at room temperature and reacts with dienophiles within minutes warrants some discussion. The only difference between Quinkert's *cisCB* and 2BzBP-ECB is the hydroxy group.

Houk's theory on *torquoselectivity* along with the Woodward-Hoffman rules for pericyclic reactions is useful in understanding these results. The Woodward-Hoffman rules predict a conrotatory ring opening for the thermal ring openings of cyclobutene to 1,3-butadiene suggesting the E-benzocyclobutenol should open to either the EE or ZZ enols. Houk's rules are useful in predicting the direction of the conrotatory process and predicts which xylylenol (EE or ZZ) will be formed.^{64,126,127} The methoxy substituent of α -methoxybenzocyclobutene causes a (ca. 9 kcal/mol) lowering of the activation



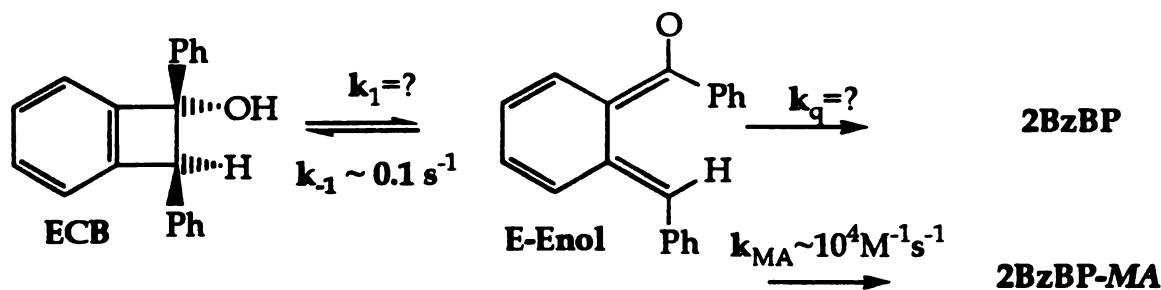
Scheme 61. Quinkert's thermal chemistry of *cis* and *trans* 1,2-diphenylbenzocyclobutene

energy for ring opening compared with the unsubstituted case.^{64,128} Houk has also reported similar values for the electrocyclic ring openings of cyclobutenes and benzocyclobutenes. The activation energy for isomerization via a conrotatory opening of *cis*-3,4-diphenylcyclobutene to *cis*-,*trans*-1,4-diphenylbuta-1,3-diene is 24.5 kcal/mol¹²⁹ compared with 32.5 kcal/mol¹²⁶ activation energy for conversion of cyclobutene to 1,3-butadiene. Huigen's activation energy for conversion of *cis*Ph₂CB to the xylene is 25 kcal/mol and combined with a 9 kcal/mol lowering of the activation energy for opening with an OH out suggests a value of $E_A = 16$ kcal/mol for 2BzBP-ECB to 2BzBP-*Eenol*. The calculated rate of 2BzBP-ECB to 2BzBP-*Eenol* using the parameters $\log A = 12$ and $T = 25^\circ\text{C}$ is 2.6 s^{-1} . This seems too fast if we assume the lifetime measured by Yang and Porter ($\sim 10\text{s}$) is the rate of cyclization ($k_1 \sim 0.1 \text{ s}^{-1}$). I observe only 2BzBP-ECB after irradiation of 2BzBP by NMR, thus $k_1 > k_2$. The estimation of E_A is probably too low and an activation energy of $\sim 10\text{-}20$ kcal/mol (corresponds



Scheme 62. Activation Energies for Electrocyclic Ring Openings of Cyclobutenes.

to k_1 values of 0.018 and 0.0034 s^{-1} respectively) for opening seems more likely. A NMR experiment revealed that approximately one half of the **2BzBP-ECB** reverted to starting ketone in ~ 6 hour. The constant k_{obs} also reflects a rate constant k_q for quenching (catalysis to the ketone) of the enol. However, it is not clear if catalysis occurs from a intermolecular reaction with a second enol molecule, from the glass or from acid impurities in the solvent, thus k_q is unknown. A k_1 value of 0.01-0.001 s^{-1} is attractive since my experiments with addition of maleic anhydride (0.1 M) showed *only* **2BzBP-MA** two minutes after the addition to a solution of **2BzBP-ECB**, with no remaining s which corresponds to a rate of $1 \times 10^{-4} \text{ s}^{-1}$ (k_{obs}). The rate constant for trapping of the E-xilylenol of 2MBP is $\sim 10^4$ (k_{MA}) with maleic anhydride and would react with 0.01 M **2BzBP-ECB** at a rate of 10 s^{-1} which is too fast to be measured by the technique I employed.



$$k_{\text{obs}} = \frac{k_1[\text{ECB}] \cdot k_q[\text{E-Enol}]}{k_1[\text{E-Enol}]} \quad \Rightarrow \quad \text{if } [\text{ECB}] = 0.01 \text{ M} \quad k_1 \cdot k_q = 10^3 \text{ M s}^{-2}$$

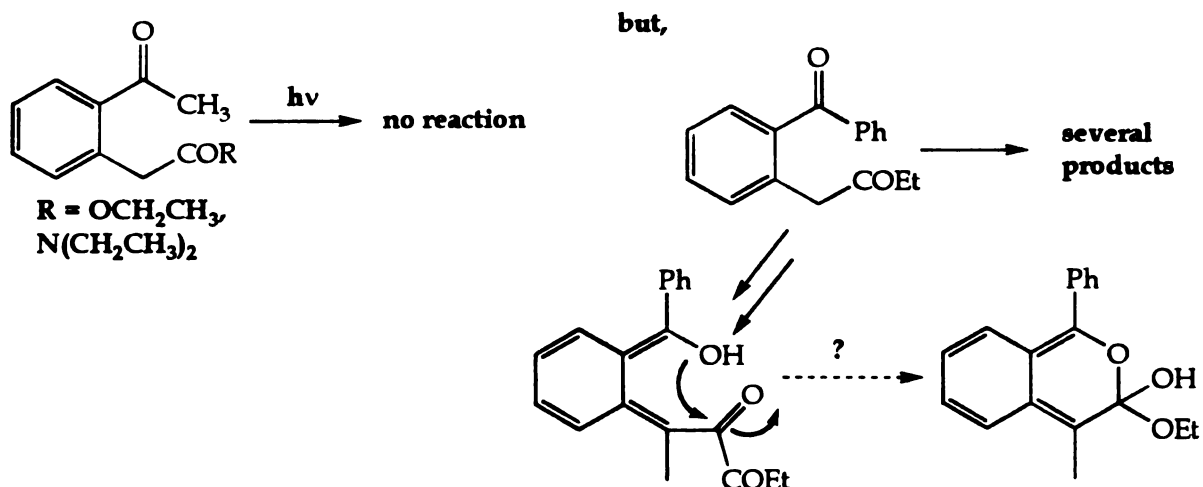
Scheme 63. Equilibrium of 2BzBP-CB with 2BzBP-Enol.

Quinkert's stereoselective trapping of *cis* and *trans* 1,2-diphenylbenzocyclobutene suggests the ring opening to xylylene is a conrotatory process, however his *cisCB* could only form one xylylene due to symmetry which would have one phenyl pointed in and the second pointed out. Thermal opening of 2BzBP-*ECB* by a conrotatory process can lead two possible xylylenols *ZZ* and *EE*. Houk's theory of torquoselectivity predicts the OH should move outward. An interesting twist would be the thermal opening of 2BzBP-*ZCB*, if the torquoselectivity rules hold, the hydroxy group would rotate outward forcing two phenyl rings inward. Trapping of this dienophile should lead to the opposite Diels-Alder product obtained from 2BzBP-*ECB*. Several attempts were made to generate 2BzBP-*ZCB* from 2BzBP-*ECB* by catalysis but failed and resulted in regeneration of the starting ketone.

B. Effect of electron withdrawing groups on formation of simple *o*-xylylenols.

Ortho acetyl and benzoyl phenylacetic acid derivatives were studied in order to examine the effect of an electron withdrawing group on the benzylic positions.

The (2-acetylphenyl)acetate and (2-acetylphenyl)acetamide derivatives were photoinert when irradiated in benzene (see Scheme 64). Ethyl (2-benzoylphenyl)acetate in benzene gave a mixture of products and was only ~10% as reactive as 2-ethylbenzophenone based on irradiation time. The *ZZ* enol

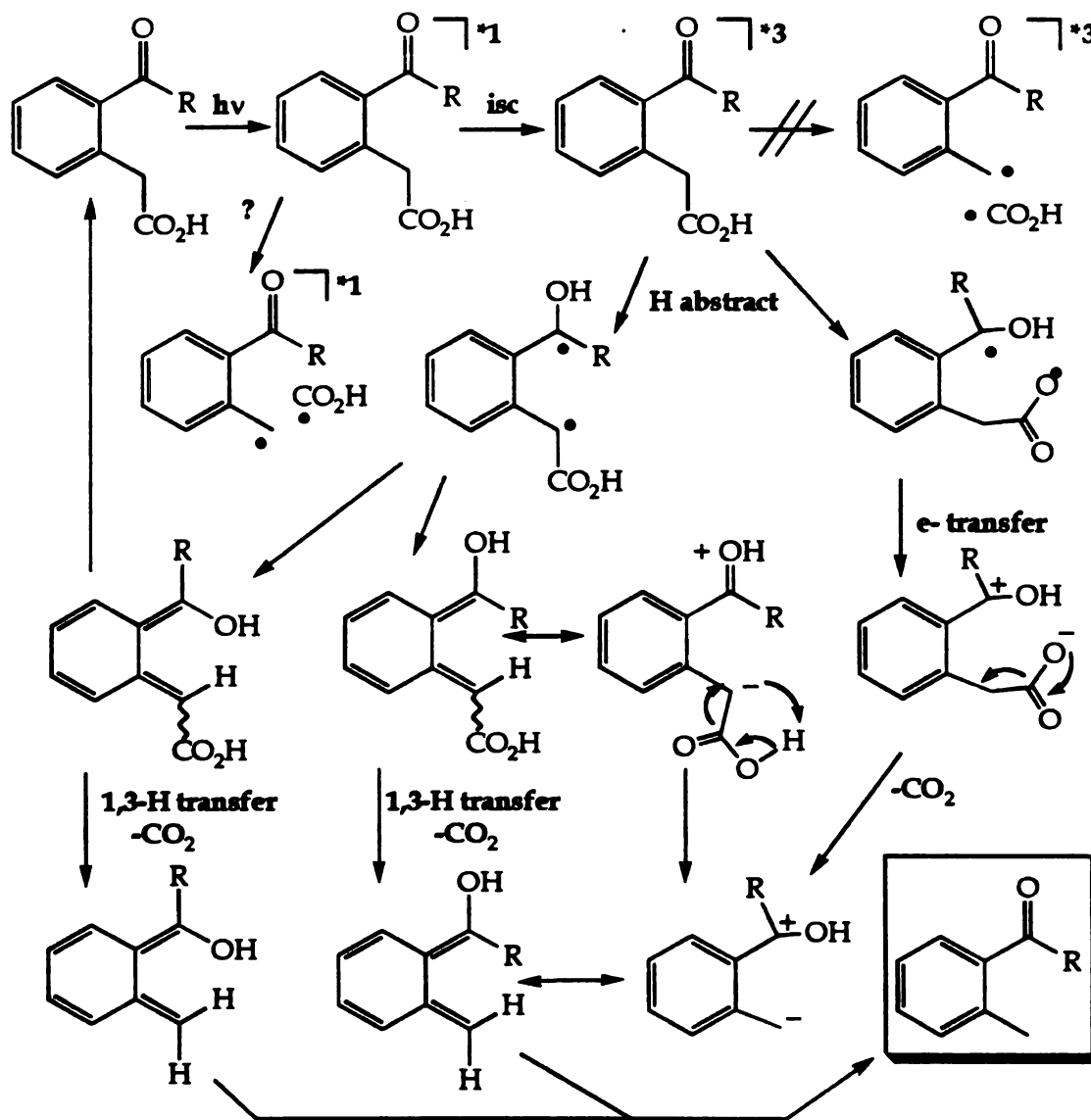


Scheme 64. Photochemistry of phenylacetic acid derivatives.

can possibly be trapped by an intramolecular reaction with the ester group, but no products were isolated (see Scheme 64). The electron withdrawing group should not affect the rate of hydrogen abstraction since the rate constant for γ -hydrogen abstraction for γ -cyanobutyrophenone is $0.40 \times 10^7 \text{ s}^{-1}$, only a factor of 2 slower than butyrophenone itself ($k_{\text{H}} = 0.80 \times 10^7 \text{ s}^{-1}$).¹³⁰ Singlet quenching may be competing for the acetophenones, since the quantum yields for isc of ortho-alkylacetophenones are only ~20-50%, but does not explain the loss in reactivity of the benzophenones.^{56,131}

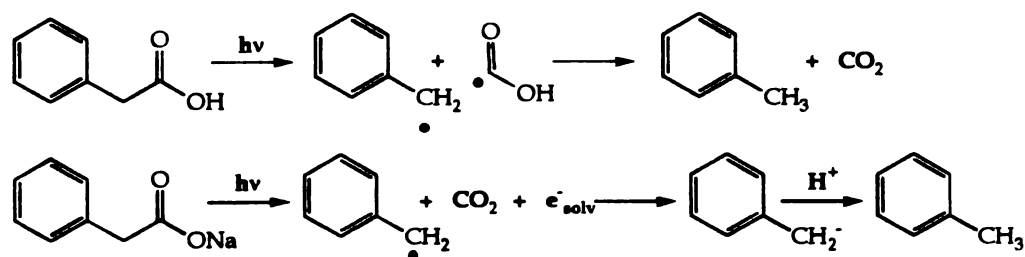
Irradiation of (2-acetylphenyl)acetic acid and (2-benzoylphenyl)acetic acid in benzene gave 2-methylacetophenone and 2-methylbenzophenone accompanied by loss of carbon dioxide within 20 minutes. This is a very short irradiation time for an ortho alkyl acetophenone to react completely; a typical irradiation time is >24 hours for complete conversion. A possible mechanism is outlined in Scheme 65.

Photodecarboxylation of phenylacetic acid has been studied in depth since it is the simplest aromatic acetic acid. Epling and Lopes conducted deuterium labeling studies of phenylacetic acid which give toluene as the major product from decarboxylation.¹³² Supporting evidence for the radical pathway was a spectral absorption assigned to the benzyl radical (or from a solvated



Scheme 65. Possible mechanism for photodecarboxylation of phenyl acetic acids.

electron) and the formation of bibenzyl. Sensitization with xanthone ($E_T = 74$ kcal/mol), and acetone ($E_T \sim 79$ kcal/mol) did not promote decarboxylation nor did quenching with myrcene produce a triplet product and it was concluded the decarboxylation was from the singlet state. A study by Givens showed that the photochemical decarboxylation of phenylacetic esters also occurred from the singlet state.¹³³ Prior to Epling and Lopes' results other groups had suggested photodecarboxylation by both anionic and radical fragmentation.¹³⁴ An important similarity in all the literature examples reported to this date is that the photochemical decarboxylation of phenylacetic acid and its derivatives only occurs when conducted in protic or mixtures of protic and aprotic solvents.



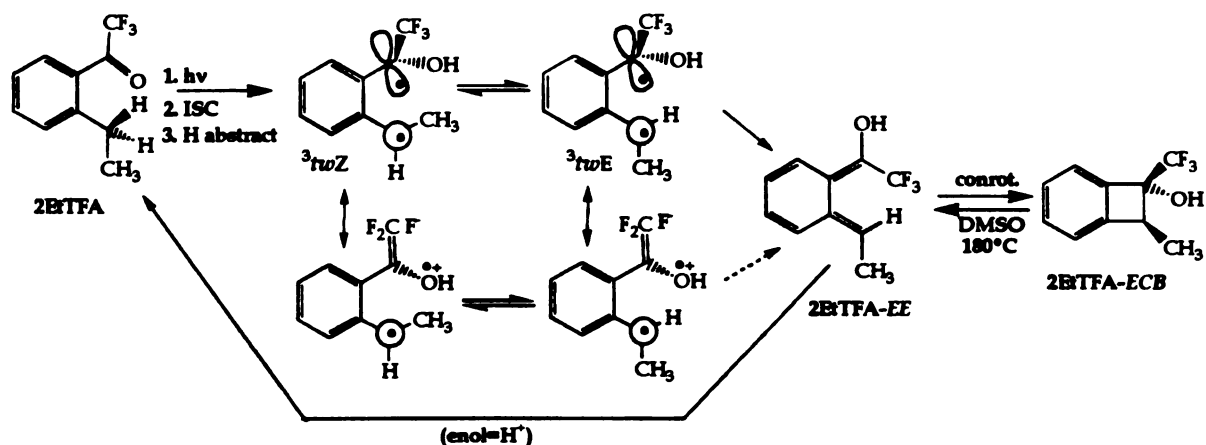
Scheme 66. Photochemistry of Phenylacetic acid.

My deuterium labeling studies provide some insight but no definitive conclusions can be drawn. The results of the labeling studies (2-benzoylphenyl)acetic and (2-acetylphenyl)acetic acid indicated deuterium incorporation occurs at the benzylic position. There is some discrepancy between results from the techniques employed for analyzing the amount of deuterium incorporated for the study of (2-benzoylphenyl)acetic: the ^1H -NMR of the ketone fragment from irradiation of 2AcMBP d_1 shows approximately a 1:1 ratio of

2MeBP : $2\text{MeBP}d_1$ while mass spec analysis suggests almost no 2MeBP but a 1:1 ratio of $2\text{MeBP}d_1$: $2\text{MeBP}d_2$. The origin of the dideuterated species is not clear but it is likely the $2\text{AcMBP}d_1$ sample had small amounts of D_2O which exchanged with the *o*-xylylenol from 2MeBP which was formed after fragmentation. Each pathway in Scheme 65 can incorporate deuterium from the acid functionality thus a decisive mechanism can not be drawn at this time.

Whatever the case may be, this photodecarboxylation is unique since it occurs in hydrocarbon solutions.¹³⁵ Further studies are necessary before any conclusions can be drawn especially quenching studies and laser flash photolysis (to see if *o*-xylylenols are intermediates).

C. Captodative Resonance-Another Example of Rotational Control?

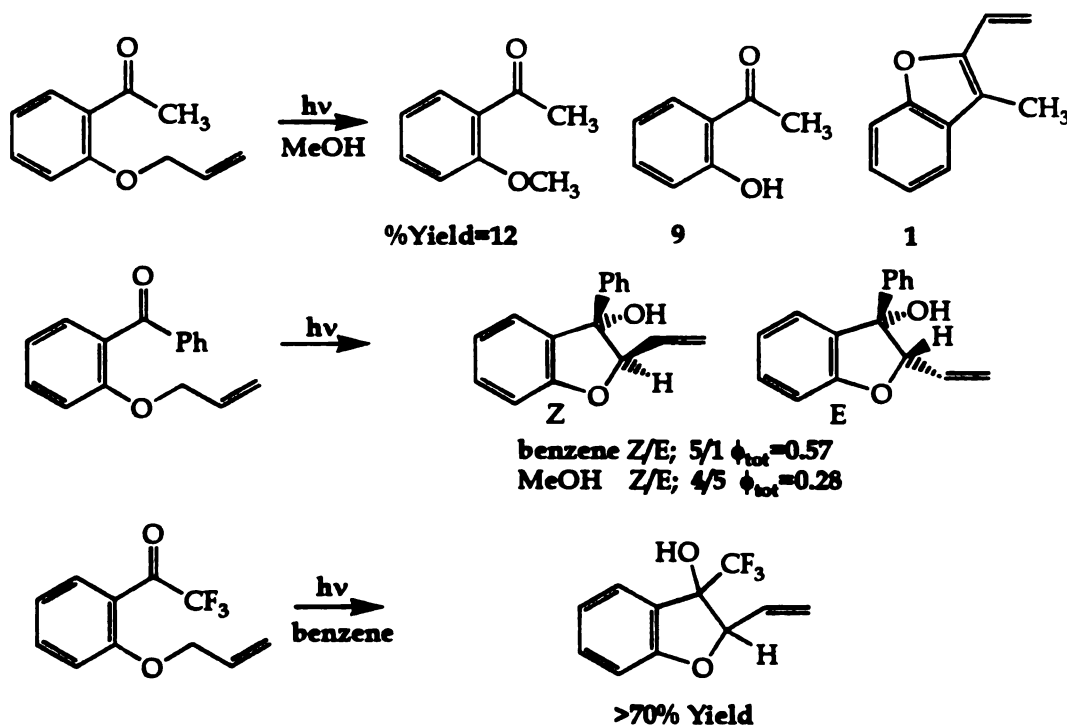


Scheme 67. Captodative resonance contributions of trifluoroacetophenone.

The ortho alkyl α,α,α -trifluoroacetophenones were synthesized to test the validity of the mechanism described in Scheme 57. Trifluoroacetophenone

derivatives exhibit capto-dative resonance stabilization due to their strong fluorine hyperconjugation which enhances the charge separated resonance form of the hydroxy radical center. This stabilization of the radical center could minimize the effect of benzylic conjugation that controls bond rotation as previously discussed for ketones 2EtBP, 2BzAP and 2BzBP.

The well behaved biradical character of α -allyloxybenzophenones¹³⁶ have successfully been mimicked using 2'-allyloxy-2,2,2-trifluoroacetophenones¹³⁷. Scheme 68 exemplifies the difference in photo and chemical behavior of aceto-¹³⁸ and benzophenones, and the similarity between trifluoroacetophenones and benzophenones. The chemical yields are greatly

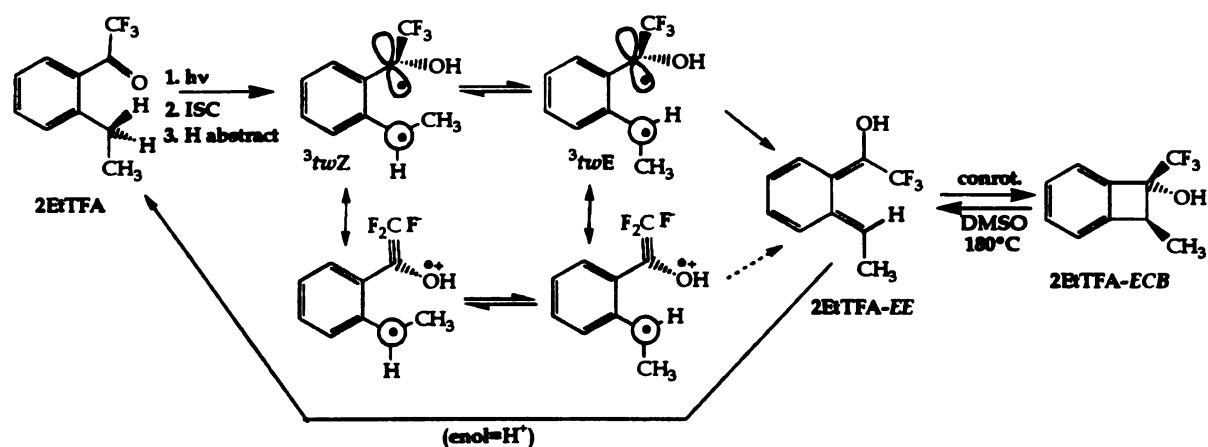


Scheme 68. An example of high stereoselectivity from trifluoroacetophenones.

enhanced when the hydroxy radical center of the biradical is stabilized with a trifluoromethyl group or a phenyl ring. We thought that the similar behavior

between ortho substituted trifluoroacetophenone and benzophenone derivatives may provide further diastereoselective control for the formation of benzocyclobutenols.

2-Ethyl-trifluoroacetophenone (2EtTFA) gives only E-benzocyclobutenol (2EtTFA-ECB) when irradiated in deaerated benzene with no trace of the Z-benzocyclobutenol. If we consider the same factors stressed in Scheme 41 and Scheme 57, then *twE* is the best geometry and preferred over *Etw* and *Ztw* since the ethyl radical prefers to be coplanar with the benzene ring. This cannot be achieved in the latter two without a loss of conjugation. Sterically *twE* is preferred over *twZ* since the methyl is pointing outward in the former case. The *twE* geometry will decay to EE and EZ enols but EE is preferred due to sterics



Scheme 69. Captodative resonance in the formation of 2EtTFA-ECB.

and would cyclize to E-benzocyclobutenol which is observed experimentally. The 2EtTFA-ECB is stable at room temp unlike 2BzBP-ECB, in fact it is much more stable than 2EtBP-ECB which opens thermally at 80°C.⁴⁵ 2EtTFA-ECB was heated at 100°C in DMSO with no decomposition after four days but reverted to

2EtTFA (plus several other products) after 27 hours in DMSO at 180°C. Houk's rules predict a ~9 kcal/mol lowering of the activation energy for ring opening when rotating a methoxy group outward,^{51,128} a 1-2 kcal/mol lowering for a methyl rotating outward,¹²⁶ and a ~5 kcal/mol increase for the CF₃ group rotating inward¹²⁶. The net lowering of the activation energy for these three groups is ~5 kcal/mol (benzocyclobutene opening to *o*-xylylene has an activation energy of ~40 kcal/mol)¹²⁸. An estimate of the rate constant for opening of 2EtTFA-ECB using $E_A = 35$ kcal/mol, $\log A = 12$ at 25°C is $2.3 \times 10^{-14} \text{ s}^{-1}$ with a corresponding half life of 9.5×10^5 years. The rate of opening at 180°C with the same parameters is $1.5 \times 10^{-5} \text{ s}^{-1}$ and corresponds to a half life of 14 hours which correlates nicely with my experiment.

IV. Results for 2' and 4' substituted 2,4,6-trialkylbenzophenones

A. General preparation of ketones

The ketones were prepared by Friedel-Crafts acylation of the 2,4,6-trialkyl substituted benzene with the appropriately substituted acid chloride. 2,4,6,2',4',6'-Hexamethylbenzophenone Me₆BP was synthesized by the reaction of mesitylene with one equivalent of oxalyl chloride in carbon disulfide. Most compounds were sufficiently pure after washing with 1N NaOH(aq) solution followed by recrystallization from petroleum ether (ligroin). Scheme 70 gives the ortho substituted 2'4'6'-trialkylbenzophenones studied.

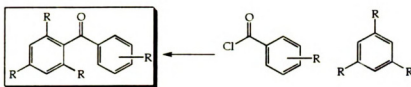
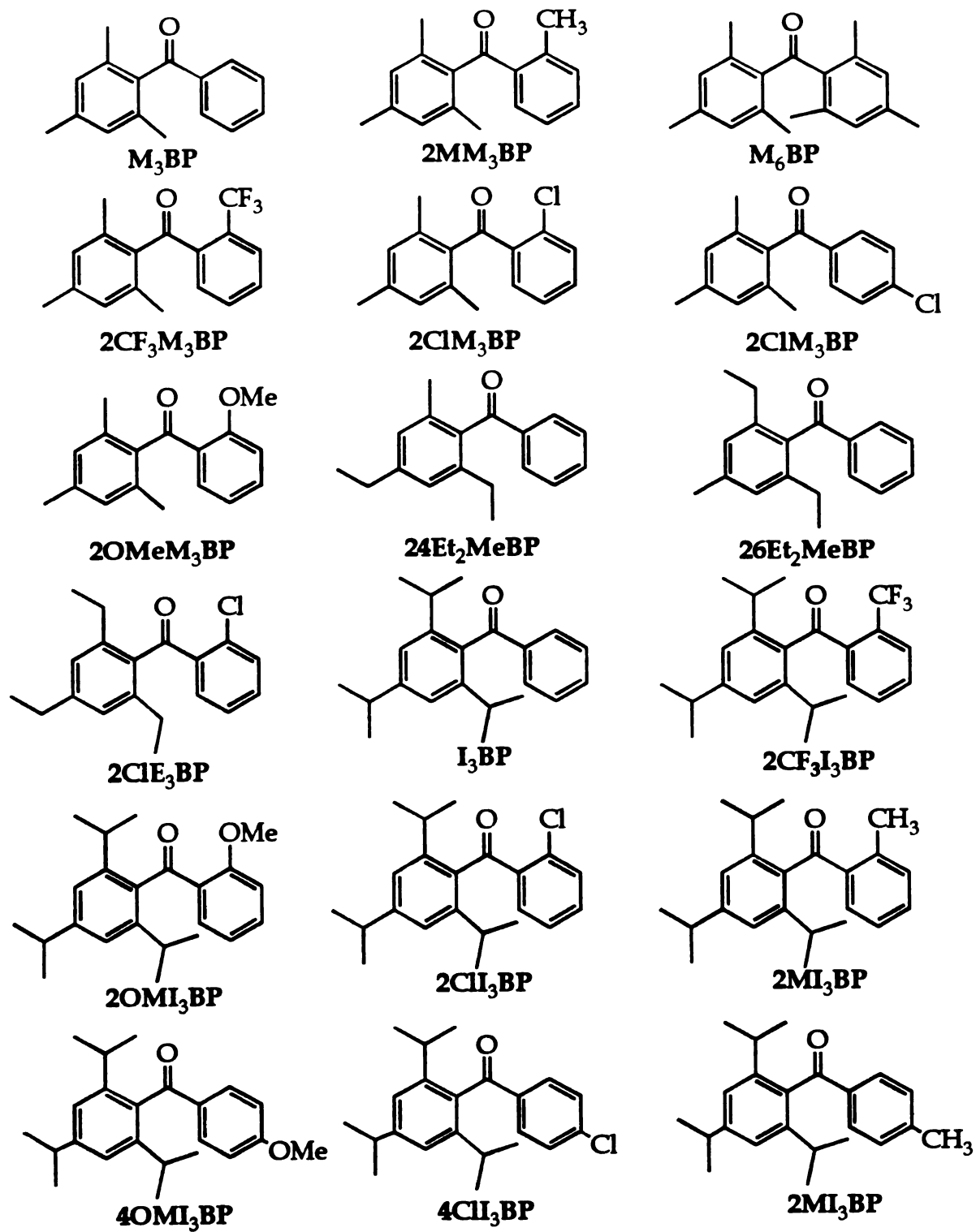


Table 16. Abbreviations for 2,4,6-trialkylbenzophenones studied.

Ketone (BP) ^a	R	R'	Abbreviation
2,4,6-triisopropylBP	i-Pr	H	I ₃ BP
2'-chloro-2,4,6-triisopropylBP	i-Pr	2'-CH ₃	2ClI ₃ BP
4'-chloro-2,4,6-triisopropylBP	i-Pr	4'-CH ₃	4ClI ₃ BP
2'-methyl-2,4,6-triisopropylBP	i-Pr	2'-Cl	2MI ₃ BP
4'-methyl-2,4,6-triisopropylBP	i-Pr	4'-Cl	4MI ₃ BP
2'-methoxy-2,4,6-triisopropylBP	i-Pr	2'-OCH ₃	2OMI ₃ BP
4'-methyl-2,4,6-triisopropylBP	i-Pr	4'-OCH ₃	4OMI ₃ BP
2'-(α,α,α -trifluoromethyl)-2,4,6-triisopropylBP	i-Pr	2'-CF ₃	2CF ₃ I ₃ BP
2'-chloro-2,4,6-triethylBP	CH ₂ CH ₃	2'-Cl	2ClE ₃ BP
2,4-diethyl-6-methylBP	2,6-diEt-4-Me	H	24Et ₂ MeBP
2,6-diethyl-4-methylBP	2,6-diEt-4-Me	H	26Et ₂ MeBP
2,4,6-trimethylBP	CH ₃	H	M ₃ BP
2'-methyl-2,4,6-trimethylBP	CH ₃	2'-CH ₃	2MM ₃ BP
2'-chloro-2,4,6-trimethylBP	CH ₃	2'-Cl	2ClM ₃ BP
4'-chloro-2,4,6-trimethylBP	CH ₃	4'-Cl	4ClM ₃ BP
2'-methoxy-2,4,6-trimethylBP	CH ₃	2'-OCH ₃	2OMM ₃ BP
2'-(α,α,α -trifluoromethyl)-2,4,6-trimethylBP	CH ₃	2'-CF ₃	2CF ₃ M ₃ BP
2,4,6-hexamethylBP	CH ₃	2',4',6'-trimethyl	M ₆ BP

^a BP = benzophenone



Scheme 70. 2'- and 4'- 2,4,6-trialkylbenophenones studied.

B. Identification of Products

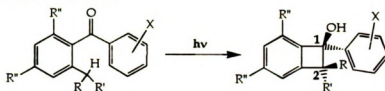
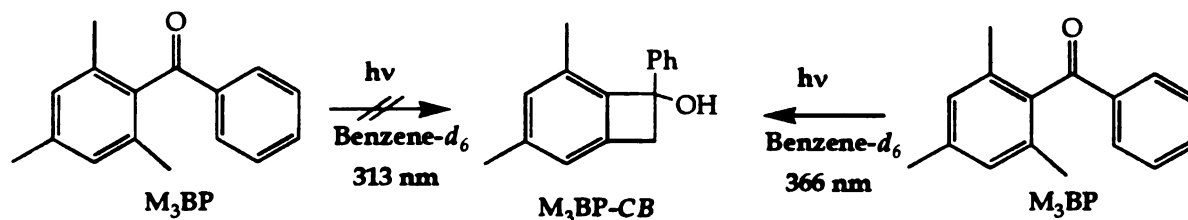


Table 17. Chemical shifts of benzocyclobutenols from 2' substituted 2,4,6-trialkylbenzophenones.

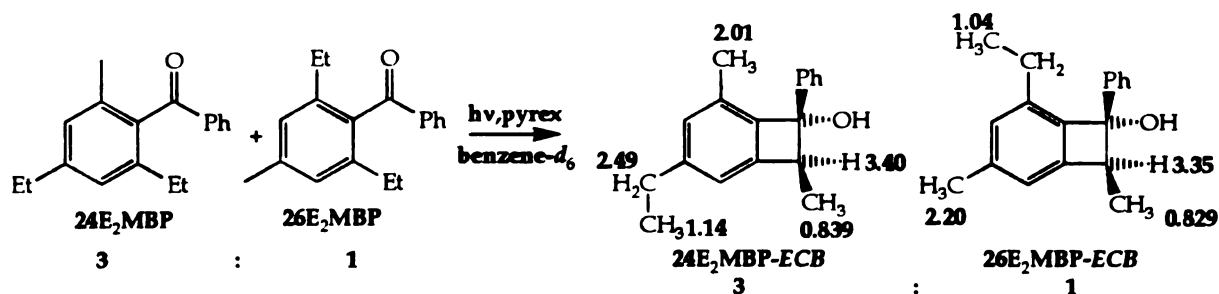
Product	solvent	R, δ (ppm)	R', δ (ppm)	X, δ (ppm)	OH, δ (ppm)	C1	C2
1 ₁ BP- CB	benzene- <i>d</i> ₆	CH ₃ , 1.33	CH ₃ , 0.886	H, —	2.18	—	—
1 ₁ BP- CB	chloroform- <i>d</i> ₁	CH ₃ , 1.49	CH ₃ , 0.85	H, —	2.58	85.86	54.54
2Cl ₁ BP- CB	benzene- <i>d</i> ₆	CH ₃ , 1.59	CH ₃ , 1.06	2Cl, —	3.69	—	—
2Cl ₁ BP- CB	chloroform- <i>d</i> ₁	CH ₃ , 1.65	CH ₃ , 1.07	2Cl, —	3.73	87.44	54.36
4Cl ₁ BP- CB	benzene- <i>d</i> ₆	CH ₃ , 1.22	CH ₃ , 0.78	4Cl, —	2.10	—	—
4Cl ₁ BP- CB	chloroform- <i>d</i> ₁	CH ₃ , 1.43	CH ₃ , 0.800	4Cl, —	2.52	85.38	54.62
2Me ₁ BP- CB	benzene- <i>d</i> ₆	CH ₃ , 1.56	CH ₃ , 0.907	2CH ₃ , 2.55	—	—	—
4Me ₁ BP- CB	benzene- <i>d</i> ₆	CH ₃ , 1.34	CH ₃ , 0.922	4CH ₃ , 2.03	2.20	—	—
4Me ₁ BP- CB	chloroform- <i>d</i> ₁	CH ₃ , 1.44	CH ₃ , 0.807	4CH ₃ , 2.32	—	85.79	54.47
2OMe ₁ BP- CB	benzene- <i>d</i> ₆	CH ₃ , 1.65	CH ₃ , 0.96	2OCH ₃ , 3.05	4.62	—	—
2OMe ₁ BP- CB	chloroform- <i>d</i> ₁	CH ₃ , 1.53	CH ₃ , 0.88	2OCH ₃ , 3.96	4.58	86.81	55.21
4OMe ₁ BP- CB	benzene- <i>d</i> ₆	CH ₃ , 1.34	CH ₃ , 0.923	4OCH ₃ , 3.21	2.18	—	—
4OMe ₁ BP- CB	chloroform- <i>d</i> ₁	CH ₃ , 1.46	CH ₃ , 0.84	4OCH ₃ , 3.79	2.56	85.57	55.09
2CF ₃ ₁ BP- CB	benzene- <i>d</i> ₆	CH ₃ , 1.33	CH ₃ , 0.915	2CF ₃ , —	2.43	—	—
2CF ₃ ₁ BP- CB	chloroform- <i>d</i> ₁	CH ₃ , 1.50	CH ₃ , 0.910	2CF ₃ , —	2.68	87.69	55.42
2ClEt ₂ BP- CB	benzene- <i>d</i> ₆	H, 3.72	CH ₃ , 1.04	2Cl, —	—	—	—
24Et ₂ MeBP- CB ^a	benzene- <i>d</i> ₆	H, 3.40	CH ₃ , 0.839	—	—	—	—
26Et ₂ MeBP- CB ^a	benzene- <i>d</i> ₆	H, 3.35	CH ₃ , 0.829	—	—	—	—
M ₁ BP- CB	benzene- <i>d</i> ₆	H, 3.10	H, 3.29	—	—	81.10	51.14
2MM ₁ BP- CB	benzene- <i>d</i> ₆	H, 3.27	H, 3.48	2,4,6-Me ₃ , 2.23(3H), 2.46(6H)	—	—	—
2OMM ₁ BP- CB ^a	benzene- <i>d</i> ₆	H, 3.40	H, 3.65	2OM, 3.04	—	—	—
M ₄ BP- CB ^a	benzene- <i>d</i> ₆	H, 3.28	H, 3.35	Ph, —	—	—	—

^a from crude ¹H-NMR.

1. 2,4,6-trimethylbenzophenone (M_3BP)

The photochemistry of M_3BP has been examined by several groups including ours.^{50,103} It was not my intention to conduct an in depth product study of M_3BP but only to determine the quantum yield of M_3BP-CB formation. Irradiation of a 0.084 M M_3BP benzene- d_6 solution with 313 nm filtered light gave no product formation after 24 hours at 25°C. The nmr sample tubes were irradiated parallel to 0.1 M valerophenone. The valerophenone had completely reacted during this time period indicating that light was reaching the samples. The reaction solution had become pale yellow after the 24 hours of irradiation. After this time, a new valerophenone solution (0.63 M in benzene- d_6) was prepared. The same M_3BP nmr sample tubes were irradiated parallel to the valerophenone solution with 366 nm filtered light. After four hours irradiation (366 nm) at 25°C 5% of the M_3BP had been converted to M_3BP-CB which was observed by the growth of the two doublets at δ 3.10 and 3.29 ppm in the 1H -NMR spectrum. The quantum yield for formation of M_3BP-CB was determined to be 0.022 at 366 nm by integration of these peaks relative to the methyl ester peak of the benzoate internal standard.

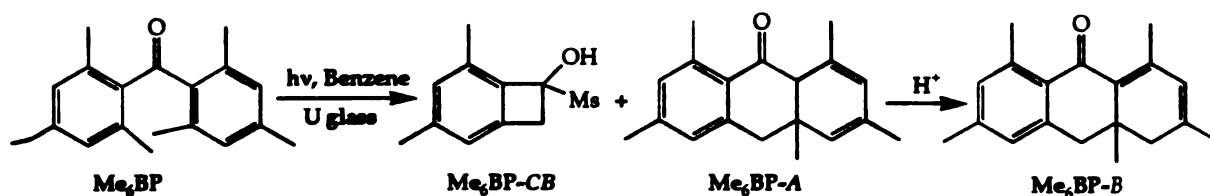
2. *2,4-diethyl-6-methylbenzophenone* (24E₂MBP) and *2,6-diethyl-4-methylbenzophenone* (26E₂MBP)



Scheme 71. Photochemistry of 24E₂MBP and 26E₂MBP.

The ketones 24E₂MBP and 26E₂MBP were irradiated as a 3:1 mixture of 24E₂MBP: 26E₂MBP. The two major products had ¹H-NMR spectra consistent with 24E₂MBP-ECB and 26E₂MBP-ECB, no other isomers were observed (no Z-CB or benzocyclobutenol from hydrogen abstraction from the ortho methyl group). The ratio of 24E₂MBP-ECB : 26E₂MBP-ECB was 3:1 and was determined by integration of the aryl methyl singlets. The benzocyclobutenols ECB-24E₂MBP and ECB-26E₂MBP from 24E₂MBP and 26E₂MBP were assigned the *E* stereochemistry due to their upfield chemical shift of their methyl doublets.

3. *2,4,6,2',4',6'-hexamethylbenzophenone* (M₆BP)



Scheme 72. Photochemistry of 2,2',4,4',6,6'-hexamethyl benzophenone

Irradiation of a 0.01 M **M₆BP** benzene-*d*₆ solution yielded one major product **M₆BP-1** and a minor product **M₆BP-CB** (see Figure 27). The reaction was complete (100% conversion) after 9 hours of irradiation after which a yellow solution remained. The formation of **M₆BP-1** and **M₆BP-CB** was independent of light source, both products formed by irradiation with either a medium pressure mercury arc lamp (Pyrex filtered, 17-20°C) or in a Rayonet reactor (300 nm lamps). However the reaction was much cleaner (i.e. no secondary products) when the temperature was maintained at 17-20°C. During purification a third product was isolated that was not apparent in the ¹H-NMR of the crude reaction mixture acquired immediately after irradiation (see Figure 28). This product had an ¹H-NMR spectrum consistent with **M₆BP-2**.

The ¹H-NMR spectrum of **M₆BP-1** has five distinct methyl signals at 0.896 (s), 1.56 (d, *J* = 1.8 Hz), 1.96 (s), 2.32 (s) and 2.63 (s) ppm, an AB quartet at 2.44 and 2.95 (, *J* = 17 Hz), a methine hydrogen at 3.27 (s) ppm, two vinyl resonances at 5.02 (s) and 5.49 (q, *J* = 1.8 Hz), and two aromatic resonances at 6.53 (s) and 6.59 (s) ppm. It is interesting that only one of the two allylic methyls has coupling with one of the vinyl hydrogens. However, the methyl signal at δ 2.32 is much broader than the other three methyl resonances with unresolved shoulders and is assigned as the second allylic methyl group. The product **M₆BP-1** was stable to heating at 50°C for 12 hours.

Treatment of the crude **M₆BP-1** in benzene-*d*₆ with a few crystals of *p*-toluenesulfonic acid caused isomerization (~50%) to **M₆BP-2** within 6 hours and

was complete after 48 hours and had turned a brilliant (canary) yellow. The isomerization was followed by ^1H NMR in which a new AB quartet at (1.50 and 1.90 ppm) was formed at the expense of the vinyl proton (5.02 ppm) and the bridgehead methine hydrogen (3.27 ppm) from $\text{M}_6\text{BP-1}$ (see Figure 29). The AB quartet (2.44 and 2.55 ppm) for the benzylic methylene in $\text{M}_6\text{BP-1}$ migrated to 2.54 and 2.16 ppm respectively while only one vinyl (5.52 ppm, q, $J = 1.5$ Hz) resonance remained.

The ^1H -NMR spectrum of the crude reaction products shows an AB quartet (at 3.4 ppm) which is consistent with the benzocyclobutenol $\text{M}_6\text{BP-CB}$, which decomposed and could not be isolated and characterized. The AB quartet assigned to $\text{M}_6\text{BP-CB}$ disappeared on heating the NMR sample at 50°C for 12 hours. The reaction was very sensitive to temperature. When the sample was irradiated while hung outside the immersion well or in the Rayonet reactor without cooling the reaction mixture became very complex with additional peaks. This problem was alleviated by controlling the reaction temperature by submerging the water cooled immersion well and the sample tube in a dewar with deionized water.

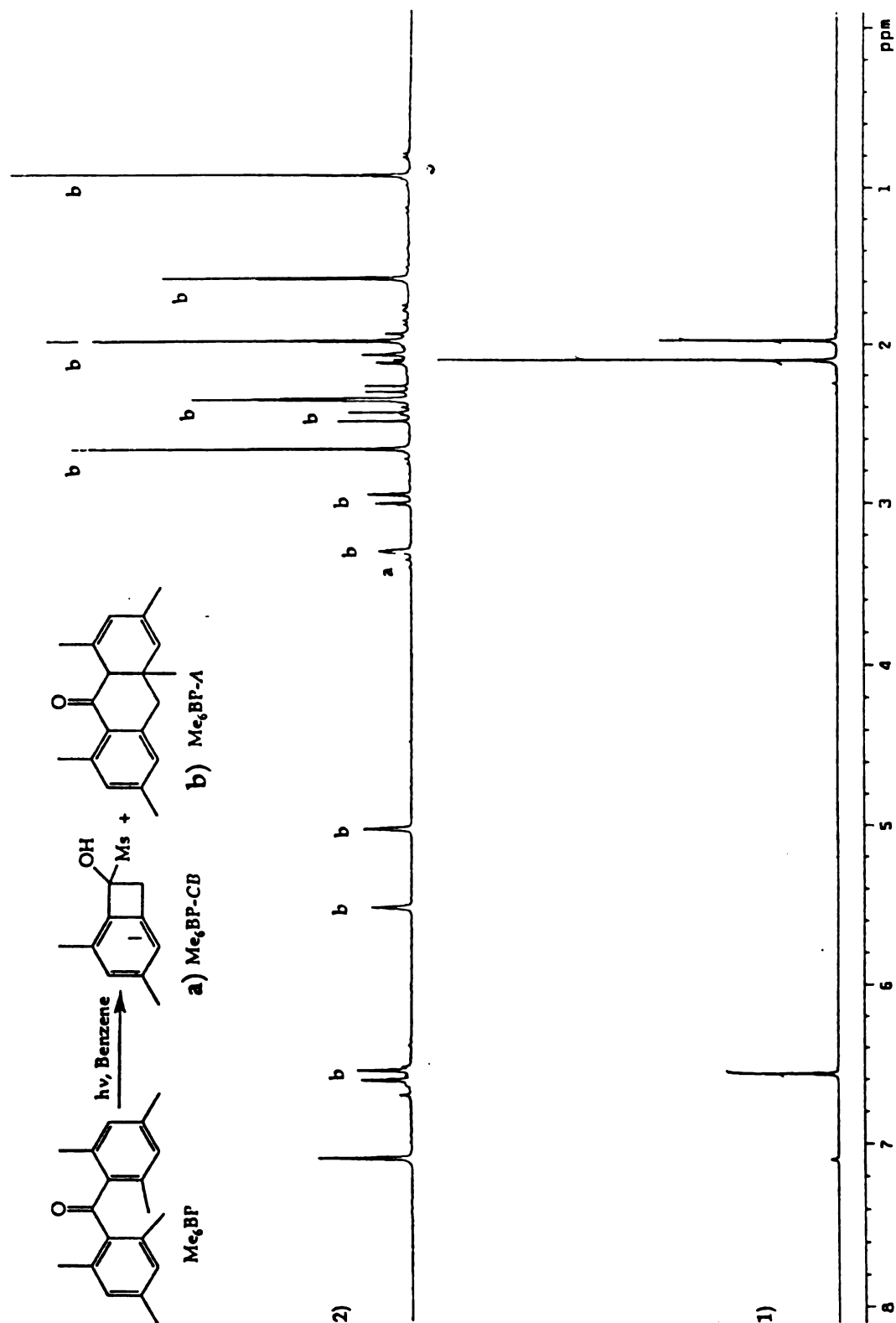


Figure 27. ¹H-NMR Spectra for Me₆BP in benzene-*d*₆ 1) before irradiation 2) after 9 hours irradiation.

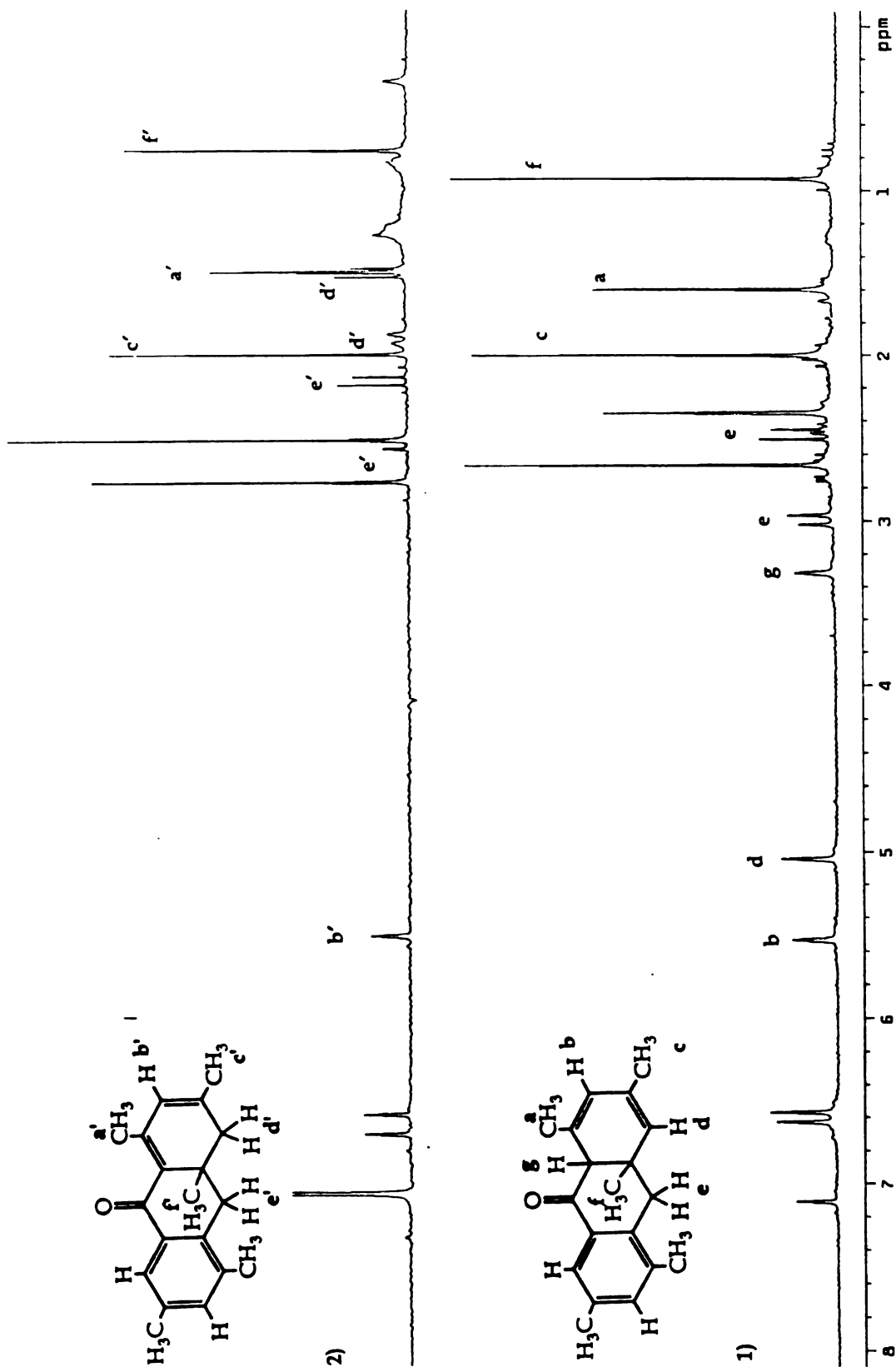


Figure 28. ^1H -NMR spectra of 1) $\text{M}_6\text{BP-1}$ and 2) $\text{M}_6\text{BP-2}$ in benzene- d_6 .

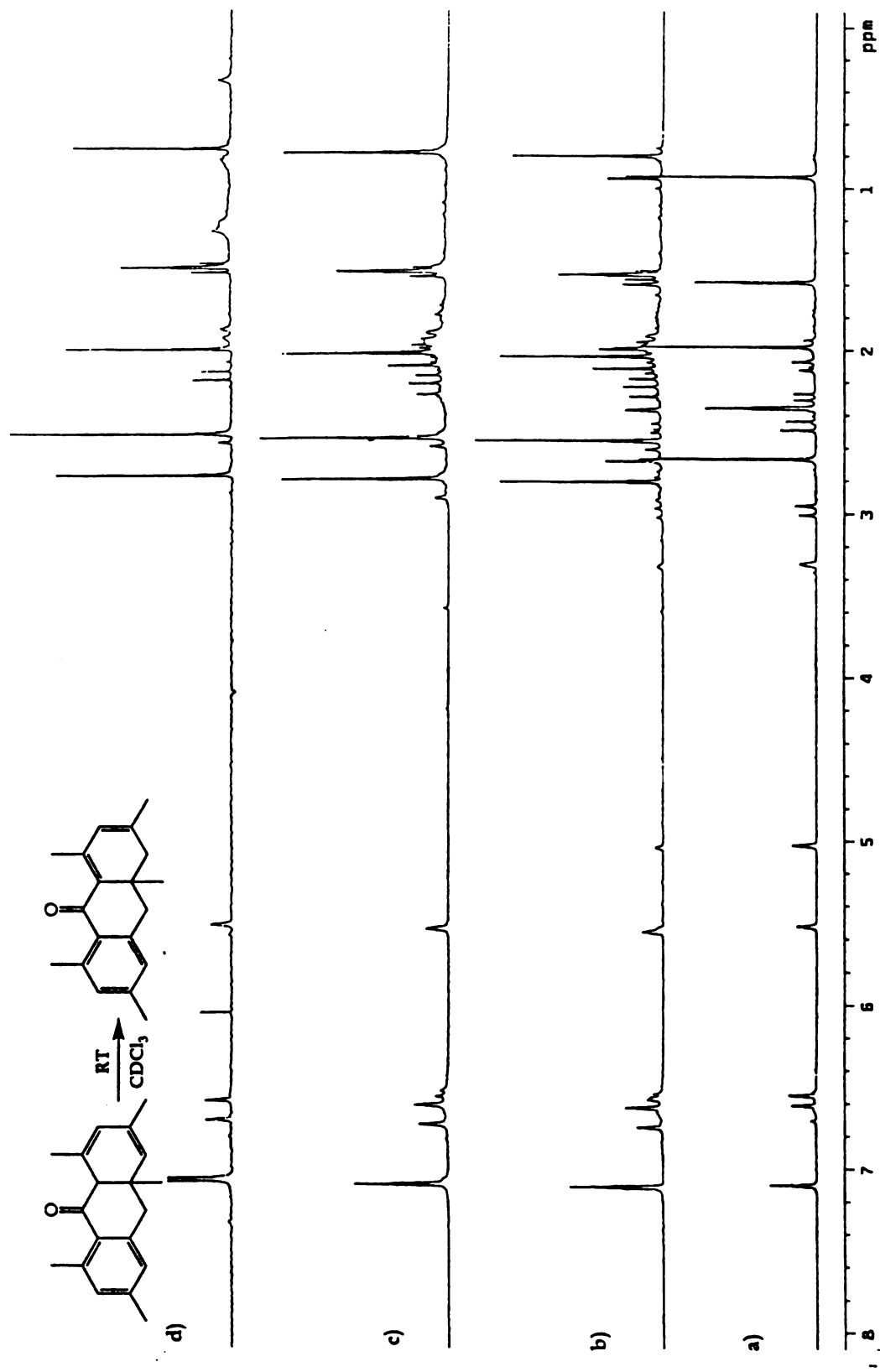
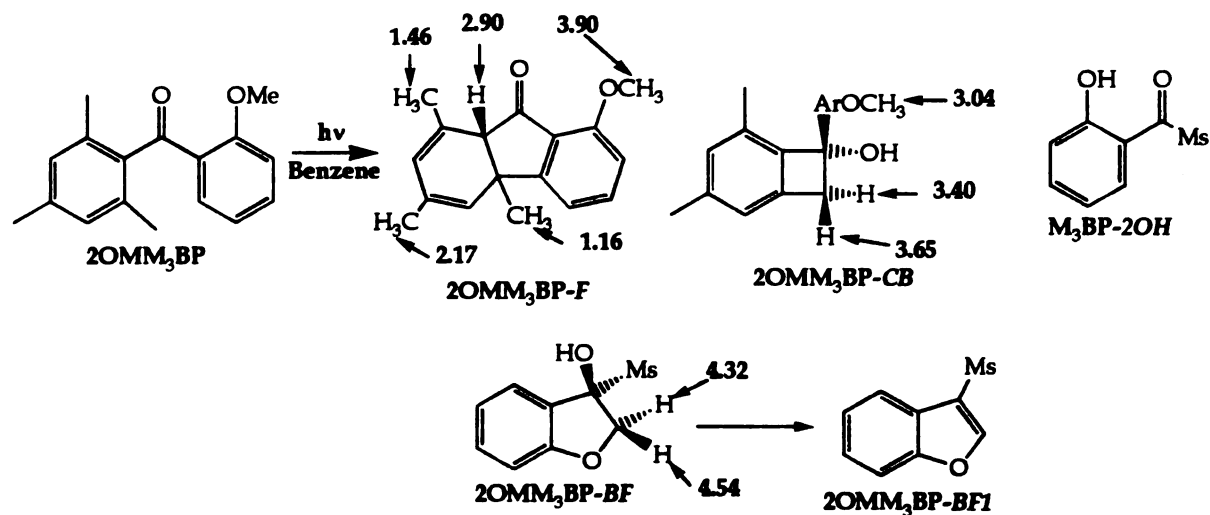


Figure 29. ¹H-NMR Spectra for isomerization of M₆BP-1 to M₆BP-2 in benzene-*d*₆ a) from NMR scale photoreaction of M₆BP b) in dark 6 hours with pTsOH c) in dark 48 hours with pTsOH d) isolated M₆BP-1.

4. 2'-methoxy-2,4,6-trimethylbenzophenone (2OMM₃BP)



Scheme 73. Photochemistry of 2'-methoxy-2,4,6-trimethylbenzophenone Chemical shifts (ppm) in benzene-*d*₆.

The photochemistry of 2OMM₃BP yielded four photoproducts 2OMM₃BP-F, 2OMM₃BP-BF, M₃BP-2OH and 2OMM₃BP-CB. The NMR scale photoreaction in benzene-*d*₆ gave different results with different photochemical reactor setups. Irradiation in the Rayonet reactor (300 nm lamps, ~45°C) of a 0.01 M benzene-*d*₆ ketone solution after 14 hours gave a product distribution of 1.0:2.9:1.5 / 2OMM₃BP-F : 2OMM₃BP-BF : 2OMM₃BP-CB. The quantum yield for 2OMM₃BP-F formation was measured at 313 nm by ¹H-NMR and found to be 0.074 (27% conversion). After 60 minutes of irradiation the sample had turned yellow. After six hours the sample had turned auburn, which remained throughout the course of the reaction. An additional product was formed at short irradiation times (~20 minutes) and possessed a doublet at 4.90 ppm, *J* = 4.80 Hz and a broad unresolved triplet at 3.81 which integrated in a 2:1 ratio.

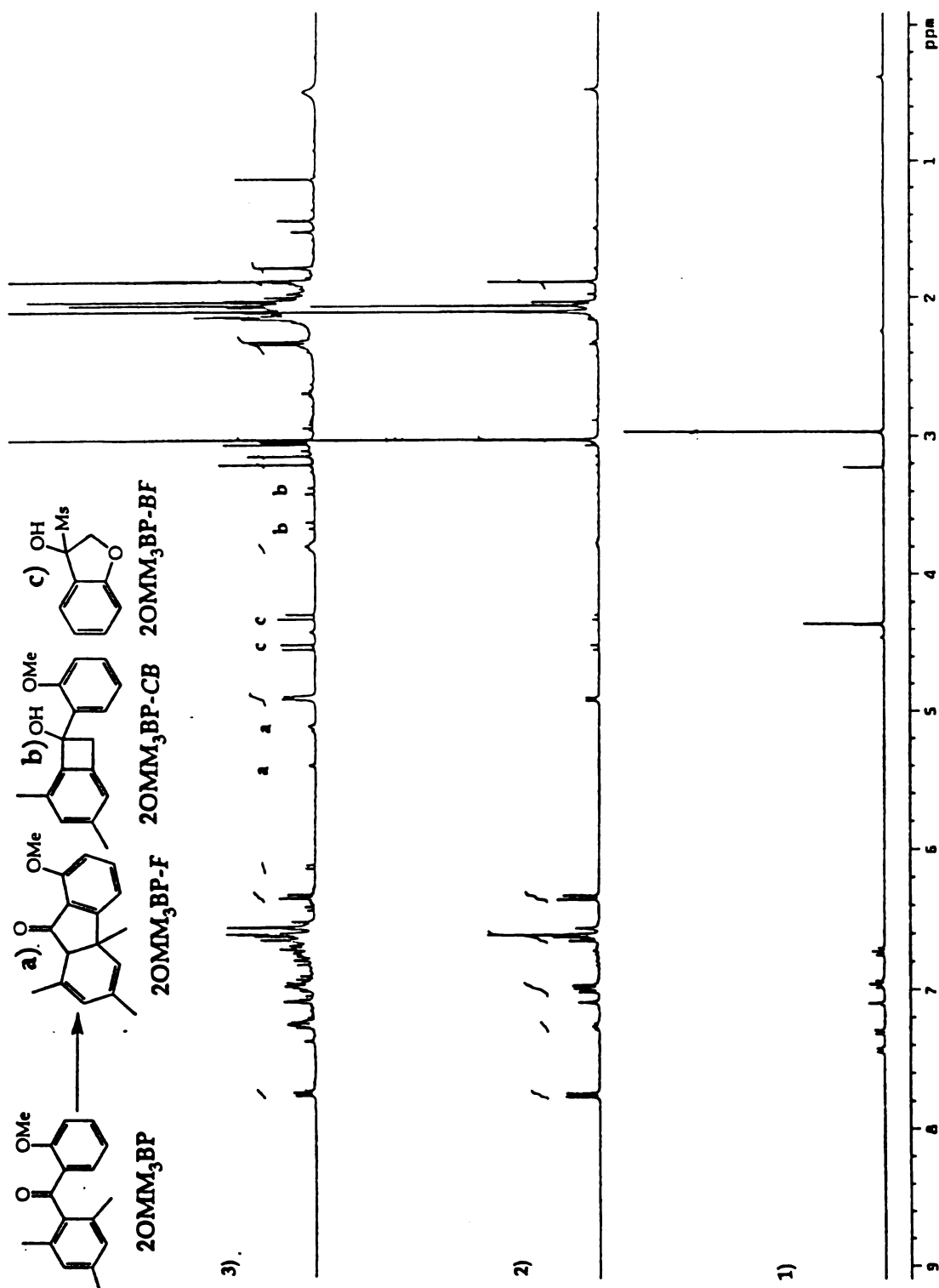
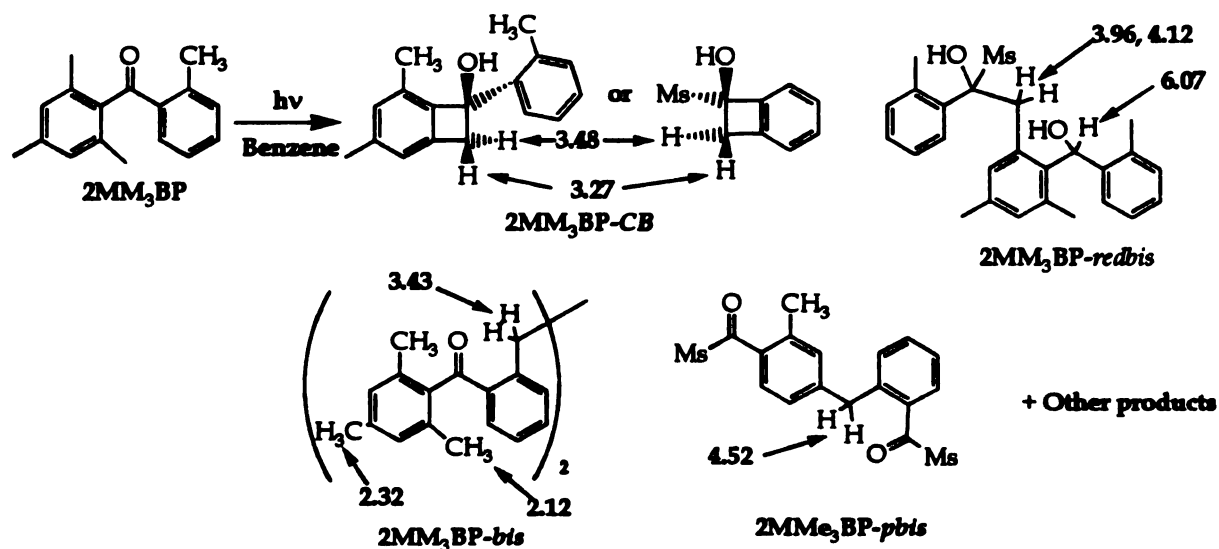


Figure 30. ¹H NMR Spectra of 2OMM₃BP in benzene-*d*₆ 1) before irradiation 2) after irradiation 1 hour 3) after irradiation 6 hours.

This unidentified product is formed in a 1:1 ratio with 2OMM₃BP-BF (assuming the unidentified product's resonance at 4.90 ppm is 2 H's). Irradiation of a similar sample in a water cooled immersion well with Pyrex filtered light from a mercury arc lamp which was submerged in a dewar with deionized water gave a product distribution 1.4:1.0:0.3/2OMM₃BP-F: 2OMM₃BP-BF : 2OMM₃BP-CB after 9 hours. However, the previously unidentified product from the Rayonet experiment was not observed under these conditions. A small amount of the product 2OMM₃BP-2OH was isolated during a preparative scale reaction, it was difficult to tell what the ratio (relative to the other products) was by ¹H-NMR due to the number of overlapping peaks (in both aliphatic and aryl regions) in the crude sample. For details of ¹H-NMR the reaction see Figure 30.

5. 2'-methyl-2,4,6-trimethylbenzophenone (2MM₃BP)



Scheme 74. 2'-methyl-2,4,6-trimethylbenzophenone, Chemical shifts (ppm) in CDCl₃.

A 0.01 M deaerated 2MM₃BP benzene solution was irradiated with uranium glass (>340 nm) filtered light from a medium pressure mercury lamp at 17-20°C. The reaction was complete after ~72 hours of irradiation and a yellow color persisted. The solvent from a small fraction of the reaction solution was removed by rotoevaporation and dissolved in chloroform-*d*₁ and ¹H-NMR analysis revealed a *very* complicated spectrum. The ¹H-NMR sample tube with the crude reaction mixture was left standing and became a very deep green in color. The crude reaction was separated by silica gel column chromatography (95:5 hexane:ethyl acetate) followed by a second purification with PTLC using the same solvent system. Four major products were identified as 2MM₃BP-*CB*, 2MM₃BP-*redbis*, 2MM₃BP-*bis*, and 2MM₃BP-*pbis* along with three minor products which I could not assign a structure to. However, the unidentified products were likely dimers since their mass spectra indicated *m/z* peaks >400. The 2MM₃BP-*pbis* eluted first from the column followed by **unknown-1**, 2MM₃BP-*bis*, **unknown-2**, 2MM₃BP-*redbis* and **unknown-3** being the last. The presumed 2MM₃BP-*CB* was not isolated due to decomposition during chromatography but was evident in the crude ¹H-NMR spectrum. The characteristic AB quartet for 2MM₃BP-*CB* was at 3.27, 3.38 ppm but it is not clear if the benzocyclobutenol was formed from hydrogen abstraction from the mesityl ring or the mono substituted ring.

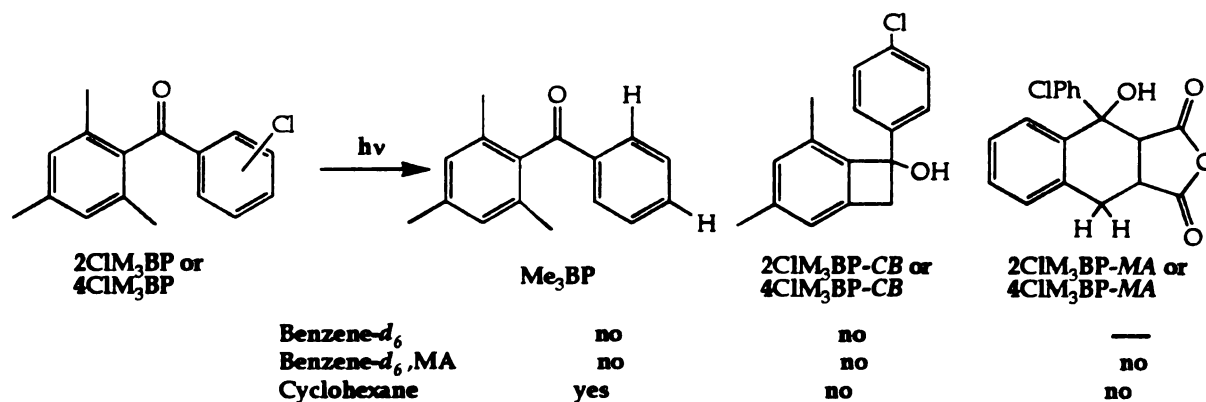
The structure for 2MM₃BP-*bis* was arrived at from the following spectral data: the ¹H-NMR in CDCl₃ showed two methyl singlets at 2.12 (12H) and

2.32(6H) ppm, two more singlets at 3.43(4H) and 6.87(4H) which were assigned to the benzylic methylene and the meta hydrogens on the mesityl ring, there were four sets of aromatic protons at 7.16(ddd, $J = 7.5, 7.5, 1.5$ Hz, 2H), 7.37(dd, $J = 7.8, 1.5$ Hz, 2H), 7.45(ddd, $J = 7.5, 7.5, 1.5$ Hz, 2H) and 7.65(dd, $J = 7.5, 1.5$ Hz, 2H). The ^{13}C -NMR in CDCl_3 showed a total of 14 resonances. Mass spectral analysis confirmed the compound being a dimer which had a m/z at 474.4(M^+).

The structure for 2MM₃BP-*pbis* was arrived at from the following spectral data: the ^1H -NMR in CDCl_3 showed 4 methyl singlets at 1.89(6H), 2.04(6H), 2.28(3H) and 2.60(3H), a methylene singlet at 4.52 ppm (2H), two 2H singlets 6.80 and 6.82 ppm which are assigned to the meta protons of the two different mesityl rings, a singlet at 7.15 (1H, meta to carbonyl), an aromatic doublet at 6.96 (1H) ppm and complicated aromatic region between 7.15-7.48 (6H). The ^{13}C -NMR in CDCl_3 showed a total of 27 resonances. Mass spectral analysis confirmed the compound being a dimer which had a m/z at 474.2(M^+).

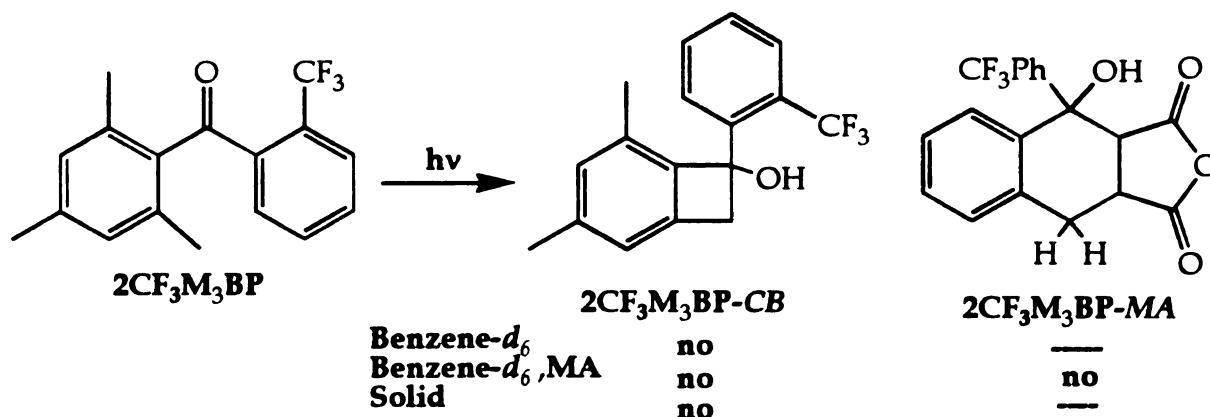
The structure for 2MM₃BP-*redbis* was arrived at from the following spectral data: the ^1H -NMR in CDCl_3 showed 5 methyl singlets at 1.94(3H), 1.98(6H), 2.17(3H), 2.26(3H), 2.45(6H), an AB quartet at 3.96, 4.12($J = 22.8$ Hz), two doublets at 6.07 ($J = 3.6$ Hz, 1H, ArCMsHOH) at 6.24 ($J = 7.8$ Hz, 1H), two aromatic singlets at 6.79 (3H) and 6.93(1H), a triplet at 7.00($J = 7.2$ Hz, 1H) and three multiplets in the ranges 6.90-6.96(1H), 7.14-7.30(4H) and 7.52-7.57(1H). The ^{13}C -NMR in CDCl_3 showed a total of 27 resonances.

6. 2' and 4'-chloro-2,4,6-trimethylbenzophenone (2ClM₃BP and 4ClM₃BP)

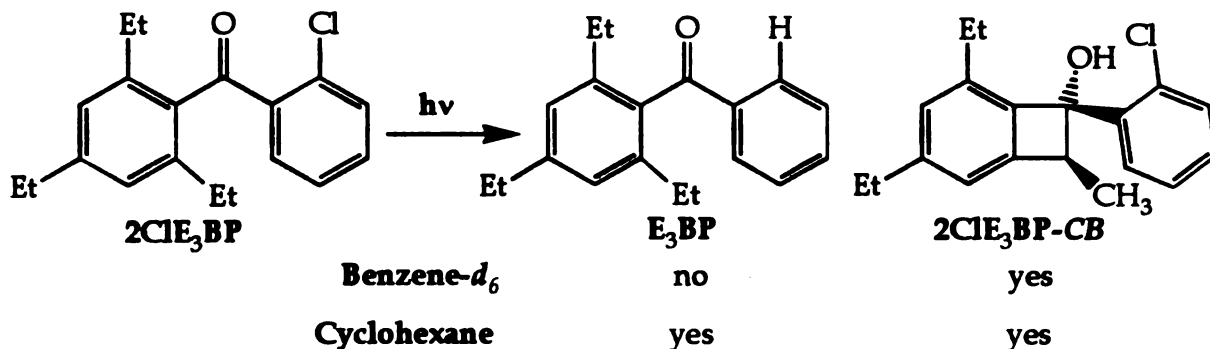


Scheme 75. Photochemistry of 2' and 4'-chloro-2,4,6-trimethylbenzophenone

Irradiation of 2ClM₃BP and 4ClM₃BP in benzene and benzene with excess maleic anhydride (0.10 M MA, 0.01M ketone) did not give any products after 24 hours of irradiation. Irradiation of 2ClM₃BP and 4ClM₃BP in cyclohexane gave M₃BP after 30 minutes irradiation. The formation of M₃BP was determined by GC analysis by comparing the chromatogram of the crude reaction mixture with authentic M₃BP.

7. 2'-(α,α,α -trifluoromethyl)-2,4,6-trimethylbenzophenone (2CF₃M₃BP)Scheme 76. Photochemistry of 2'-(α,α,α -trifluoromethyl)-2,4,6-trimethylbenzophenone

Irradiation of 2CF₃M₃BP in benzene, benzene with excess maleic anhydride or in the solid state gave no products after 50 hours of irradiation through Pyrex.

8. 2'-chloro-2,4,6-triethylbenzophenone (2ClE₃BP)

Scheme 77. Photochemistry of 2'-chloro-2,4,6-triethylbenzophenone

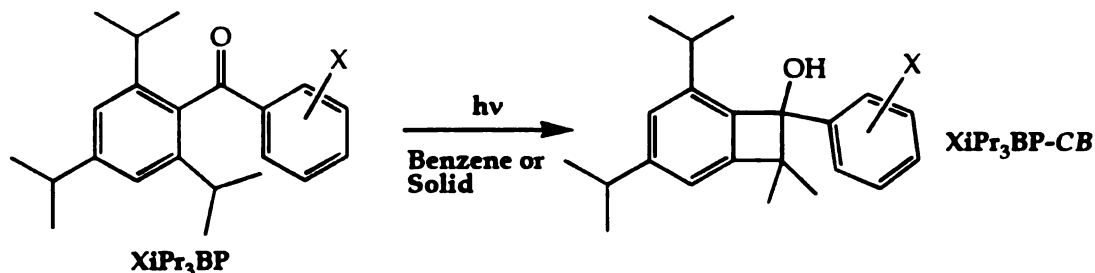
Irradiation of 2ClE₃P in benzene-*d*₆ gave a complex mixture of products. The major product of the crude mixture possessed a quartet at 3.72 ppm with J=

6.9 Hz coupling, it also contained a doublet at 1.04 ppm with a $J = 6.9$ Hz coupling. The chemical shift of the methyl doublet is in agreement with the chemical shift of the methyl cis to the 2-chlorophenyl ring in CB-2Cl₃BP which is 1.06 ppm thus the benzocyclobutenol 2ClE₃BP-ECB is assigned the *E* configuration.

Irradiation of 2ClEt₃P in cyclohexane gave a mixture of products including 2ClE₃BP-ECB and E₃BP. The cyclohexane reaction mixture after irradiation had a stench that was attributed to HCl(g) that was noticed when the septum was removed. The solution also caused the septum to become brittle and turn black. The reaction solution was filtered through a small plug of anhydrous sodium bicarbonate and sodium sulfate and then analyzed by GC. The chromatogram gave a peak (~4%) with a retention time of 5.45 minutes after 30 minutes irradiation, the peak grew to ~20% of total area after 4 hours but decreased to 16% of total area after 25 hours. A standard solution of 2,4,6-triethylbenzophenone gave a retention time of 5.56 minutes while the starting ketone 2ClE₃BP had a retention time of 11.65 minutes. A second peak was also visible after 30 minutes irradiation with a retention time of 15.11 minutes and ~6% of total area. This peak grew to 15% of the total area after 4 hours irradiation but decreased to 11% of the total area after irradiating the sample 25 hours. No attempt was made to isolate any of the photoproducts.

9. Products from 2' substituted 2,4,6-triisopropylbenzophenones

a) Effect of phase



Scheme 78. Photochemistry of 2' substituted 2,4,6-triisopropylbenzophenones

Table 18. Solution vs. Solid State Reactivity of 2'-2,4,6-triisopropylbenzophenones.

Ketone	Product	Reacts in benzene	Reacts in solid
I ₃ BP	I ₃ BP-CB	yes	yes
2ClI ₃ BP	2ClI ₃ BP-CB	yes	yes
4ClI ₃ BP	4ClI ₃ BP-CB	yes	yes
2MI ₃ BP ^a	2MI ₃ BP-CB ^a	yes	no
4MI ₃ BP	4MI ₃ BP-CB	yes	yes
2OMeI ₃ BP	2OMeI ₃ BP-CB	yes	yes
4OMeI ₃ BP	4OMeI ₃ BP-CB	yes	yes
2CF ₃ I ₃ BP	2CF ₃ I ₃ BP-CB	yes	no

All ketones in Table 18 were subjected to irradiation in degassed benzene solutions and the solid state. All ketones reacted in solution and gave only one product with the exception of 2MI₃BP, in contrast two of the ketones, 2MI₃BP and 2CF₃I₃BP did not react in the solid after 24 hours of irradiation. A typical solid state experiment was conducted by placing ~250 mg of finely powdered XPr₃BP between two glass slides. The reaction was monitored by periodically

washing a small amount of solid from the glass plates with chloroform- d_1 followed by analysis by $^1\text{H-NMR}$. No precautionary steps were taken to exclude oxygen from the solid state reactions.

b) Identification of Products

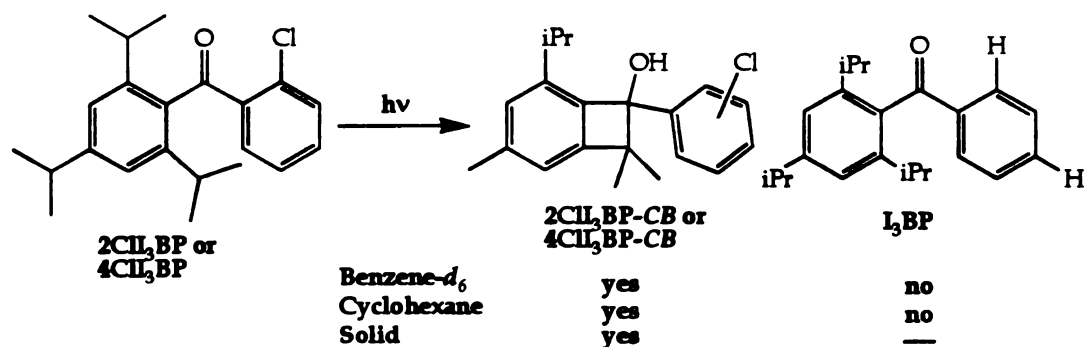
The structural assignments were based on a combination of spectroscopic techniques. FTIR spectroscopy showed the loss of the carbonyl stretching frequency that ranged from $1660\text{--}1690\text{ cm}^{-1}$ with the formation of a sharp alcohol stretching frequency in the range of $3555\text{--}3620\text{ cm}^{-1}$. The structural assignment are consistent with previous literature reports of 2,4,6-triisopropylbenzophenones.¹³⁹

The significant values for the chemical shifts of the benzocyclobutenols are given in Table 18. $^1\text{H-NMR}$ analysis was useful in assigning the two methyl singlets which were formerly a doublet from an isopropyl group. The new singlets differed in their respective chemical shifts by $\sim 0.5\text{ ppm}$ due to the relative configuration to the ortho phenyl substituent. One of the singlets typically appears near $\sim 1.0\text{ ppm}$, this methyl group is *cis* to the phenyl substituent and its large upfield shift stems from being in the shielding cone of the adjacent phenyl ring. The second methyl singlet typically has a chemical shift near $\sim 1.5\text{ ppm}$ and is assigned to a configuration *cis* to the hydroxyl group.

$^{13}\text{C-NMR}$ decoupled spectra were consistent with their $^1\text{H-NMR}$ counterpart for the number of methyl groups. The $^{13}\text{C-NMR}$ spectra revealed

two new aliphatic peaks in the ranges of 51.1-55.5 and 81.0-87.7 ppm. The resonance near 55 ppm is assigned to the gem dimethyl benzylic carbon while the resonance near 85 ppm is assigned to the benzylic alcohol carbon peak (C1).

c) chloro-2,4,6-trisopropylbenzophenone (2ClI₃BP)



Scheme 79. Photochemistry of 2' and 4'-chloro-2,4,6-trisopropylbenzophenone

A summary of the irradiations of 2ClI₃BP and 4ClI₃BP under different conditions are given in Scheme 79. Irradiation of either ketone gives quantitatively the respective benzocyclobutenol 2ClI₃BP-CB or 4ClI₃BP-CB in high chemical yield (>95%) in either solution or the solid state. The ketones were irradiated in degassed cyclohexane and the progress of the reaction monitored by HPLC. No I₃BP was observed and only their respective benzocyclobutenols were formed.

C. Quantum yields

Table 19. Quantum yields for products from 2' substituted 2,4,6-trialkylbenzophenones.

Ketone	Product	Φ_{313}	Φ_{366}
M₃BP	M₃BP-CB	—	0.022
I₃BP	I₃BP-CB	0.710	—
2OMI₃BP	2OMI₃BP-CB	0.510	—
4OMI₃BP	4OMI₃BP-CB	0.770	—
4MI₃BP	4MI₃BP-CB	0.640	—
2CF₃I₃BP	2CF₃I₃BP-CB	0.013	—

D.Semi Empirical Calculations

In order to gain a better understanding of the ground state geometries of the 2' and 4' substituted 2,4,6-trialkylbenzophenones AM1 level semi empirical calculations were conducted. All calculations were performed on a 7100/80 Power Macintosh computer with *Cache* molecular modeling software. The AM1 protocol was used from the *MOPAC6* module in the *Cache* software. The calculations were done by generating an input structure from the *Editor* which was minimized with molecular mechanics (MM2). The purpose of the MM2 calculation was to provide MOPAC with a better input structure. Global minimizations were carried out by using double dihedral drives (the "optimized search|grid" option) in the *Cache* software. The keyword "GEO-OK" was implemented during the double dihedral drive. The starting geometry always started with the 2' or 4' ring (β dihedral angle) twisted orthogonal and was rotated in 10-15° increments until 180° was reached from the starting geometry. The 2,4-disubstituted ring (α dihedral angle) was rotated likewise. The combined searches were automated by the software to give a three dimensional grid of data. The rings were only rotated 180° and not the full 360° due to the symmetry. To minimize the computation time the para alkyl group (for the 2,4,6-trialkyl ring) was excluded from the calculation and it is assumed that this group does not affect the geometries significantly.

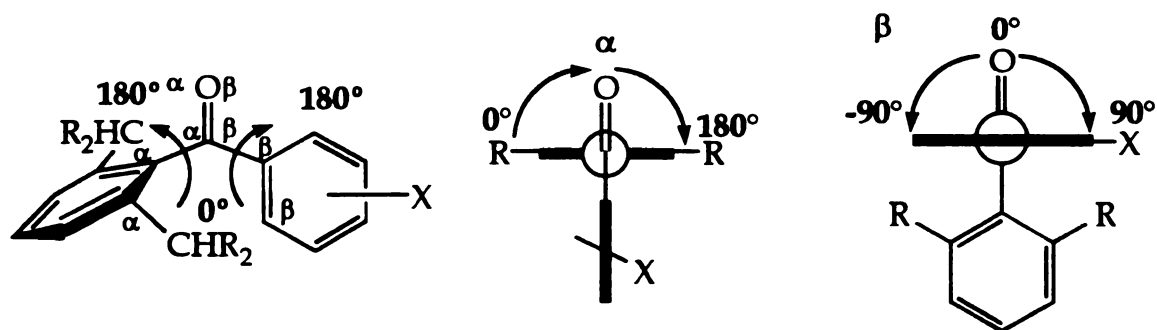


Figure 31. Definition of α and β torsion angles and direction of sign.

Table 20. Bond angles and atom distances of 2' and 4' substituted 2,6-dimethylbenzophenones.

Entry	Ketone (BP=benophenone)	α torsion angle ^b	β torsion angle ^b	C=O ⁰ H distance ^b	C=O ¹⁸⁰ H distance ^b
1	2'-chloro-2,6-dimethylBP	89	-52	3.13	2.57
2	2'-trifluomethyl-2,6-dimethylBP	111	-37	3.09	2.51
3	2'-methoxy-2,6-dimethylBP	84	-24	2.67	3.05
4	2'-methyl-2,6-dimethylBP	99	-22	2.92	2.66
5	4'-cyano-2,6-dimethylBP	84	-7.9	2.64	3.02
6	2,6-dimethylBP	84	-8.1	2.66	3.19
7	4'-chloro-2,6-dimethylBP	84	-8.1	2.65	3.02
8	4'- methoxy-2,6-dimethylBP	81	-7.0	2.64	2.96

^b see Figure 31.

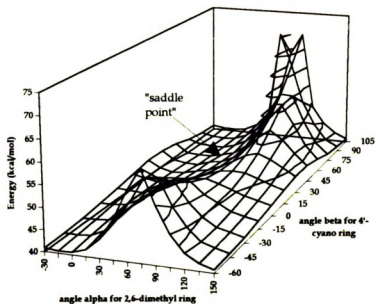


Figure 32. Three dimensional plot of data for 4'-cyano-2,6-dimethylbenzophenone.

Table 21. AM1 energies for double dihedral drive of 4'-cyano-2,6-dimethylbenzophenone.*

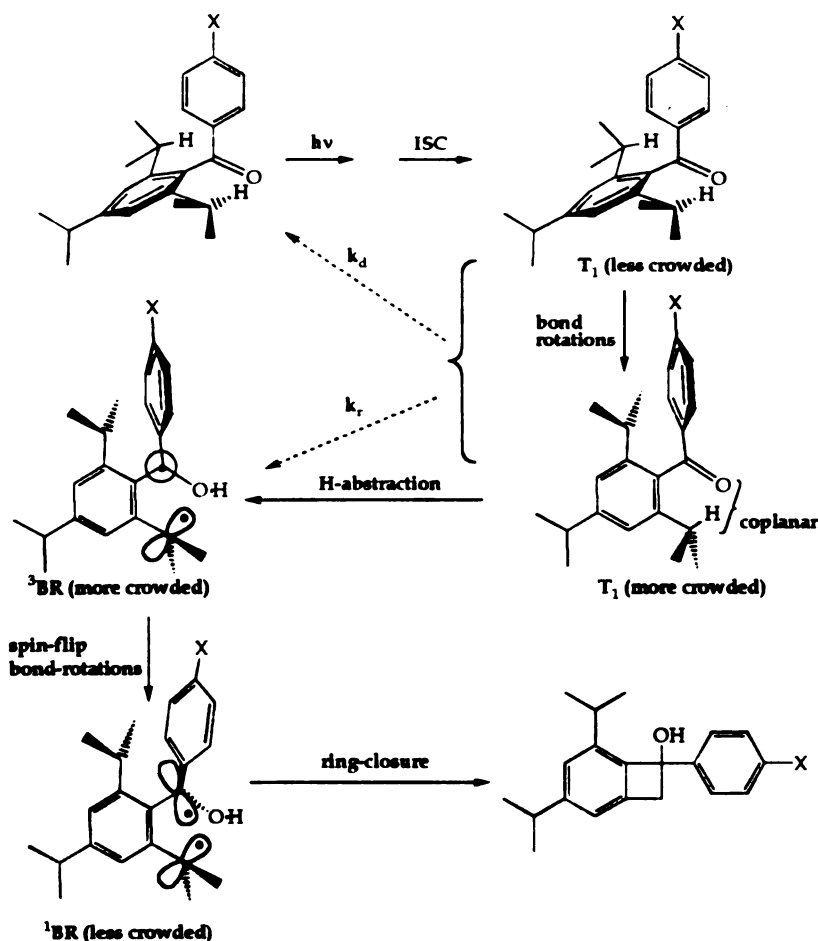
$\alpha \backslash \beta$	-60	-45	-30	-15	0	15	30	45	60	75	90	105
-30	40.86	41.03	41.36	41.94	42.62	43.42	44.31	44.06	43.32	42.06	41.35	41.01
-15	40.54	40.95	41.38	41.91	42.43	42.6	42.62	42.03	41.29	40.98	40.6	40.61
0	40.62	41.16	41.65	42.29	42.24	42.11	41.79	41.42	41.01	40.79	40.56	40.53
15	41.53	42.62	43.51	43.7	43.24	42.46	42.03	41.36	40.98	40.8	40.75	40.95
30	44.28	45.69	46.14	45.58	44.25	43.27	42.78	42.32	41.68	41.54	41.82	42.43
45	48.98	50.36	49.82	47.71	45.87	44.3	43.37	42.85	42.55	43.15	44.08	45.84
60	55.68	55.85	52.96	49.95	47	45.38	44.61	44.16	44.57	45.76	48.11	51.37
75	60.88	55.92	52.03	49.43	47.44	46.46	46.22	46.71	48.02	50.48	70.74	63.62
90	53.19	49.81	47.85	46.82	46.43	46.84	48.02	49.99	52.76	56.72	62.45	69.1
105	47.32	45.69	44.87	45.2	45.4	46.63	48.87	52.24	56.32	56.41	52.56	48.93
120	43.53	42.82	42.87	43.46	44.25	45.6	47.67	50.11	51.49	49.68	46.72	44.66
135	41.77	41.85	42.19	42.64	43.43	44.43	45.85	46.86	46.35	44.52	42.87	42.18
150	40.72	40.92	41.29	41.98	42.55	43.4	44.02	44.01	43.04	41.8	41.19	40.77

* The values in bold represent the least energy pathway for concerted rotation of the phenyl rings. The bold boxed value is the "saddle point".

Table 20 lists relevant bond angles and atom distances. The activation energy for the concerted bond rotation of the two phenyl rings was estimated from the three dimensional grid of ("saddle point") by the lowest energy path. An example of a plot of the energies obtained from the double dihedral drive is given in Table 20. Table 21 has the numerical values of the plot (see Figure 32), the bold values represent the lowest energy path for the concerted rotation of the phenyl rings. The bold boxed value is the "saddle point" and the activation energy for the rings rotating was calculated from the lowest energy geometry to this point.

V. Discussion of photoenolization in 2,4,6-trialkylbenzophenones

There is a considerable amount of literature on 2,4,6-trialkylbenzophenones which was pioneered by Matsuura and coworkers in the early 70's.^{50,140} This group was the first to report benzocyclobutenol formation and concluded the cyclization was promoted by steric congestion (i.e. the equilibrium favored the benzocyclobutenol over the sterically crowded xylylenol). Initial reports suggested that enols were intermediates but direct cyclization from the biradical introduced some controversy.^{50,141,45} The mechanistic dilemma has been complicated by the facts that the 2,4,6-trialkylbenzophenone do not readily undergo photodeuteration and do not react with dienophiles as o-alkyl systems do. Matsuura's proposed mechanism is outlined in Scheme 80.



Scheme 80. Matsuura's view of benzocyclobutenol formation from trialkylbenzophenones.

A more recent laser flash photolysis study of 2,4,6-trialkyl benzophenones has found that the *o*-xylylenols do exist.¹⁴² The authors detected a relatively long lived triplet (compared to monosubstituted benzophenones) from 2,4,6-triisopropylbenzophenone with a lifetime $>2 \mu\text{s}$ in acetonitrile. 2,4,6-Triisopropylbenzophenone gave an equal mixture of E and Z xylylenols but the biradical was not detected. Irradiation of 2,4,6-triisopropylbenzophenone in methanol- $\text{O-}d_1$ gave 30-40 % monodeuterated ketone,¹⁴² presumably the other 60% cyclizes ($\Phi_{CB} = 0.60$)¹⁴¹. The laser flash photolysis of 2,4,6-

triimethylbenzophenone is puzzling in that it led to no observable transients (no xilylenols or biradicals could be detected) but the triplet was detected and had a lifetime of 280 ns in acetonitrile.

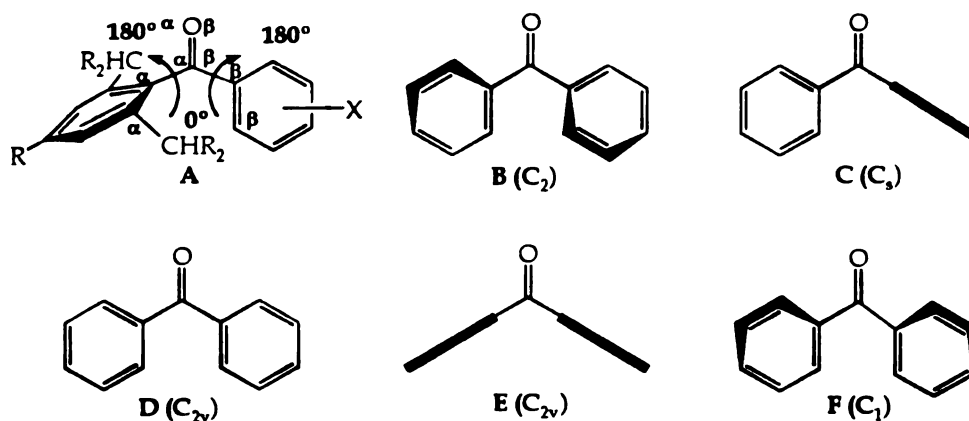


Figure 33. Possible conformations for diaryl carbonyls (symmetry point group).

Matsuura's and Ito's work on the para substituent effects of 2,4,6-trialkylbenzophenones prompted my study of several 2'- and 4'-2,4,6-trialkylbenzophenones. One requirement for hydrogen abstraction in Scheme 80 is that the X-phenyl group must be perpendicular to the carbonyl which is coplanar with the trialkylbenzene ring (T_1 (less crowded) in Scheme 80). In support, they found that 1-isopropylanthrone has only one subnanosecond triplet but does not form benzocyclobutenol.¹⁴³ This geometry (T_1 (more crowded) in Figure 33) for hydrogen abstraction seemed very unlikely based on it being significantly higher in energy from the steric congestion introduced by this rotation, also several 2,4,6-triisopropylbenzophenones react in the solid with known geometries. The crystal structure of 4'-methoxy-2,4,6-triisopropylbenzophenone has the triisopropyl ring nearly perpendicular with a

torsion angle $\alpha = 82^\circ$ (see Figure 33, torsion angle between the triisopropyl ring and the carbonyl plane) while the second ring deviates slightly from coplanarity with a torsion angle $\beta = 15^\circ$ (see Figure 33, torsion angle between the X substituted ring and the carbonyl plane).¹⁴⁴ The crystal structure of 2,4,6-triisopropylbenzophenone has the triisopropyl ring twisted $\alpha = 86^\circ$ while the second ring is nearly coplanar $\beta = 4^\circ$.¹⁴⁴

Ito and coworkers have investigated a number of 4'-substituted 2,4,6-triisopropylbenzophenones by variable temperature NMR and determined $\Delta G^\ddagger$ values for rotation of the triisopropyl ring.^{145,146} The rates of rotation were dependent on the resonance interaction between the carbonyl group and the 4' substituent and steric energy introduced by a 2' substituent. Ito's experimental

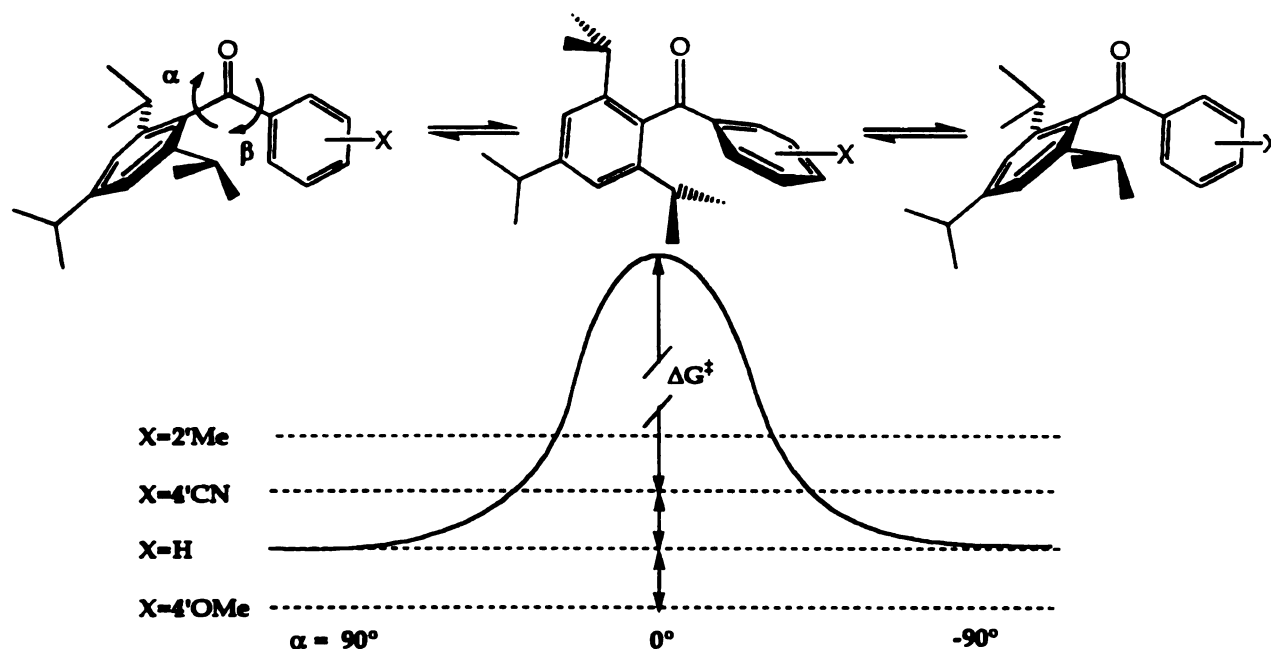


Figure 34. Rotational barriers of substituted triisopropylbenzophenones.

values of $\Delta G^\ddagger$ for $X = 4'$ -methoxy (4OI₃BP), H (I₃BP), $4'$ -cyano- (4CNI₃BP), $2'$ -methyl (2MI₃BP) benzophenone are 17.6, 16.2, 15.3 and <13.8 kcal/mol respectively. The 4-methoxy substituent stabilizes the ground state conformation by π -conjugation while the $4'$ -cyano is destabilizing. The $2'$ -methyl substituted also destabilizes the ground state geometry due to steric interactions with the carbonyl group and raising its zero point energy. A similar decrease of a rotational barrier in spite of the increased steric congestion about the bond under consideration has been reported previously.¹⁴⁷ Thus, the rate of rotation of the triisopropyl ring can be altered both sterically and electronically. Matsuura's "coplanar" hydrogen abstraction mechanism cannot be correct since electron withdrawing groups decrease the rotation about the α torsion angle and should lead to an increase in quantum yields for benzocyclobutenol formation. However a decrease in the efficiency for benzocyclobutenols is observed (i.e. Φ_{CB} (I₃BP) = 0.60, Φ_{CB} (4CNI₃BP) = 0.06). The dynamic NMR studies showed that the rotations are very slow in the ground state, $\sim 14 \text{ s}^{-1}$. Since conjugation is more important in the excited states, it is difficult to understand how rotation rates can be 10^6 times faster than in the ground state.

Table 20 lists calculated activation energies for rotation of a 2,6-dialkyl ring. The calculated using double dihedral driver about the α and β torsion angles and reflect the difference of the lowest energy geometry to the transition state ("saddle point") by the lowest energy path. Several $2'$ - and $4'$ - substituted 2,4,6-trimethyl and 2,4,6-triisopropylbenzophenones were studied in order to

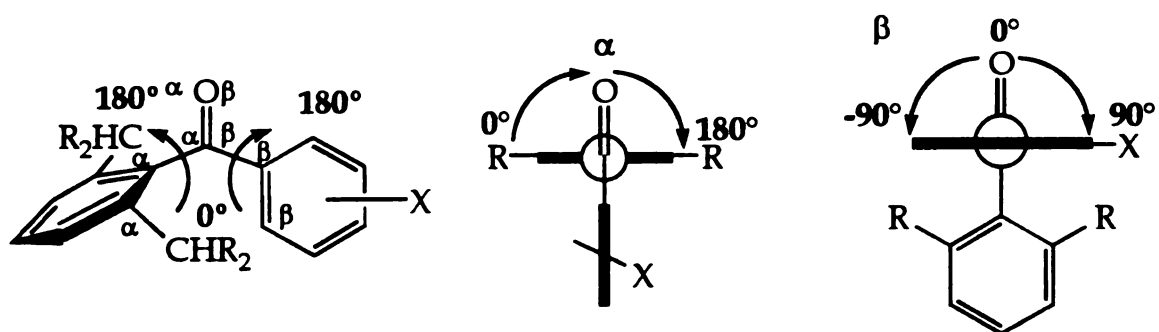


Figure 35. Definition of α and β torsion angles and direction of sign.

Table 22. AM1 calculated activation energies for rotation of 2,6-dimethylphenyl ring in diarylbenzophenones.

Entry	Ketone	E _a kcal/mol	α torsion angle ^b	β torsion angle ^b	C=O ⁰ H distance ^b	C=O ¹⁸⁰ H distance ^b
1	2'-chloro-2,6-dimethylBP	4.79	89	-52	3.13	2.57
2	2'-trifluomethyl-2,6-dimethylBP	4.98	111	-37	3.09	2.51
3	2'-methoxy-2,6-dimethylBP	5.23	84	-24	2.67	3.05
4	2'-methyl-2,6-dimethylBP	6.28	99	-22	2.92	2.66
5	4'-cyano-2,6-dimethylBP	6.30	84	-7.9	2.64	3.02
6	2,6-dimethylBP	6.72	84	-8.1	2.66	3.19
7	4'-chloro-2,6-dimethylBP	6.98	84	-8.1	2.65	3.02
8	4'- methoxy-2,6-dimethylBP	7.17	81	-7.0	2.64	2.96

^a rotation of 2,6-dimethylphenyl ring ^b see Figure 31.

elucidate substitution effects on benzocyclobutenol formation. I found that the 2'- and 4'- 2,4,6-triisopropylbenzophenones were well behaved (i.e. gave good yields of benzocyclobutenol). All the 2'- and 4'-2,4,6-triisopropylbenzophenones studied reacted in solution and the solid to give benzocyclobutenols except for 2'-methoxy-2,4,6-triisopropylbenzophenone (2OI₃BP) and 2'-methyl-2,4,6-triisopropylbenzophenone (2MI₃BP) which were photoinert in the crystal. The

photochemistry of the 2'- and 4'- trimethylbenzophenones was unpredictable. Several did not react while others gave a wide distribution of products, some unprecedented. It is not clear why there is such diverse chemistry in structurally similar molecules.

2'-Chloro-2,4,6-trimethylbenzophenone (2ClM₃BP) is photostable in benzene but undergoes photoinduced dechlorination in cyclohexane to give 2,4,6-trimethylbenzophenone as the major product. To account for this photoinertness we considered several possibilities: 1) a "bad" geometry for hydrogen abstraction; 2) the hydrogen abstraction occurs but is reversible thus the products are "invisible" by conventional photolysis; 3) radical cleavage occurs but radical recombination predominates in benzene; 4) there is quenching of the excited state.

I thought the lack of product formation in benzene was due to a "bad" geometry for hydrogen abstraction introduced by the 2'-chloro substituent. Semi empirical calculations predict the ortho methyl hydrogen to be ~2.6 Å from the carbonyl oxygen in the lowest energy geometry, well within the requirements described in the introduction. Also, 4'-chloro-2,4,6-trimethylbenzophenone (4ClM₃BP) also gave no photoproducts in benzene but underwent dechlorination in cyclohexane. It appears the 2'-chloro group is not introducing steric constraints impeding hydrogen abstraction, the calculated lowest energy geometries for 2,4,6-trimethylbenzophenone (M₃BP) and 2ClM₃BP are quite similar (compare entries 1 and 6 in Table 20) and both have abstractable

hydrogens ≤ 2.7 Å and M₃BP forms benzocyclobutenol. There is some confusion about the actual geometry of 2ClM₃BP in solution. A recent study of the conformation of sterically hindered benzophenones by means of the Kerr effect and dipole moment methods predicted 2ClM₃BP was in a strange geometry with the mesityl ring and carbonyl nearly coplanar (i.e. see Figure 33, $\alpha = \sim 0^\circ$, $\beta = \sim 90^\circ$).¹⁴⁸ The authors arrived at this conclusion since the roots were absent for the vector addition of the dipole moments. This meant the conformation of 2ClM₃BP could not be a helical one (B in Figure 33). I could not reproduce this geometry with AM1 level calculations but the average of the two lowest energy geometries (these geometries are ~ 0.6 kcal different in energy) predicts the aryl-Cl ring nearly perpendicular to the carbonyl plane (see Figure 37 and Figure 38). The dihedral angles α and β for 4ClM₃BP were also calculated in this same study with values of 72° and -20° (compare to entry 7 in Table 20) respectively which were measured in dioxane.

Deuterium incorporation into the benzylic position is a common probe to test whether a xylylenol has been formed since it is assumed the incorporation stems from protonation of the enol. Irradiation of 2ClM₃BP in methanol-*d*₄ was inconclusive. Analysis by ¹H-NMR revealed the spectrum had changed significantly in the aromatic region after irradiation but the intensity of the methyl signals did not decrease and was attributed to photodechlorination. At this point there is no evidence that hydrogen abstraction is occurring but the possibility of a back hydrogen transfer cannot be ignored.

Another viable pathway to account for the lack of benzocyclobutenol formation is self quenching of an excited ketone (T_1) by a ground state molecule (S_0). This bimolecular self quenching of several benzophenones has been studied by Singer and coworkers.¹⁴⁹ The quenching occurs via two deactivation pathways via "n-type" and " π -type" exciplexes (see Figure 36). The rate

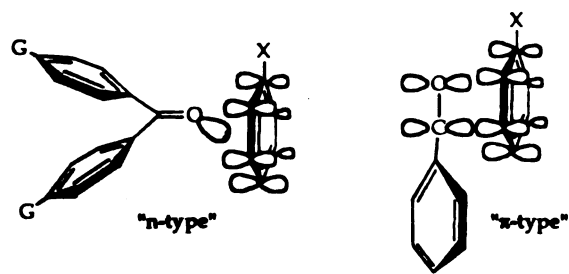


Figure 36. Self quenching of benzophenone.

- | | | |
|-----|------------------------------|--------------------|
| (1) | $S_0 \rightarrow S_1$ | excitation |
| (2) | $S_1 \rightarrow T_1$ | ISC |
| (3) | $T_1 \rightarrow S_0$ | phosphorescence |
| (4) | $T_1 \rightarrow S_0$ | nonradiative decay |
| (5) | $T_1 + Q_1 \rightarrow S_0$ | quenching |
| (6) | $T_1 + S_0 \rightarrow 2S_0$ | self quenching |

constant for the self quenching of 4,4'-dichlorobenzophenone in benzene is $4.7 \pm 0.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. The lifetime for the triplet of M_3BP in benzene is $>4 \mu\text{s}$,¹⁴² thus the triplet would not be quenched sufficiently using the rate constant from 4,4'-dichlorobenzophenone at 0.01 M (my experiments were conducted at this concentration). However, not knowing the lifetime of the triplet for $2ClM_3BP$, its self quenching is still questionable. In addition, the reported triplet lifetime for M_3BP is questionable since it is difficult to imagine why M_3BP gave no transients (that were assigned to the biradical or xylylenols) considering xylylenols have been detected by flash spectroscopy for a large number of aryl ketones. Since photodechlorination is occurring for both $2ClM_3BP$ and $4ClM_3BP$,

it is likely that the energy from excitation is going to break the carbon-chlorine bond. In benzene the radicals recouple but are trapped in cyclohexane.

The 2'-chloro (2ClI₃BP) and 4'-chloro (4ClI₃BP) 2,4,6-trisopropylbenzophenones reacted smoothly in both solution and the solid. The reaction was $\sim 1/3$ as fast as for 2,4,6-trisopropylbenzophenone (I₃BP) in benzene and only gave benzocyclobutenol in cyclohexane without dechlorination. Interestingly, semi-empirical (AM1) predicts the chlorine atom is pointing underneath the triisopropyl opposite the carbonyl presumably to minimize electronic repulsion of the two electron rich species (see Figure 37) and is not the same geometry as predicted for 2'-chloro-2,6-dimethylbenzophenone (see entry 1 in Table 20). However, the calculated geometry in Figure 37 is also a local minimum for 2'-chloro-2,6-dimethylbenzophenone but is 0.6 kcal/mol (see Figure 38) higher in energy than the reported geometry in Table 20

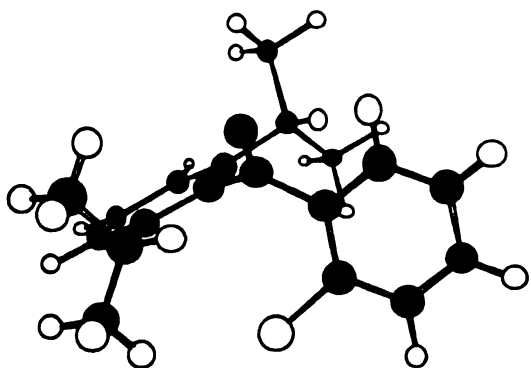


Figure 37. AM1 minimized structure of 2'-chloro-2,6-diisopropylbenzophenone.

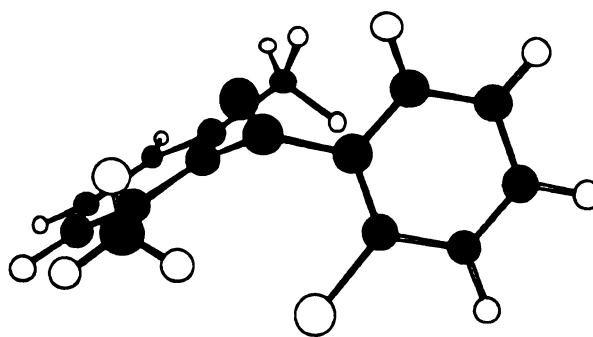
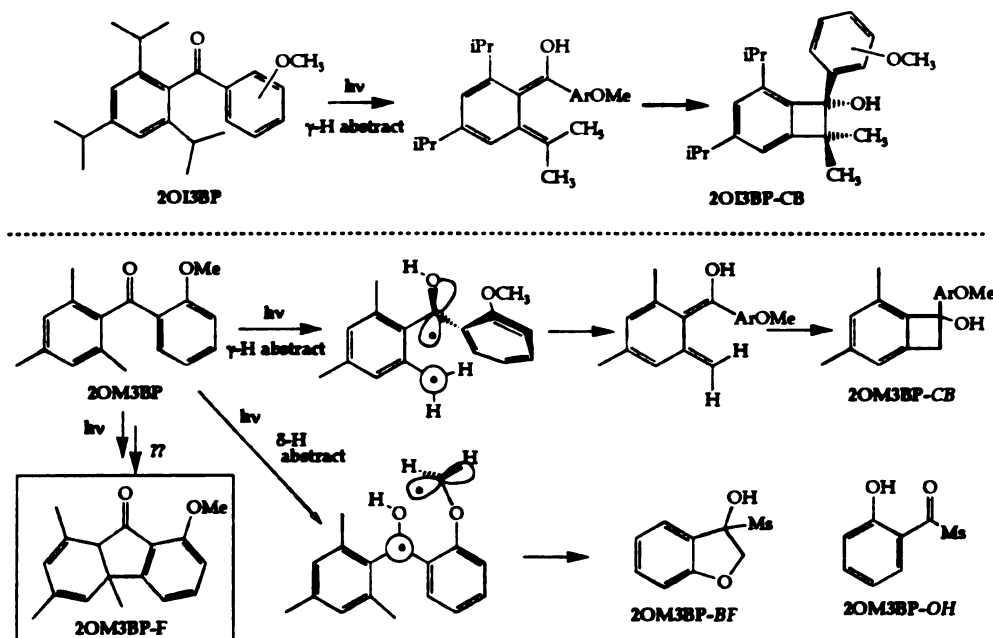


Figure 38. 0.6 kcal/mol higher than global minimum of 2'-chloro-2,6-dimethylbenzophenone.

Introduction of a 2'- or 4'-methoxy substituent did not have a significant impact on the efficiency for benzocyclobutenol formation from the 2,4,6-triisopropylbenzophenones. The quantum yields for formation of 2OI₃BP-CB and 4OI₃BP-CB in benzene were 0.55 and 0.77 respectively. However, irradiation of 2'-methoxy-2,4,6-trimethylbenzophenone (2OM₃BP) resulted in a distribution of products derived from γ and δ hydrogen abstraction. Ortho



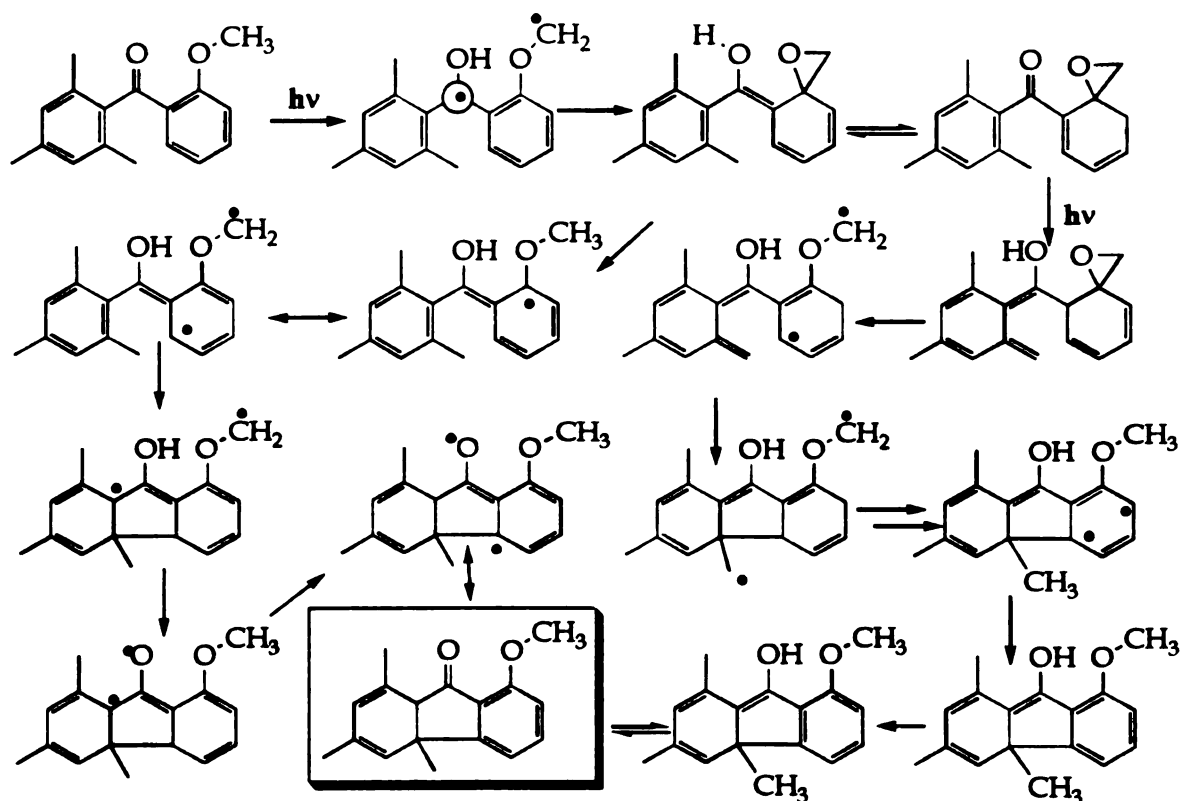
Scheme 81. Photochemistry of 2'-methoxy-2,4,6-trialkylbenzophenones.

alkoxy benzophenones are known to undergo δ hydrogen abstraction with rate constants 10^5 - 10^7 s⁻¹ and cyclize to benzodihydrofuranols with quantum yields as high as 0.95 for 2-benzyloxybenzophenone.¹¹ The rate constant for hydrogen abstraction for 2-methoxybenzophenone is 5×10^5 s⁻¹ which cyclizes with a quantum efficiency of 0.30. The reciprocal triplet lifetime of 2,4,6-trimethylbenzophenone, presumably the rate constant for γ -hydrogen

abstraction by its n,π^* lowest triplet in benzene, is $2.5 \times 10^5 \text{ s}^{-1}$.¹⁴² The ratio of quantum yields for 2OM₃BP-BF/2OM₃BP from 2OI₃BP in benzene is ~2, from values of 0.019 and 0.010 respectively and may represent the ratio of the rate constants for hydrogen abstraction for 2-methoxybenzophenone and 2,4,6-trimethylbenzophenone. However the quantum yield for formation of 2OM₃BP-BF is a factor of 15 lower than benzodihydrofuranol formation from 2-methoxybenzophenone. The competing γ -hydrogen abstraction alone can not account for this inefficiency. Two other products are formed during the reaction, one has been identified as *2-methoxy-4b,6,8-trimethyl-4b,8a-dihydrofluorene-9-one* (2OM₃BP-F) the second product was not isolated but was formed at ~3 times the efficiency of 2OM₃BP-BF at low conversion. The 2OM₃BP-F is likely formed from the unidentified species since 2OM₃BP-F is not formed at low conversion and the unidentified product is not observed at high conversion. A viable mechanism could involve a spiro epoxide intermediate which have been suggested as intermediates from irradiation of o-alkoxybenzophenones and is presented in Scheme 82.

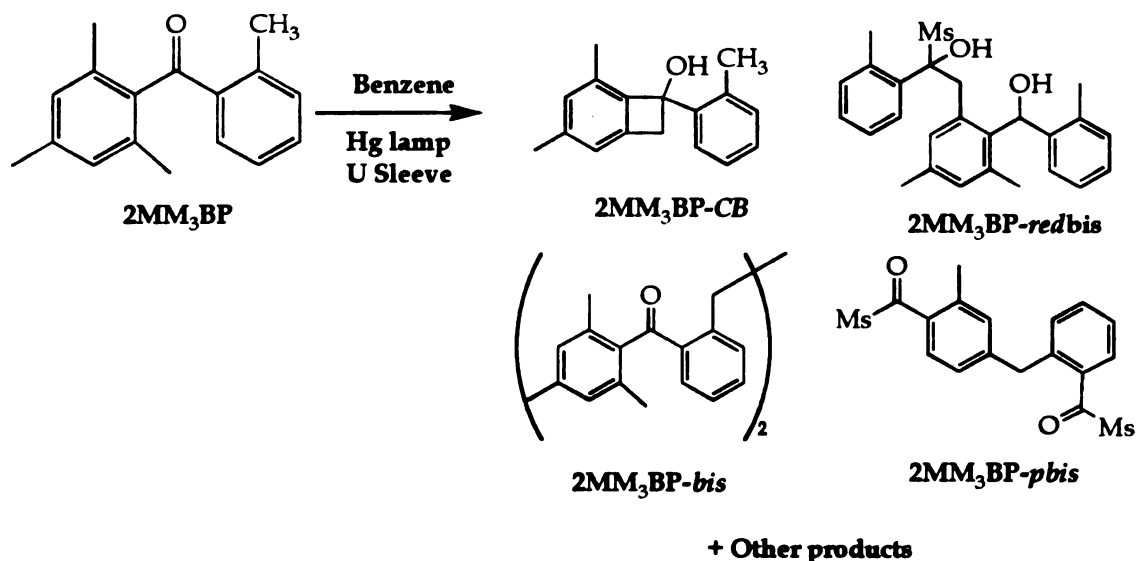
The 2'- and 4'- methyl substituted triisopropylbenzophenones both gave benzocyclobutenols. 2'-Methyl-2,4,6-trisopropylbenzophenone (2MI₃BP) reacted in solution from both the 2'-methyl and 2-isopropyl positions but favored hydrogen abstraction from the methyl group. However, 2MI₃BP did not give products when irradiated in the solid while 4'-Methyl-2,4,6-trisopropylbenzophenone (4MI₃BP) yielded benzocyclobutenol The lack of

product formation from 2MI₃BP is likely due to a reversible hydrogen abstraction from the 2' methyl position, 2OI₃BP reacts efficiently in the solid and has a similar ground state geometry (see entry 3 and 4 in Table 20). The

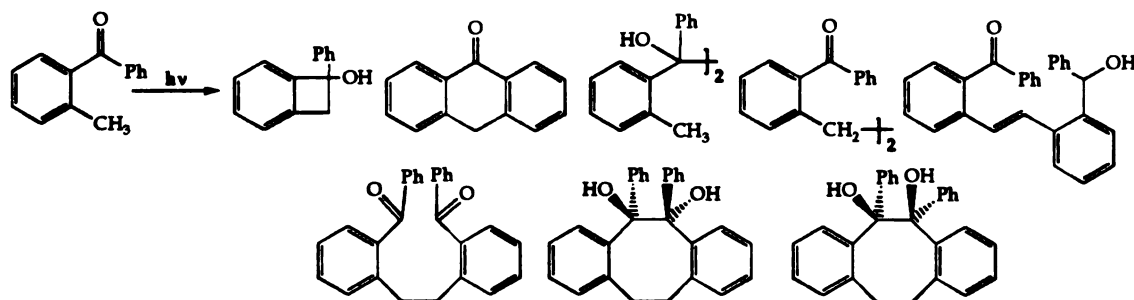


Scheme 82. Possible mechanism for formation of 2OM₃BP-F.

photochemistry of 2'-methyl-2,4,6-trimethylbenzophenone (2MM₃BP) gave a complex mixture of products via hydrogen abstraction from the 2 and 2' methyl positions (see Scheme 83). Several intermolecular coupling products were identified and probably derived from either xylylenol dimerization or radical coupling which have been reported in similar ketones. Wilson has isolated several dimeric products from 2-methylbenzophenone by conventional laser photolysis (see Scheme 84).⁵²

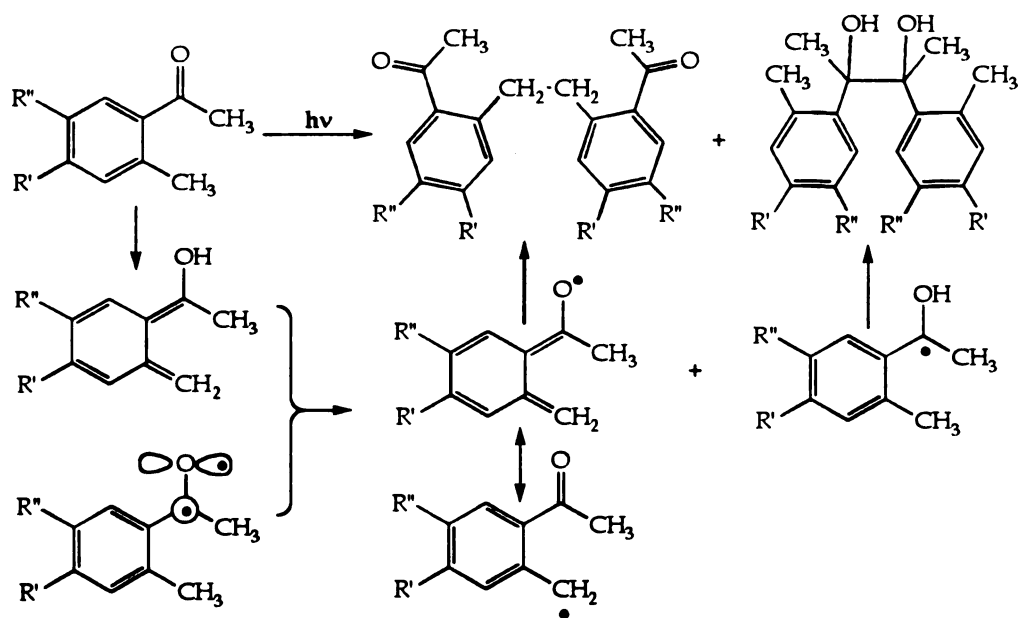


Scheme 83. Product distribution from photochemistry of 2MM₃BP in benzene.



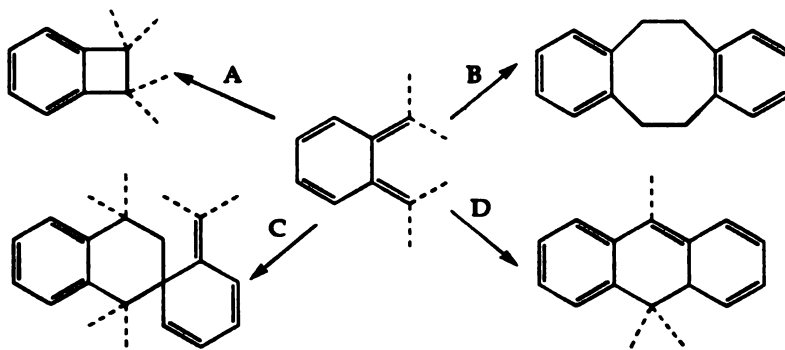
Scheme 84. Dimerization reactions during conventional photolysis of 2-methylbenzophenone.

Becker has reported the photoinduced dimerization of 2-methylacetophenone to give bibenzyl and pinacol derivatives (see Scheme 84).¹⁵⁰ The proposed mechanism involved an intermolecular hydrogen abstraction from a ground state xylylenol by a triplet ketone. Simple *o*-

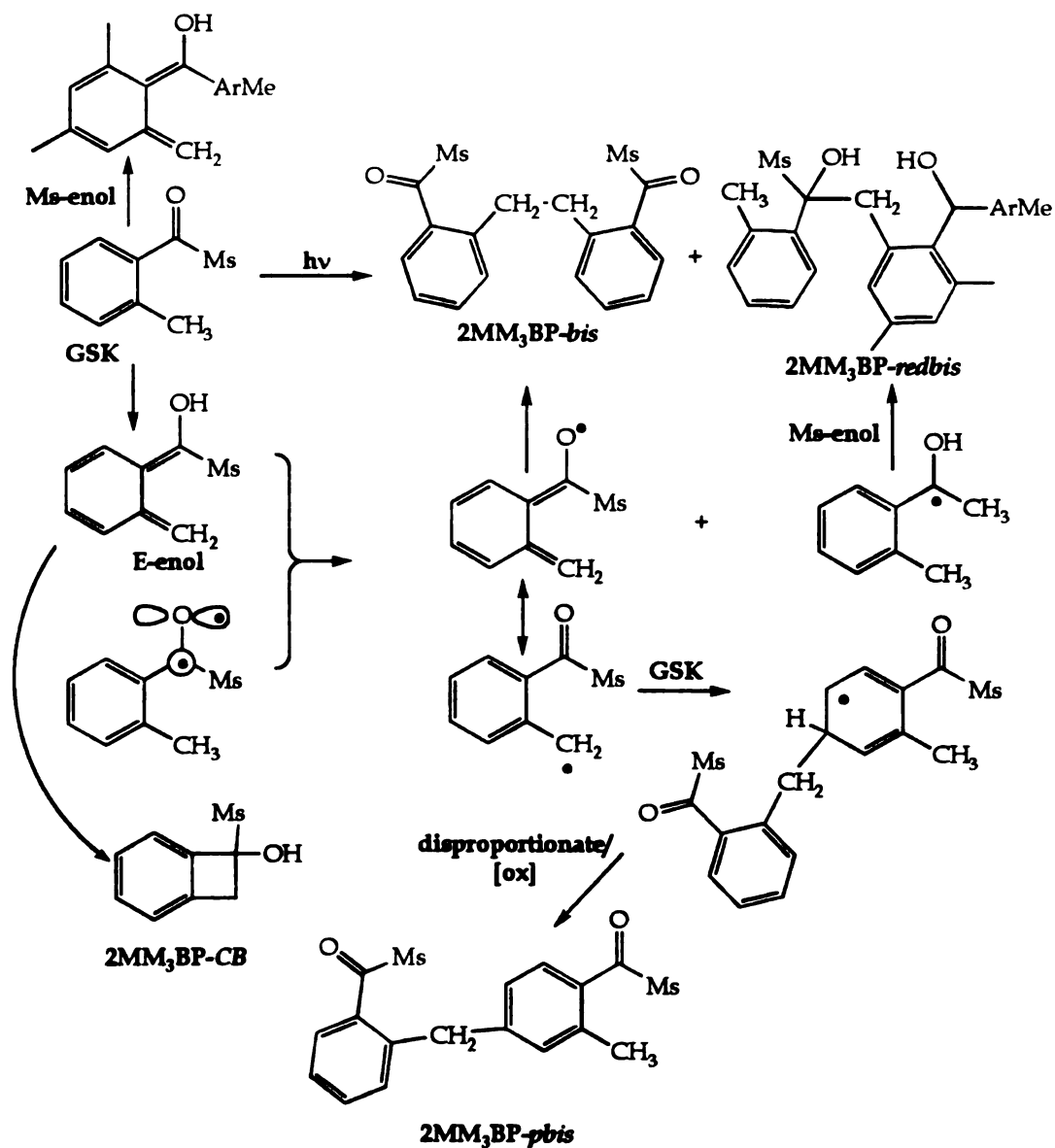


Scheme 85. Dimerization reactions during conventional photolysis of 2-methylacetophenone.

xylenes are known to undergo dimerization reactions similar to those reported by Wilson (path B, Scheme 86). At low temperatures the spiro-dimer (path C) is favored and has been isolated by several groups.¹⁵¹



Scheme 86. Fate of o-xylenes.



Scheme 87. Possible mechanism for product formation from 2MM₃BP.

The products observed by Wilson, Becker and myself may represent alternative pathways that predominate under certain circumstances. Careful studies of temperature, light intensity, concentration, excitation wavelength and irradiation time are required in understanding when these alternative pathways can effectively compete with benzocyclobutenol formation. A possible

mechanism than may help explain the formation of 2MM₃BP-CB, 2MM₃BP-CB, 2MM₃BP-*bis*, 2MM₃BP-*pbis* and 2MM₃BP-*redbis* is outlined in Scheme 87.

A. Conformational effects in the solid state.

The photochemistry of triisopropylbenzophenones in the solid state may offer a new insight into the factors effect both hydrogen abstraction and product formation. The correlation between experiments and theoretical calculations support one another. The conformations of substituted 2,6-diemethylbenzophenones were calculated using semi-empirical methods and are assumed to represent the geometries for the analogous triisopropylbenzophenones studied by Matsuura and myself. The calculated difference in steric and electronic effects for rotation of the dialkyl group are in agreement with the experimental solution values (compare Table 20 with

Figure 34). Although the magnitude of the values differ, the trend is identical. The ketones 2OI₃BP, 4OI₃BP, I₃BP, 2ClI₃BP, 4ClI₃BP all react in the solid while 2CF₃I₃BP and 2MI₃BP are photoinert. This finding is explained by assuming their calculated geometries are representative of the crystal structure (value for the angles are not exact but the direction and twist of the rings are correct). In all 2,6-dimethyl ketones in Table 20 except for 2'CF₃, 2'Me and 2'Cl(for unknown reasons this geometry is not representative of the 2,6-diisopropyl case, see Figure 37) the ortho carbon of the X substituted ring is the closest carbon of the ring to the ortho benzylic carbon in which hydrogen

abstraction will occur. I believe this orientation of the X-substituted ring dictates if the photochemistry will occur in the crystalline phase. For ketones

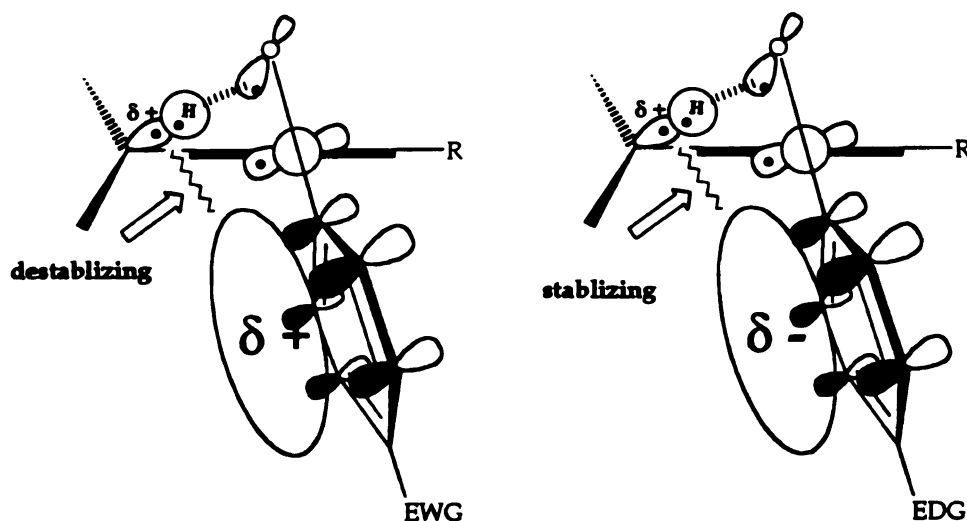


Figure 39. Stabilization of transition state for hydrogen abstraction by X-phenyl ring.

2MI₃BP and 2CF₃I₃BP the 2' substituent forces the ring to twist in an opposite direction (see entries 2 and 4 in Table 20), probably due to steric and electronic factors. For the 4' substituted ketones the ortho carbons of the X-substituted ring are equivalent due to symmetry. The forming radical center at the ortho benzylic carbon is stabilized by overlap of the X substituted phenyl ring. The electron donating groups are the best at stabilizing the electron deficient center while the CF₃ group has a repulsive effect. It is possible that overlap of the CF₃-phenyl ring destabilizes the transition state for hydrogen abstraction. If destabilization is occurring then the rate of hydrogen abstraction should decrease with electron withdrawing substituents on the X-phenyl ring, moreover the triplet lifetime should be longer than in the unsubstituted case. In fact, the lifetime of triplets do increase with electron withdrawing groups at the para substituent. The lifetimes

for have been reported for I₃BP, 4'-trifluoromethyl-2,4,6-trisopropylbenzophenone (4CF₃I₃BP), 4'-cyano-2,4,6-trisopropylbenzophenone (4CNI₃BP) and are 90, 179 and 190 ns respectively from quenching with dienes.¹³⁹ Wagner, Scaiano and Truman have reported the substituent effects on the decay rates of triplet benzophenones in cyclopentane: *p*-methoxyBP, *p*-methylBP, BP, *p*-chloroBP, *p*-trifluormethylBP, and *p*-cyanoBP are 3.4, 4.5, 5.3, 6.3, 10.3 and 11.0 × 10⁶ s⁻¹ respectively.¹⁵² The electron-withdrawing ring substituent does not deactivate the triplet towards hydrogen abstraction in substituted benzophenones but actually increases the rate of hydrogen abstraction as compared to benzophenone (BP) itself. In the crystal only the lowest energy geometry is populated but in solution this repulsive effect of the electron with-drawing groups can be reduced by the molecule assuming slightly different conformations, thus 2CF₃I₃BP reacts in solution. The quantum yield for benzocyclobutenol formation from 4CNI₃BP and 2CF₃I₃BP are 0.060 and 0.013 respectively and probably reflect the decrease in the rate of hydrogen abstraction.

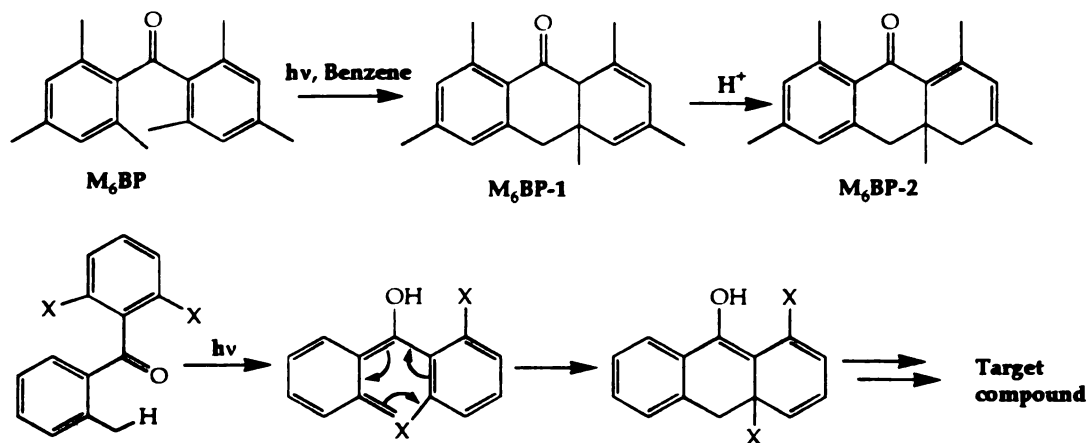
The lack of product formation of 2MI₃BP in solid is attributed to a competing γ -hydrogen abstraction from the 2'-methyl position (2'-methyl hydrogen is closer than the 2-isopropyl hydrogen), due to constraints in the crystal lattice the xylylenol can not cyclize since the 2,4,6-trisopropyl ring must rotate. In solution, a small bond rotation (rotation about the carbonyl-

triisopropyl ring bond) will bring the ortho methine close enough for hydrogen abstraction to compete from this position.

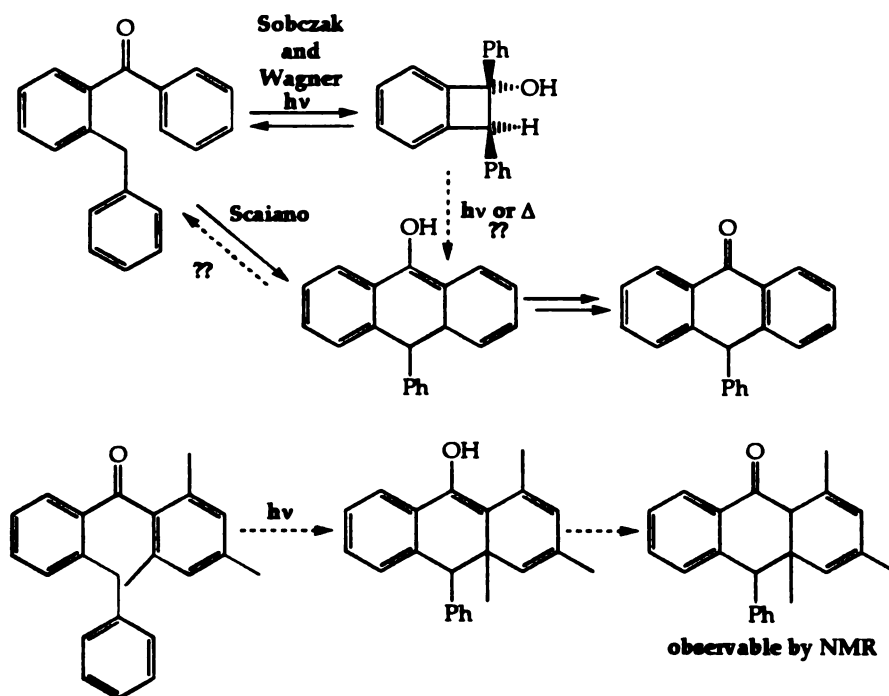
B. A new intramolecular trap for xylylenols.

The photochemistry from the substituted mesitylbenzophenone derivatives may introduce a fruitful area of photochemistry that has not been explored. The ketone 2,4,6,2',4',6'-hexamethylbenzophenone (**M₆BP**) may be an example of an efficient intramolecular trap for o-xylylenols with synthetic implications. Anthrol has been generated by an intramolecular [4+2] cyclization of the E-enol from 2-methylbenzophenone. There is some confusion in the present literature if the closure is a photochemical or thermal transformation.^{52,153,154} Once the hexadiene structure has formed oxidation occurs readily due to rearomatization. However, with substituents at the 2'- and 6'-positions the hexadiene unit cannot rearomatize because of the bridgehead substituents as I observed for the cyclization of **M₆BP**.

This idea of an intramolecular trap could be useful in identifying intermediates that are difficult to observe by NMR. Scaiano¹²¹ has reported that 9-phenylanthrone is a major product from 2-benzylbenophenone but I only observed formation of **2BzBP-ECB**, it is possible that the anthrol is rearomatizing and the vinyl resonances are never observed on the NMR timescale. What ever the case may be, replacement of the phenyl group with a mesitylene ring could



serve as a trap not allowing rearomatization, this is especially true if the 9-phenylanthrol is reverting to starting ketone (see Scheme 88). This trapping may also have synthetic utility if X is chosen properly since the product could be subjected to the appropriate chemical transformations.



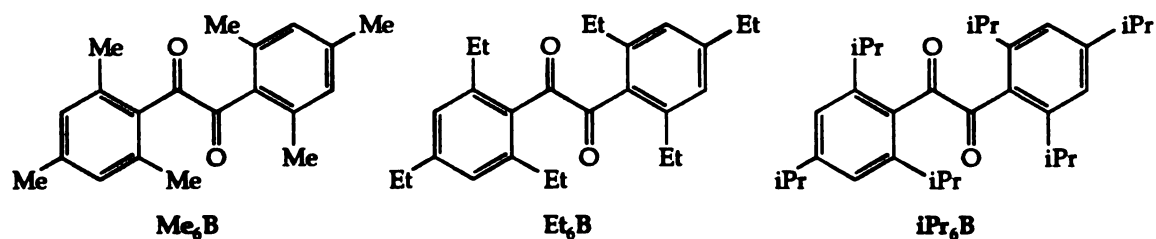
Scheme 88. Possible application using mesityl ring to trap *o*-xylenols.

VI. Results for congested α -hydroxyindanones and their Photoproducts

A. General preparation of ketones

The benzils studied were originally gifts from Professor Zvi Rappoport of Hebrew University in Jerusalem but more were prepared by standard literature methods. The hexaalkylbenzils were prepared by a modified method of Fuson *et al* in which a binary mixture of I_2 and MgI are used to reduce the carbon-chlorine bond of the appropriate trialkylbenzoyl chloride. Fuson used this method to prepare enediols with yields as high as 40% and the byproduct of his preparation was the 1,2-diketone. The benzil yield can be greatly increased by a slight modification in the work up procedure (93% isolated yield for Et_6B). Instead of conducting the workup procedure quickly to prohibit air oxidation of enediol to benzil, the combined washed extracts are stirred for six hours and protected from light in aerobic conditions.

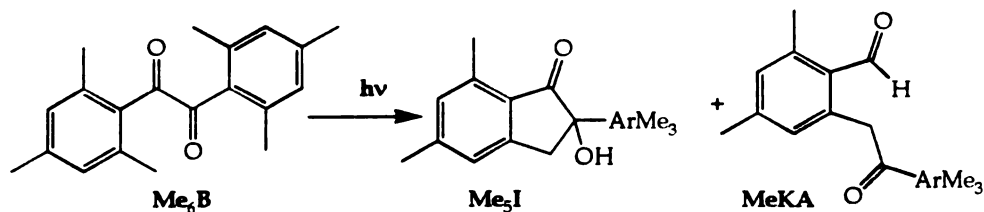
The diketones Me_6B , Et_6B , iPr_6B were studied by previously by Park.¹⁵⁵



Scheme 89. Studied 2,4,6,2',4',6'-hexaalkylbenzils

B. Identification of products

1. 2,4,6,2',4',6'-hexamethylbenzil (Me₆B)



Scheme 90. Photochemistry of 2,4,6,2',4',6'-hexamethylbenzil

The preliminary study of Me₆B was conducted by Bong-Ser Park in which he identified Me₅I and MeKA, but the products were not isolated. The products that I observed are consistent with Park's results. The ¹H-NMR of Me₅I had four unique methyl resonances which all appeared as singlets at 2.12(3H), 2.24(6H), 2.38(3H), and 2.63 ppm (3H). The benzylic methylene appeared as an AB quartet 3.36(J=17.9 Hz, 1H) and 3.57 ppm (J=17.8 Hz, 1H) which is consistent with the previously reported 2-hydroxy-2-phenylindane-1-one (KA in Figure 40) in which the chemical shifts for the two benzylic methylene hydrogens are 3.54 and 3.65 ppm.¹⁵⁶ The aromatic region had three resonances which all appeared as singlets at 6.81(2H), 6.98(1H), 7.02(1H) ppm.

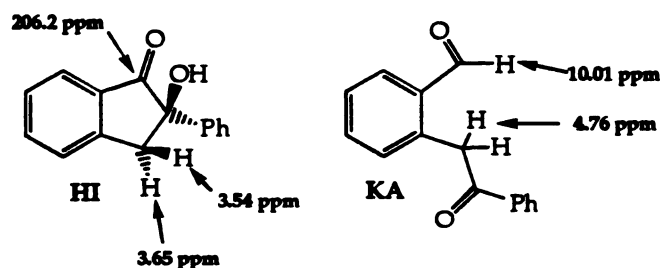
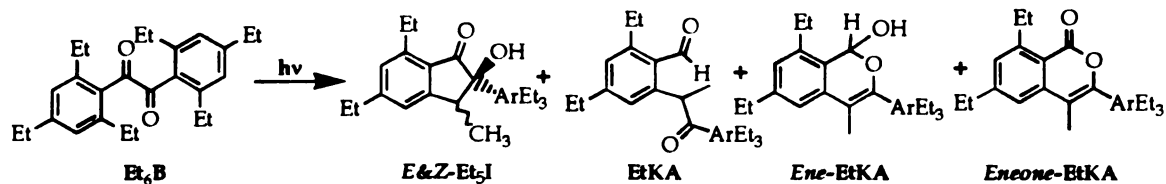


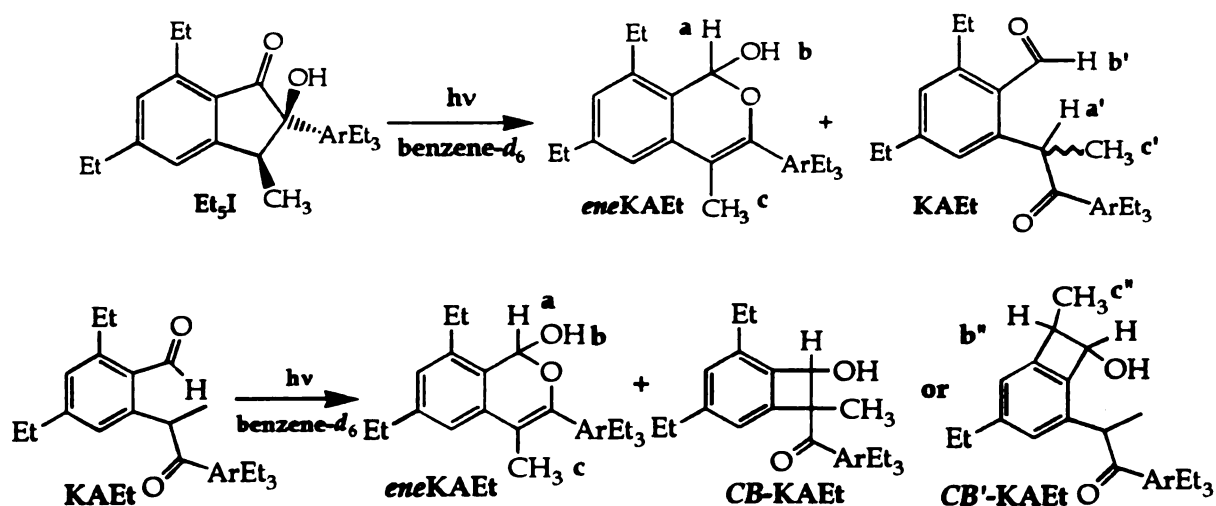
Figure 40. Model compounds from independent researchers.

2. 2,4,6,2',4',6'-hexaethylbenzil (Et₆B)



Scheme 91. Photochemistry of 2,4,6,4', 2', 6'-hexaethylbenzil

The photochemistry of Et₆B and its products were quite complex and the final isolated product depended on wavelength, conversion and temperature. Table 23 summarizes the photochemistry of Et₆B and its products. The *Et₅Ione-EtKA* was only isolated during solid state preparative chemistry when no precautionary measures were taken to exclude air. The wavelength had a significant impact on the product distribution as previously reported by Park. Irradiation at ~438 nm gave only Z-Et₅I and E-Et₅I in a 2:1 ratio, while irradiation with Pyrex filtered light gave Z&E-Et₅I, EtKA and *eneEtKA* (see Figure 40) This product distribution was dependent on conversion and the length of irradiation since the products also underwent photochemistry. The products Z/E-Et₅I, EtKA and *eneEtKA* were isolated (see Figure 42) and irradiated independently. One important fact was that irradiation of Z-Et₅I did not yield E-Et₅I nor did irradiation of E-Et₅I give Z-Et₅I which indicates they do not interconvert. The results of various reaction conditions during the irradiation of Z and E-Et₅I and their photoproducts are summarized in Table 23.



Scheme 92. Photochemistry of Et_3I and KAEt .

Irradiation of E - Et_3I and Z - Et_3I yielded KAEt and eneKAEt and their ratios depended on wavelength, irradiation time and temperature. Irradiation of KAEt formed eneKAEt and an unidentified product, possibly the benzocyclobutenol CB- or CB'-KAEt . Irradiation of eneKAEt gave no products after 12 hours. However, on one occasion, a product had formed after 24 hours irradiation of eneKAEt in $\text{benzene-}d_6$ but the sample had warmed considerably. This result could not be reproduced when the temperature was maintained at 17-20°C.

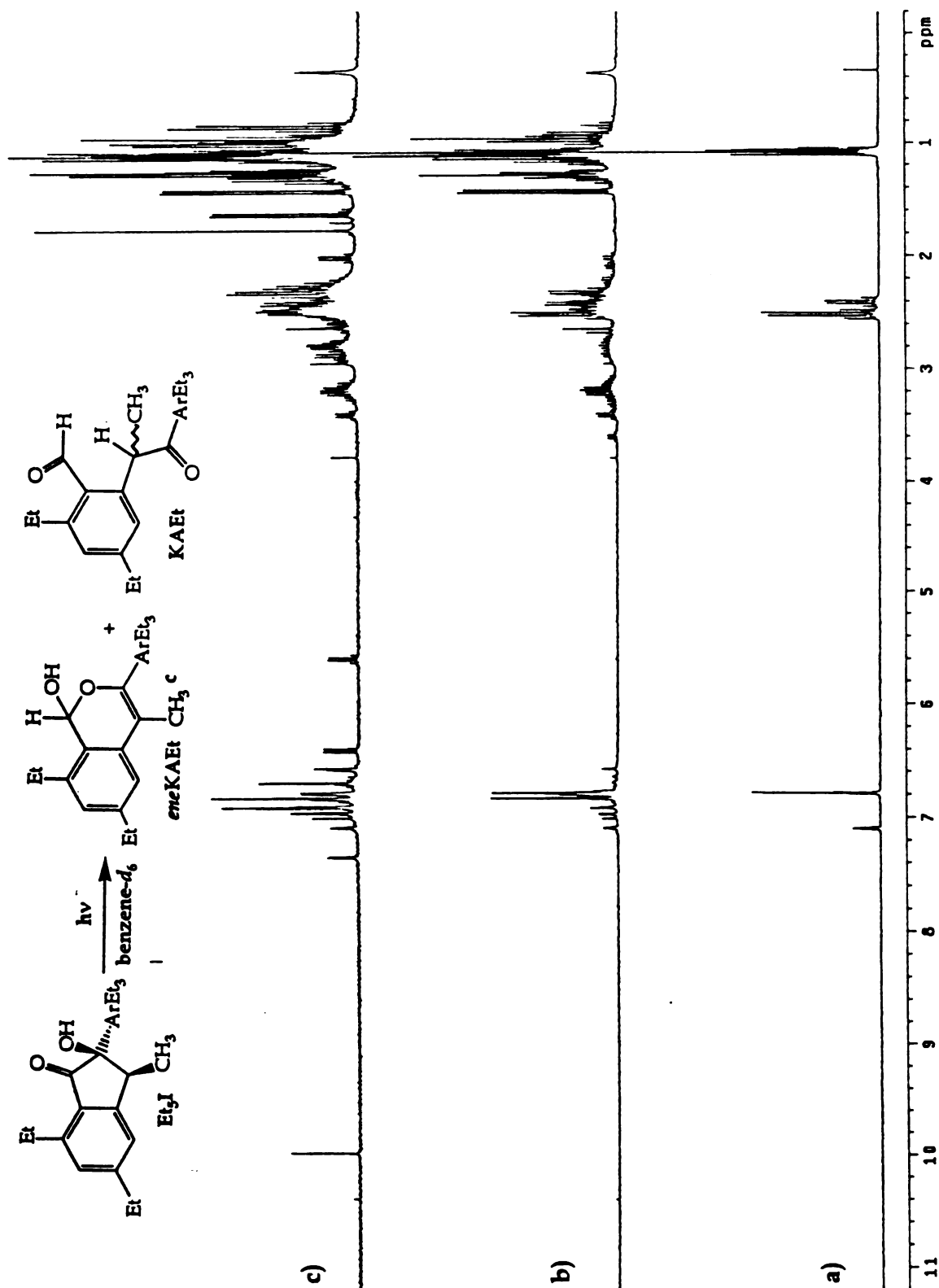


Figure 41. ^1H -NMR Spectra for K-Et₆ in benzene- d_6 , a) before irradiation b) after 24 hours irradiation at ~ 438 nm c) after 4 hours irradiation at $\lambda > 290$ nm.

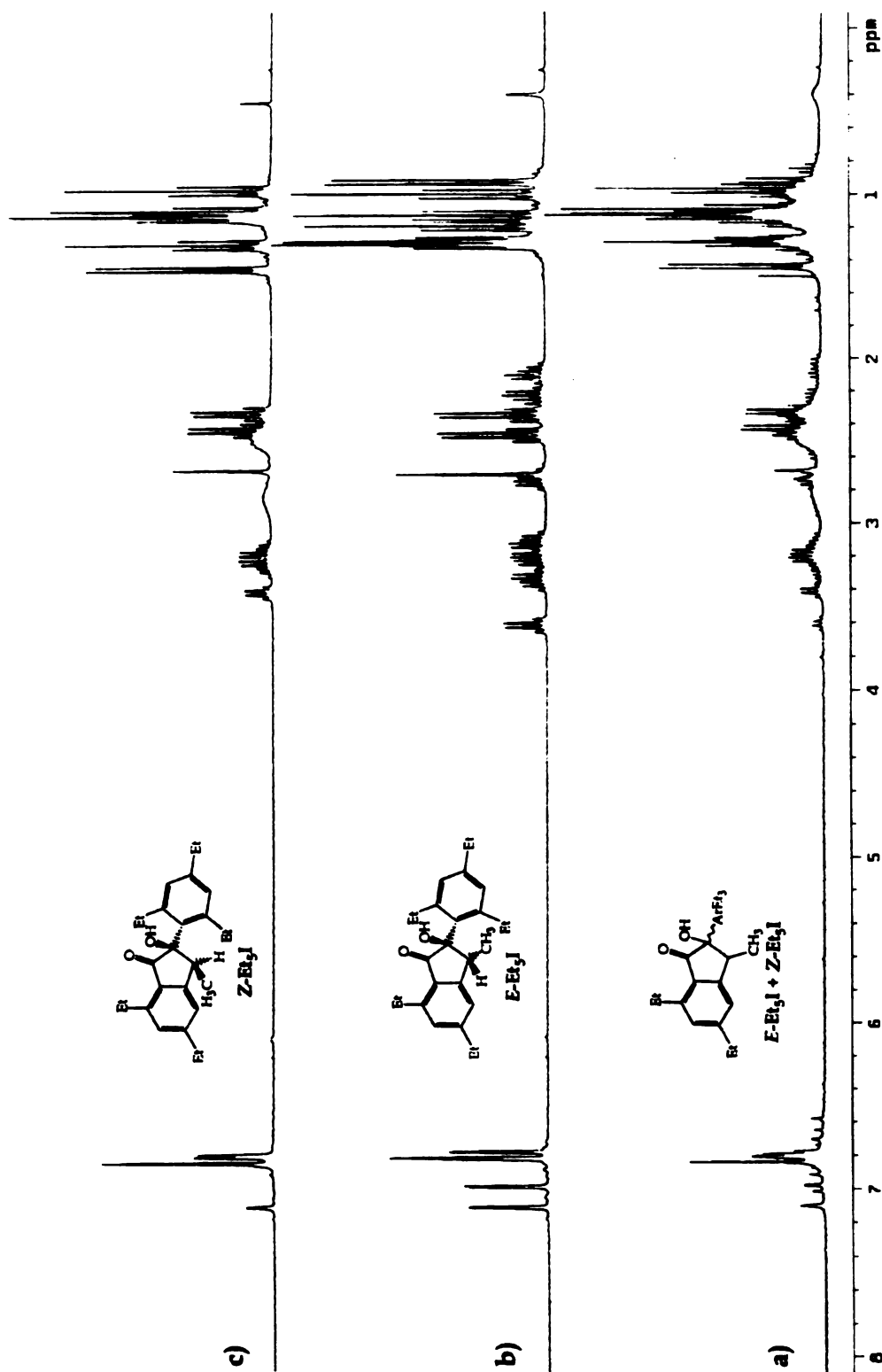
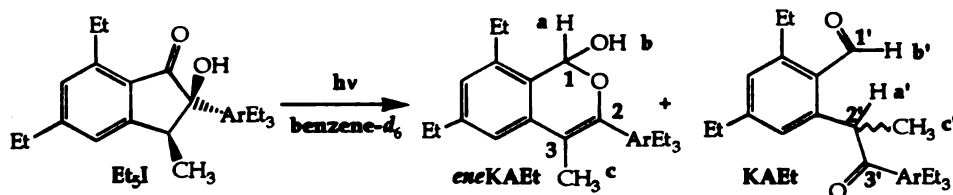


Figure 42. ^1H -NMR Spectra for in $\text{benzene-}d_6$ a) mixture of E- Et_3I and Z- Et_3I after irradiation b) purified E- Et_3I c) purified Z- Et_3I .

Table 23. Chemical yields of irradiated benzils and their photoproducts.

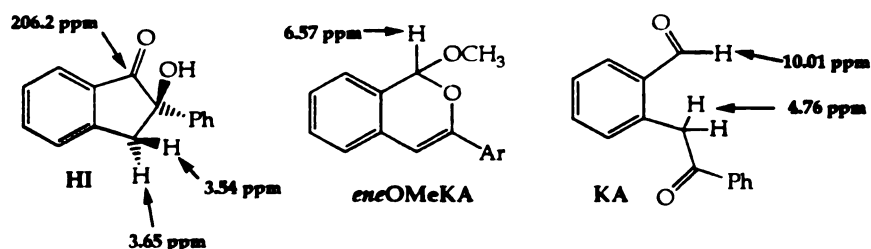
Irradiation of	h ν , λ , nm	temp, °C	solvent	%conv.	ZEt ₃ I	EEt ₃ I	EtKA	eneEtKA
Et ₃ B	>290	25	benzene- <i>d</i> ₆	60	39	13	6	1
Et ₃ B	>290	25	benzene- <i>d</i> ₆	83	48	8	20	7
Et ₃ B	>290	25	benzene- <i>d</i> ₆	>95	31	<3	22	26
Et ₃ B	~438	25	benzene- <i>d</i> ₆	>95	65	22	0	0
Et ₃ B	>290	25	solid	>95	55	9	7	0
Z-Et ₃ I	>340	25	benzene- <i>d</i> ₆	20	—	0	11	9
Z-Et ₃ I	>340	25	benzene- <i>d</i> ₆	40	—	0	21	19
Z-Et ₃ I	>340	25	benzene- <i>d</i> ₆	73	—	0	21	44
Z-Et ₃ I	>340	25	benzene- <i>d</i> ₆	>95	—	0	17	60
Z-Et ₃ I	>340	25	toluene- <i>d</i> ₈	20	—	0	8	5
Z-Et ₃ I	>340	25	toluene- <i>d</i> ₈	26	—	0	15	10
Z-Et ₃ I	>340	25	toluene- <i>d</i> ₈	44	—	0	21	18
Z-Et ₃ I	>340	25	toluene- <i>d</i> ₈	61	—	0	27	34
Z-Et ₃ I	>340	25	toluene- <i>d</i> ₈	79	—	0	20	28
Z-Et ₃ I	>340	25	toluene- <i>d</i> ₈	92	—	0	10	27
Z-Et ₃ I	>340	-72	toluene- <i>d</i> ₈	23	—	0	10	8
Z-Et ₃ I	>340	-72	toluene- <i>d</i> ₈	33	—	0	10	10
E-Et ₃ I	>340	-72	toluene- <i>d</i> ₈	25	0	—	11	2
E-Et ₃ I	>340	-72	toluene- <i>d</i> ₈	75	0	—	37	28
EtKA	>340	25	benzene- <i>d</i> ₆	68	0	0	—	12
EtKA	>340	25	benzene- <i>d</i> ₆	84	0	0	—	11

The ketoaldehyde KAet was isolated from irradiation of Et₆B, E-Et₅I and Z-Et₅I. The products were separated using PTLC with 97:3 hexane:ethyl acetate as the eluent which gave two bands with R_f values of 0.21 and 0.13. The first band (R_f = 0.21) contained two compounds Z-Et₅I and KAet, the second band (R_f = 0.13) consisted of *ene*KAet. The mixture of Z-Et₅I and KAet was rechromatographed using benzene as the eluent. Two bands were isolated with R_f values of 0.26 and 0.22. The first band (R_f = 0.26) contained KAet while the second band (R_f = 0.26) consisted of only Z-Et₅I. The ¹H-NMR in benzene-*d*₆ had a aldehydic resonance at 9.99 ppm (s, 1H, a) and revealed five distinct methyl



resonances, four of which were triplets at 0.865(J = 7.5 Hz, 3H), 0.970(J = 7.5 Hz, 3H), 1.01(J = 7.5 Hz, 6H), 1.04 ppm (J = 7.5 Hz, 3H), and one being a doublet at 1.65 ppm (J = 6.9 Hz, 3H, c'). The region between 2.0 and 2.5 ppm was quite complicated with five distinct methylene resonances at 2.18-2.28(broad m, 4H), 2.27(q, J = 7.5 Hz, 2H), 2.35(q, J = 7.5 Hz, 2H), 2.41(q, J = 7.5 Hz, 2H). The benzylic methine a' that is coupled to the methyl group c' of has a chemical shift of 5.62 ppm (J = 7.2 Hz, 1H, c') and appears as a quartet. The aromatic region is simple with only three resonances, one appears as a singlet at 6.71(2H) while the other two appear as doublets at 6.59(J = 1.5 Hz, 1H), 7.36 ppm (J = 1.5 Hz, 1H). The ¹H-

NMR spectrum of KAet closely resembles the previously reported 2(*o*-formylphenyl)-1-phenylethanone.¹⁵⁷



Scheme 93. Model compounds from independent researchers.

The hemiacetal *eneKA*Et was isolated from irradiation of Et₃B, *E*-Et₃I, *Z*-Et₃I and KAet in separate experiments. Separation was accomplished using PTLC with 97:3, hexane:ethyl acetate and eluted with a R_f value of 0.13. For ¹H-NMR spectral details see Figure 43. The ¹H-NMR spectrum in chloroform-*d*₁ had five distinct methyl resonances, four of which are triplets at 1.09(*J*= 7.5 Hz, 3H), 1.18(*J*= 7.5 Hz, 3H), 1.24(*J*= 7.5 Hz, 3H), 1.27 (*J*= 7.5 Hz, 3H), 1.30 ppm (*J*= 7.5 Hz, 3H) and one which is a singlet at 1.81 ppm (3H, b). The benzylic methine appeared as doublet at 6.56 ppm (*J*= 7.2 Hz, 1H, a) with ³*J* vicinal coupling to the hydroxyl proton which disappeared after washing with D₂O. The aromatic region was simple with three singlets at 6.95(s, 1H), 6.97(s, 1H) and 7.02 ppm (s, 2H). The ¹³C-NMR in chloroform-*d*₁ three resonances that are consistent with *eneKA*Et structure have chemical shifts of 89.96 (1'), 107.4 (3') and 188.9 ppm (2'). The assigned structure of *eneKA*Et is in agreement with the previously reported 1-methoxy-4-phenyl-1*H*-2-benzopyran (*Et*₃IOMeKA in Scheme 93) in which the hemiacetal benzylic hydrogen's chemical shift is a 6.57 ppm in CCl₄.¹⁵⁷

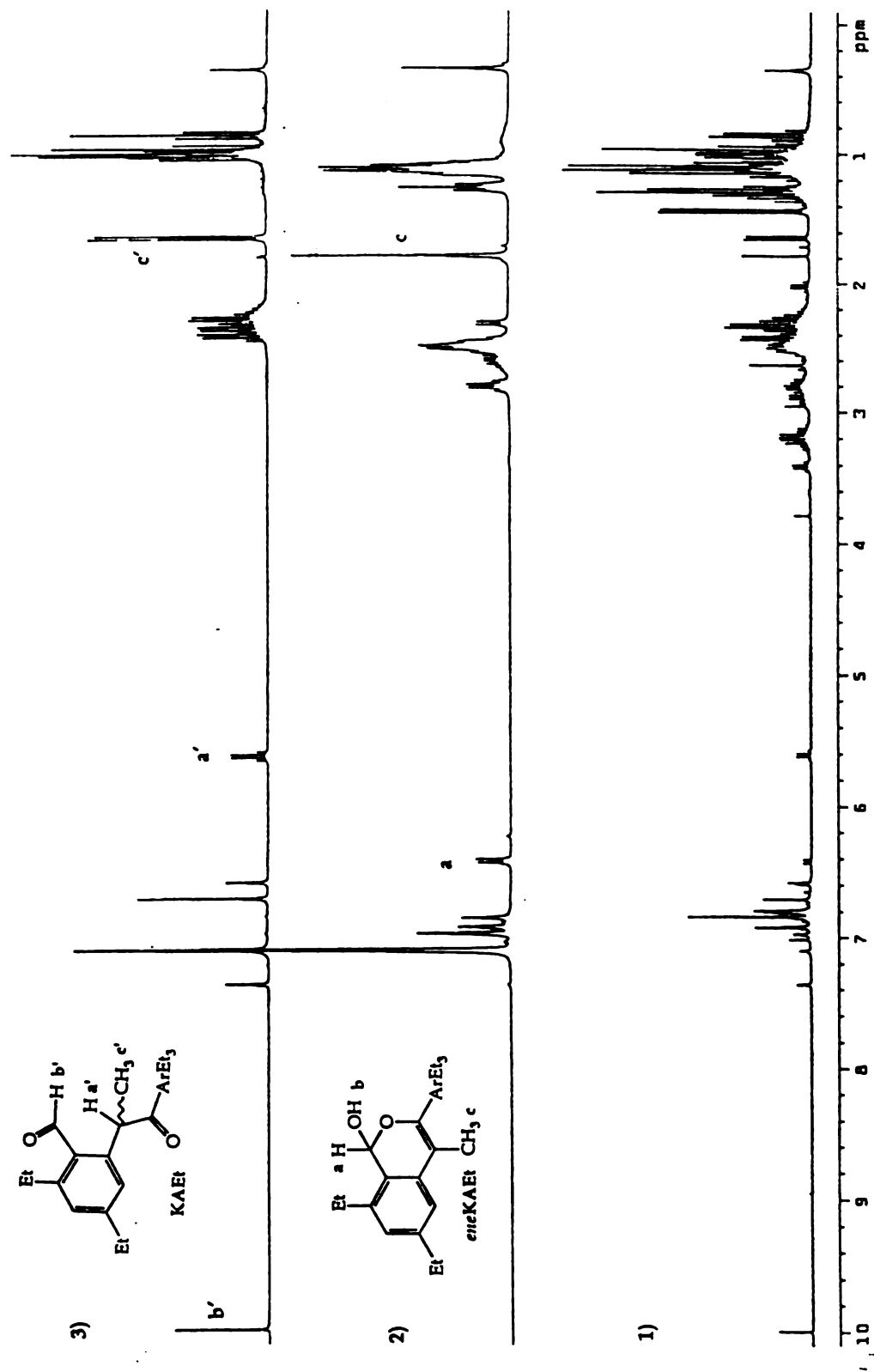


Figure 43. ^1H -NMR Spectra in benzene- d_6 1) mixture of *ene*KAEt and KAEt after irradiation of Z-E-I 2) purified *ene*KAEt 3) purified KAEt.

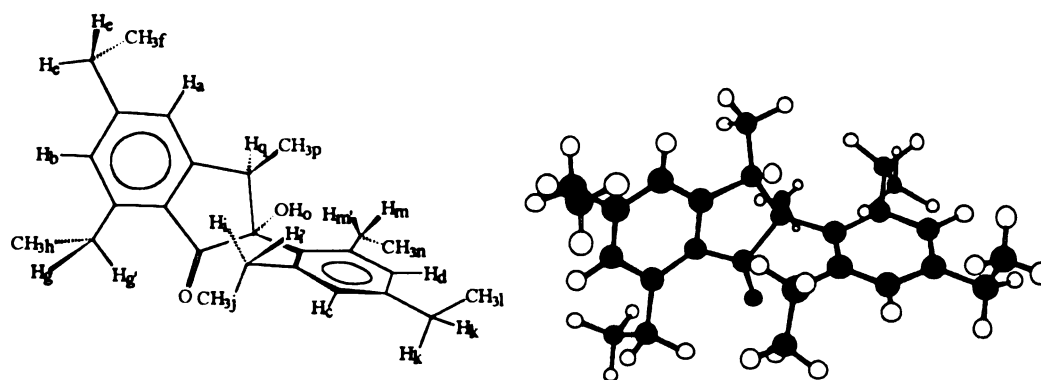


Figure 44. MM2 minimized geometry of *E*-Et₅I

The *Z* and *E* Et₅I isomers were subjected to selective decoupling, ¹HNOE, and temperature dependent ¹H-NMR studies. We were able to identify and assign all the ¹HNMR resonances for each of the isomers. The most noticeable difference in ¹HNMR spectra for the two isomers is the large difference in chemical shifts of the methyl substituent (p) on the indanone ring. Another distinct difference in the spectra is the broadening of the ortho methylenes of the triethylphenyl substituent for the *Z* isomer. In benzene-*d*₆ the three remaining ortho methylenes give rise to six different hydrogen resonances in the *E*-isomer at room temperature, all of which are doublets of quartets. However, the three remaining ortho methylene groups of the *Z*-isomer give rise to 4 resonances, two of them are AB quartet of quartets (H's=g and g') and the other two are very broad singlets with line widths at ½ height from 225 to ~300Hz. The ¹HNMR spectrum of the *Z* isomer at reduced temperatures resembles the *E*-isomer at room temperature. This increased similarity is attributed to the reduced rotation of the triethylphenyl substituent alpha to the carbonyl group.

The Z-isomer has a methyl doublet with a chemical shift of σ 1.46 ppm (p, d, J=7.0 Hz; 3H) which is deshielded compared to the methyl doublet for the E-isomer, 0.986 ppm (p, d, J=7.5 Hz; 3H) in chloroform- d_1 . The large difference in chemical shifts for the two methyl groups of the isomers is attributed to E-isomer having the methyl and triethylphenyl groups cis. This cis configuration orientates the methyl group in the ring current of the benzene ring. A similar phenomenon is encountered for one of the ortho methyl groups of the ethyl on the triethylphenyl ring substituent for the E isomer. The methyl triplet with a chemical shift of 1.22 ppm (J=7.5Hz; 3H) in chloroform- d_1 is the most shielded of the methyl triplets. This can be explained with aid from a minimized MM2 geometry in Figure 44. The minimized molecular mechanics geometry shows the ortho methyl group being directly above the carbon-oxygen double bond. The carbonyl group also has a shielding cone similar to the ring current found in benzene analogues.

It is worth noting that in the Z-isomer, the methine hydrogen (q) is in the same position as the methyl group (p) of the E isomer, cis to the triethylphenyl substituent of indanone ring. Even though the methyl group (p) and methine hydrogen (q) are both substituents of the indanone ring in the same position, there is only a small difference in chemical shifts, 0.16 ppm, of the methine hydrogen (q) of the two isomers. This contrasts with the large difference in chemical shifts, 0.5 ppm, of the methyl group (p) of the E-isomer that is shielded as compared to the Z-isomer. It appears that the hydrogens on the methyl group

(p) are approximately one angstrom farther from the indanone ring than the methine hydrogen (q). This increased distance of the methyl group from the indanone ring orientates it in the ring current of the benzene ring resulting in a resonance at higher field.

^1H -NOE provided pertinent information on the relative through space relations of the different types of hydrogens in the isomers. The ^1H -NOE results enabled us to assign which aryl hydrogens were neighbors to which methylene hydrogens of the ethyl groups. For example, irradiation of hydrogen g and g' gave an adsorption of the aryl hydrogen b, irradiation of b gave an adsorption of e, irradiation of a gave an adsorption of e. This information suggests that a-e-b-gg' are in close proximity and suggests their relative positions on the benzene ring. The selective decoupling experiment also confirms the large ^1H -NOE effect of g and g', -23%, and showed that they are clearly coupled through bond. Once the methylene (g and g') resonances were identified, the selective decoupling experiment was used to determine the through bond relation of the methylene group (g and g') with the methyl group (h).

The Z-isomer was subjected to temperature studies from -77°C to 105°C in toluene- d_8 . This experiment was especially useful in the analysis of the Z-isomer because it was not possible to distinguish i and i' from m and m' by selective decoupling or NOE experiments. Prior to this experiment the identity of i, i', m, m' was unclear.

The hydrogens that are affected the most when the temperature is varied are the three ortho methylene hydrogens (**g** and **g'**, **i** and **i'**, **m** and **m'**). The results suggest that at or near room temperature **i** and **m**, and **i'** and **m'** are at point of coalescence with chemical shifts of 2.53 and 2.94 ppm respectively. When the sample is warmed gradually from 20°C to 105°C the broad peaks of **i**, **i'**, **m**, and **m'** become more resolved, but their chemical shifts remain nearly constant. At

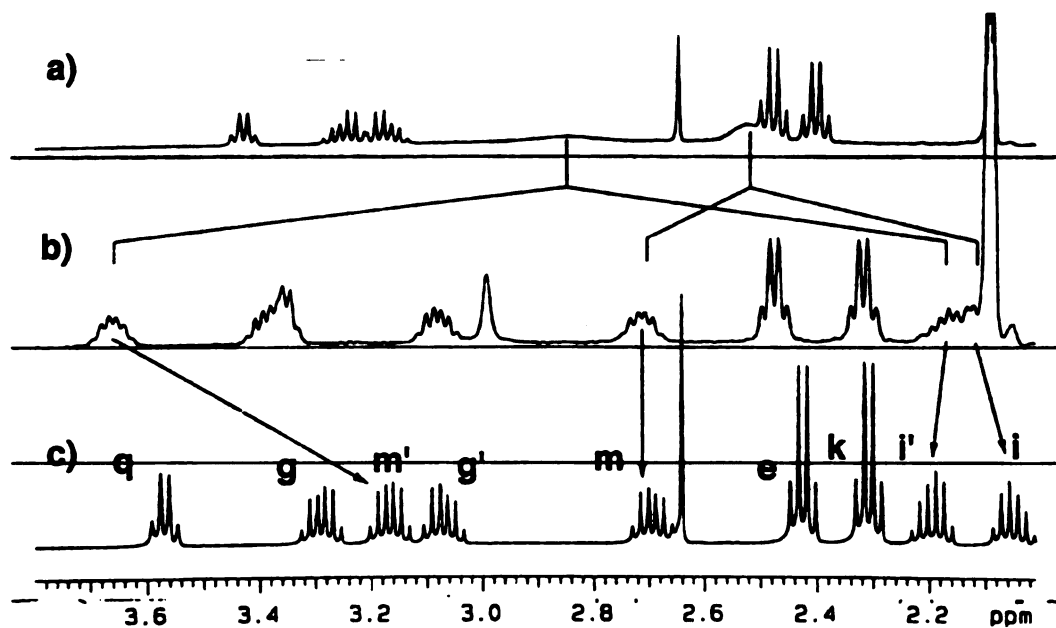
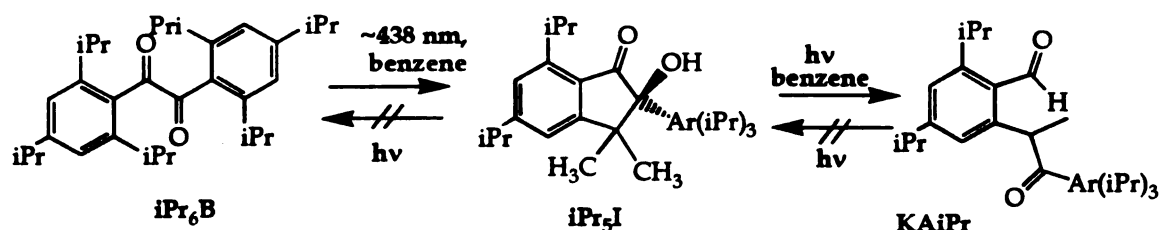


Figure 45. *Z*-Et₃I, toluene-*d*₈, 20°C. b) *Z*-Et₃I, toluene-*d*₈, -60°C c) *E*-Et₃I, benzene-*d*₆, 20°C.

105°C **i** and **m** and **i'** and **m'** have the same chemical shift, both sets appear as a quartet of a doublet and integrate for two hydrogens. The two hydrogens of each respective set have become rotationally equivalent. This suggests that the hydrogens **i** and **m** or **i'** and **m'** are rapidly interconverting by a C₂ rotation of the triethylphenyl substituent of the indanone ring. When the sample is heated

to 105°C the rotation of this bond is now faster relative to the NMR time scale (10^{-3} sec) and the peaks appear to be more resolved. As the temperatures are decreased the bond rotation becomes slower and **i**, **i'**, **m**, and **m'** have unique resonances (see Figure 45).

3. 2,4,6,2',4',6'-hexaisopropylbenzil (**iPr₆B**)



Scheme 94. Photochemistry of 2,4,6,2',4',6'-hexaisopropylbenzil

The products from **iPr₆B** have been previously characterized by Park.¹⁰³ Irradiation of **iPr₅I** gave **KAiPr** quantitatively. Irradiation of **KAiPr** gave no products after 50 hours of irradiation in benzene-*d*₆ through Pyrex filtered light. For details of this reaction see Figure 46.



Figure 47. $^1\text{H-NMR}$ Spectra of KAlPr in benzene- d_6 with MB internal standard 1) before irradiation 2) after 9 hours irradiation.

C. Quantum yields and Stern-Volmer quenching studies

The quantum yield measurements were conducted at 313 and 366 nm with filtered light. The irradiation conducted with the light source mounted in the center of a merry-go-round setup. For NMR tubes, the 14 mm merry-go-round hole size was adapted with Teflon disk adapters (1 mm x 12 Teflon wafer

Table 24. Quantum Yields for α -hydroxyindanone formation from 2,2',4,4',6,6'-hexaalkylbenzils

Ketone	Indanone	$\epsilon_{313\text{nm}}$ (benzene)	$\Phi, 313\text{nm}^a$	$\Phi, 313\text{nm}$ (% conv) ^b	$\Phi, 366\text{nm}$ (% conv) ^a	$k_q\tau(\text{M}^{-1})$	$\tau, \text{ns}^{b,c}$
Me ₆	Me ₃ -I	1340	0.006	—	0.009(5)	404	67
Et ₆	E-Et ₃ -I	2190	0.012	0.013(17)	0.013(18)	570	95
Et ₆	Z-Et ₃ -I	2190	0.026	0.026(17)	0.017(18)	570	95
Ip ₆	I ₃ -I	2810	0.042	0.042(7)	0.034(17)	420	70

^a GC analysis, degassed benzene ^b NMR analysis, degassed benzene-*d*₆ ^c pyrene as quencher in degassed benzene at 25.0°C, based on assumption quenching is diffusion controlled ($k_q = 6 \times 10^9 \text{M}^{-1}\text{s}^{-1}$).

Table 25. Quantum Yields for formation of ketoaldehyde from α -hydroxyindanone.

Indanone	Ketoaldehyde	$\epsilon_{313\text{nm}}$ (benzene)	$\Phi, 313\text{nm}^a$	% conversion
Me ₃ -I	KA-Me ₃	689	0.041	5
E-Et ₃ -I	KA-Et ₃	700	0.096	7
Z-Et ₃ -I	KA-Et ₃	705	0.067	12
I ₃ -I	KA-I ₃	734	0.100	26

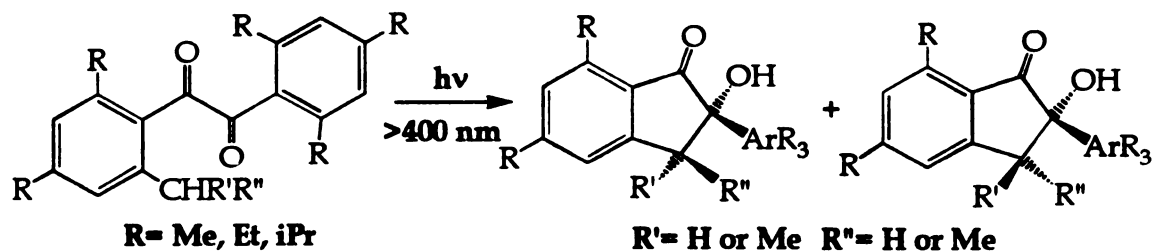
^b NMR analysis, degassed benzene-*d*₆ at 25°C with 0.10 M valerophenone as actinometer.

with a 5 mm centered bore) to ensure the NMR tube fit snug inside of the **standardized** test tube. The portion of the NMR tube above the merry-go-round **was** wrapped with black electrical tape since the 0.7 mL volume was above this **level** and would have absorbed reflected light. The use of the Teflon adapter **ensured** the NMR sample tubes were equal distance from the light source which **was** mounted in the center.

VII. Discussion for α -Cleavage of congested α -hydroxyindanones

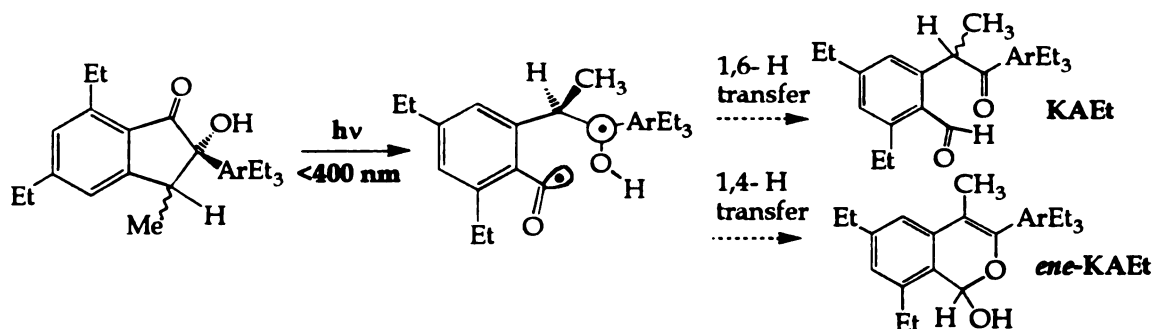
Our continued interest in the effects of steric congestion on photoreactivity¹² has led to the study of 2,4,6,2',4',6'-hexaalkylbenzils and their photoproducts.

Previously we reported that the primary photoproducts of hexaalkylbenzils are α -hydroxyindanones formed from a 1,5-biradical after δ -hydrogen abstraction.¹⁵⁵ However, these initial hydroxyindanones are photolabile and can undergo the Norrish Type I reaction followed by biradical disproportionation to yield ketoaldehydes.^{89,97}



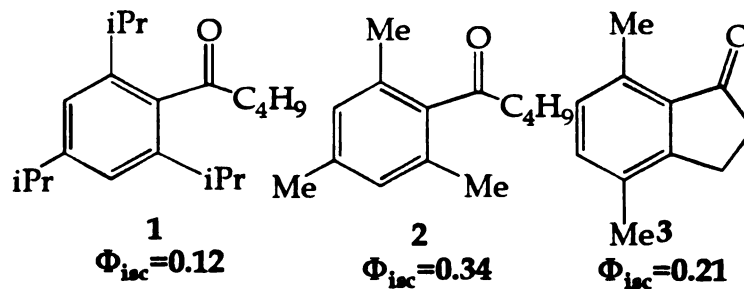
My studies have revealed subtleties in this secondary photochemistry, in particular a second disproportionation pathway for the biradical which involves a 1,4 hydrogen transfer rather than a 1,6 transfer and gives the benzopyran derivative *eneKA*Et, which is photostable. The ketoaldehyde itself can be photolabile and can give several photoproducts, *eneKA*Et being the major one.

This study provides insight into the effects of steric congestion on photoreactivity. An increase in steric congestion ($\text{Me}_6\text{I} < \text{Z-Et}_6\text{I} < \text{E-Et}_6\text{I}$, iPr_6I)



Scheme 95. Disproportionation of a 1,5-biradical by 1,4 and 1,6 pathways.

seems to facilitate the α -cleavage process, as reflected in the quantum yields for ketoaldehyde formation. The quantum yields for product formation from these α -hydroxyindanones are surprisingly low considering their similarity to benzoin derivatives which are efficient photoinitiators for polymerization.¹⁵⁸ Since 1M piperylene did not quench KAiPr formation, either the reaction occurs from the excited singlet or the triplet cleavage rate constant is $>10^{10}\text{ s}^{-1}$. The latter is probable since α -cleavage is known to be much faster from an $^3n,\pi^*$ state than from a $^1n,\pi^*$ state. Lewis has shown that benzaldehyde formation from benzoin is quenched with naphthalene to give a triplet lifetime of 1.2 ns.¹⁵⁹ An important difference between our α -hydroxyindanones and previous literature examples is the substituent ortho to the carbonyl moiety: it introduces steric congestion and provides competing decay modes. I believe that the low quantum yields for α -cleavage are due primarily to efficient singlet state quenching, given the quantum yields for triplet formation reported for model ketones 1-3.¹³¹



The quantum yields for product formation from iPr_3I and Et_3I fit nicely with the quantum yield for triplet formation of 1 and suggest that nearly all the triplet molecules formed α -cleave to give a 1,5-biradical. When the isopropyl groups are replaced by methyl groups the quantum yield for triplet formation presumably increases, as for 2, but our product quantum yield decreases. Apparently the biradical from iPr_3I only disproportionates, since cyclization would regenerate severe steric congestion. With less steric congestion the biradical from Me_3I can recyclize as well as disproportionate.

A. Chemistry of biradicals from Et_3I and $KAEt$

1. 1-(α -hydroxy),5(acyl)-biradical from Et_3I

The biradical formed by α -cleavage of Et_3I disproportionates by two pathways involving either a 1,4 or 1,6-hydrogen shift to give nearly equal amounts of $KAEt$ and *ene* $KAEt$. Similar results have been previously documented.^{87,89,160} In the case of iPr_3I this mode of disproportionation is prevented by the benzylic gem dimethyl group. The biradical does not recyclize since *E*- Et_3I and *Z*- Et_3I do not interconvert photochemically. Semiempirical

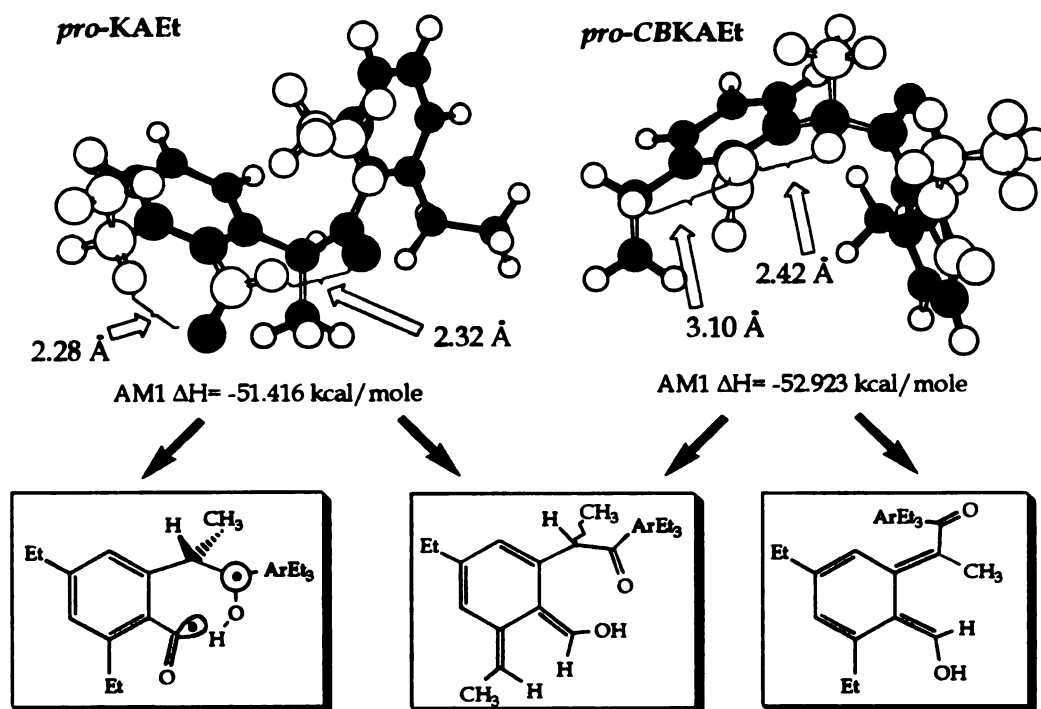


Figure 47. Conformations of ground state KAEt.

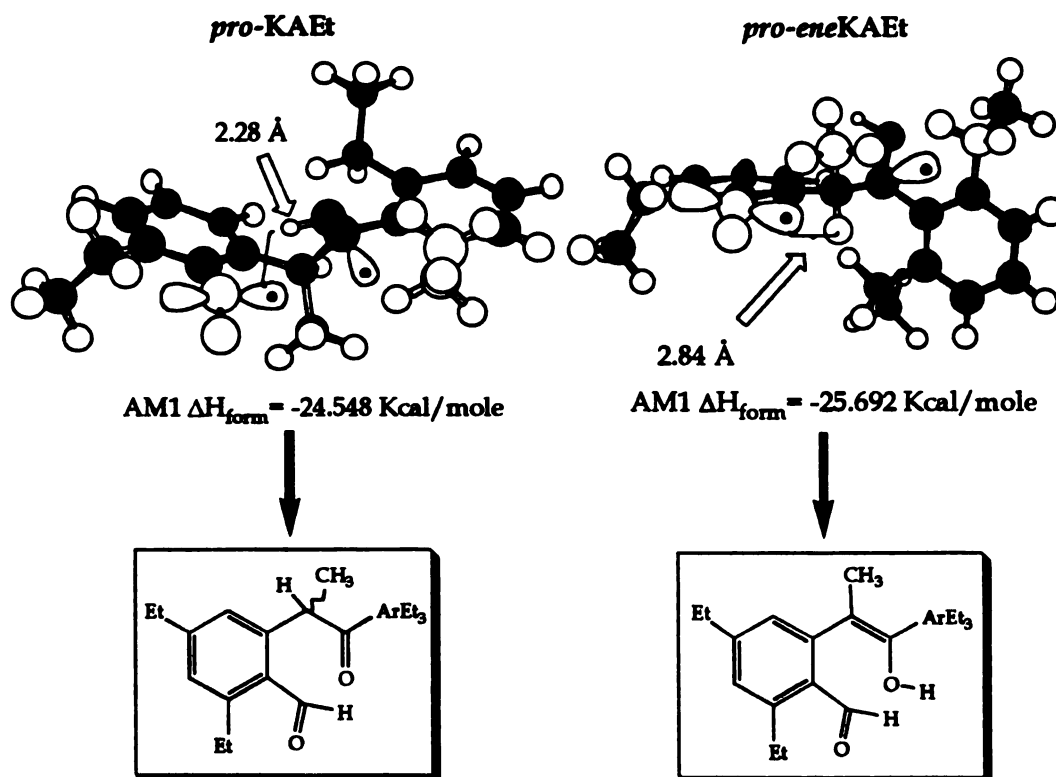


Figure 48. Conformations of the biradical KAEt.

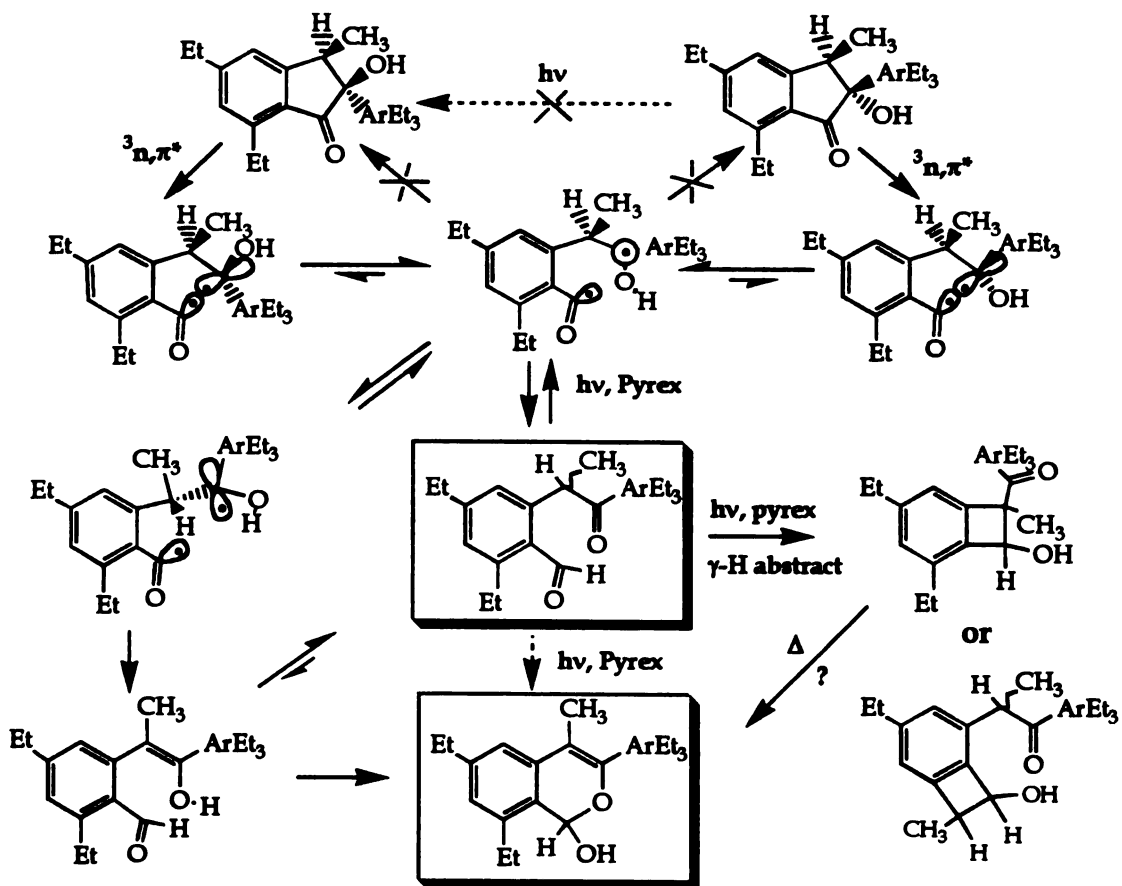
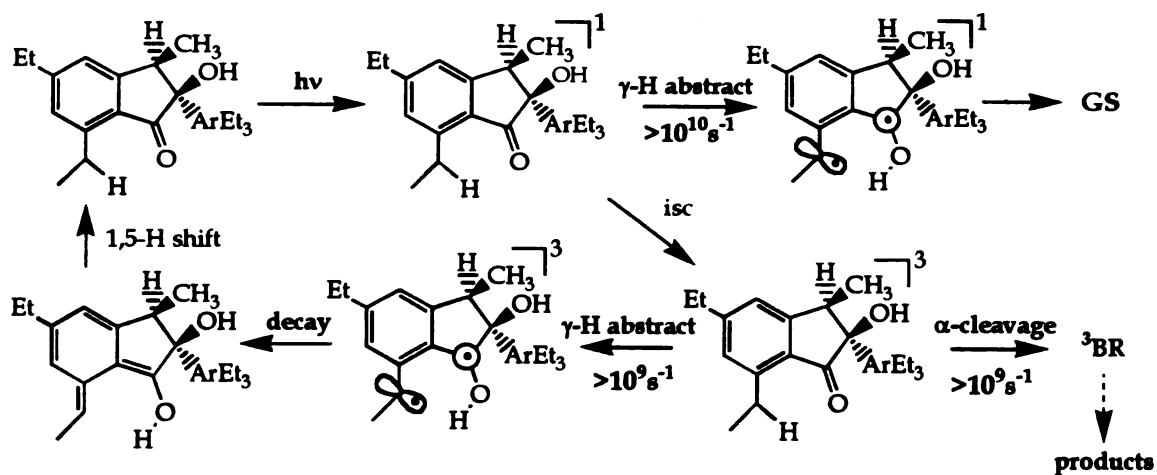


Figure 49. Proposed mechanism for α -cleavage of sterically congested α -hydroxyindanones.

calculations suggest that *pro-CBKAEt* and *pro-eneKAEt* biradical geometries are the lowest energy conformations that lead to the two competing products (see Figure 48).

2. Biradicals from KAEt.

KAEt undergoes secondary photoreactions to give both 1,4 and 1,5 biradicals. KAEt can generate, by δ -hydrogen abstraction the same noncyclizing biradical formed by α -cleavage of either *Et*₃*I* isomer. The eventual predominance of *eneKAEt* represents, at least partially, continued interconversion between KAEt and this 1,5-biradical. Semiempirical calculations suggest that the two lowest energy conformations of ground state KAEt both can undergo γ -hydrogen abstraction to form photoenols that could cyclize to *CB-KAEt* or *CB'-KAEt*, and possibly also to *eneKAEt* by a Diels-Alder reaction (see Figure 47). Only one conformer can undergo δ -hydrogen abstraction.

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FACTORS INFLUENCING THE
PHOTOCHEMISTRY OF ORTHO ALKYL PHENYL KETONES.

VOLUME II

By

Martin Sobczak

A DISSERTATION

Submitted to
Michigan State University
In partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1997

Experimental

I. General Procedures

Fourier Transform Infrared (FTIR) spectra were recorded using a Nicolet IR/42 Fourier Transform spectrometer. Samples were prepared in a 0.025 mm solution cell with carbon tetrachloride as the solvent. Both background and solvent reference were subtracted. Compounds with low solubility in carbon tetrachloride were prepared as thin films on a NaCl plate by dissolving in an appropriate solvent then pipetting the solution on the salt plate. The solvent was allowed to evaporate and the cycle repeated until an acceptable film was achieved.

^1H -NMR and ^{13}C -NMR spectra were obtained using several Varian spectrometers but with the same acquisition parameters. The Varian models used were Gemini 300 MHz, VXR 300 MHz, VXR 500 MHz, UNITY 300 MHz with VXR software. Deuterated NMR solvents were used as obtained from Aldrich Chemical. Chemical shifts are reported in ppm from chloroform- d_1 (7.24 ppm for ^1H , 77.0 ppm for ^{13}C), benzene- d_6 (7.10 ppm for ^1H , 128.0 ppm for ^{13}C), acetonitrile- d_3 (1.93 ppm for ^1H , 1.29 ppm for ^{13}C), toluene- d_8 (2.09

ppm for ^1H). It was essential when the FID's (free induction decay) were acquired for quantitative experiments that a long delay (parameter D1) be employed. The value of D1 was generally 10-20 seconds and was tested by increasing the value of D1 until integration values were constant and did not change with the increasing D1. The NMR sample tubes used for quantitative experiments were model 535pp (pyrex, ID= 4.000 mm $\pm \leq 0.005''$) from Wilmad Glass. ^2H -NMR was conducted using a Varian VXR 300 MHz NMR spectrometer with the lock channel off. A blank sample of the analogous deuterated solvent was locked and shimmed. The probe was then tuned to ^2H (frequency) and the lock turned off.

Absorption spectra (UV-VIS) were obtained on a Shimadzu UV-160 spectrometer with matched 1.0 cm quartz cells. A Perkin-Elmer MPF-44A spectrofluorimeter was used to record both fluorescence and phosphorescence spectra attached to a Houston instruments Omnigraphic model 2000 XY-recorder. Phosphorescence spectra was recorded at 77K in a 2-methyltetrahydrofuran or ethanol glass in a 4 mm Pyrex NMR sample tube. Absorption and emission spectra were digitized with version 2.0 UN-SCANT software by Silk Scientific and plotted using KaleidaGraph graphing software.

Low resolution mass spectra (LRMS) were recorded using a Hewlett-Packard 5890 GC/MS Trio-1; high resolution mass spectra (HRMS) using a Joel JMS-HX110 double focusing mass spectrometer, with exact masses determined by peak matching in the FAB.

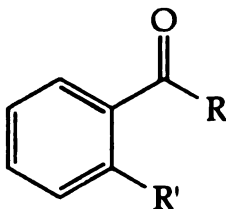
Gas Chromatographic analyses were performed on a Varian 3400 chromatograph equipped with flame ionization detector, splitless capillary injector and a Megabore DB210 (J. & W. Science) capillary column. The chromatograms were recorded with either a Hewlett-Packard 3393A or 3392 integrating recorder. High Pressure Liquid Chromatography (HPLC) was conducted using a Rainin system equipped with two solvent delivery pumps (25 mL heads), a Dynamax UV-D detector, a 20 μ L loop and a normal phase Rainin Microsorb Si80-125-CS silica gel column. The data were acquired using a Macintosh Classic personal computer with Rainin Dynamax software.

Melting points were determined using a capillary Uni-Melt melting point apparatus. All melting and boiling points are uncorrected.

Analtech Uniplate silica gel plates (20 cm x 20 cm, 1000 micron) were used for preparative thin layer chromatography (PTLC).

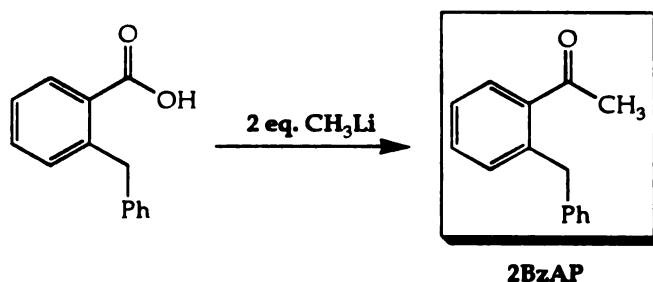
II.Synthesis: Preparation of Starting ketones

A.Substituted 2-akyl aceto-, trifluoroaceto- and benzo- phenones



Ketone	R	R'
2BzAP	CH ₃	CH ₂ Ph
2AcMAP	CH ₃	CH ₂ COOH
2AcMAP_{d1}	CH ₃	CH ₂ COOD
2EsMAP	CH ₃	CH ₂ COOEt
2AmMAP	CH ₃	CH ₂ CONEt ₂
2MeTFA	CF ₃	CH ₃
2EtTFA	CF ₃	CH ₂ CH ₃
2MOTFA	CF ₃	CH ₂ OCH ₃
2EtBP	Ph	CH ₂ CH ₃
2BzBP	Ph	CH ₂ Ph
2BzBP_{d2}	Ph	CD ₂ Ph
2AcMBP	Ph	CH ₂ COOH
2AcMBP_{d1}	Ph	CH ₂ COOD
2EsMBP	Ph	CH ₂ COOEt
2AmMBP	Ph	CH ₂ CONEt ₂
Me₂BP	2'-MePh	CH ₃

1. 2-benzylacetophenone (BzAP)



reference: Bradsher, C. K. and S. T. Webster, *J. Amer. Chem. Soc.* **1957**, 393

2'-Benzylacetophenone was prepared by standard literature methods. Methyl lithium, 90 mL (1M, Aldrich chemical) was added to 7.5 g of *o*-benzylbenzoic acid (0.035 moles, Aldrich Chemical) dissolved in 250 mL of dry diethyl ether and stirred for 2 hours at room temperature. The mixture then was treated with ice and extracted three times with diethyl ether, washed with saturated aqueous NaHCO₃ and concentrated. The crude product was distilled (bp 149-152°C/3 mm Hg) and recrystallized from petroleum ether (60-90°C). The mass of the recrystallized product was 6.0 g (80 % yield). The crystals melted at 45-48°C, lit.¹⁶¹ 49-50°C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 2.48 (s, 3H), 4.26 (s, 2H), 7.10-7.26 (m, 5H), 7.29 (dd, J = 7.4, 1.5 Hz, 1H), 7.38 (ddd, J = 7.4, 7.4, 1.5 Hz, 1H), 7.63 (dd, J = 7.4, 1.5 Hz, 2H).

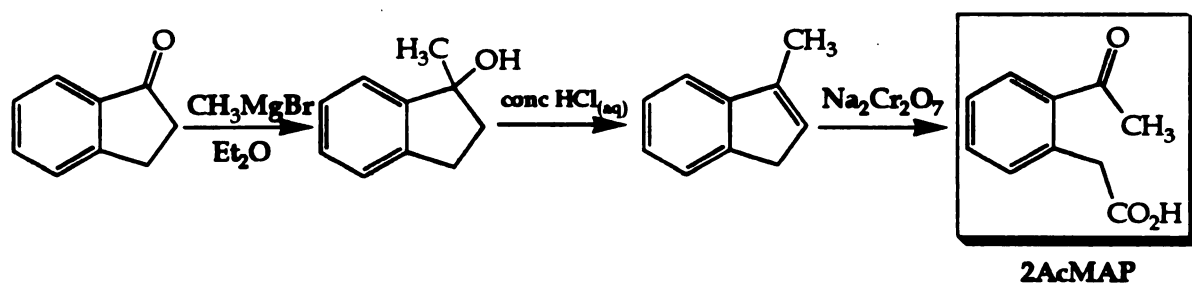
¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 29.74, 39.17, 125.9, 126.1, 128.3, 128.9, 129.1, 131.3, 131.7, 138.3, 140.5, 140.8, 202.3.

FTIR (0.025mm CCl_4 , cm^{-1}) 1211.46(vs), 1246.17(s), 1489.24(w), 1691.79(s), 2922.53(w), 3030.56(w), 3067.21(w).

HRMS, Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_1$, 210.10446, found 210.1045.

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Cyclohexane, 284 (1,260), 239 (8,040), 218 (10,400), $\epsilon_{313} = 80.6 \text{ M}^{-1}$, $\epsilon_{366} = 4.86 \text{ M}^{-1}$.

2. (2-acetylphenyl)acetic acid (2AcMAP)



1-methylindene

reference: Jackson, R. A.; C. J. Rhodes, *J. Chem. Soc. Perk. Trans. 2*, 1993, 53.

1-Indanone (Aldrich Chemical, 10g, 76 mmol) was dissolved in 50 mL of freshly distilled diethyl ether and added slowly, with stirring, to the Grignard reagent from 6.3 mL (14.4 g, 100 mmol) methyl iodide and 3.4 g (140 mmol) of freshly ground magnesium turnings. The reaction solution was refluxed for one hour and cooled to room temperature. The solution was poured into a mixture of 100 g of crushed ice and 25 mL concentrated sulfuric acid. The ether layer was separated and dried over anhydrous MgSO_4 and the solvent removed, 25 mL of concentrated sulfuric acid was added and the mixture refluxed for 1 hour. The 1-

indene was steam distilled and extracted with three 30 mL portions of diethyl ether. Evaporation gave 4.4 g (45% yield).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 2.12(s, 3H), 3.30 (s, 2H), 6.22(s, 1H), 7.2-7.6(m, 4H).

(2-acetylphenyl)acetic acid

reference: Halford, J. O. and B. Weissmann, *J. Org. Chem.* 1953, 31, 30.

The oxidative cleavage of 1-methylindene was conducted using a literature method with sodium dichromate hydrate, although ozonolysis is probably a more efficient method. A solution of 8.8 g (30 mmol) of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$, 0.5 g sodium benzene sulfonate (3 mmol) and 24 mL of concentrated sulfuric acid in 130 mL distilled water was stirred mechanically. A solution of 3.5 g (270 mmol) 1-methylindene in 10 mL methanol was added over a 30 minute period and the solution was warmed to 55°C for 25 minutes. The mixture was cooled in a refrigerator for 3 hours and a green gummy solid was collected by vacuum filtration and washed with cold 5% H_2SO_4 and water. Recrystallization with water gave a poor yield (200 mg, 4% yield) and the crystals melted at $163\text{-}165^\circ\text{C}$, literature¹⁶² $165\text{-}166^\circ\text{C}$. Thus, the filtrate was extracted with three 50 mL portions of ethyl acetate and yielded an additional 1.1 g of crude o-acetylphenylacetic acid.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 2.64(s, 3H), 3.87(s, 2H), 7.34(dd, J = 7.5, 1.5 Hz, 1H), 7.40(ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 7.50(ddd, 7.5, 7.5, 1.5 Hz, 1H), 7.81(dd, J = 7.5, 1.5 Hz, 1H).

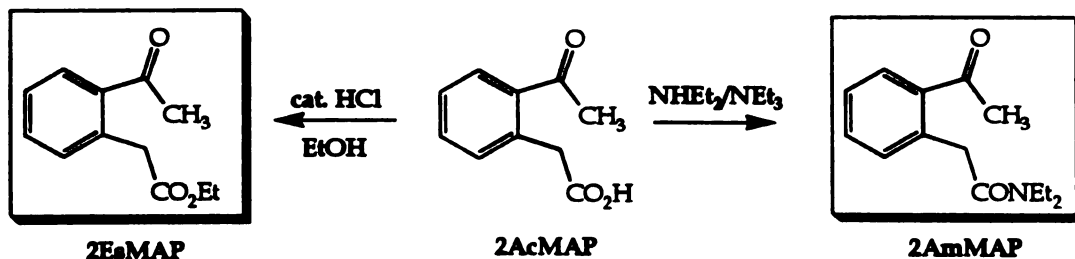
$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 1.92(s, 3H), 3.53(s, 2H), 6.76(d, J = 7.5 Hz, 1H), 6.78(ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 6.90(ddd, J = 7.5, 7.5, 1.5, 1H), 7.04(dd, J = 7.5, 1.5 Hz, 1H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 28.56, 40.44, 127.5, 129.9, 132.4, 132.6, 133.6, 136.9, 174.5, 202.6.

FTIR (film-NaCl plate, cm^{-1}) 1261.61(vs, broad), 1292.47(s), 1383.14(s, broad), 1448.73(m), 1491.16(m), 1550.97(m, broad), 1577.97(m), 1601.12(m), 1703.36(vs, broad), 2800-3550(m, very broad).

LRMS, m/z : (M^+) 178.1, (100%) 149.1, 132.0, 118.9, 105.2.

3. *ethyl (2-acetylphenyl)acetate* (2EsMAP) and *N,N*-diethyl (2-acetylphenyl)acetamide (2AmMAP)



N,N-diethyl (2-acetylphenyl)acetamide

reference: Shimada, K. and T. Mukaiyama, *Bull. Chem. Soc. Japan* **1977**, 50, 1863.
Mukaiyama T.; Y. Aikawa; S. Kobayashi, *Chemical Letters* **1976**, 57.

To a solution of 170 mg (Aldrich Chemical, 0.67 mmol) 1-methyl-2-chloropyridinium iodide in 5 mL of dichloromethane was added 60 μ L (0.56 mmol) freshly distilled diethylamine, 180 μ L (1.3 mmol) freshly distilled triethylamine and 100mg (0.56 mmol) (2-acetylphenyl)acetic acid dissolved in 1 mL dichloromethane. The mixture was heated to reflux under an argon atmosphere with stirring for one hour. The solution was cooled to room temperature and 10 mL of diethyl ether was added followed by washing with three 5 mL portions of 5% HCl_(aq) and once with 5 mL deionized water. The organic layer was dried over anhydrous CaCl₂ and concentrated under reduced pressure. The crude N,N-diethyl (2'-acetyl)phenylacetamide was purified by PTLC with 95:5 hexane:ethyl acetate as the eluent.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 1.08(t, J= 7.0 Hz, 3H), 1.26(t, J= 7.0 Hz, 3H), 2.56(s, 3H), 3.36(q, J=7.0 Hz, 2H), 3.41(q, J= 7.0 Hz, 2H), 3.98(s, 2H), 7.20(dd, J= 8.4, 1.0 Hz, 1H), 7.35(ddd, J= 7.7, 7.6, 1.4 Hz, 1H), 7.42(ddd, J= 7.5, 7.4, 1.5 Hz, 1H), 7.35(dd, J= 7.6, 1.4 Hz, 1H)

ethyl (2-acetylphenyl)acetate

reference: Anzalone, L. and J.. A. Hirsh, *J. Org. Chem.* **1985**, 50, 2128. Chatterjee, S. and E.-I. Negishi, , *J. Org. Chem.* **1986**, 51, 3407.

The ethyl ester of (2-acetylphenyl)acetic acid was synthesized by dissolving 100 mg (0.56 mmol) of (2-acetylphenyl)acetic acid in 20 mL of absolute ethanol and adding three drops of concentrated $\text{HCl}_{(\text{aq})}$. The solution was refluxed overnight and cooled to room temperature and evaporated to dryness followed by the addition of 5 mL diethyl ether and washing with 2 mL saturated $\text{NaHCO}_{3(\text{aq})}$. The ether solution was dried by passing through a 1 inch plug of basic alumina. ^1H -NMR analysis revealed the pure ester with no impurities.

^1H -NMR (CDCl_3 , 300 MHz), δ ppm: 1.25(t, J = 7.1 Hz, 3H), 2.58(s, 3H), 3.92(s, 2H), 4.14(q, J = 7.1 Hz, 2H), 7.23(dd, J = 7.8, 1.0 Hz, 1H), 7.37(ddd, J = 7.5, 7.4, 1.0 Hz, 1H), 7.45(ddd, J = 7.4, 7.4, 1.5 Hz, 1H), 7.79(dd, J = 7.6, 1.5 Hz, 1H).

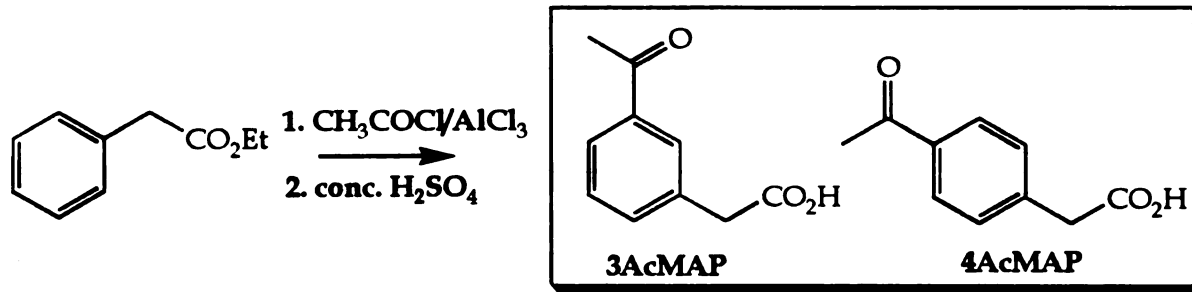
^1H -NMR (Benzene- d_6 , 300 MHz), δ ppm: 0.935(t, J = 7.1 Hz, 3H), 2.12(s, 3H), 3.91(s, 2H), 3.95(q, J = 7.1 Hz, 2H), 6.79(dd, J = 7.8, 1.0 Hz, 1H), 6.86(ddd, J = 7.5, 7.4, 1.0 Hz, 1H), 6.96(ddd, J = 7.4, 7.4, 1.5 Hz, 1H), 7.17(dd, J = 7.6, 1.5 Hz, 1H).

^{13}C -NMR (CDCl_3 , 75 MHz), δ ppm: 14.04, 28.63, 40.97, 60.49, 127.2, 129.6, 131.7, 132.4, 134.3, 137.3, 171.4, 201.1.

FTIR (0.025mm CCl_4 , cm^{-1}) 1032.05(w), 1163.22(m), 1174.80(m), 1213.38(m), 1257.75(s), 1689.86(s), 1740.01(vs), 2936.03(w), 2984.26(m), 3069.14.

LRMS, m/z : (M^+) 206.1, 160.1, (100%) 132.1, 119.2.

4. (3')-& (4'-acetylphenyl)acetic acid (3PAAP or 4PAAP)



reference: D. Papa, E. Schwenk and A. Klingsberg, *J. Amer. Chem. Soc.* **1946**, 68, 2133-2134.

ethyl (3' and 4'-acetylphenyl)acetate

3.30 g (0.02 moles) of ethyl phenylacetate was dissolved in 30 ml of dry carbon disulfide. The mixture was cooled to 0°C and 5.32 g (0.04 moles) of finely powdered anhydrous aluminum chloride was added slowly, with stirring. The temperature was maintained between 0 - 5°C during the addition of the aluminum chloride. To the resulting suspension, at 0°C , 2.5 g of acetyl chloride was added in one portion and the reaction mixture stirred for 20 hours at room temperature. The reaction mixture was then put in a separatory funnel and the two layers separated. The lower layer was slowly added to a mixture of 10 mL conc. HCl in 25 g crushed ice followed by extraction with three 25 mL portions of ether. The combined extracts were washed with water and dried over sodium sulfate. The residue was esterified by dissolving in 5 mL absolute ethanol and adding slowly (with cooling) 1 mL of acetyl chloride. The solvent was removed and solidified partially overnight. The viscous liquid (meta isomer) was removed with a pipette and the remaining solid washed several

times with petroleum ether. The mass of the crude solid was 1.3 g and was not purified further.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: from mixture.

meta- 1.239(t, J= 7.2, 3H), 2.59(s, 3H), 3.72(s, 2H), 4.14(q, J= 7.2 Hz, 2H), 7.40-7.50(m, 2H), 7.82-7.96(m, 2H).

para- 1.234(t, J= 7.2, 3H), 2.58(3H), 3.65(s, 2H), 4.14(q, J= 7.2 Hz, 2H), 7.38(d, J= 8.1 Hz, 2H), 7.92(d, J= 8.1 Hz).

¹³C-NMR (CDCl₃, 75 MHz), δ ppm, only observed *para* substituted: 14.13, 26.60, 41.31, 61.13, 127.14, 128.59, 129.52, 134.027, 135.97, 139.48, 170.80, 197.73.

4'-acetylphenylacetic acid

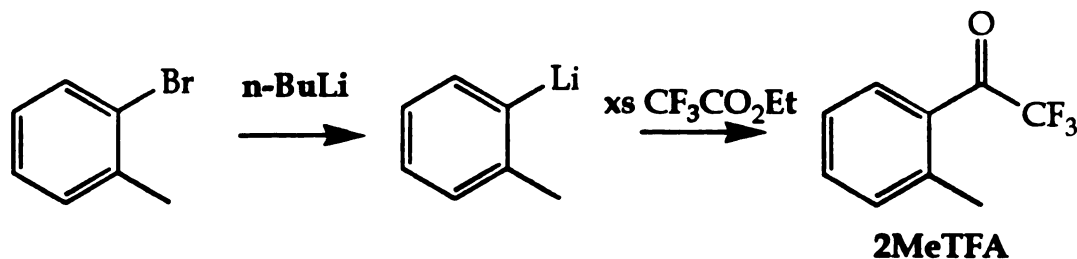
reference: Morgan, E. D. *Tetrahedron*. 1967, 23, 1735. Papa, D.; E. Schwenk; A. Klinsberg J. *Amer. Chem. Soc.* 1946, 68, 2133-2134.

To 1 g of the ester was added 10 mL of a 50% aqueous sulfuric acid solution. The mixture was allowed to stand overnight. In the morning the solution was diluted with water and filtered. The solid filtrate was collected and recrystallized from benzene yielding 0.5 grams of the acid which contained a minor component of the *meta* isomer (*para:meta*, 6:1). The acid was used without further purification and melted at 110-115 °C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 2.575(s, 3H), 2.584(*meta* isomer, from mixture of *m:p*-6:1, s, 3H), 3.70(s, 2H), 7.35(d, J=8.1 Hz, d), 7.91(d, J=8.3 Hz).

^{13}C -NMR (CDCl_3 , 75 MHz), δ ppm: 28.56, 40.44, 127.5, 129.9, 132.4, 132.6, 133.6, 136.9, 174.5, 202.6.

5. 2'-methyl-2,2,2-trifluoroacetophenone (2MeTFA)



ethyl α,α,α -trifluoroethylacetate

reference: Bergman, E. *J. Org. Chem* 1958, 23, 476.

The ethyl ester from α,α,α -trifluoroacetic acid was prepared by a known literature method. A 1L flask with 135 mL (200g, 1.75 mol) α,α,α -trifluoroacetic acid was cooled in an ice bath and 132 mL (103g, 2.11 mol) 95% ethanol was added slowly via an addition funnel followed by careful addition of ~200 mL concentrated sulfuric acid. The solution was heated at reflux for 30 minutes and then cooled. The ester was distilled through a 35 cm fractionating column and 223 g (90% yield) was collected at 58–62°C, literature 60–62°C.

^1H -NMR (CDCl_3 , 300 MHz), δ ppm: 1.39(t, J = 7.2 Hz, 3H), 4.39(q, J =7.2 Hz, 2H).

^{13}C -NMR (CDCl_3 , 75 MHz), δ ppm: 13.67, 64.43, 114.5(q, $J_{\text{C-F}}$ = 283 Hz), 157.7(q, $J_{\text{C-F}}$ = 42.1 Hz).

2'-methyl-2,2,2-trifluoroacetophenone

reference: Bégué, J.-P. and D. Bonnet-delpont, *Tetrahedron* **1991**, 47, 3207. Chen L. S.; G. G. Chen; C. Tamborski *J. Fluorine Chem.* **1981**, 18, 177. Creary, X. *J. Org. Chem* **1987**, 52, 5026.

The introduction of the trifluoroacetyl group was accomplished by a standard literature procedure. The aryllithium species could be added to the ester or the ester added to it; both gave similar results. The bromine-lithium exchange was successfully carried out by first purging the reaction setup with argon. Then 25 mL of freshly distilled THF was added via syringe, followed by 10 g (Eastman-Kodak, 60 mmol) 1-bromotoluene. The solution was cooled to -78°C and 60 mL (Aldrich Chemical, 2M cyclohexane solution) of n-butyl lithium was added via syringe and stirred for 10 minutes. The solution was warmed to 0°C and stirred for 20 minutes after which a yellow color persisted. The flask was then cooled to -78°C and stirred for 20 minutes and 32 mL (280 mmol) of neat ethyl α,α,α -trifluoroacetate was added all at once. The solution was stirred for 30 minutes and warmed to 0°C, the ice bath was allowed to melt and the reaction was stirred for 24 hours at room temperature. The reaction was quenched by pouring the reaction solution into 100 mL of saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ solution, extracted with three 100 mL portions of ether, washed with brine and dried over anhydrous MgSO_4 . Nearly all the solvent was removed by rotoevaporation. However, it is crucial that the concentrated crude reaction solution not be exposed to reduced pressure for an extended period of time. The

2'-methyl-2,2,2-trifluoroacetophenone is extremely volatile and was lost due to evaporation on several occasions. The remaining ether and ester were distilled through a 10 cm vigreux column and provided 6.1 g (60% yield) of colorless 2'-methyl-2,2,2-trifluoroacetophenone which boiled at 162-165 °C.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 2.56(s, 3H), 7.30-7.38(m, 2H), 7.52(ddd, J = 7.5, 7.2, 1.2 Hz, 1H), 7.87(distorted dd, J = 8.1, 2.1 Hz).

$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 2.22(s, 3H), 6.40-6.72(m, 2H), 6.84(ddd, J = 7.5, 7.2, 1.2 Hz, 1H), 7.55(ddd, 7.8, 1.8, 1.5 Hz, 1H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 21.85, 116.5(q, $J_{\text{C-F}}$ = 291 Hz), 126.0, 129.2, 130.5(q, $J_{\text{C-F}}$ = 3.38 Hz), 132.6, 134.0, 142.4, 182.3(q, $J_{\text{C-F}}$ = 34.1 Hz).

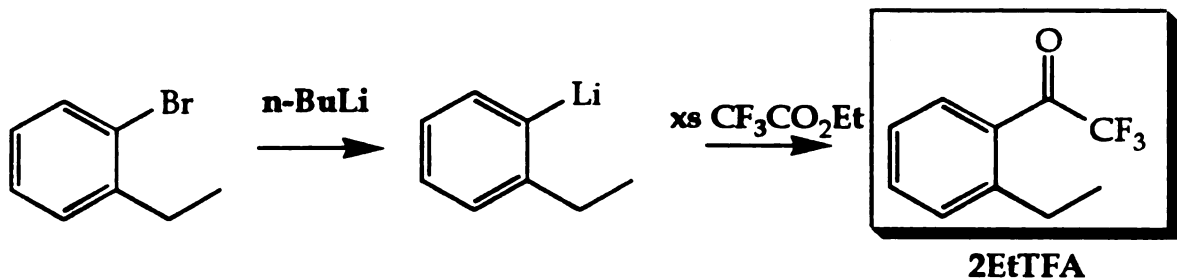
FTIR (neat, NaCl plate, cm^{-1}): 1288.6(m), 1323.3(s), 1385.1(m), 1460.3(s), 1572.2(s), 1604.98(s), 1714.9(vs), 2936.0(w), 2976.5(w), 3073.0(w).

LRMS. m/z : 188.0(19.0%, M^+), 119.1(89%), 91.1(100%), 65.1(27%).

HRMS. m/z : Calcd. for $\text{C}_9\text{H}_7\text{O}_1\text{F}_3$ 188.0449, found .

UV (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Cyclohexane, 297 (1780), 253 (11,400), 209 (14,200). Benzene, ϵ_{313} = 1300 M^{-1} .

6. 2'-ethyl-2,2,2-trifluoroacetophenone (2EtTFA)



reference: Bégué, J.-P. and D. Bonnet-delpont, *Tetrahedron* **1991**, 47, 3207. Chen L. S.; G. G. Chen; C. Tamborski *J. Fluorine Chem.* **1981**, 18, 177. Creary, X. *J. Org. Chem* **1987**, 52, 5026.

The introduction of the trifluoroacetyl group was exactly as described for 2MeFTA, except that 2-ethylbromobenzene was used in place of 2-bromotoluene. The mass of reagents used were 4 mL (Aldrich Chemical, 5g, 28 mmol) 95% 1-bromo-2-ethylbenzene, 30 mL (Aldrich Chemical, 2M cyclohexane solution) of n-butyl lithium and 16 mL (140 mmol) of neat ethyl α,α,α -trifluoroethylacetate. The 2'-ethyl-2,2,2-trifluoroacetophenone also is extremely volatile and was lost due to evaporation on several occasions. Distillation through a 10 cm vigreux column provided 4.5 g (80% yield) of colorless 2'-ethyl-2,2,2-trifluoroacetophenone, bp= 118-121°C.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 1.22(t, $J=7.5$ Hz, 3H), 2.88(q, $J= 7.5$ Hz, 2H), 7.30-7.39(m, 2H), 7.54(ddd, $J= 7.8, 7.8, 1.2$ Hz, 1H), 7.82(ddd, $J= 7.8, 7.8, 1.5$ Hz, 1H).

$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 0.979 (t, $J= 7.5$ Hz, 3H), 2.61(q, $J= 7.5$ Hz, 2H), 6.69(ddd, $J= 7.5, 7.5, 1.5$ Hz, 1H), 6.77(dd, 7.5, 0.90 Hz), 6.90(ddd, $J= 7.5, 7.5, 1.5$ Hz), 7.51(q of dd, $J_{\text{CF}}=1.5$ Hz, $J= 7.5, 1.5$ Hz, 1H)

^{13}C -NMR (CDCl_3 , 75 MHz), δ ppm: 15.54, 27.34, 117.2(q, $J_{\text{C-F}} = 293$ Hz), 125.88, 129.27, 130.0(q, $J_{\text{C-F}} = 3.68$ Hz), 131.1, 134.0, 147.95, 184.0(q, $J_{\text{C-F}} = 34.4$ Hz).

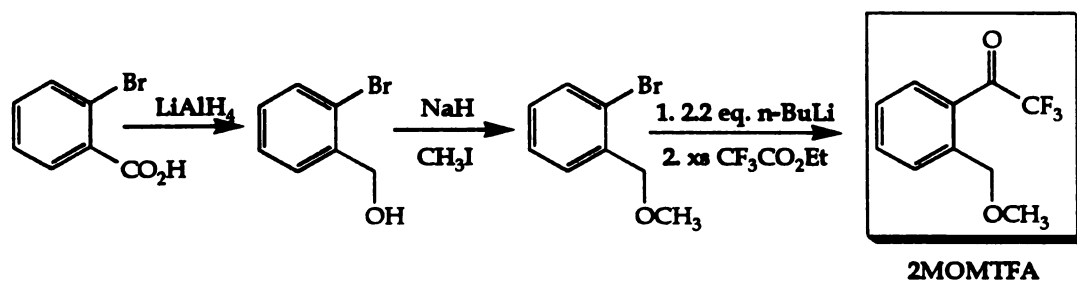
FTIR (0.025 mm CCl_4 , cm^{-1}): 2974.61(m), 2936.03(m), 2876.23(m), 1724.58(s), 1205.58, 1205.66(vs), 1169.06(vs), 1149.72(vs).

LRMS, m/z : 202(M^+), 187(3.1%), 167(5.4%), 153(2.2%), 133(100%), 115(25.9%), 105(76.1%), 77(73.3%).

HRMS, m/z : Calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_1$ 202.06055, found 202.0613.

UV (n-Pentane) λ_{max} (nm): 293.5, 253.5.

7. 2'-(methoxymethyl)-2,2,2-trifluoroacetophenone (2MOMTFA)



2-bromobenzyl alcohol

To a flask containing 500 mL of dry diethyl ether and 7.1 g (0.187 mol) lithium aluminum hydride was added dropwise 50 g (0.246 mol) of 2-bromobenzoic acid dissolved in ~500 mL of diethyl ether. The benzoic acid solution was added over a period of one hour while the flask was cooled with an ice bath. After complete addition of the benzoic acid the flask was maintained at 0°C with stirring for one hour. The reaction solution was then warmed to room

temperature and stirred overnight. The reaction solution was then poured carefully into crushed ice and acidified with 50 mL of concentrated HCl. The aqueous layer was separated and extracted with three 100 mL portions of diethyl ether, the combined ether layers were washed several times with saturated sodium bicarbonate solution, brine and dried over anhydrous sodium sulfate. The crude alcohol was recrystallized twice from ligroin and weighed 32 g (70% yield).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 2.65(s, 1H, OH), 4.70(s, 2H), 7.14(ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 7.30(ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 7.45(dd, J = 7.5, 1.8 Hz, 1H), 7.52(dd, J = 7.5, 1.2 Hz, 1H).

methyl 2-bromobenzyl ether

reference: Bos, M. E.; W. D. Wulff; R. A. Miller; S. Chamberlin; T. A. Baandvold, *J. Amer. Chem. Soc.* **1991**, 113, 9311.

Under an argon blanket, 2.4 g of NaH (60 wt % in mineral oil, 60 mmol) was washed twice with 10 mL of hexane, slurried with 60 mL of freshly distilled THF, and cooled to 0°C. A solution of 9.37 g of 2-bromobenzyl alcohol (50 mmol) in 30 mL of THF was added slowly via syringe and was washed with an additional 10 mL of THF. After 30 minutes at 0°C, 3.75 mL of methyl iodide (60 mmol) was added all at once via syringe. The reaction was stirred at 0°C for 30 minutes and then at room temperature for 1 hour. After cooling to 0°C, the

reaction was quenched with water and poured into ether. The combined ether extracts were washed with brine and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and gave methyl 2-bromobenzyl ether as a slightly yellow oil weighing 9.5 g (94% yield).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 3.45(s, 3H), 4.51(s, 2H), 7.13(ddd, J = 7.5, 8.1, 1.5 Hz, 1H), 7.30(ddd, J = 8.1, 7.5, 1.5 Hz, 1H), 7.44(distorted dd, J =7.8, 1.5 Hz, 1H), 7.53(dd, J = 7.8 Hz, 1.5 Hz, 1H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 58.59, 73.87, 122.7, 127.4, 128.88, 128.93, 132.5, 137.5.

2'-(methoxymethyl)-2,2,2-trifluoroacetophenone

reference: Bégué, J.-P. and D. Bonnet-delpont, *Tetrahedron* **1991**, 47, 3207. Chen L. S.; G. G. Chen; C. Tamborski *J. Fluorine Chem.* **1981**, 18, 177. Creary, X. *J. Org. Chem* **1987**, 52, 5026.

The introduction of the trifluoroacetyl group was exactly as described for 2MeFTA, except that methyl 2-bromobenzyl ether was used in place of 2-bromotoluene. 3.6 g (18 mmol) of methyl 2-bromobenzylether, 4 mL (Aldrich Chemical, 10M cyclohexane solution) of n-butyl lithium and 5.6 g (40 mmol) of ethyl α,α,α -trifluoroacetate were used. The ketone was distilled through a 10 cm vigreux column and 3g (76% yield) of colorless 2'-(methoxymethyl)-2,2,2-trifluoroacetophenone (~95% purity) was collected at 145-155°C. The remaining

impurity was removed by column chromatography (SiO₂, 75:25, pentane:diethyl ether).

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 3.45(s, 3H), 4.73(s, 2H), 7.43(distorted ddd, J= 7.5, 7.2, 1.5 Hz, 1H), 7.63(ddd, J= 7.5, 7.2, 1.5 Hz, 1H), 7.69(distorted dd, J= 7.5, 1.5 Hz, 1H), 7.82(distorted dd, J= 7.2, 1.5 Hz, 1H).

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 2.97(s, 3H), 4.36(s, 2H), 6.73(distorted, ddd, J= 7.8, 7.5, 0.6 Hz, 1H), 6.96(ddd, J= 7.8, 7.2, 1.5 Hz, 1H), 7.31(dd, J= 7.8, 1.5 Hz, 1H), 7.44(ddd, J= 8.1, 1.5, 0.9 Hz).

¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 58.71, 72.33, 116.3(q, J_{C-F}= 290.1 Hz), 127.2, 127.7, 128.7, 129.7(q, J_{C-F}= 3.22 Hz), 133.8, 142.2, 183.30(q, J_{C-F}= 34.4 Hz)

FTIR (0.025mm CCl₄, cm⁻¹): 939.45(m), 976.11(w), 1006.97(w), 1105.35(w), 1120.78(w), 1149.72(vs), 1186.37(s), 1201.81(vs), 1550.97(m, broad), 1714.94(m), 2828.00(w), 2882.02(w), 2932.17(m), 2964.97(w).

LRMS, m/z: 218.1(M⁺, 10%), 203(25%), 187.0(5%), 167.0(3%), 155.0(18%), 127.0(15%), 119.1(15%), 83.8(100%), 77.0(15%).

HRMS, m/z: Calcd. for C₁₀H₉O₂F₃ 218.0554, found 218.0556.

UV-VIS (path= 1 cm, λ_{max} nm (ε_{max} M⁻¹): Cyclohexane, 298 (1440), 256 (8780), 211 (7,300). Benzene, 298 (1220), 256 (1560), 311 (910).

8. 2-ethylbenzophenone (EtBP)

2-Ethylbenzophenone had been prepared by Dr. Bong-Ser Park and was used without further purification.

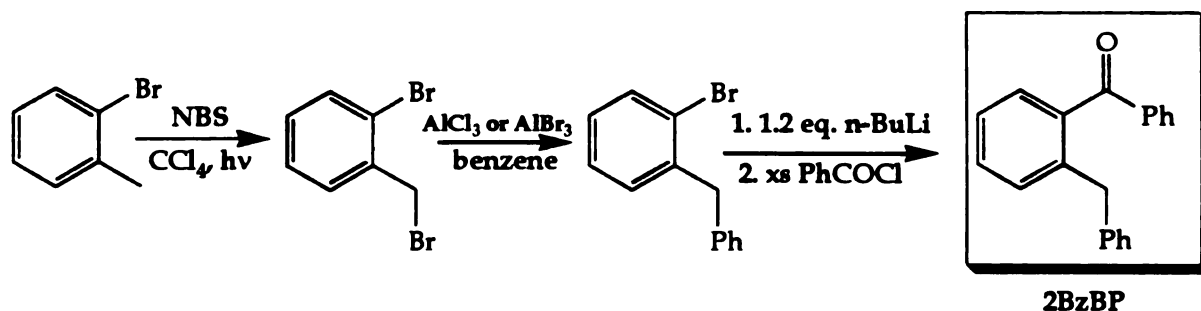
$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 1.03(t, J = 7.5 Hz, 3H), 2.64(q, J = 7.5 Hz, 1H), 6.85(ddd, J = 7.8, 7.2, 1.8 Hz, 1H), 6.94(ddd, J = 7.0, 7.0, 1.2, 1H), 6.96(d, J = 7.8 Hz, 1H), 6.98-7.05(m, 4H), 7.06(ddd, J = 7.5, 7.2, 1.5 Hz, 1H), 7.77(distorted dd, J = 7.8, 1.2 Hz, 2H).

$^1\text{H-NMR}$ (Toluene- d_8 , 300 MHz), δ ppm: 1.10(t, J = 7.8 Hz, 3H), 2.61(q, J = 7.5 Hz), 6.91(ddd, J = 7.8, 7.2, 1.8 Hz, 1H), 6.96-7.07(m, 4H), 7.08-7.15(m, 2H), 7.77(distorted dd, J = 7.8, 1.2 Hz, 2H).

$^1\text{H-NMR}$ (Acetonitrile- d_4 , 300 MHz), δ ppm: 1.11(t, J = 7.8 Hz, 3H), 2.61(q, J = 7.8 Hz, 7.24-7.29(m, 1H), 7.30(ddd, J = 7.8, 7.5, 1.5, 1H), 7.40(distorted d, 1H), 7.45-7.56(m, 4H), 7.66(ddd, J = 7.5, 7.2, 1.5 Hz, 1H), 7.75-7.80(distorted d, 2H).

$^1\text{H-NMR}$ (Acetone- d_6 , 300 MHz, -85°C), δ ppm: 1.05(t, J = 7.5 Hz, 3H), 2.59(q, J = 7.5 Hz, 2H), 7.27-7.33(m, 1H), 7.34(ddd, J = 7.2, 7.2, 1.2 Hz, 1H), 7.44(d, 1H), 7.46-7.57(m, 2H), 7.59(d, J = 6.0 Hz, 1H), 7.73(ddd, J = 7.2, 7.0, 1.5 Hz, 1H), 7.76(distorted d, 2H).

9. 2-benzylbenzophenone (2BzBP)



2-bromobenzylbromide

To a 1 L three-neck flask was added 85 mL (Eastman-Kodak, 91 g, 0.5 mol) 2-bromotoluene, 85 g (0.48 mol) n-bromosuccinimide and 300 mL of carbon tetrachloride. Benzoyl peroxide (0.5 g) that was freshly pressed between filter paper was added to the reaction solution and allowed to stand for 30 minutes followed by refluxing for 1 hour. Gas chromatographic analysis revealed no reaction had occurred. The reaction flask was cooled to 0°C and several crystals of iodine previously dissolved in 5 mL of carbon tetrachloride were added. The reaction was heated to reflux and maintained for 5 hours. GC analysis showed most of the 2-bromotoluene had reacted (70%) conversion. The flask was heated to reflux for an additional 2 hours without an increase in conversion. The succinimide was collected by vacuum filtration and the carbon tetrachloride removed by rotoevaporation. The benzyl bromide was not purified but crystallized during storage in the refrigerator. The liquid 2-bromotoluene was removed by pipette and the crystalline 2-bromobenzylbromide was rinsed with hexane.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 4.59(s, 2H), 7.15(ddd, J = 7.7, 7.5, 1.8 Hz, 1H), 7.30(ddd, J = 7.7, 7.5, 1.8 Hz, 1H), 7.44(dd, 7.5, 1.7 Hz, 1H), 7.56(d, 7.9 Hz, 1H).

2-bromodiphenylmethane

The 2-bromodiphenylmethane was synthesized by a standard literature method. Similar results were obtained with either aluminum trichloride or aluminum tribromide; both catalysts gave diphenylmethane as a major byproduct. The reaction flask was charged with 1.33 g (100 mmol) aluminum trichloride and 50 mL of 1,2-dichloroethane and cooled to 0°C , with stirring; 5 g (200 mmol) of 2-bromobenzylbromide was then added. The reaction flask was then cooled to -40°C and 2.7 mL (2.34 g, 300 mmol) benzene dissolved in 5 mL of 1,2-dichloroethane was added via syringe over a 10 minute period. The reaction was quenched by pouring the contents of the flask into a mixture of 50 mL of concentrated HCl and 50 g of crushed ice, the aqueous layer was extracted with three 30 mL portions of diethyl ether, washed with saturated aqueous NaHCO_3 until neutral and dried over anhydrous MgSO_4 . The crude product was purified by silica gel column chromatography by first eluting with hexane to remove diphenylmethane followed by 90:10 (Hexane : Ethyl Acetate). The purified 2-bromodiphenylmethane was isolated as a white solid which melted at $75\text{--}78^\circ\text{C}$ and weighed 0.6g (12% yield).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 4.11(s, 2H), 7.05-7.38(m, 8H), 7.56(dd, $J=7.92, 1.29\text{Hz}$, 1H).

LRMS, m/z : 246 and 248($\text{M}^{+\cdot}$), 165 and 167(100%).

2-benzylbenzophenone

2'-benzylbenzophenone was prepared by reacting 1 g (40 mmol) 2-bromodiphenylmethane with 3 mL (60 mmol) of 2M n-butyl lithium. The bromolithium exchange was conducted by first adding the aryl bromide to the flask, evacuating and purging with argon. This cycle was repeated three times followed by the addition of 25 mL of freshly distilled THF. The reaction flask was cooled to -78°C and the n-butyl lithium added via syringe. The flask was then warmed to 0°C and stirred for 15 minutes. A small aliquot was quenched with 5% HCl, but GC analysis showed only 54% conversion to the aryl lithium species by comparing the peak areas of diphenylmethane(from quenching the aryl lithium species) and the starting bromodiphenylmethane. The flask was then cooled to -78°C and an additional 1.5 mL (20 mmol) of 2M n-butyl lithium was added, after being warmed to 0°C , the solution was stirred for 30 minutes. GC analysis showed no increase in conversion. The aryl lithium species was added via syringe to 0.6 mL (0.70 g, 50 mmol) benzoyl chloride dissolved in 20 mL of freshly distilled THF under an argon. The benzoyl chloride/THF solution was cooled to -78°C prior to the addition of the nucleophile. The reaction solution was then warmed to room temperature and stirred for 5 hours. The reaction was quenched with 25 mL of 5% HCl(aq), the aqueous layer was

extracted with 3-30 mL portions of diethyl ether, washed with saturated aqueous NaHCO_3 until neutral and dried over anhydrous MgSO_4 . Analysis by GC revealed one major product and 2-bromodiphenylmethane. The crude 2'-benzylbenzophenone was purified by silica gel column chromatography by first eluting with hexane to remove 2-bromodiphenylmethane followed by 90:10 (Hexane : Ethyl Acetate). Purification by a second silica gel column gave 0.40 g (38% yield) of pure 2'-benzylbenzophenone. The white crystals melted at 47-50°C, lit.¹⁶¹ 50-52°C.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 4.09(s, H), 7.04-7.15(m, 3H), 7.15-7.23(m, 2H), 7.24-7.34(m, 3H), 7.52-7.59(distorted ddd, 1H), 7.70-7.76(m, 2H).

$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 4.02(s, 2H), 6.82-7.09(m, 12H), 7.72(distorted d, 2H).

$^1\text{H-NMR}$ (Acetonitrile- d_3 , 300 MHz, -30°C), δ ppm: 4.02(s, 1H), 7.00-7.10(m, 3H), 7.13(d, J = 7.5 Hz, 1H), 7.14(ddd, J = 7.0, 6.3, 1.5 Hz, 1H), 7.30(dd, J = 7.2, 1.2 Hz, 2H), 7.36(d, J = 7.5, 1H), 7.40-7.44(m, 3H), 7.47(ddd, J = 7.4, 7.2, 1.5 Hz, 1H), 7.55-7.68(m, 2H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 38.79, 125.5, 126.0, 128.23, 128.26, 128.57, 129.13, 130.10, 130.26, 130.76, 133.07, 137.63, 138.76, 140.05, 140.40, 198.49.

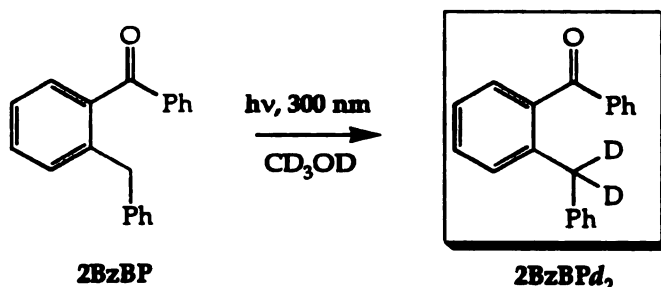
FTIR (0.025mm CCl_4 , cm^{-1}) 937.52(w), 1269.32(m), 1315.62(w), 1448.73(w), 1495.02(w), 1599.19(w), 1668.64(vs), 3028.63(w), 3065.28(w).

LRMS, m/z: 272(100%), 271(M⁺·), 194, 165.

UV ($\lambda_{\text{max nm}}$ ($\epsilon_{\text{max M}^{-1}}$): Cyclohexane, 248 (15,200), 211 (21,700), $\epsilon_{313} = 50.1$, $\epsilon_{366} =$

41.0. Benzene, $\epsilon_{313}=104$, $\epsilon_{366}=53.0$.

2-benzylbenzophenone- d_2 (2BzBP d_2)

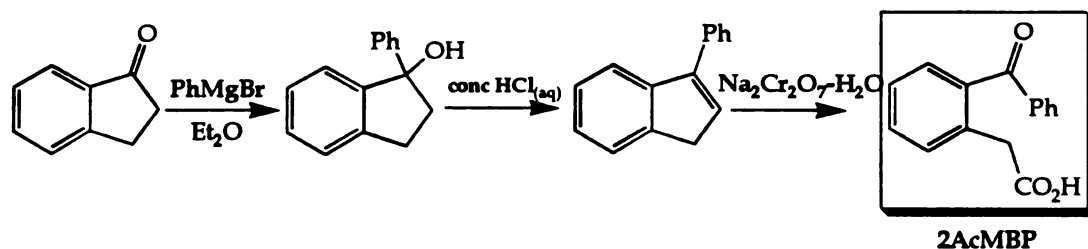


Reference: Yang, N. C. and C. Rivas, J. Am. Chem. Soc. **1961**, *83*, 2213.

The benzylic hydrogens were exchanged photochemically by irradiating 2-benzylbenzophenone in methanol- d_4 . A methanol- d_4 solution was prepared by dissolving 6.2 mg of 2'-benzylbenzophenone (0.042M) in 0.6 mL of solvent. The solution was degassed by purging the sample with a continuous stream of oxygen free argon for 20 minutes. The nmr sample tube was irradiated at 300 nm in a Rayonet reactor for 16 hours. The sample was monitored by ^1H -NMR analysis which showed complete disappearance of the benzylic methylene protons without any change to the aromatic region.

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 6.82-7.09(m, 12H), 7.72(distorted d, 2H).

10. (2-benzoylphenyl)acetic acid (2AcMBP)

*1-phenylindene*

1-Indanone (Aldrich Chemical, 5g, 38 mmol) was dissolved in 50 mL of freshly distilled diethyl ether and added slowly, with stirring to the Grignard reagent from 8.0 mL (11.9 g, 75 mmol) bromobenzene and 1.8 g (75 mmol) of freshly ground magnesium turnings. The reaction solution was refluxed for one hour and cooled to room temperature. The solution was poured into a mixture of 100 g of crushed ice and 25 mL concentrated sulfuric acid. The ether layer was separated and dried over anhydrous MgSO_4 and the solvent removed. The crude 1-phenylindan-1-ol was dissolved in 25 mL of dichloromethane with 20 mg p-toluenesulfonic acid and stirred at room temperature for two hours followed by washing with 1N $\text{NaOH}_{(\text{aq})}$, deionized water and drying with anhydrous CaCl_2 . Evaporation gave 6.1 g (84% yield) of a viscous liquid. The indene was sufficiently pure for the following step and was not purified.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 3.50(d, $J = 2.0$ Hz, 2H), 6.58(t, $J = 2.0$ Hz, 1H), 7.22-7.40(m, 3H), 7.45(dd, $J = 8.4, 8.0$ Hz, 2H), 7.53(d, $J = 7.2$ Hz, 1H), 7.56-7.64(m, 3H)

LRMS, m/z: 274(M^{+}), 273(100%), 105, 77.

(2-benzoylphenyl)acetic acid

A solution of 9.9 g (33 mmol) $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$, 0.54 g sodium benzenesulfonate (3 mmol) and 24 mL concentrated sulfuric acid in 130 mL distilled water was stirred mechanically. A solution of 5.8 g (300 mmol) 1-phenylindene in 10 mL methanol was added over a 30 minute period and the solution was warmed to 55°C for 25 minutes. The mixture was cooled in a refrigerator for 3 hours and a green gummy solid was collected by vacuum filtration and washed with cold 5% aqueous H_2SO_4 and water. Recrystallization with water gave a poor yield (200 mg, 3% yield) and the crystals melted at 128-130° C, literature¹⁶³ 130-131° C. The filtrate was extracted with three 50 mL portions of ethyl acetate and yielded an additional 100 mg of crude o-benzoylphenylacetic acid. The additional crude acid was recrystallized from benzene to give 50mg of pure acid.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 3.80(s, 2H), 7.38(ddd, $J=7.1, 7.4, 1.2$ Hz, 2H), 7.42-7.58(m, 4H), 7.64(dd, $J=7.4, 7.4$ Hz, 1H), 7.82(d, $J=7.4$ Hz, 2H).

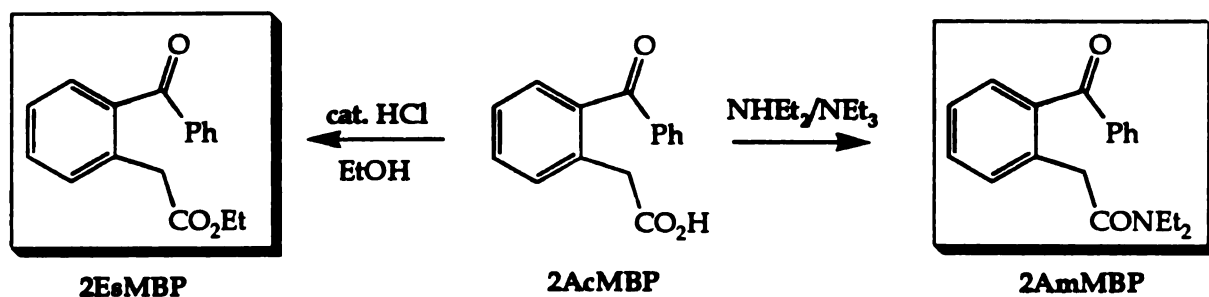
$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 3.59(s, 2H), 6.74(ddd, $J=7.5, 7.5, 1.5$ Hz, 1H), 6.85-6.99(m, 5H), 7.03(dd, $J=7.5, 7.5$ Hz, 1H), 7.65(d, $J=7.5$ Hz, 2H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 39.81, 126.6, 128.3, 130.69, 130.72, 131.7, 131.8, 133.5, 133.9, 137.0, 137.2, 173.6, 199.2.

FTIR (0.025mm CCl_4 , cm^{-1}): 1159.37(m), 1215.31(m), 1288.61(s), 1448.73(w), 1550.97(w), 1579.90(w), 1597.26(w), 1664.78(s), 1736.16(s), 2986.19(w), 3020.00(w), 3065.28(w), 3500(broad).

LRMS, m/z : 240.0(M^+), 195.2, 194.1, 182.1, 165.0, 149.1, 105.1, (100%), 77.1.

11. *ethyl (2-benzoylphenyl)acetate* (2EsMBP) and *N,N-diethyl (2-benzoylphenyl)acetamide* (2AmMBP)



N,N-diethyl (2-benzoylphenyl)acetamide

reference: Shimada, K. and T. Mukaiyama, *Bull. Chem. Soc. Japan* 1977, 50, 1863.

Mukaiyama T.; Y. Aikawa; S. Kobayashi, *Chemical Letters* 1976, 57.

To a solution of 130 mg (Aldrich Chemical, 0.50 mmol) 1-methyl-2-chloropyridinium iodide in 5 mL of dichloromethane was added 45 μL (0.42 mmol) freshly distilled diethyl amine, 140 μL (1.0 mmol) and 100mg (0.42 mmol) o-acetylphenylacetic acid dissolved in 1 mL dichloromethane. The mixture was heated to reflux under an argon atmosphere with stirring for one hour. The solution was cooled to room temperature and 10 mL of diethyl ether was added followed by washing with three 5 mL portions of 5% aqueous HCl and once with 5 mL deionized water. The organic layer was dried over anhydrous CaCl_2

and concentrated under reduced pressure. The crude N,N-diethyl (2-acetyl)phenylacetamide was purified by PTLC with 95:5 (Hexane : Ethyl Acetate) as the eluent.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 0.965(t, J= 7.2Hz, 3H), 1.10(t, J= 7.2 Hz, 3H), 3.26(t, J= 7.2 Hz, 2H), 3.27(t, J= 7.2 Hz, 2H).

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 0.699(t, J= 7.1 Hz, 3H), 0.718(t, J= 7.1 Hz, 3H), 2.70(q, J=7.1 Hz, 2H), 2.95(q, J= 7.1 Hz, 2H), 3.78(s, 2H), 6.88(dd, J= 7.7, 7.6 Hz, 1H), 6.92-7.13(m, 4H), 7.15(dd, J= 7.6, 7.0 Hz, 2H), 7.94(distorted d, J= 6.8 Hz, 2H),

¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 12.75, 13.99, 37.51, 40.27, 42.11, 125.8, 128.1, 129.3, 130.2, 130.4, 131.1, 132.7, 135.2, 137.8, 138.2, 169.4, 198.3.

ethyl (2-benzoylphenyl)acetate

reference: Anzalone, L. and J.. A. Hirsh, *J. Org. Chem.* **1985**, 50, 2128. Chatterjee, S. and E.-I. Negishi, , *J. Org. Chem.* **1986**, 51, 3407.

The ethyl ester of 2-benzoylphenylacetic acid was synthesized by dissolving 100 mg (0.42 mmol) of 2-benzoylphenylacetic acid in 20 mL of absolute ethanol and adding three drops of concentrated HCl. The solution was refluxed overnight, cooled to room temperature, and evaporated to dryness. The crude ester was dissolved in diethyl ether (5 mL) and washed with 2 mL saturated NaHCO₃. The ether solution was dried by passing through a 1 inch

plug of basic alumina. Evaporation of the solvent left a viscous liquid whose ^1H -NMR revealed only pure ester with no impurities.

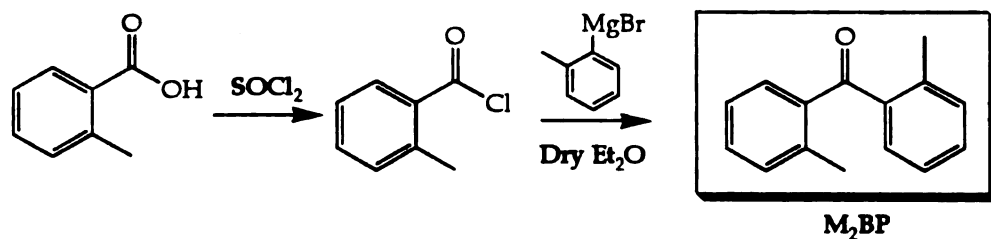
^1H -NMR (CDCl_3 , 300 MHz), δ ppm: 1.09(t, $J = 7.1$ Hz, 3H), 3.87(s, 2H), 4.00(q, $J = 7.1$ Hz, 2H), 7.27-7.40(m, 3H), 7.40-7.50(m, 3H), 7.56(distorted ddd, $J = 7.4, 7.2, 1.3$ Hz, 1H), 7.80(distorted d, 2H).

^1H -NMR (Benzene- d_6 , 300 MHz), δ ppm: 0.727(t, $J = 7.1$ Hz, 3H), 3.71(q, $J = 7.1$ Hz, 2H), 3.87(s, 2H), 6.82(ddd, $J = 7.4, 7.3, 1.5$ Hz, 1H), 6.92-7.10(m, 6H), 7.80(distorted d, 2H).

^{13}C -NMR (CDCl_3 , 75 MHz), δ ppm: 13.86, 38.71, 60.62, 126.3, 128.1, 129.8, 130.2, 130.6, 131.6, 132.7, 133.8, 137.7, 138.2, 171.0, 197.8.

FTIR (0.025mm CCl_4 , cm^{-1}): 918.23(w), 947.17(w), 1032.05(w), 1163.22(m), 1215.31(m), 1269.32(s), 1288.61(m), 1448.73(w), 1599.19(w), 1666.71(vs), 1738.08(vs), 2907.10(w), 2936.03(w), 2984.26(w), 3028.63(w), 3067.21(w).

LRMS, m/z : 268.1(M^+), 239.1, 223.1, 195.2, (100%), 194.1, 177.2, 165.2, 105.1, 77.1.

12. 2,2'-dimethylbenzophenone (Me₂BP)

The preparation of *o*-toluoylbenzoyl chloride is described in the preparation of 2'-chloro-2,4,6-trimethylbenzophenone. The Grignard reagent was prepared with 1 g of 2-bromotoluene (5.8 mmol) and 0.2 g (7.5 mmol) of freshly ground magnesium turnings. The ethereal solution was refluxed for ~2 hours after which time nearly all the magnesium had been consumed. The Grignard reagent was cooled to room temperature and added via syringe to a solution of 1.0 mL (1.17 g, 7.6 mmol) *o*-toluoylbenzoyl chloride in 25 mL diethyl ether under an argon atmosphere at -78°C. Upon addition of the Grignard reagent to the acid chloride the solution turned yellow. The solution was stirred at -78°C for twenty minutes and then warmed to room temperature and stirred overnight. The reaction was quenched by pouring it into a 5% aqueous HCl followed by three 15 mL extractions with diethyl ether and several washings with saturated aqueous NaHCO₃. The combined ether extracts were then washed with saturated aqueous NaCl solution and dried over anhydrous MgSO₄. The crude ketone was purified by PTLC with 98:2 hexane:ethyl acetate as the eluent, after evaporation a clear viscous liquid remained and weighed 450 mg (37%).

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 2.42(s, 6H), 7.18(ddd, J= 8.0, 7.3, 1.2 Hz; 2H), 7.26(dd; J= 8.0, 1.5Hz, 2H), 7.29(dd, J= 7.3, 1.8, 2H) 7.37(ddd, 7.8, 7.3, 1.5Hz; 2H).

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 2.33(s, 6H), 6.76(dd, J= 7.7, 7.7 Hz, 2H), 6.86(d, J= 7.9 Hz, 2H), 6.95(dd, J= 7.7, 7.1 Hz, 2H), 7.11(d, J= 7.8 Hz, 2H).

¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 20.23, 124.96, 129.87, 130.63, 130.97, 137.73, 138.52, 200.35.

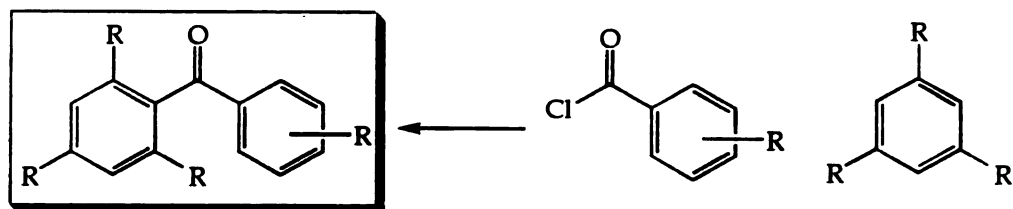
FTIR (0.025mm CCl₄, cm⁻¹) 924.02(s), 1255.82(s), 1302.12(m), 1666.71(vs), 2930(w), 3022.84(w), 3069.14(w).

LRMS, m/z: 210(M⁺). 195(100%).

HRMS, m/z: Calcd. for C₁₅H₁₄O₁ 210.10446, found .

UV (path= 1 cm, λ_{max} nm (ε_{max} M⁻¹)): Cyclohexane, 282 (2790), 248 (13,500), 211 (17,700), ε₃₁₃=74.7, ε₃₆₆= 61.4.

B. Substituted 2,4,6-Trialkyl benzophenones.

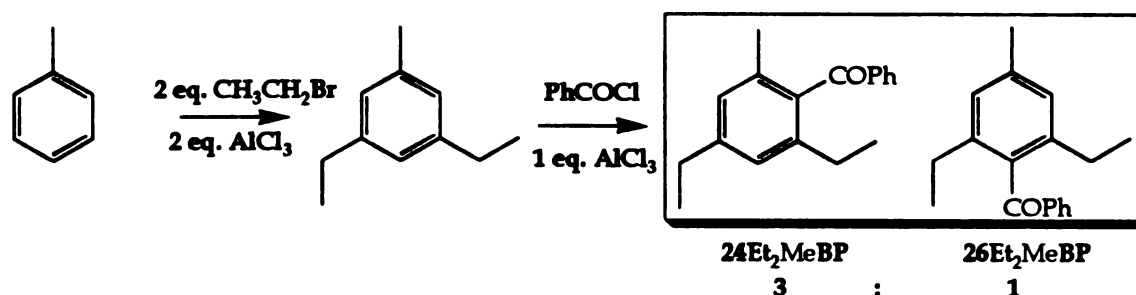


Ketone	R	R'
I ₃ BP	i-Pr	H
2ClI ₃ BP	i-Pr	2'-CH ₃
4ClI ₃ BP	i-Pr	4'-CH ₃
2MI ₃ BP	i-Pr	2'-Cl
4MI ₃ BP	i-Pr	4'-Cl
2OMI ₃ BP	i-Pr	2'-OCH ₃
4OMI ₃ BP	i-Pr	4'-OCH ₃
2CF ₃ I ₃ BP	i-Pr	2'-CF ₃
2ClEt ₃ BP	Et	2'-Cl
24E ₂ MBP	2,4-diethyl-6-methyl	H
26E ₂ MBP	2,6-diethyl-4-methyl	H
M ₃ BP*	CH ₃	H
2MM ₃ BP	CH ₃	2'-CH ₃
2ClM ₃ BP	CH ₃	2'-Cl
4ClM ₃ BP	CH ₃	4'-Cl
2OMM ₃ BP	CH ₃	2'-OCH ₃
2CF ₃ M ₃ BP	CH ₃	2'-CF ₃
M ₆ BP	CH ₃	2',4',6'-trimethyl

*Aldrich chemical.

All 2,4,6-Trialkyl benzophenones were prepared by Friedel-Crafts acylation with the appropriate acid chloride. Washing with alkaline solution followed by recrystallization was sufficient for purification in most cases. Column or Thin Layer chromatography was applied to separate minor impurities.

1. **2,4-diethyl-6-methylbenzophenone (24E₂MBP)** and **2,6-diethyl-4-methylbenzophenone (26E₂MBP)**.



3,5-diethyltoluene

reference: Norris, J. F.; Rubinstein, D. J. *Amer. Chem. Soc.* **1939**, 1163.

The 3,5-Diethyltoluene was prepared by a standard literature method. A 500 mL three neck round bottom flask equipped with mechanical stirrer, 125 mL addition funnel and condenser was cooled in ice-salt (NaCl) bath. Aluminum chloride (Spectrum Chemical, 59 g, 0.2 mol) was added to the flask along with one half of the ethyl bromide (Fischer Chemical, 75 g, 51 mL, 0.2 mol) and the flask shaken. The toluene (28 g, 0.3 mol) was added slowly with the addition funnel over a 30 minute period while the temperature was maintained between -10 and -5°C. The remaining ethyl bromide was added while cooling, after which the flask was allowed to warm to room temperature and stirred overnight. The

reaction solution was poured into a mixture of 100 g of crushed ice with 20 mL of concentrated HCl with mechanical stirring. The clear yellow product was washed three times with 1N aqueous NaOH and dried over anhydrous CaCl_2 . The crude product was fractionally distilled (20 cm vigreux column); 35 g (84% yield) of 3,5-diethyltoluene was obtained and boiled at 198-200°C (literature 199.8.0-200°C).

^1H -NMR (CDCl_3 , 300 MHz), δ ppm: 1.21(t, J = 7.4 Hz, 6H), 2.31 (s, 3H), 2.59(q, J = 7.4 Hz, 4H), 6.83(s, 3H).

A three neck flask equipped with a drying tube was charged with 100 mL of dry 1,2-dichloroethane and 5.45 g of anhydrous aluminum chloride (0.041 moles, Fischer Chemical). The solution was cooled to -4°C with aid of a NaCl/ice bath and 8.3 mL (10 g, 0.041 moles) of freshly distilled benzoyl chloride was added via syringe. The solution was then allowed to cool to -10°C and 5 g of 3,5-diethyltoluene was added dropwise over a 10 minute period. The reaction mixture was allowed to stir at -10°C for an additional one half hour. The reaction mixture was poured into 100 g of crushed ice and 30 mL of concentrated HCl. The organic layer was separated, washed with water, and extracted three times with 2N aqueous NaOH. The ^1H -NMR of the crude product indicated a mixture of isomers in a 3:1 ratio. The crude product was purified by a bulb to bulb distillation with a Kugelrohr apparatus and boiled at 145°C /1 mm Hg. The

purified product was distilled through a 10 cm vigreux column; 5.5 g of liquid was collected at constant temperature (165°C/0.8 mm Hg). Capillary Gas Chromatography (DB210, isothermal 180°C) revealed two products in a 66:34 (24Et₂MeBP: 26Et₂MeBP) ratio which were identified by ¹H-NMR analysis as regioisomers *2,4-diethyl-6-methylbenzophenone* (24E₂MBP) and *2,6-diethyl-4-methylbenzophenone* (26E₂MBP). The isomers could not be separated by repeated fractional distillation or column chromatography with a variety of solvent systems.

2,4-diethyl-6-methylbenzophenone (24E₂MBP), from mixture.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 1.08(t, J= 7.5 Hz, 3H), 1.28(t, J= 7.5 Hz, 3H), 2.09(s, 3H), 2.41(q, J= 7.5 Hz, 2H), 2.66(q, J= 7.5 Hz, 2H), 6.92(s, 1H), 6.97(s, 1H), 7.45(dd, J=7.8, 7.8 Hz, 1H), 7.46(d, J= 7.8 Hz, 1H), 7.55(dd, J= 7.8, 7.8 Hz, 1H), 7.81(d, J= 7.8 Hz, 2H).

¹H-NMR (benzene-*d*₆, 300 MHz), δ ppm: 1.00(t, J= 7.5 Hz, 3H), 1.11(t, J= 7.5, 3H), 1.98(s, 3H), 2.37(q, J= 7.5 Hz, 2H), 2.43(q, J= 7.5 Hz, 2H), 6.70(s, 1H), 6.80(s, 1H), 6.92-7.06(m, 3H), 7.86(d, J= 7.0 Hz, 2H).

¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 15.46, 15.64, 19.45, 26.23, 28.66, 125.5, 126.6, 127.2, 128.7, 129.4, 133.5, 134.9, 136.5, 137.5, 140.6, 144.9, 200.8.

LRMS, m/z: 252(M⁺).

UV-VIS (path= 1 cm, $\lambda_{\max}$ nm ($\epsilon_{\max}$ M⁻¹)): Cyclohexane, 272 (2,850), 243 (16,100), 209 (15,100), $\epsilon_{313}=43.5$ M⁻¹, $\epsilon_{366}=57.4$ M⁻¹.

2,6-diethyl-4-methylbenzophenone (26E₂MBP), from mixture.

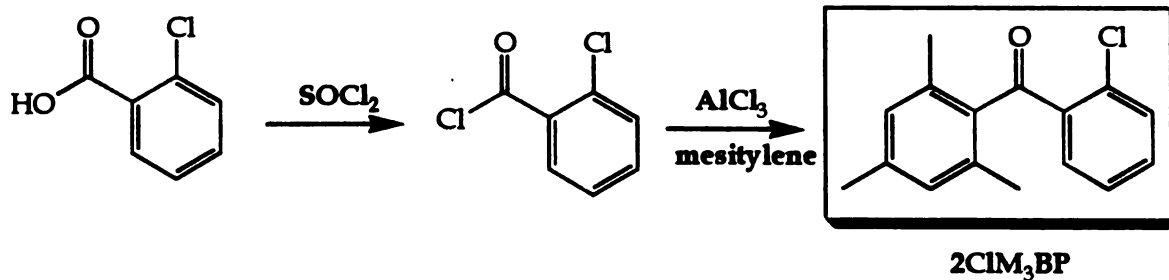
¹H-NMR (CDCl₃, 300 MHz), δ ppm: 1.07(t, J= 7.5 Hz, 6H), 2.38(q, J=7.5 Hz, 4H), 2.39(s, 3H), 6.97(s, 2H), 7.45(dd, J=7.8, 7.8 Hz, 1H), 7.46(d, J= 7.8 Hz, 1H), 7.55(dd, J= 7.8, 7.8 Hz, 1H), 7.81(d, J= 7.8 Hz, 2H).

¹H-NMR (benzene-*d*₆, 300 MHz), δ ppm: 0.981(t, J= 7.5 Hz, 6H), 2.13(s, 3H), 2.35(q, J= 7.5 hz, 4H), 6.75(s, 2 H), 6.92-7.06(m, 3H), 7.86(d, J= 7.0 Hz, 2H).

¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 15.46, 21.36, 26.37, 125.5, 126.6, 127.2, 128.7, 129.4, 130.1, 135.7, 137.8, 138.7, 140.4, 144.9, 199.8.

UV-VIS (path= 1 cm, $\lambda_{\max}$ nm ($\epsilon_{\max}$ M⁻¹)): Cyclohexane, 272 (2,850), 243 (16,100), 209 (15,100), $\epsilon_{313}=43.5$ M⁻¹, $\epsilon_{366}=57.4$ M⁻¹.

2. 2'-chloro-2,4,6-trimethylbenzophenone (2ClM₃BP)



o-chlorobenzoyl chloride

A mixture of *o*-chlorobenzoic acid (Aldrich Chemical, 50 g, 320 mmol) and 125 mL thionyl chloride was stirred at 25°C for 24h. The excess thionyl chloride was removed in vacuo with the aid of a water aspirator. The crude acid chloride was distilled (bp 233°C; literature 238°C, Aldrich Chemical) and yielded 55 g of colorless liquid.

2'-chloro-2,4,6-trimethylbenzophenone

The Friedel-Crafts reaction of *o*-chlorobenzoyl chloride (3.0 mL, 24 mmol) with mesitylene (Aldrich Chemical, 3.5 g, 29 mmol) and aluminum chloride (3.8g, 29 mmol) was carried out in 50 mL 1,2-dichloroethane. The flask was charged with the mesitylene, aluminum chloride and 1,2-dichloroethane and cooled to 0°C. The temperature was maintained between 0-5°C while the acid chloride was added dropwise via syringe. The ice bath was allowed to melt and the reaction was stirred overnight at room temperature. The reaction mixture was then poured into mixture of 15 mL concentrated HCl and 60g crushed ice with manual stirring. The organic layer was separated and the aqueous layer extracted with three portions of methylene chloride. The combined organic layers were washed with distilled water and 5M aqueous NaOH until precipitation of alkaline wash with dilute acid ceased. The organic layer was dried with anhydrous CaCl₂. The crude product was recrystallized from

petroleum ether (ligroin). The mass of purified ketone was 3.1 g (41% yield) and melted at 93-96°C, literature¹⁶⁴ 99-101°C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 2.12(s; 6H), 2.31(s; 3H), 6.87(s; 2H), 7.26(ddd, 7.7 Hz, 7.3 Hz, 1.5 Hz; 1H), 7.41(ddd, 7.1, 7.2, 1.7; 1H), 7.64(m; 2H).

¹H-NMR (benzene-*d*₆, 300 MHz), δ ppm: 2.01(s, 3H), 2.03(s, 6H), 6.57(s, 2H), 6.60(ddd, *J* = 6.9, 7.5, 0.6 Hz, 1H), 6.66(ddd, 7.5, 7.0, 1.5 Hz, 1H), 7.02(dd, *J* = 7.5, 1.5 Hz, 1H). 7.34(dd, 7.8, 1.5 Hz, 1H).

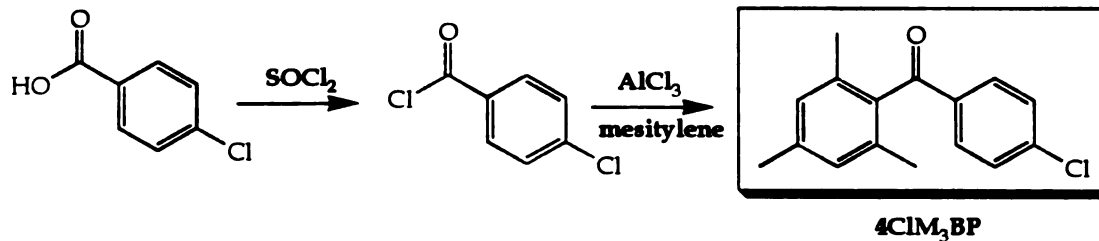
¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 19.68, 21.12, 126.79, 128.74, 131.42, 131.68, 132.73, 133.14, 134.99, 137.23, 137.51, 139.33, 198.98.

FTIR (0.025mm CCl₄, cm⁻¹) 910.52(s), 1286.68(m), 1435.22(m), 1684.07(vs), 2922.53(w), 3000(w, broad).

LRMS, *m/z*: 258(M⁺), 223(100%), 208.3(56%), 147.3(46%), 119.2(31%), 91.1(28%), 77.1(25%).

UV-VIS (path= 1 cm, $\lambda_{\max}$ nm ($\epsilon_{\max}$ M⁻¹)): Benzene, 284 (3,310), ϵ_{313} =473 M⁻¹, ϵ_{366} =88.2 M⁻¹. Cyclohexane, 221 (11,700), 243 (11,400), 280 (3,250), 340 (61.4), ϵ_{313} =322 M⁻¹, ϵ_{366} =87.1 M⁻¹.

3. 4'-chloro-2,4,6-trimethylbenzophenone (4ClM₃BP)



p-chlorobenzoyl chloride

A mixture of *p*-chlorobenzoic acid (Aldrich Chemical, 50 g, 320 mmol) and 125 mL thionyl chloride was stirred at 25°C for 24h. The excess thionyl chloride was removed in vacuo with the aid of a water aspirator. The crude acid chloride was distilled (bp 223°C; literature 221°C; Aldrich Chemical) and yielded 48 g of colorless liquid.

4'-chloro-2,4,6-trimethylbenzophenone

This ketone was prepared exactly like its ortho isomer except that *p*-chlorobenzoyl chloride (3.0 mL, 24 mmol) was used. The mass of purified ketone was 3.8 g (51% yield) and melted at 64–67°C, literature¹⁶⁵ 68–69.5°C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 2.05(s, 6H), 2.31(s, 3H), 6.88(s, 2H), 7.41(d, J= 8.2 Hz),), 7.73(d, J= 8.3 Hz)

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 1.92(s, 6H), 2.05(s, 3H), 6.59(s, 2H), 6.90(d, J= 9 Hz, 2H), 7.54(d, J= 8.7 Hz, 2H).

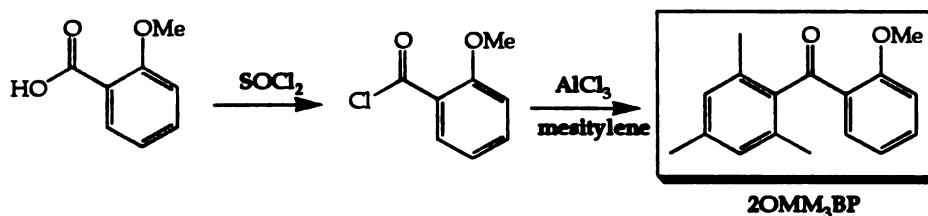
^{13}C -NMR (CDCl_3 , 75 MHz), δ ppm: 19.31, 21.13, 128.40, 129.14, 130.75, 134.11, 135.62, 136.27, 138.74, 140.07, 199.80.

FTIR (0.025mm CCl_4 , cm^{-1}) 846.86(m), 908.59(s), 1265.46(s), 1587.62(m), 1676.35(vs), 2875.00(w), 2922.53(w), 2850.00(w).

LRMS, m/z : 258(M^+), 223(100%), 208(45%), 147(73%), 119.1(40%), 111(42%), 91.6(44.4), 77.0(28.2).

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Benzene, 281 (3,550), $\epsilon_{313}=185 \text{ M}^{-1}$, $\epsilon_{366}=76.7 \text{ M}^{-1}$. Cyclohexane, 216 (16,900), 254 (20,700), 353(94.5), $\epsilon_{313}=73.4 \text{ M}^{-1}$, $\epsilon_{366}=69.1 \text{ M}^{-1}$.

4. 2'-methoxy-2,4,6-trimethylbenzophenone (2OMM₃BP)



o-anisoyl chloride

The *o*-anisoyl chloride was prepared by a known method. During the purification step it was important to distill at reduced pressure or the acid chloride became a thick syrup probably due to polymerization. A mixture of *o*-anisic acid (Aldrich Chemical, 50 g, 330 mmol) and 125 mL thionyl chloride was stirred at 25°C for 24h. The excess thionyl chloride was removed in vacuo with

the aid of a water aspirator. The crude acid chloride was distilled (bp 100°C/0.3 mm Hg, lit. 68°C/0.05 mm Hg) and yielded 50 g of a colorless liquid.

2'-methoxy-2,4,6-trimethylbenzophenone

This ketone was prepared exactly like *2'-chloro-2,4,6-trimethylbenzophenone* except that *o*-anisoyl chloride (3.0 mL, 20 mmol) was used. The Friedel-Crafts reaction was carried out with mesitylene (Aldrich Chemical, 2.64 g, 22 mmol) and aluminum chloride (2.95 g, 22 mmol). The crude product was recrystallized from ligroin and melted at 111-113°C, literature¹⁶⁶ 112-113°C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 2.09(s, 6H), 2.28(s, 3H), 3.78(s, 3H), 6.82(s, 2H), 6.91(ddd; 7.4 Hz, 7.5 Hz, 2.8 Hz; 1H), 6.97(d; 8.2Hz, 1H), 7.47(ddd; 7.4 Hz, 8.3 Hz, 1.8 Hz; 1H), 7.50(dd; 7.7 Hz, 1.5 Hz; 1H).

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 2.06(s, 3H), 2.11(s, 6H), 3.02(s, 3H), 6.35(d, J= 8.7 Hz, 1H), 6.62(s, 2H), 6.63(dd, J= 7.5, 7.5, 0.9 Hz, 1H), 7.00(ddd, J= 7.2, 7.2, 1.8 Hz, 1H), 7.77(dd, J= 7.5, 1.8 Hz, 1H).

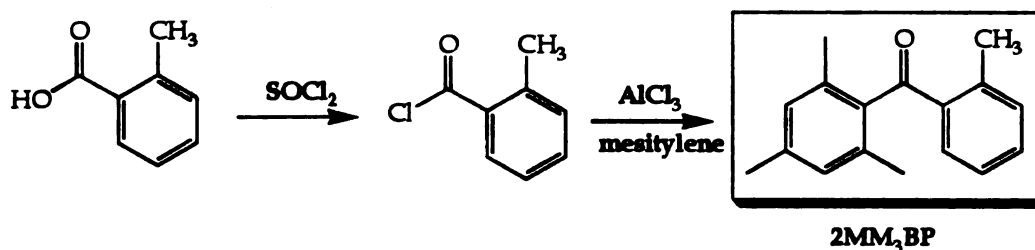
¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 19.42, 21.11, 55.86, 112.20, 120.32, 127.78, 128.21, 132.34, 133.99, 134.32, 138.00, 139.25, 159.48, 199.85.

FTIR (0.025mm CCl₄,cm⁻¹) 908.59(s), 1255.82(vs), 1296.33(s), 1435.22(m), 1464.16(m), 1485.38(m), 1597.26(s), 1672.50(s).

LRMS, m/z: 254(M⁺), 239(100%), 233.2(40%), 208.1(21%), 195.1(5%), 165.0(10%), 147.1(41%), 135.0(57%), 119.1(36%), 91.0(37%), 77.0(55%).

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M⁻¹): Benzene, 307 (4,300), $\epsilon_{313}=3,870$ M⁻¹, $\epsilon_{366}=75.3$ M⁻¹. Cyclohexane, 304 (4,130), 249 (10,700), 205 (34,100), 340 (129), $\epsilon_{313}=3,360$ M⁻¹, $\epsilon_{366}= 950$ M⁻¹.

5. 2'-methyl-2,4,6-trimethylbenzophenone (2MM₃BP)



o-toluoyl chloride

A mixture of *o*-toluic acid (Aldrich Chemical, 50 g, 370 mmol) and 125 mL thionyl chloride was stirred at 25°C for 24h. The excess thionyl chloride was removed in vacuo with the aid of a water aspirator. The crude acid chloride was distilled (bp 223°C; literature 88-90°C/12mm, Aldrich Chemical) and yielded 41 g (72% yield) of colorless liquid.

2'-methyl-2,4,6-trimethylbenzophenone

This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that *o*-toluoyl chloride (3.0 mL, 23 mmol) was used. The Friedel-Crafts reaction was carried out with mesitylene (Aldrich Chemical, 3.4 g, 28 mmol) and

aluminum chloride (3.7 g, 28 mmol). The mass of purified ketone was 5.1 g (93% yield) and melted at 109-111°C, literature¹⁶⁷ 111.9-112.2°C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 2.08(s, 6H), 2.31(s, 3H), 2.67(s, 3H), 6.86(s, 2H), 7.14(dd, J= 7.4 , 7.7 Hz, 1H), 7.29(d, J= 7.1 Hz, 1H), 7.34(d, J= 8.3 Hz, 1H), 7.38(dd, J= 7.4, 7.6 Hz, 1H).

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 1.99(s, 6H), 2.05(s, 3H), 2.71(s, 3H), 6.60(s, 2H), 6.74(ddd, J= 7.5, 6.9, 1.8, 1H), 6.90-7.00(m, 2H), 7.35(d, J= 7.5 Hz, 1H).

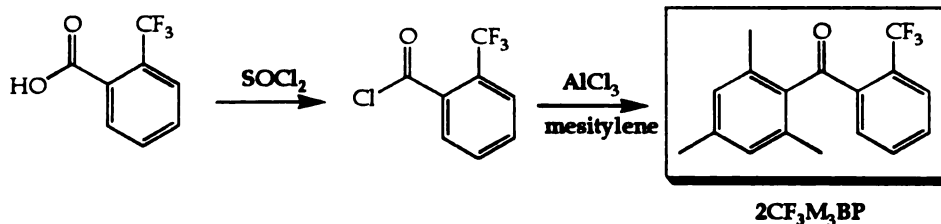
¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 19.41, 21.15, 21.81, 125.90, 128.47, 131.88, 132.10, 134.35 (2 carbons), 136.96, 138.46, 138.49, 139.94, 202.69.

FTIR (0.025mm CCl₄, cm⁻¹) 852.65(w), 908.59(s), 1255.82(s), 1672.50(vs), 2850.00(w), 2926.39(w), 2975.00(w), 3000.00(w), 3050.00(w).

LRMS, m/z: 238(M⁺), 223(100%), 208(27%), 193.1(3%), 165.1(7%), 147.1(27%), 119.1(32%), 91.1(58%), 77.0(18%)..

UV-VIS (path= 1 cm, λ_{max} nm (ε_{max} M⁻¹): Benzene, 285 (3,230), ε₃₁₃=65.5 M⁻¹, ε₃₆₆=135 M⁻¹. Cyclohexane, 245 (14,600), 206 (33,700), 344 (101), ε₃₁₃=64.7 M⁻¹, ε₃₆₆= 66.5 M⁻¹.

6. 2'-(α,α,α -trifluoromethyl)-2,4,6-trimethylbenzophenone (2CF₃M₃BP)



This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that α,α,α -trifluorotoluoyl chloride (Aldrich Chemical, 1.0mL, 7.1 mmol) was used. The Friedel-Crafts reaction was carried out with mesitylene (Aldrich Chemical, 0.93g, 7.8 mmol) and aluminum chloride (1.04 g, 7.8 mmol) in 25 mL 1,2-dichloroethane. The mass of purified ketone was 1.5g (66% yield) which melted at 112-114°C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 2.10(s, 6H), 2.30(s, 3H), 6.87(s, 2H), 7.38(dd; 6.8Hz, 0.70 Hz; 1H), 7.50(ddd; 6.8 Hz, 7.5 Hz, 0.70 Hz; 1H) 7.60(ddd; 7.5 Hz, 7.8Hz, 1.3Hz; 1H), 7.85(dd; 7.5Hz, 0.80 Hz; 1H).

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 1.97(s, 6H), 2.00(s, 3H), 6.55(s, 2H), 6.67(dd, *J* = 7.2, 7.5 Hz, 1H), 6.75(dd, *J* = 7.5, 6.9 Hz, 1H), 7.1(d, *J* = 7.5 Hz, 1H), 7.41(d, *J* = 7.8 Hz, 1H).

¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 198.71, 139.83, 138.84, 136.39, 135.74, 131.79, 131.04, 128.96, 128.81, 128.57, 127.85 (q, *J* = 5.9 Hz), 123.56 (q, *J* = 272.2 Hz), 21.15, 19.94.

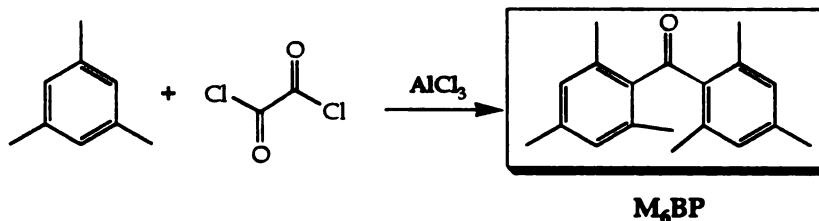
FTIR (0.025mm CCl_4 , cm^{-1}) 910.52(m), 1167.08(vs), 1311.76(vs), 1691.79(m), 2900(w, broad).

LRMS, m/z : 292(M^+). 277(67%), 256.1(12%), 223.0(100%), 208(42%), 147.1(87%), 119.2(54%), 91.0(57%), 77.0(34%).

HRMS, m/z : Calcd for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_1$ 292.10750, found 292.1083.

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Cyclohexane, 272 (4,390), 235 (13,600), 217 (13,900), 341 (144), $\epsilon_{313}=197 \text{ M}^{-1}$, $\epsilon_{366}= 89.3 \text{ M}^{-1}$.

7. 2,4,6,2',4',6'-hexamethylbenzophenone (M_6BP)



The procedure for the preparation of 2,4,6-trimethylbenzoic acid was modified with the reaction being conducted at low temperature. The Friedel-Crafts reaction was carried out with 3.35 g (0.025 mol) anhydrous aluminum chloride and 2.1 mL (3.0 g, 0.025 mol) oxalyl chloride dissolved in 25 mL of fresh 1,2-dichloroethane. To the ice cooled solution, 5.8 mL (5g, 0.042 mol) mesitylene was added via syringe while not allowing the solution to warm above 5°C. The solution was allowed to warm to room temperature and stirred for 24 hours. The reaction was quenched by carefully pouring the deep red reaction solution into 10 mL concentrated HCl with 50 g of crushed ice and then stirred. The aqueous

layer was extracted with three 25 mL portions of methylene chloride. The organic layer was washed with saturated NaHCO_3 and saturated NaCl . The NaHCO_3 washings were continued until acidification no longer gave a white precipitate (2,4,6-trimethylbenzoic acid). Evaporation gave a yellow-green solid which was decolorized with activated carbon. Recrystallization of the crude solid gave 1.8 g (32% yield) with petroleum ether (ligroin) and melted at 133-136°C, literature¹⁶⁸ 138-140°C.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 2.10(s, 12H), 2.66(s, 6H), 6.82(s, 4H).

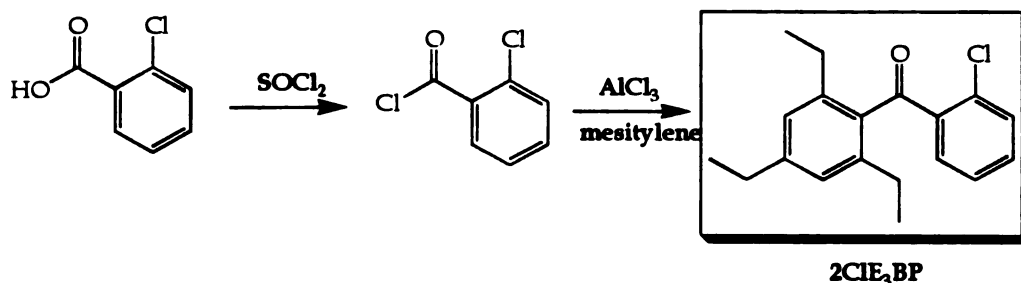
$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 1.98(s, 6H), 2.10(s, 12H), 6.57(s, 4H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 20.7, 21.12, 129.76, 136.56, 138.40, 139.94, 202.63.

FTIR (0.025mm CCl_4 , cm^{-1}) 852.65(m), 891.23(m), 1608.84(s), 1658.99(vs), 2926.39(m).

LRMS, m/z : 266.1(M^+), 251(100%), 236(28%), 221.0(4%), 193.0(5%), 165(3%), 147.0(20%), 119.0(21%), 91.0(30%).

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Benzene, 280 (7,400), $\epsilon_{313}=430 \text{ M}^{-1}$, $\epsilon_{366}=108 \text{ M}^{-1}$. Cyclohexane, 265 (12,300), 213 (12,300), 340(191), $\epsilon_{313}=214 \text{ M}^{-1}$, $\epsilon_{366}=22,500 \text{ M}^{-1}$.

8. 2'-chloro-2,4,6-triethylbenzophenone (2ClE₃BP)

This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that *o*-chlorobenzoyl chloride (2.3 mL, 18 mmol) and 1,3,5-triethylbenzene (3.0 g, 18 mmol) were used. The preparation of *o*-chlorobenzoyl chloride is described in the preparation of 2'-chloro-2,4,6-trimethylbenzophenone. The Friedel-Crafts reaction was carried out with 1.04 g aluminum chloride (7.8 mmol) was carried out in 50 mL 1,2-dichloroethane. The crude product was recrystallized from petroleum ether (ligroin). The mass of purified ketone was 3.1 g (41% yield) which melted at 35-38°C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 1.08(t, J= 7.5 Hz, 6H), 1.25(t, J= 7.5 Hz, 3H), 2.44(q, J= 7.5 Hz, 4H), 2.64(q, J= 7.5 Hz, 2H), 6.93(s, 2H), 7.22(ddd, J= 7.5, 7.5, 1.5 Hz, 1H), 7.39(ddd, J= 7.5, 7.5, 1.5 Hz, 1H), 7.44(dd, J= 7.5, 1.5 Hz, 1H), 7.47(dd, J= 7.5, 1.5 Hz, 1H).

¹H-NMR (benzene-*d*₆, 300 MHz), δ ppm: 1.02(t, J= 7.8 Hz, 6H), 1.08(t, J=7.8 Hz, 3H), 2.41(q, J= 7.8 Hz, 2H), 2.42(q, J= 7.8 Hz, 4H), 6.56(ddd, J= 7.5, 7.2, 1.5 Hz, 1H), 6.65(ddd, J= 7.8, 7.5, 1.8 Hz, 1H), 6.77(s, 2H), 7.05(dd, J= 7.8, 1.5 Hz, 1H), 7.38(dd, J= 7.5, 1.8 Hz, 1H).

^{13}C -NMR (CDCl_3 , 75 MHz), δ ppm: 15.33, 15.57, 26.48, 28.73, 125.9, 126.5, 131.6, 132.4, 132.8, 133.3, 136.6, 137.3, 141.0, 145.7, 199.0.

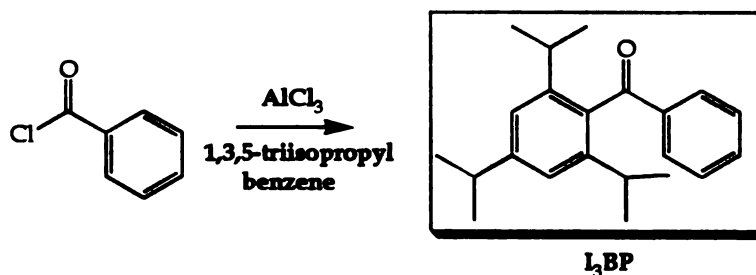
FTIR (0.025mm CCl_4 , cm^{-1}): 873.86(m), 931.74(vs), 1037.83(m), 1060.98(m), 1134.29(w), 1176.73(w), 1238.46(w), 1288.61(m), 1307.90(w), 1435.22(m), 1464.16(m), 1587.62(m), 1606.91(m), 1662.85(m), 1684.07(vs), 2876.23(m), 2936.03(m), 2868.83(vs).

LRMS, m/z : (M^+) 300.2 and 302.3, 285.3(5%), 284.0(7%), (100%) 265.1, 250(45%), 235.9(48%), 189.0(20.8), 178.0(11%), 165.0(7%), 139.0(23%), 105.1(27%).

HRMS, m/z : Calcd for $\text{C}_{19}\text{H}_{21}\text{Cl}_1\text{O}_1$ 300.1281, found 300.1278. Calcd for $\text{C}_{19}\text{H}_{21}^+\text{Cl}_1\text{O}_1$ 302.1241, found 302.1246.

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Cyclohexane, 218 (16,900), 243 (11,600), 284 (2,770), 344 (121), $\epsilon_{313}=276 \text{ M}^{-1}$, $\epsilon_{366}=78.6 \text{ M}^{-1}$.

9. 2,4,6-trisopropylbenzophenone (I_3BP)



This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that benzoyl chloride (Fisher Chemical, 5.0mL, 29 mmol) and 1,3,5-

triisopropylbenzene (Aldrich Chemical, 5.9g, 29 mmol) were used. The Friedel-Crafts reaction was carried out with 3.8 g aluminum chloride (29 mmol) in 50 mL 1,2-dichloroethane. The crude product was recrystallized from petroleum ether (ligroin) and gave 7.1 g (79% yield) of pure *2,4,6-triisopropylbenzophenone* which melted at 97-99°C, literature 97-99°C.¹⁶⁹

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 1.03(d, J= 6.9 Hz, 6H), 1.16(d, J= 6.9 Hz, 6H), 1.27(d, J= 6.9 Hz, 6H), 2.60(septet, J= 6.9 Hz, 2H), 2.92(septet, J= 6.9 Hz, 1H), 7.05(s, 2H), 7.43(dd, J= 7.5, 7.5 Hz, 2H), 7.55(tt, J= 7.2, 1.2 Hz, 1H), 7.82(dd, J= 7.2, 1.5 Hz, 2H).

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 0.981(d, J= 6.9, 6H), 1.14(d, J= 7.2 Hz, 6H), 1.20(d, J= 6.9 Hz, 6H), 2.75(septet, J= 6.9 Hz, 1H), 2.81(septet, J= 6.9 Hz, 2H), 6.91(ddd, J= 7.8, 7.5, 1.2 Hz, 2H), 7.01(tt, J= 7.2, 1.2 Hz, 1H), 7.12(s, 2H), 7.91(d, J= 6.9 Hz, 2H).

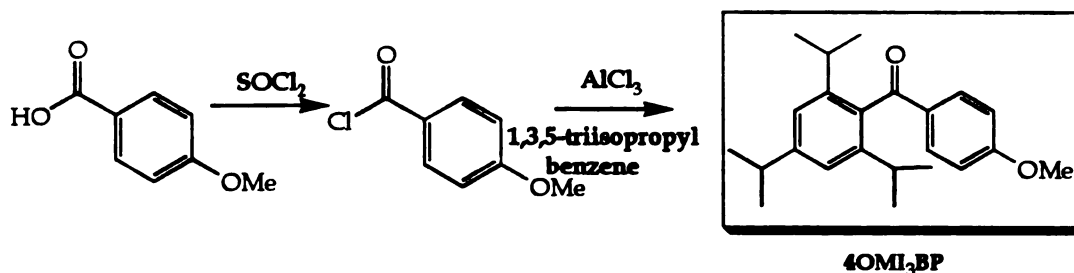
¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 23.36, 24.02, 24.87, 31.01, 34.35, 120.96, 128.54, 129.45, 133.46, 135.02, 138.15, 144.93, 149.68, 201.20.

FTIR (0.025mm CCl₄, cm⁻¹). 877.2(m), 918.23(m), 947.17(m), 1604.989w), 1670.57(vs), 2850.00(m), 2900.00(m), 2964.97(vs).

LRMS, m/z: 308.2(M, 100%), 293.1(46%), 278.1(17%), 265.0((39%), 250(34%), 231.1(47%), 104.9(55%), 91.0(27%), 77.0(55%).

UV-VIS (path= 1 cm, $\lambda_{\max}$ nm ($\epsilon_{\max}$ M⁻¹)): Benzene, 281 (1,300), $\epsilon_{313}= 58$ M⁻¹, $\epsilon_{366}= 51$ M⁻¹. Cyclohexane, 211 (15,000), 271 (19,100), 348(77), $\epsilon_{313}=40$ M⁻¹, $\epsilon_{366}=52$ M⁻¹.

10. *4'-methoxy-2,4,6-triisopropylbenzophenone* (4OMI₃BP)



p-anisoyl chloride

A mixture of *p*-anisic acid (Aldrich Chemical, 50 g, 330 mmol) and 125 mL thionyl chloride was stirred at 25°C for 24h. The excess thionyl chloride was removed in vacuo with the aid of a water aspirator. The crude acid chloride was distilled (bp 134°C/6 mm Hg, lit. 145°C/14 mm Hg) and yielded 38 g (67% yield) of colorless liquid. During the purification step it was important to distill at reduced pressure or the acid chloride became a thick syrup probably due to polymerization.

4'-methoxy-2,4,6-triisopropylbenzophenone

This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that benzoyl chloride *p*-anisoyl chloride (3.0 mL, 20 mmol) and 1,3,5-

triisopropylbenzene (Aldrich Chemical, 5.9g, 29 mmol) were used. The Friedel-Crafts reaction was carried out with 3.36 g aluminum chloride (25 mmol) in 50 mL 1,2-dichloroethane. Recrystallization gave 2.4 g (24% yield) of 4'-methoxy-2,4,6-triisopropylbenzophenone which melted at 108-110°C, literature¹⁷⁰ 108-110°C.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 1.04(d, J=6.8 Hz, 6H), 1.16(d, J=6.8 Hz, 6H), 1.27(d, J= 7.0 Hz, 6H), 2.63(septet, J=6.7 Hz, 2H), 2.91(septet, J=6.9 Hz, 1H), 3.84(s, 3H), 6.90(d, J= 9.0 Hz, 2H), 7.03(s, 2H), 7.79(d, J=8.2 Hz, 2H).

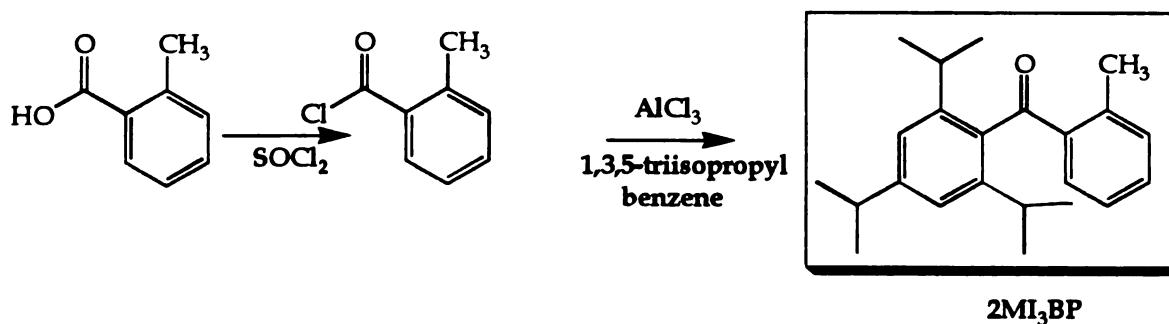
¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 1.05(d, J= 6.8 Hz, 6H), 1.18(d, J= 6.8 Hz, 6H), 1.22(d, J= 6.9 Hz, 6H), 2.80(septet, J= 6.9 Hz, 1H), 2.92(septet, J= 6.8 Hz, 2H), 3.04(s, 3H), 6.47(d, J= 9.1 Hz, 2H), 7.15(s, 2H), 7.89(broad d, J=9.0 Hz, 2H).

¹³C-NMR (CDCl₃, 75 MHz), δ ppm: 23.50, 24.05, 24.89, 30.96, 34.34, 55.45, 113.71, 120.92, 131.56, 131.86, 135.36, 144.86, 149.48, 163.81, 199.73.

FTIR (0.025mm CCl₄, cm⁻¹).848.79(m), 850.00(m), 920.16(m), 947.17(m), 1035.91(m), 1253.89(vs), 1601.12(s), 1662.85, 2870.44(m), 2934.10(m), 2963.04(s).

LRMS, m/z: 338.4(M⁺). 323.3(100%), 307.3(64%), 280.3(25%), 231.3(25%), 135.1(82%), 121.1(45%), 107.1(17%), 77.1(32%).

UV-VIS (path= 1 cm, λ_{max} nm (ε_{max} M⁻¹)): Benzene 281 (18,300), ε₃₁₃=141 M⁻¹, ε₃₆₆=39 M⁻¹. Cyclohexane, 218 (22,500), 271 (24,400), 348(132), ε₃₁₃=84 M⁻¹, ε₃₆₆=43 M⁻¹.

11. 2'-methyl-2,4,6-triisopropylbenzophenone (2MI₃BP)

This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that *o*-toluoyl chloride (3.0 mL, 23 mmol) and 1,3,5-triisopropylbenzene (Aldrich Chemical, 5.9g, 29 mmol) were used. The preparation of *o*-toluoyl chloride is described for the preparation of 2'-methyl-2,4,6-trimethylbenzophenone. The crude product was recrystallized from petroleum ether (ligroin) and gave 4.8 g (53% yield) of pure 2'-methyl-2,4,6-triisopropylbenzophenone which melted at 100-102°C, literature 103-104°C¹⁴⁵.

¹H-NMR (CDCl₃, 300 MHz), δ ppm: 1.10(d, J= 5.5 Hz, very broad, 12H), 1.27(d, J= 6.9 Hz, 6H), 2.64(septet, J= 6.7 Hz, 2H), 2.73(s, 3H), 2.91(septet, J= 6.9 Hz, 1H), 7.02(s, 2H), 7.13(ddd, J= 7.8, 7.8, 1.3 Hz, 1H), 7.29(d, J= 7.4 Hz, 1H), 7.37(ddd, J= 7.8, 7.8, 1.3 Hz, 1H), 7.39(d, J=7.4 Hz, 1H).

¹H-NMR (Benzene-*d*₆, 300 MHz), δ ppm: 1.09(broad s, 12H), 1.20(d, J= 7.0 Hz, 6H), 2.77(septet, J= 6.9 Hz, 1H), 2.86(septet, J= 6.6 Hz, 2H), 6.67(m, 1H), 6.90-6.96(m, 2H), 7.12(s, 2H), 7.47(d, J= 7.8 Hz, 1H).

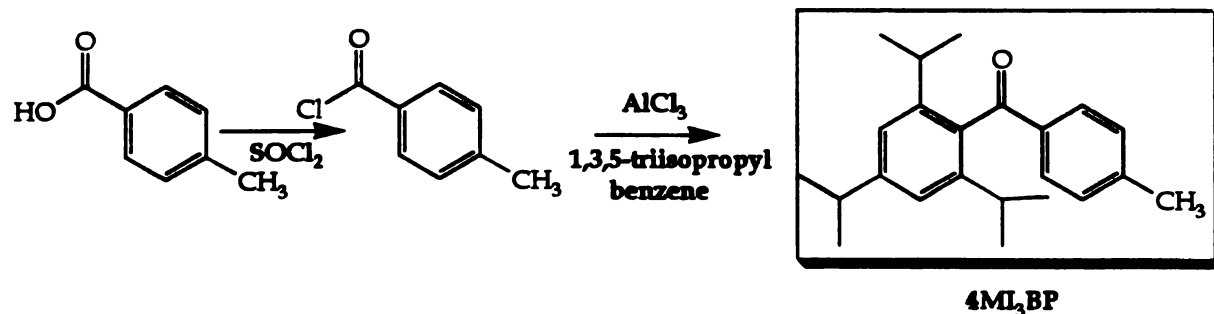
^{13}C -NMR (CDCl_3 , 75 MHz), δ ppm: 22.22, 23.75, 24.02, 24.28, 30.95, 34.35, 120.99, 125.54, 132.21, 132.27, 132.99, 136.82, 137.35, 139.96, 144.86, 149.54, 203.13.

FTIR (0.025mm CCl_4 , cm^{-1}): 877.72(w), 918.23(w), 945.24(w), 1248.10(m), 1462.23(m), 1603.05(m), 1666.71(s), 2870.44(m), 2928.32(m), 2963.04(vs).

LRMS, m/z : 322.4(M^+). 307.3(100%), 292.3(13%), 279.3(13%), 265.3(7%), 250.3(3%), 231.2(9%), 119.1(10%), 91.1(15%).

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Benzene, 287 nm (2370), ϵ_{313} = 114 M^{-1} , ϵ_{366} = 55 M^{-1} . Cyclohexane, 212 (18,400), 244 (15,400), 270 (2,430), 340(112), ϵ_{313} = 60 M^{-1} , ϵ_{366} = 58 M^{-1} .

12. 4'-methyl-2,4,6-triisopropylbenzophenone (4MI₃BP)



p-toluoyl chloride

This acid chloride was prepared exactly as its ortho isomer except that *p*-toluic acid (Aldrich Chemical, 50 g, 370 mmol) was used. The crude acid chloride was distilled in vacuo (bp 105°C/4 mm Hg, literature 225-227°C) and yielded 36 g (64% yield) of colorless liquid.

4'-methyl-2,4,6-triisopropylbenzophenone

This ketone was prepared exactly like *2'-chloro-2,4,6-trimethylbenzophenone* except that *p-toluoyl chloride* (3.0 mL, 23 mmol) and 1,3,5-triisopropylbenzene (Aldrich Chemical, 5.7 g, 28 mmol) were used. The crude product was recrystallized from petroleum ether (ligroin) and gave 5.9 g (68% yield) of pure *4'-methyl-2,4,6-triisopropylbenzophenone*I and melted at 85-87°C, literature (ito joc 1981) 87-87.5°C.

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.04(d, J= 6.8 Hz, 6H), 1.16(d, J= 6.8 Hz, 6H), 1.28(d, J= 6.9 Hz, 6H), 2.40(s, 3H), 2.61(septet, J= 6.8 Hz, 2H), 2.92(septet, J= 6.9 Hz, 1H), 7.04(s, 2H), 7.22(d, J= 8.2 Hz, 2H), 7.72(d, J= 8.0 Hz, 2H).

¹H-NMR(Benzene-*d*₆, 300 MHz), δ ppm: 1.03(d, J= 6.9 Hz, 6H), 1.16(d, J=6.8 Hz, 6H), 1.21(d, J=6.9 Hz, 6H), 1.85(s, 3H), 2.78(septet, J= 6.9 Hz, 1H), 2.88(septet, J= 6.8 Hz, 2H), 6.76(d, J= 7.8 Hz, 2H), 7.14(s, 2H), 7.88(d, J= 7.5 Hz, 2H).

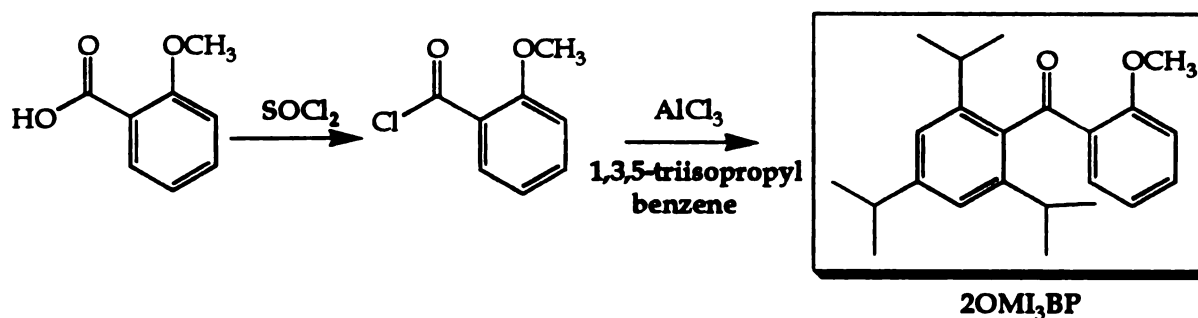
¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 21.76, 23.45, 24.05, 24.88, 30.99, 34.37, 120.93, 129.28, 129.66, 135.31, 135.85, 144.37, 144.91, 149.54, 200.83.

FTIR(0.025mm CCl₄,cm⁻¹). 846.86(w), 877.72(w), 918.23(m), 945.24(m), 1255.82(m), 1604.98(s), 1666.71(s), 2870.44(m), 2928.32(vs).

LRMS, m/z: 322.4(M⁺·). 307.3(100%), 292.3(20%), 265.3(16%), 231.3(20%), 119.1(40%), 91.1(44%).

UV-VIS (path= 1 cm, $\lambda_{\max}$ nm ($\epsilon_{\max}$ M⁻¹)): Benzene, 281 (3150), ϵ_{313} =57 M⁻¹, ϵ_{366} =46 M⁻¹. Cyclohexane, 214 (16,700), 254 (21,100), 344(87), ϵ_{313} = 48 M⁻¹, ϵ_{366} = 52 M⁻¹.

13. 2'-methoxy-2,4,6-triisopropylbenzophenone (2OMI₃BP)



This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that *o*-anisoyl chloride (3.0 mL, 20 mmol) and 1,3,5-triisopropylbenzene (Aldrich Chemical, 5.17 g, 25 mmol) were used. The preparation of *o*-anisoyl chloride is described for the preparation of 2'-methoxy-2,4,6-trimethylbenzophenone. The crude product was recrystallized from petroleum ether (ligroin), however, crystal formation required nearly three weeks at -40°C in a freezer. Recrystallization gave 1.8 g (21% yield) of pure 2'-methoxy-2,4,6-triisopropylbenzophenone which melted at 71-72°C.

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.08(d, J= 6.6 Hz, 12 H), 1.25(d, J= 6.6 Hz, 6H), 2.70(septet, J= 6.6 Hz, 2H), 2.89(septet, J= 6.9 Hz, 1H), 3.77(s, 3H), 6.92(dd,

$J = 6.7, 8.4, 1.2$ Hz, 1H), 6.96(d, $J = 8.1$ Hz, 1H), 6.99(s, 2H), 7.47(ddd, $J = 7.2, 7.5, 1.5$ Hz, 1H), 7.57(dd, $J = 8.1, 1.8$ Hz, 1H).

$^1\text{H-NMR}$ (benzene- d_6 , 300 MHz), δ ppm: 1.11(d, $J = 6.9$ Hz, 12H), 1.20(d, $J = 6.9$ Hz, 6H), 2.77(septet, $J = 6.9$ Hz, 1H), 2.99(septet, $J = 6.9$ Hz, 2H), 3.08(s, 3H), 6.37(d, $J = 8.2$ Hz, 1H), 6.57(dd, $J = 7.4, 7.7$ Hz, 1H), 6.99(ddd, $J = 7.7, 7.4, 1.7$ Hz, 1H), 7.08(s, 1H), 7.10(s, 1H), 7.87(dd, $J = 7.7, 1.7$ Hz, 1H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 23.62, 23.88, 30.77, 31.03, 34.19, 55.51, 112.08, 119.89, 120.57, 127.90, 132.97, 134.28, 137.80, 144.26, 148.92, 159.44, 199.68.

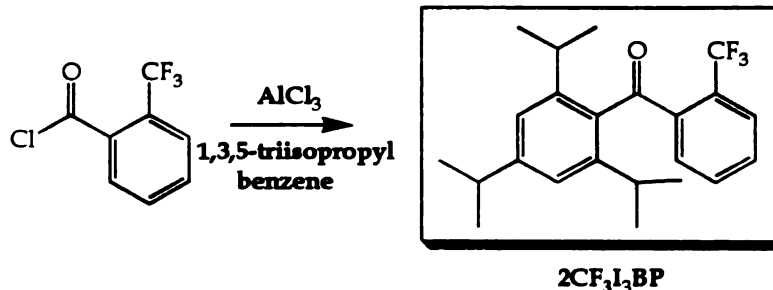
FTIR(0.025mm CCl_4 , cm^{-1}). 877.72(w), 916.30(m), 947.17(m), 1028.19(m), 1250.03(s), 1597.26(s), 1668.64, 2870.44(m), 2934.10(m), 2963.04(vs).

LRMS, m/z : 338.4(M^+). 323.3(100%), 307.3(70%), 295.3(36%), 265.3(12%), 250.2(7%), 135.1(82%), 91.1(19%), 77.1(32%).

HRMS, m/z : Calcd. for $\text{C}_{23}\text{H}_{30}\text{O}_2$ 338.2246, found 338.2245.

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Benzene, 311 (4770), $\epsilon_{313}=4730$ M^{-1} , $\epsilon_{366}=76$ M^{-1} ; Cyclohexane, 216 (61,200), 250 (28,000), 348(121), $\epsilon_{313}=9680$ M^{-1} , $\epsilon_{366}=60$ M^{-1} .

14. 2'-(α,α,α -trifluoromethyl)-2,4,6-triisopropylbenzophenone (2CF₃I₃BP)



This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that α,α,α -trifluorotoluoyl chloride (Aldrich Chemical, 1.0 mL, 7.1 mmol), 1,3,5-triisopropylbenzene (Aldrich Chemical, 1.67 g, 7.8 mmol) and aluminum chloride (1.10 g, 8.2 mmol) were used. Recrystallization from ligroin gave 2.1 g (80% yield) of pure 2'-methoxy-2,4,6-triisopropylbenzophenone which melted at 95-96°C.

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.12(s, very broad, 12H), 1.29(d, J=6.9 Hz, 6H), 2.75(septet, J= 6.8 Hz, 2H), 2.94(septet, J= 6.9 Hz, 1H), 7.07(s, 2H), 7.62(ddd, J= 6.9 , 6.9, 0.78 Hz, 1H), 7.45-7.55(m, 2H), 7.90(d, J= 7.7Hz, 1H).

¹H-NMR(Benzene-*d*₆, 300 MHz), δ ppm: 1.06(broad s, 12H), 1.16(d, J= 6.9 Hz, 6H), 6.61(dd, J= 7.5, 7.8 Hz, 1H), 6.73(dd, J= 7.8, 7.5 Hz, 1H), 7.10(s, 2H), 7.34(d, J= 7.5 Hz, 1H), 7.43(d, J= 7.5 Hz, 1H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 23.94 (2 carbons), 30.74, 34.36, 121.25, 122.9(q, J_{13C-19F}=280Hz), 128.00(q, J_{13C-19F}=25Hz), 128.4, 131.50, 132.15, 132.74, 135.23, 138.50, 145.81, 150.46, 199.17.

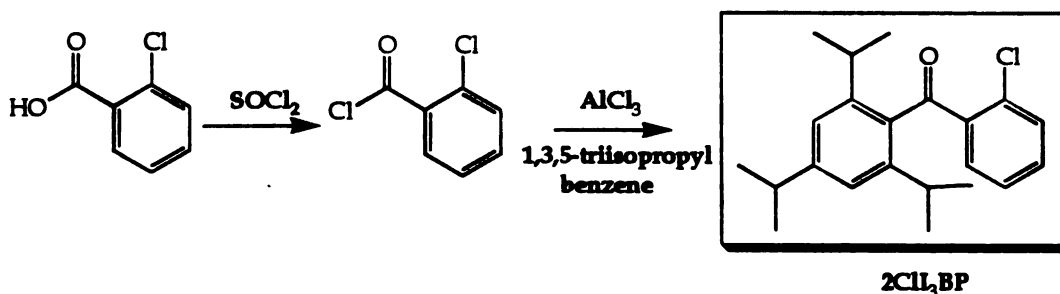
FTIR(0.025mm CCl₄,cm⁻¹) 918.23(w), 947.17(w), 1161.29(s), 1309.83(vs), 1693.72(m), 2872.37(w), 2950.00(w), 2964.97(s).

LRMS, m/z: 376(M⁺). 307(91%), 231.2(20%), 190.0(62%), 173.1(100%), 145.1(83%).

HRMS, m/z: Calcd. for C₂₃H₂₇F₃O₁ 376.20140, found 376.2007.

UV-VIS (path= 1 cm, λ_{max} nm (ε_{max} M⁻¹)): Benzene, 281 (2960), ε₃₁₃=171 M⁻¹, ε₃₆₆=76 M⁻¹; Cyclohexane, 236 (13,500), 277 (2,720), 346(92), ε₃₁₃=101 M⁻¹, ε₃₆₆=65 M⁻¹.

15. 2'-chloro-2,4,6-triisopropylbenzophenone (2ClI₃BP)



This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that o-chlorobenzoyl chloride (3.0 mL, 24 mmol) and 1,3,5-triisopropylbenzene (Aldrich Chemical, 1.67 g, 7.8 mmol) used. The preparation of o-chlorobenzoyl chloride is described for the preparation of 2'-chloro-2,4,6-trimethylbenzophenone. The crude product was recrystallized from petroleum ether (ligroin). The mass of purified 2'-chloro-2,4,6-triisopropylbenzophenone was 2.7 g (33% yield) which melted at 105-107°C.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 1.14(d, J = 6.6 Hz, 12H), 1.29(d, J = 6.9 Hz, 6H), 2.72(septet, J = 6.6 Hz, 2H), 2.93(septet, J = 6.9 Hz, 1H), 7.05(s, 2H), 7.26(ddd, J = 6.3, 7.5, 1.5 Hz, 1H), 7.42(ddd, J = 6.9, 7.8, 1.5 Hz, 1H), 7.50(dd, J = 6.9, 1.5 Hz, 1H), 7.52(d, J = 6.3, 1.5 Hz, 1H).

$^1\text{H-NMR}$ (benzene- d_6 , 300 MHz), δ ppm: 1.09(d, J = 6.9 Hz, 12H), 1.162(d, J = 6.9 Hz, 3H), 1.165(d, J = 6.9 Hz, 3H), 2.73(septet, J = 6.9 Hz, 1H), 2.91(septet, J = 6.9 Hz, 2H), 6.51(dd, J = 7.1, 7.5 Hz, 1H), 6.64(dd, 7.1, 7.5 Hz, 1H), 7.08(d, J = 7.2 Hz, 1H), 7.10(s, 2H), 7.45(d, J = 7.6 Hz, 1H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 23.97, 24.11, 31.06, 34.37, 121.16, 126.47, 131.85, 132.87, 132.92, 133.47, 135.88, 137.08, 145.25, 150.22, 199.36.

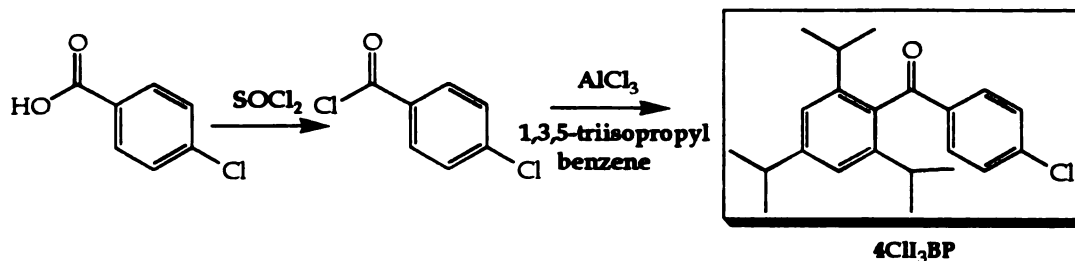
FTIR(0.025mm CCl_4 , cm^{-1}) 877.72(w), 918.23(m), 947.17(m), 1238.46(m), 1288.61(m), 1464.16(m), 1684.07(s), 2870.44(m), 2932.17(m), 2694.97(vs).

LRMS, m/z : 342.3(M^+). 307.4(100%), 292.3(25%), 265.3(11%), 250.3(6%), 231.3(5%), 139.0(13%), 91.1(4%), 77.1(3%).

HRMS, m/z : Calcd. For $\text{C}_{22}\text{H}_{27}\text{Cl}_1\text{O}_1$ 342.1750, found 342.1750. Calcd. For $\text{C}_{22}\text{H}_{27}^+\text{Cl}_1\text{O}_1$ 344.1655, found 342.1718.

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Benzene, 289 (2410), $\epsilon_{313}=327 \text{ M}^{-1}$, $\epsilon_{366}=73 \text{ M}^{-1}$; Cyclohexane, 243 (11,500), 270 (1,770), 286 (2,260), 340 (117), $\epsilon_{313}=204 \text{ M}^{-1}$, $\epsilon_{366}=68 \text{ M}^{-1}$.

16. 4'-chloro-2,4,6-triisopropylbenzophenone (4ClI₃BP)



This ketone was prepared exactly like 2'-chloro-2,4,6-trimethylbenzophenone except that *p*-chlorobenzoyl chloride (3.0 mL, 24 mmol) and 1,3,5-triisopropylbenzene (Aldrich Chemical, 5.9 g, 29 mmol) used. The preparation of *p*-chlorobenzoyl chloride is described for the preparation of 4'-chloro-2,4,6-trimethylbenzophenone. The mass of purified 4'-chloro-2,4,6-triisopropylbenzophenone was 3.4 g (41% yield) which melted at 87-89°C, literature 92-94°C.

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.03(d, J= 6.6 Hz, 6H), 1.14(d, J= 6.9 Hz, 6H), 1.27(d, J= 1.27, 6H), 2.55(septet, J= 6.9 Hz, 2H), 2.91(septet, J=6.6 Hz, 1H), 7.04(s, 2H), 7.40(d, J= 8.7 Hz, 2H), 7.76(d, J=8.4 Hz, 2H).

¹H-NMR(benzene-*d*₆, 300 MHz), δ ppm: 0.97(d, J= 6.9 Hz, 6H), 1.13(d, J= 6.9 Hz, 6H), 1.19(d, J=6.9 Hz, 6H), 2.72(septet, J= 6.9 Hz, 2H), 2.74(septet, J= 6.9 Hz, 2H), 6.86(d, J= 8.2 Hz, 2H), 7.10(s, 2H), 7.63(d, J=8.2 Hz, 2H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 23.60, 24.00, 24.87, 31.08, 34.38, 121.0, 128.94, 130.82, 134.52, 136.66, 139.97, 145.00, 150.00, 199.85.

FTIR(0.025mm CCl_4 , cm^{-1}) 850.72(w), 877.72(w), 918.23(m), 947.17(m), 1091.85(m), 1672.50(s), 2870.44(m), 2900.00(m), 2964.97(vs).

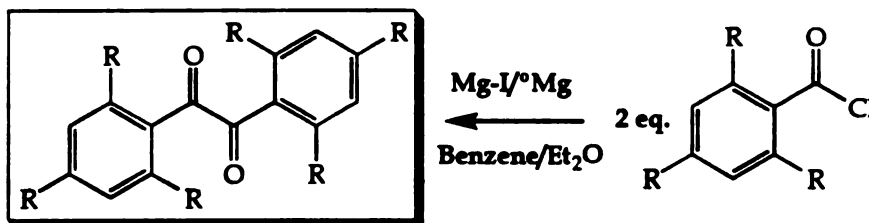
LRMS, m/z : 342(M^+), 307(100%), 292, 231.

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1}): Benzene, 280 (2990), $\epsilon_{313}=98 \text{ M}^{-1}$,

$\epsilon_{366}=57 \text{ M}^{-1}$. Cyclohexane, 214 (17,600), 256 (18,000), 270 (5,980), $\epsilon_{313}=101 \text{ M}^{-1}$,

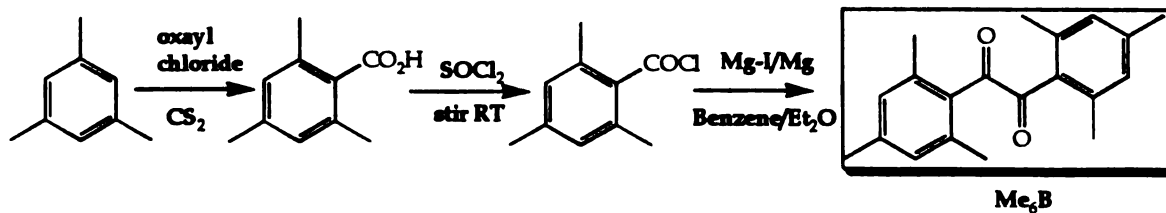
$\epsilon_{366}=88 \text{ M}^{-1}$.

C. Preparation of 2,4,6,2',4',6'-triaklybenzils



Ketone	R
Me_6B	$-\text{CH}_3$
Et_6B	$-\text{CH}_2\text{CH}_3$
$i\text{Pr}_6\text{B}$	$-\text{CH}(\text{CH}_3)_2$

1. 2,4,6,2',4',6'-hexamethylbenzil (Me_6B)



2,4,6-trimethylbenzoic acid

reference: P. E. Sokol, Organic Synthesis Coll. Vol., pg 706.

To a 2 Liter flask equipped with a mechanical stirrer, a 250 mL addition funnel, and a condenser protected by a drying tube, 146 g(Spectrum Chemical, 1.10 moles) of anhydrous aluminum chloride and 700 mL of carbon disulfide were added. The suspension was cooled to 10-15°C in an ice bath, and oxalyl chloride (EM Science, 139 g, 1.10 moles) was added dropwise with stirring over a 30 minute period and stirred for an additional 30 minutes. A solution of mesitylene (Aldrich Chemical, 120 g, 1.00 mole) in 200 mL carbon disulfide was added dropwise with stirring over a 1 hour period to the mixture while the temperature was maintained at 10-15°C. During this time hydrogen chloride was evolved and a dark red complex formed. The reaction mixture was refluxed for 1 hour and allowed to cool to room temperature. The solution was then poured into a mixture of 2 kg of crushed ice and 300 mL of concentrated HCl. The solution was then extracted with three 200 mL portions of dichloromethane. The combined organic extracts were washed with two 200 mL portions of deionized water and then extracted with three 200 mL portions of aqueous 5N NaOH. The aqueous extract was then acidified with concentrated HCl. The trimethylbenzoic acid was collected by vacuum filtration and washed with water and thoroughly dried. The trimethylbenzoic acid weighed 124g (76% yield) and melted at 151-153°C (lit. 149-150°, Aldrich chemical).

$^1\text{H-NMR}(\text{CDCl}_3, 300 \text{ MHz}), \delta \text{ ppm: } 2.28(\text{s}, 3\text{H}), 2.40(\text{s}, 6\text{H}), 6.87(\text{s}, 2\text{H})$

$^{13}\text{C-NMR}(\text{CDCl}_3, 75 \text{ MHz}), \delta \text{ ppm: } 20.29, 21.12, 128.8, 129.3, 136.1, 140.0, 175.5.$

2,4,6-trimethylbenzoyl chloride

To a 500 mL round bottom flask was added 100 g of 2,4,6-trimethylbenzoic acid (0.61 moles) equipped with a magnetic stirrer and a reflux condenser protected by a Drierite drying tube. Enough thionyl chloride was added to dissolve the benzoic acid. The reaction solution was allowed to stir at room temperature overnight (~20 hours). The thionyl chloride was then removed by simple distillation with the aid of heat and a water aspirator. Once the majority of the thionyl chloride was removed, the crude acid chloride was transferred to 250 mL round bottom flask equipped with a magnetic stir bar. A one piece fractional distillation setup with a 10 cm vigreux column was attached to the greased joint of the round bottom flask. The distillation pot was first wrapped with glass wool, followed by aluminum foil and finally cotton roll. The entire distillation column was wrapped with cotton roll and then aluminum foil to facilitate the distillation process. The purified acid chloride distilled as a colorless liquid. The mass of the 2,4,6-trimethylbenzoyl chloride was 88 g (0.44 moles, 72 % yield).

$^1\text{H-NMR}(\text{CDCl}_3, 300 \text{ MHz}), \delta \text{ ppm: } 2.23(\text{s}, 3\text{H}), 2.41(\text{s}, 6\text{H}), 6.88(\text{s}, 2\text{H}).$

2,4,6,2',4',6'-hexamethylbenzil

reference: Fuson, R. C. ; McKeever, C. H. ; Corse, J. *Am. Chem. Soc.* **1940**, 62, 600.

Gomberg, M. ; Bachmann, W. E., *J. Am. Chem. Soc.* **1927**, 49, 236.

The 2,4,6,2',4',6'-hexamethylbenzil was prepared by a known procedure using a binary mixture of magnesium iodide and magnesium. The procedure was followed as previously reported with no modifications. It was necessary to heat the MgI/⁰Mg to reflux to obtain the clear gray solution as reported by Gomberg and Bachmann. The binary mixture was prepared by combining 3 g of freshly crushed magnesium turnings with 60 mL of freshly distilled diethyl ether and 120 mL of dry benzene. To this solvent mixture was added a total of 15.3 g of iodine in several small portions (~ 1 g/portion). On addition of the iodine the reaction solution warmed and often refluxed. The solution maintained a deep red/purple color and had not become clear after one hour as reported. The solution was then warmed and reflux was maintained for approximately two hours after which the solution became clear and gray in color. The reaction vessel was allowed to cool to room temperature and the air was swept out by a constant stream of Argon. A solution of 11 g of the acid chloride dissolved in 10 mL of dry diethyl ether was added via an addition funnel over a period of fifteen minutes. The solution was allowed to stir at room temperature, protected from light, in an Argon atmosphere for a period of twenty four hours. At the end

of this period the magnesium turnings had nearly disappeared and the solution was a deep red in color.

The reaction was worked up by pouring the reaction mixture into a 1000 mL beaker containing 8 mL of glacial acetic acid and 100 mL of ice water. The ether-benzene layer was washed rapidly with water, with 5% sodium thiosulfate solution, again with water, then with saturated sodium bicarbonate solution and finally once more with water. The solution was then dried over anhydrous calcium chloride, filtered and evaporated to yield a mixture of an orange and white solid. The white solid (enediol) was separated from the benzil by recrystallization from 50 mL of petroleum ether, in which it precipitated first. The benzil was recrystallized a second time from petroleum ether to yield 7.5 g (85% yield) of pure 2,2',4,4',6,6'-hexamethybenzil, the orange crystals melted at 118-119 °C, lit. 136-137°C.¹⁷¹

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 2.21(s, 6H), 2.23(s, 12H), 6.80(s, 4H).

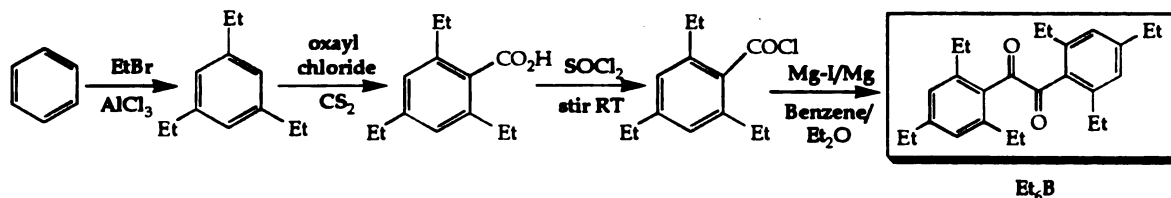
¹H-NMR(Benzene-*d*₆, 300 MHz), δ ppm: 2.04(s, 6H), 2.16(s, 12H), 6.61(s, 3H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 20.1, 21.2, 128.8, 133.6, 135.4, 140.1, 197.4.

FTIR(0.025mm CCl₄.cm⁻¹) 1698.

UV-VIS (path= 1 cm, λ_{max} nm (ε_{max} M⁻¹)): Cyclohexane, 216 (21,600), 288 (3,130), 464 (49.7), 494(57.8).

2. 2,4,6,2',4',6'-hexaethylbenzil (Et₆B)



2,4,6-triethyl benzoic acid

reference: P. E. Sokol, Organic Synthesis Coll. Vol., pg 706.

The method for synthesis for 2,4,6-trimethyl benzoic acid was adapted to prepare 2,4,6-triethylbenzoic acid. The synthetic procedure for preparation of 1,3,5-triethylbenzene has been previously described in the synthesis of 2'-chloro-2,4,6-triethylbenzophenone. To a 1 Liter flask equipped with a mechanical stirrer, a 125 mL addition funnel, and a condenser protected by a drying tube was added, 72 g(Spectrum Chemical, 0.55 moles) of anhydrous aluminum chloride and 350 mL of carbon disulfide. The suspension was cooled to 10-15°C in an ice bath, and oxalyl chloride (EM Science, 70 g, 0.55 moles) was added dropwise with stirring over a 30 minute period and stirred for an additional 30 minutes. A solution of 1,3,5-triethylbenzene (81 g, 0.50 mole) and 100 mL carbon disulfide was added dropwise with stirring over a 1 hour period to the mixture while the temperature maintained at 10-15°C, during this time hydrogen chloride was evolved and a dark red complex forms. The reaction mixture was refluxed for 1 hour and allowed to cool to room temperature. The solution was then poured into a mixture of 1 kg of crushed ice and 150 mL of concentrated HCl. The solution was then extracted with three 100 mL portions of dichloromethane. The

combined organic extracts were washed with two 100 mL portions of deionized water and then extracted with three 100 mL portions of aqueous 5N NaOH. The aqueous extract was then acidified with concentrated HCl. During the extraction there were three layers, the organic, aqueous and a third dark layer between the other two. The third layer contains a significant amount of the benzoic acid and is not completely soluble in the dichloromethane. The 2,4,6-triethylbenzoic acid was collected by vacuum filtration and washed with water and thoroughly dried. The 2,4,6-triethyl benzoic acid weighed 35g (37% yield), the white crystals melted at 112-113°C, lit. 113-113.5°C.¹⁷²

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.23(t, J= 6.9 Hz, 3H), 1.26(t, J= 6.9 Hz, 6H), 2.62(q, J= 6.9 Hz, 2H), 2.73(q, J= 6.9 Hz, 4H), 6.94(s, 2H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 15.33, 15.83, 27.02, 26.76, 125.9, 129.1, 141.4, 146.3, 176.0.

2,4,6-triethylbenzoyl chloride

reference: Fuson, R. C. ; McKeever, C. H. ; Corse, *J. Am. Chem. Soc.* **1939**, 61, 2010.
Gomberg, M. ; Bachmann, W. E., *J. Am. Chem. Soc.* **1927**, 49, 236.

2,4,6-Triethylbenzoyl chloride was prepared by the same procedure as 2,4,6-trimethylbenzoyl chloride except 30 g of 2,4,6-triethylbenzoic acid (0.16

moles) was used. The purified acid chloride distilled as a colorless liquid. The mass of the 2,4,6-triethyl benzoyl chloride was 25 g (0.11, 70% yield).

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.22(t, J= 6.9 Hz, 3H), 1.24(t, J= 6.9 Hz, 6H), 2.62(q, J= 6.9 Hz, 2H), 2.69(q, 4H), 6.92(s, 2H).

2,4,6,2',4',6'-hexaethylbenzil

reference: Fuson, R. C. ; McKeever, C. H. ; Corse, J. *Am. Chem. Soc.* **1939**, 61, 2010.

The *2,4,6,2',4',6'-hexaethylbenzil* was prepared by a known literature preparation that was modified slightly. A binary mixture of magnesium and magnesium iodide was prepared from 4.5 g of magnesium turnings and 23 g of iodine according to the method of Gombery and Bachmann.¹⁷³ The details of this reaction are give for in the synthesis of *2,4,6,2',4',6'-hexamethybenzil*. A stream of Argon was passed through the vessel throughout the period of the reaction.

A solution of 16.3 g of 2,4,6-triethylbenzoyl chloride in 15 mL of freshly distilled diethyl ether was added dropwise to the binary mixture. The reaction mixture was stirred for 24 hours and nearly all the magnesium had been consumed. The reaction mixture was poured into a 1 liter beaker which contained 100 g of cracked ice and 8 mL of glacial acetic acid. The acidified reaction solution was protected from light and stirred for 4 hours while exposed to air. This modification allowed for the complete conversion of the enediol to the benzil by air oxidation. The ether-benzene solution was separated and

washed three times with saturated NaHCO_3 , once with distilled water, twice with 5 % sodium thiosulfate and twice more with water. The solvent was removed to yield a crude orange solid. This workup procedure did not yield enediol. The crude benzil was recrystallized from petroleum ether (ligroin) to yield 12.8 g (93 % yield) of pure benzil. The yellow-orange crystals melted at 75-77 °C, literature 75-75.5 °C.¹⁷²

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 1.16 (t, J = 7.5 Hz, 12H), 1.25 (t, J = 7.5 Hz, 6H), 2.47(t, J =7.5 Hz, 8H), 2.64(t, J = 7.5 Hz, 4H), 6.96 (s, 4H).

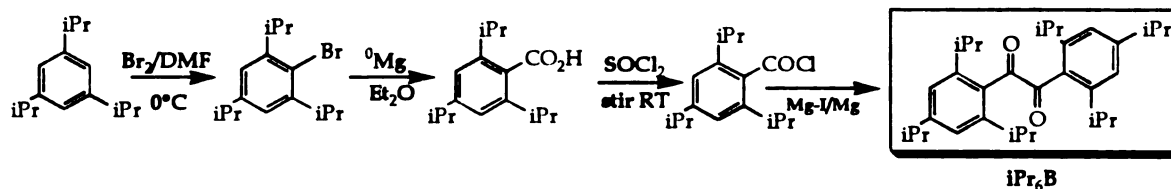
$^1\text{H-NMR}$ (benzene- d_6 , 300 MHz), δ ppm: 1.07 (t, J = 7.5 Hz, 6H), 1.09 (t, J = 7.5 Hz, 12H), 2.41(t, J =7.5 Hz, 4H), 2.50(t, J = 7.5 Hz, 8H), 6.77(s, 4H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: .15.25, 15.84, 26.86, 28.78, 125.85, 132.96, 141.54, 146.54, 198.02.

FTIR(0.025mm CCl_4 , cm^{-1}) 1700.

UV-VIS (path= 1 cm, λ_{max} nm (ϵ_{max} M^{-1})): Cyclohexane, 216 (23,000), 304 (2,180), 466 (55.3), 493 (59.6).

3. 2,4,6,2',4',6'-hexaisopropylbenzil (iPr₆Bz)



2-bromo-1,3,5-trisopropylbenzene

reference: Miller, A. R. and D. Y. Curtin *J. Am. Chem. Soc.* **1976**, 98, 1860.

An ice cold Br₂/dimethylformamide(DMF) solution was prepared by slowly adding 16 g (0.10 mol) of Br₂ with stirring, to 150 mL of chilled DMF. This solution was added to a light protected, ice cooled solution of 51 g (0.25 mol) 1,3,5-triisopropylbenzene in 250 mL of DMF. Addition at such a rate as to maintain the reaction temperature below 30°C and required 10 minutes. Stirring was continued for 20 minutes and the solution was then poured into an iced mixture of 100g of sodium sulfite and 500 mL of water. The oil was extracted into pentane and worked up to give 70 g (>99% yield) of a nearly colorless oil, whose NMR spectrum indicated no starting material, di- or tri- brominated products. The crude bromide was sufficiently pure for the subsequent step.

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.20(d, J= 6.9 Hz, 18H), 2.86(septet, J= 6.9 Hz, 1H), 3.47(septet, J= 6.9 Hz, 2H), 6.97(s, 2H).

1,3,5-triisopropylbenzoic acid

reference: Fuson, R. C. and E. C. Horning *J. Am. Chem. Soc.* **1940**, 62, 2962.

The Grignard of 2-bromo-1,3,5-triisopropylbenzene was prepared from freshly crushed magnesium (3.1 g, 0.13 mol) turnings and 30 g (0.11 mol) of 2-bromo-1,3,5-triisopropylbenzene in 100 mL of ether. The ethereal solution was heated to reflux under an argon atmosphere for three hours after which nearly all the magnesium had disappeared. The Grignard solution was then poured slowly onto crushed dry ice and was allowed to warm to room temperature. The solution was acidified and extracted with three 100 mL portions of diethyl ether. The combined organic layers were washed with saturated NaCl solution and dried over anhydrous Na₂SO₄. Evaporation gave a slightly yellow solid which was recrystallized from petroleum ether (ligroin) to give 19.8 g of 1,3,5-triisopropylbenzoic acid (73% yield) which melted at 185-188°C literature 186-187°C.¹⁷⁴

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.24(d, J= 6.9 Hz, 6H), 1.27(d, J= 6.9 Hz, 12H), 2.89(septet, J= 6.9 Hz, 1H), 3.04(septet, J= 6.9 Hz, 2H), 7.01(s, 2H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 23.92, 24.21, 31.54, 34.43, 121.0, 129.3, 144.8, 150.5, 176.7.

1,3,5-triisopropylbenzoyl chloride

reference: Fuson, R. C. and E. C. Horning *J. Am. Chem. Soc.* **1940**, 62, 2962.

The acid chloride from 1,3,5-triisopropylbenzoic acid was prepared by stirring 20g of the acid with 50 mL of freshly distilled thionyl chloride. The excess thionyl chloride was removed under reduced pressure with the aid of a water aspirator. The *1,3,5-triisopropylbenzoyl chloride* was purified by a short path distillation using a kugelrohr distillation apparatus. The acid chloride was collected when the air bath temperature was 110°C/2 mm Hg. The purified acid chloride melted at 79-82°C (literature 79-81°C, Fuson and Horning).

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.24(d, J= 6.9 Hz, 6H), 1.27(d, J= 6.9 Hz, 12H), 2.89(septet, J= 6.9 Hz, 1H), 3.04(septet, J= 6.9 Hz, 2H), 7.01(s, 2H).

2,4,6,2',4',6'-hexaisopropylbenzil

reference: Fuson, R. C. and E. C. Horning *J. Am. Chem. Soc.* **1940**, 62, 2962.
Fuson, R. C. ; McKeever, C. H. ; Corse, *J. Am. Chem. Soc.* **1940**, 62, 600. Gomberg, M. ; Bachmann, W. E., *J. Am. Chem. Soc.* **1927**, 49, 236.

2,4,6,2',4',6'-hexaisopropylbenzil was prepared by the identical procedure as *2,4,6,2',4',6'-hexamethylbenzil*. The binary mixture of magnesium and magnesium iodide was prepared with 0.46 g (0.019 mol) magnesium and 2.40 g (0.0094 mol) in a 10 mL ether/20 mL benzene solution. Addition of 2.85 g (0.0094 mol) of 1,3,5-triisopropylbenzoyl chloride to the binary mixture yielded 1.2 g (55%

yield) after recrystallization with methanol. The yellow benzil needles melted at 155-156°C, literature 155-156°C.¹⁷⁴

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.13(d, J= 6.9 Hz, 24H), 1.23(d, J= 6.9 Hz, 12H), 2.59(septet, J= 6.9 Hz, 4H), 2.88(septet, J= 6.9 Hz, 2H), 7.01(s, 4H).

¹H-NMR(Benzene-*d*₆, 300 MHz), δ ppm: 1.16(d, J= 6.9 Hz, 24H), 1.18(d, J= 6.9 Hz, 12H), 2.74(septet, J= 6.9 Hz, 2H), 2.97(septet, J= 6.9 Hz, 4H), 7.08(s, 4H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 23.88, 23.98, 31.97, 34.39, 121.2, 132.2, 145.8, 150.9, 200.8.

FTIR(0.025mm CCl₄, cm⁻¹) 1698.

UV-VIS (path= 1 cm, λ_{max} nm (ε_{max} M⁻¹)): Cyclohexane, 206 (38,800), 278 (1,900), 318(1,180) 466 (48.9), 493 (51.5).

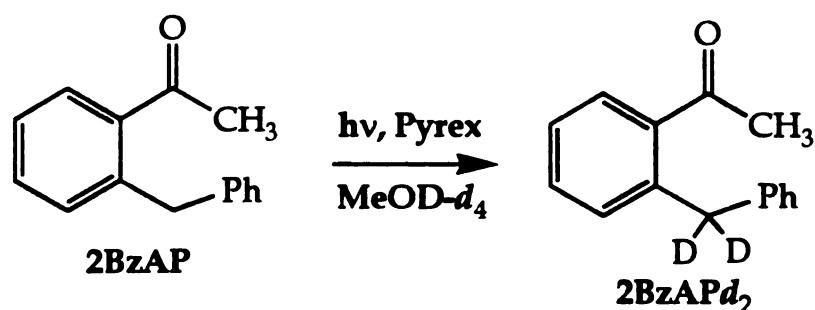
III. Identification of photoproducts

Preparative photochemistry was carried out in either a Rayonet reactor equipped with 300 nm lamps or in a Pyrex, water-cooled immersion well with a 450W medium pressure mercury arc light source. The temperature in the Rayonet reactor averaged 45°C. Submerging the immersion well in deionized water in a mirrored dewar maintained the temperature between 17-23°C, which fluctuated with the temperature of the cooling water. The immersion well was fitted with either a Pyrex (>290 nm) or Uranium glass (>330 nm) sleeve. Emission at 436 nm was isolated with a Uranium glass filter sleeve and filter solution of 20 g CuSO₄, 25g of NaNO₂ and 34 mL of concentrated ammonium hydroxide diluted into 500 mL of water. Quantum yields and Stern-Volmer quenching studies were measured with filtered light at 313 nm or 366 nm. The 313 nm band was isolated from a medium pressure 450 W Hanovia mercury arc lamp using a solution of alkaline potassium chromate (0.002 M K₂CrO₄ in 1% aqueous potassium carbonate). The 366 nm light was isolated by filtration with Corning 7-83 filters.

All samples were degassed by purging with argon for twenty minutes prior to irradiation with a continuous stream of oxygen free argon (99.996 %). The outlet needle was then be removed to maintain a positive pressure. After removal of the Argon source the septum was wrapped several times with teflon tape to ensure an air tight seal. If irradiation took longer than 24 hours, the

samples were degassed at each 24 hour interval in case oxygen had leaked in through the septa.

Products from 2'-benzylacetophenone (2BzAP)



NMR experiment

The reaction was repeated five times with similar results each time. In a typical experiment a 0.75 mL methanol- d_4 solution of 5.9 mg (0.028 mmol, 0.037 M) of 2BzAP was degassed. The sample was irradiated in a Rayonet reactor setup with 300 nm lamps. After 20 hours of irradiation complete deuterium exchange had occurred at the benzylic position accompanied by incorporation into the acetyl methyl peak. Also a new product had formed with a singlet at ~ 1.00 ppm but could not be isolated or identified.

preparative experiment

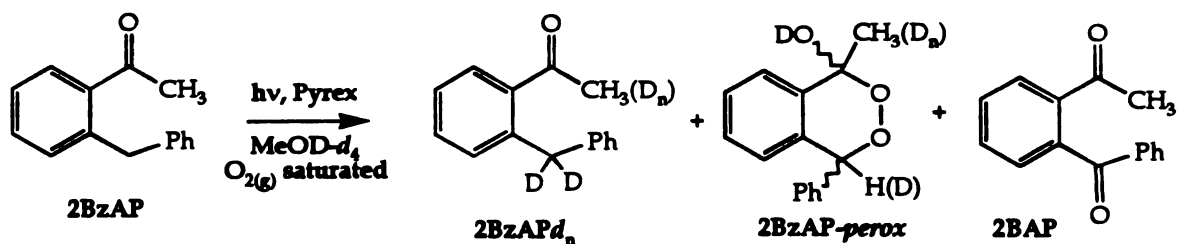
A 3.0 mL solution of methanol and 20 mg (mmol, M) of 2BzAP was degassed with argon and irradiated in a NMR tube in a Rayonet reactor setup with 300 nm lamps for 36 hours. The methanol was removed by evaporation with a continuous stream of air for 1 hour. The clear viscous liquid was

dissolved in chloroform- d_1 which had been passed through a plug of sodium bicarbonate and oven dried sodium sulfate in a pasteur pipette. The ^1H -NMR spectrum revealed no new products and only starting ketone.

dark reaction

A 0.01M methanol- d_4 of 2BzAP solution was left standing in the dark and the reaction was monitored by ^1H -NMR analysis periodically. After 3 days about there was ~30% loss of the acetyl methyl singlet at 2.39 ppm relative to the benzylic methylene peak at 4.22 ppm. There was a slight upfield shift of the methyl peak at 2.39 ppm and the peak appeared as a 1:1:1 triplet due to deuterium coupling.

NMR experiment in the presence of oxygen.



This reaction was performed four times each with similar results. In a typical experiment a 0.75 mL methanol- d_4 solution of 5.9 mg (0.028 mmol, 0.037 M) of 2BzAP was purged with pure oxygen for 20 minutes. The sample was irradiated in the Rayonet reactor setup with 300 nm lamps. After 24 hours of irradiation complete deuterium exchange had occurred at the benzylic position. In addition to deuterium incorporation three products (2 peroxides and 2-

acetylbenzophenone) were identified in ^1H -NMR spectrum of the reaction solution in methanol- d_4 . The methanol- d_4 was removed by rotoevaporation and the ^2H -NMR acquired in methanol. The methanol was removed by rotoevaporation and the ^1H -NMR spectrum was acquired in chloroform- d_1 . 2-Benzylacetophenone was isolated after irradiating 20 mg (0.10 mmol, 0.001 M) of ketone in oxygen saturated methanol. The solution was irradiated for 36 hours in a Rayonet reactor (300 nm lamps) and the solvent was removed by rotoevaporation. The ^1H -NMR spectrum showed three products. Thin layer chromatography with 95:5 hexane:ethyl acetate gave only one product identified as 2-acetylbenzophenone while the others decomposed. The ^1H -NMR spectrum acquired in chloroform- d_1 of the crude reaction mixture before chromatography was identical to the NMR scale reaction.

Note: The amount of peroxide that was formed was a function of dissolved oxygen. Complete conversion of ketone to peroxide occurred when the ketone concentration was ~ 0.001 M.

2-acetylbenzophenone

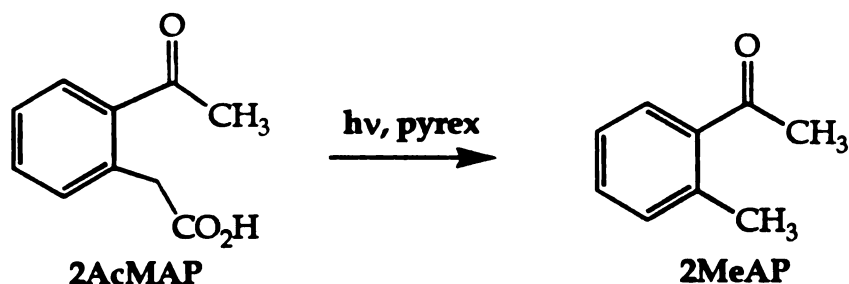
^1H -NMR(CDCl_3 , 300 MHz), δ ppm: 2.50(s, 3H), 7.35-7.45(m, 3H), 7.52(distorted ddd, $J = 7.4$ Hz, 1H), 7.55-7.65 (m, 2H), 7.57(distorted d, 2H), 7.87(dd, $J = 7.0, 2.0$ Hz, 1H).

two peroxides from crude mixture

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 1.70 (3H) and 1.74(3H), 3.56(1H broad, exchangeable with D_2O), 3.69(1H broad, exchangeable with D_2O), 5.98 (1H) and 6.29 (1H), 6.76 (d, J = 8.1 Hz, 1H), 7.05 (d, J =7.8 Hz, 1H), 7.15-7.44 (m, 16 H)

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 24.01, 24.10, 82.10, 83.96, 99.22, 99.81, 125.5, 125.8, 126.0, 126.4, 127.7, 127.9, 128.0, 128.1, 128.3 (2 peaks), 128.6(2peaks), 128.7(2 peaks), 129.2(2 peaks), 129.5(2 peaks), 129.9 (2 peaks).

Product from 2'-acetylphenylacetic acid (2AcMAP)

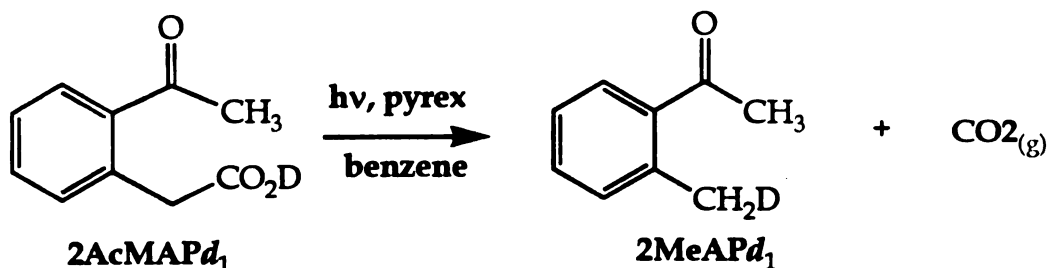


NMR experiment

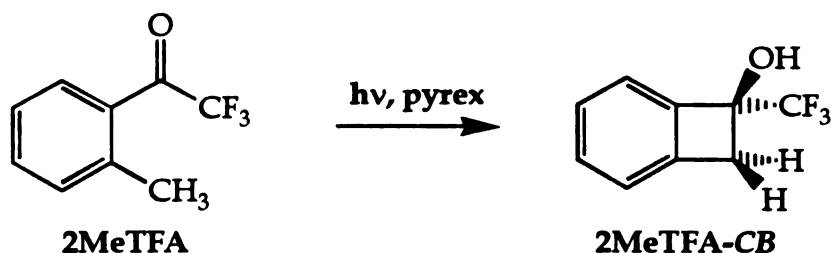
This reaction was repeated three times each with the identical result as the others. A 0.75 mL benzene- d_6 solution of 3.0 mg (0.014 mmol, 0.019 M) of 2AcMAP was degassed and irradiated in a Rayonet reactor equipped with 300 nm lamps. The reaction was nearly complete after 20 minutes of irradiation. The major product (>95%) had a $^1\text{H-NMR}$ spectrum consistent with 2-methylacetophenone. The NMR solution was also injected into the gas chromatograph and had a peak with an identical retention time as 2-methylacetophenone. The NMR solution was also spiked with authentic 2-

methylbenzophenone and reinjected into the gas chromatograph, only one peak was visible in the chromatogram.

Product from deuterio 2'-acetylphenylacetic acid (2AcMAPd₁)



To a 2.0 mL benzene solution of 9.5 mg (0.045 mmol, 0.023 M) 2AcMAPd₁ was added ~1 mL of 99.9% D₂O which had been stored under argon in a desiccator. The solution was shaken vigorously and the benzene phase removed and dried with oven dried anhydrous sodium sulfate which had been cooled in a desiccator. The solution was degassed and irradiated in a Rayonet reactor equipped with 300 nm lamps. The progress of the reaction was monitored by ²H-NMR and was complete after 110 minutes. ²H-NMR analysis showed the disappearance of a broad peak at 0.60 ppm with the simultaneous growth of a sharp singlet at 2.50 ppm. This new singlet is consistent with the formation of 2MeAP-d₁.

Product from 2'-methyl-2,2,2-trifluoroacetophenone (2MeTFA)

Irradiation of 20.0 mg (0.099 mmol, 0.130 M) 2MeTFA in benzene- d_6 gave only one product in quantitative yield. The reaction was monitored by ^1H -NMR analysis periodically. The singlet at 2.22 ppm for the *o*-toluoyl methyl group disappeared at the same rate as the growth of an AB quartet at 2.68 ppm ($J = 14.9$ Hz, 1H) and 3.33 ($J = 14.1$ Hz, 1H) ppm in benzene- d_6 . The reaction was complete (100% conversion) after 13 hours of irradiation. The product was determined to be 1-(α,α,α -trifluoromethyl)-benzocyclobuteneol (2MeTFA-CB) based on its ^1H and ^{13}C -NMR spectra. The formation of 2MeTFA-CB was independent of the light source employed. The benzocyclobutenol was formed by irradiation with a medium pressure mercury arc lamp (Pyrex filtered, 17-20°C) and 300 nm lamps in a Rayonet reactor. Each reactor gave identical results.

1-(α,α,α -trifluoromethyl)-benzocyclobutenol (2MeTFA-CB)

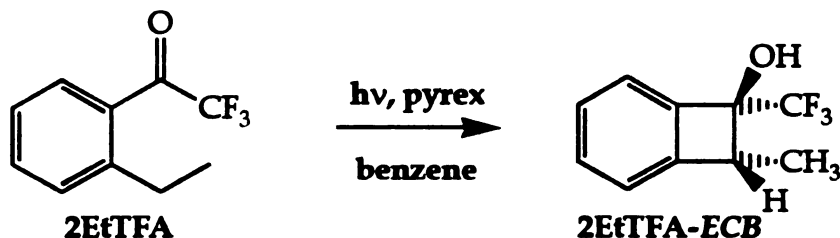
^1H -NMR(benzene- d_6 , 300 MHz), δ ppm: 2.04(broad s, 1H), 2.68(d, $J = 14.4$ Hz, 1H), 3.33(d, $J = 14.1$ Hz, 1H), 6.70(ddd, $J = 7.2, 0.9, 0.9$ Hz, 1H), 6.82-6.93(m, 2H), 6.96(ddd, $J = 7.5, 7.2, 1.8$ Hz, 1H).

¹H NMR (CDCl₃, 300 MHz), δ ppm: 2.84 (broad s, 1H), 3.27 (d, J = 14.7 Hz, 1H), 3.71 (d, J = 17.2 Hz, 1H), 7.20 (distorted d, J = 7.2 Hz, 1H), 7.25 (distorted d, J = 7.5 Hz, 1H), 7.3 (dd, J = 7.5, 7.5 Hz, 1H), 7.39 (ddd, J = 7.5, 7.2, 1.8 Hz, 1H).

¹H NMR (acetonitrile-*d*₄, 300 MHz), δ ppm: 3.23(d, J = 14.7 Hz, 1H), 3.64(d, J = 15.0 Hz, 1H), 5.01(s, 1H), 7.24(distorted d, J = 7.5 Hz, 1H), 7.27(d, J = 7.5 Hz, 1H), 7.32(distorted dd, J = 7.5, 7.0 Hz, 1H), 7.41(ddd, J = 7.5, 6.9, 1.8 Hz, 1H).

¹³C-NMR(acetonitrile -*d*₄, 75 MHz), δ ppm: 42.18, 78.54(J_{CF}= 32.2 Hz), 122.9, 124.6, 126.3(J_{CF}= 278.9 Hz), 128.9, 131.9, 143.0(J_{CF}= 2.38 Hz), 143.2.

Product from 2'-ethyl-2,2,2-trifluoroacetophenone (2EtTFA)



NMR experiment

In a typical experiment, a 1.0 mL benzene-*d*₆ solution of 12.1 mg (0.05 mmol, 0.060 M) 2EtTFA was degassed in a NMR sample tube. Irradiation gave only one product. The reaction was monitored by ¹H-NMR and was complete (100% conversion) after 12 hours of irradiation with Pyrex filtered light (medium pressure mercury arc lamp). The ¹H-NMR spectra showed the disappearance of the *o*-ethyl group (triplet at 0.979 ppm and quartet at 2.61 ppm) with the simultaneous growth of a quartet at 3.08 ppm (*J* = 7.4 Hz) and a doublet of

quartets at 1.24 ($J = 7.4, 1.8$ Hz) ppm. The product was identified as 2EtTFA-ECB. No trace of a second isomer (2EtTFA-ZCB) was apparent in the ^1H -NMR spectrum.

Preparative experiment

A preparative reaction was carried out with 280mg (0.72 mmol, 0.01 M) of 2EtTFAP in 70 mL of benzene. The preparatory scale reaction gave a identical results as the NMR scale reaction. Silica gel column chromatography with hexane gave a single product.

(E)2-methyl-1-(α,α,α -trifluoromethyl)-benzocyclobutenol (2EtTFA-ECB)

^1H -NMR(benzene- d_6 , 300 MHz), δ ppm: 1.24(dq, $J = 7.4, 1.75$ Hz, 3H), 3.08(q, $J = 7.4$ Hz, 1H), 6.25(distorted dd, $J = 7.2, 1.0$, 1H), 6.85–6.97(m, 2H), 6.99(ddd, $J = 7.3, 7.3, 1.4$ Hz, 1H).

^1H NMR(CDCl_3 , 300 MHz), δ ppm: 1.49(dq, $J = 7.2, 1.75$ Hz, 3H), 3.73(qd, $J = 7.5, 0.06$ Hz, 1H), 7.17–7.32(m, 3H), 7.39(ddd, $J = 7.2, 7.2, 1.5$ Hz, 1H).

^{13}C -NMR(CDCl_3 , 75 MHz), δ ppm: 13.47(q, $J_{13\text{C}-19\text{F}} = 2.12$ Hz), 52.34, 80.89(q, $J_{13\text{C}-19\text{F}} = 30.7$ Hz), 122.5, 122.95, 125.5(q, $J_{13\text{C}-19\text{F}} = 282$ Hz), 128.1, 132.0, 140.5, 147.8.

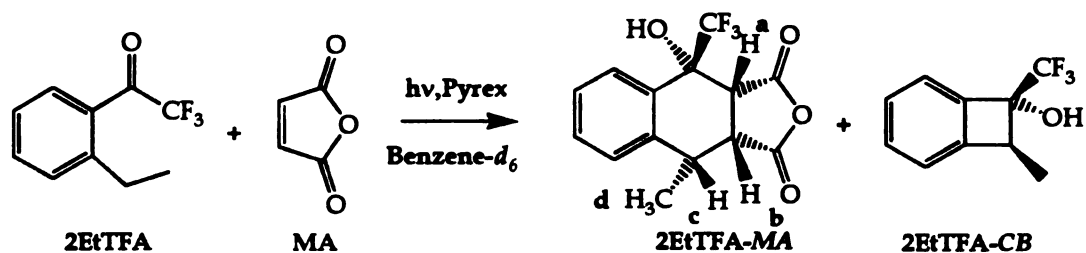
FTIR(cm^{-1}) 3611.20(m,broad), 2993.90(w), 2970.75(w), 2939.89(w), 1180.59(s), 1163.22(s), 1113.07(s).

Mass Spec, m/z: 202(M^+ , 21%). 251(100%), 133(100%), 105(48%), 103(35%), 91(11%), 77(47%).

Attempted acid catalysed isomerization of 2EtTFA-ECB

To a NMR sample tube that contained 2EtTFA-ECB (~0.01 M) dissolved in benzene- d_6 was added 5 mg of *p*-toluenesulfonic acid (pTsOH). The tube was degassed by purging with argon and placed in the dark. The reaction was monitored periodically by 1H -NMR. After one week at room temperature the 1H -NMR spectrum showed no new product formation. The same sample tube was placed in an oil bath and heated to reflux. 1H -NMR analysis showed no new product formation after 72 hours of heating.

Irradiation of 2EtTFA in the presence of maleic anhydride



NMR experiment 1

A 0.75 mL toluene- d_8 solution of 5.5 mg (0.027 M) of 2EtTFA and 1.8 mg (0.018 M) of maleic anhydride was degassed in a NMR sample tube. Within 2 hours of irradiation through Pyrex with a mercury arc lamp, most of the 2EtTFA had disappeared with the formation of two photostable products. The

irradiation was continued for 8 hours, after this time the 2EtTFAP had disappeared completely. The two photostable product possessed a ^1H -NMR spectrum consistent with 2EtTFA-*MA* and 2EtTFA-*ECB* in a 3.5:1 ratio.

Note: The ratio of 2EtTFA-*MA* : 2EtTFA-*ECBI* was found to be a function of the amount of maleic anhydride used. Complete trapping occurred when a ~10 molar excess of maleic anhydride : 2EtTFA was employed.

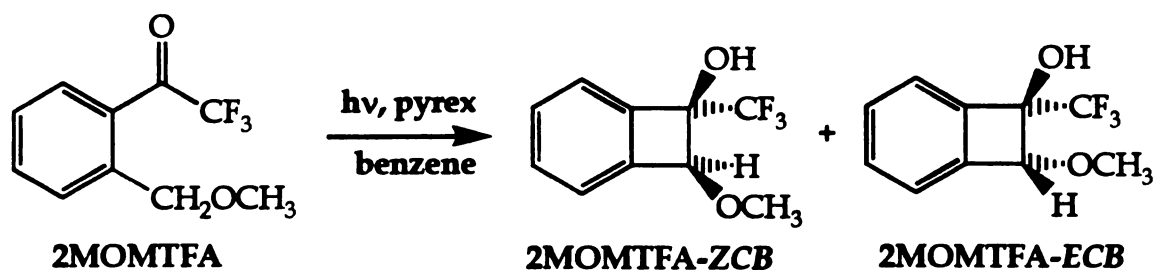
NMR experiment 2 (excess maleic anhydride)

A 0.75 mL toluene-*d*₈ solution of 3.5 mg (0.017 mmol, 0.023 M) of 2EtTFA and 11.4 mg (0.116 mmol, 0.155 M) of maleic anhydride was degassed in a NMR sample tube. Within 2 hours of irradiation through pyrex with a mercury arc lamp all of the 2EtTFA had disappeared, with the formation of only one product. The photostable product possessed a ^1H -NMR spectrum consistent with 2EtTFA-*MA*.

^1H -NMR(benzene-*d*₆, 300 MHz), δ ppm: 1.15(d, J = 7.0 Hz, 3H, d), 2.47(dd, J = 9.5, 9.2 Hz, 1H, b), 2.80(d, J = 9.5 Hz, 1H, a), 2.83(dq, J = 9.3, 6.6 Hz, 1H, c), 6.75-6.82(m, 1H), 6.93-6.97(m, 2H), 7.78-7.84(m, 1H).

Table 26. ^1H -NMR homonuclear selective decoupling (benzene- d_6 , 300 MHz)

irrad $\text{H}_x \Rightarrow \text{decoup } \text{H}_y$	decoupler frequency(ppm)	frequency decoupled(ppm),
d $\Rightarrow$ c	1.15	2.83 (dq $\Rightarrow$ d)
b $\Rightarrow$ a&c	2.47	2.80 (d $\Rightarrow$ s) : 2.83 (dq $\Rightarrow$ q)
a&c $\Rightarrow$ b&d	2.79	1.15 (dd $\Rightarrow$ s) & 2.47 (dd $\Rightarrow$ s)

Products from 2'-(methoxymethyl)-2,2,2-trifluoroacetophenone (2MOMTFA)*NMR experiment*

A 0.5 mL benzene- d_6 solution of 4.4 mg (0.020 mmol, 0.04 M) of 2MOMTFA was degassed and irradiated through Pyrex with a 450W medium pressure mercury arc lamp. The sample was hung outside the immersion well setup and the reaction was complete after 5.5 hours. The ^1H -NMR showed only one product in the benzene- d_6 reaction solvent consistent with 2MOMTFA-ECB.

Preparative experiment

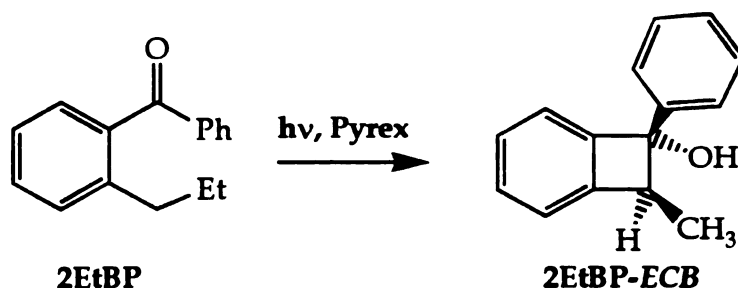
A preparative scale reaction was carried out in 70 mL benzene with 133 mg (0.61 mmol, 0.009 M) of 2MOMeTFA. The reaction was complete after 16 hours of irradiation with Pyrex filtered light. The benzene was removed by rotoevaporation and the residual solvent removed at reduced pressure with an oil pump for 2 hours. The resulting viscous crude liquid was orange in color and weighed 126 mg. ¹HNMR in CDCl₃ analysis of the crude mixture revealed two major products which were isolated and separated by column chromatography (SiO₂) with a 60:40 mixture of n-pentane:diethyl ether, as the eluent. The products had spectra consistent with 2MOMTFA-ZCB and 2MOMTFA-ECB in a 10:1 ratio.

E-2-methoxy-1-(α,α,α -trifluoromethyl)- benzocyclobutene-1-ol

¹HNMR(CDCl₃, 300 MHz), δ ppm: 2.80(s, broad), 3.65(s, 3H), 4.88(s, 1H), 7.36(distorted ddd, 7.2, 6.0, 1.8 Hz, 1H), 7.41(d, J=6.0 Hz, 1H), 7.43(d, J= 6.0 Hz, 1H), 7.46(ddd, J= 7.2, 6.0, 1.5, 1H).

Z-2-methoxy-1-(α,α,α -trifluoromethyl)-benzocyclobutene-1-ol

¹HNMR(CDCl₃, 300 MHz), δ ppm: 3.59(s, 3H), 5.09(s, 1H), 7.34-7.46(m, 4H).

Products from 2-ethylbenzophenone (2EtBP)*NMR experiment in acetonitrile- d_4*

A 0.8 mL acetonitrile- d_4 solution of 14.7 mg (0.074 mmol, 0.092 M) of 2EtBP was degassed. The sample was irradiated with Pyrex filtered light in an immersion well setup. The well was submerged in deionized water and the reaction temperature was maintained between 17-20°C during the reaction period. The lamp was turned on 20 minutes prior to introduction of the sample. After thirty minutes of irradiation the sample had become a brilliant (canary) yellow in color. The reaction was continued for 13 hours and the starting ketone had been completely consumed, the solution had turned from a brilliant yellow to a faint yellow with the prolonged irradiation. The major product had ^1H -NMR and ^{13}C -NMR consistent with 2EtBP-ECB.

NMR experiment in acetone- d_6

A 0.75 mL acetone- d_6 solution of 12.4 mg (0.06 mmol, 0.08 M) of 2EtBP was degassed and irradiated in an immersion well setup. The reaction was complete after 1 hour of irradiation and gave one major product although the

reaction solution had turned faint yellow. The product had a ^1H -NMR spectrum consistent with 2EtBP-ECB.

NMR experiment in toluene- d_8

A 0.75 mL toluene- d_8 solution of 10.5 mg (0.05 mmol, 0.07 M) of 2EtBP was degassed and irradiated. The sample was irradiated with Pyrex filtered light in an immersion well setup. The reaction was complete after 13 hours of irradiation and gave one major product although the reaction solution had turned faint yellow. The product had a ^1H -NMR spectrum consistent with 2EtBP-ECB. A few crystals of p-toluene sulphonic acid was added to the same sample and left in the dark for 24 hours. The ^1H -NMR spectrum was obtained after this time and showed the formation of a new product. The 2EtBP-ECB had isomerized to 2EtBP-ZCB with a Z/E ratio of 1.3/1 and only a trace of starting ketone (<5%) formed. The toluene solvent was removed with a constant stream of air and the remaining viscous film was dissolved in acetonitrile- d_4 and the ^{13}C -NMR spectrum obtained. For details of these reactions see Figure 50.

E-1-phenyl-2-methyl-1,2-benzocyclobuten-1-ol (2EtBP-ECB)

^1H -NMR(acetonitrile- d_4 , 300 MHz), δ ppm: 0.813(d, J = 6.9 Hz, 3H), 3.66(q, J = 6.9 Hz, 1H), 4.18(broad s, 1H), 7.22-7.37(m, 9H).

^1H -NMR(acetone- d_6 , 300 MHz), δ ppm: 0.821(d, J = 7.5 Hz, 3H), 3.70(q, J = 7.5 Hz, 1H), 5.19(s, 1H), 7.22-7.35(m, 9H).

¹H-NMR(toluene-*d*₈, 300 MHz), δ ppm: 0.835(d, J= 7.2 Hz, 3H), 1.98(s, 3H), 3.48(q, J= 7.2 Hz, 1H), 6.95-7.17(m, 7H), 7.30(distorted dd, J= 7.8, 1.2 Hz, 2H).

¹³C-NMR(acetonitrile -*d*₃, 75 MHz, -30°C), δ ppm: 15.65, 54.86, 84.67, 122.9, 123.7, 127.6, 127.9, 128.5(2 resonances), 130.1, 142.9, 148.0, 148.2.

Z-1-phenyl-2-methyl-1,2-benzocyclobuten-1-ol (**2EtBP-ECB**)

¹H-NMR(toluene-*d*₈, 300 MHz), δ ppm: 1.22(d, J= 7.2 Hz, 3H), 3.54(q, J= 7.2 Hz, 1H), 6.95-7.17(m, 7H), 7.40(distorted dd, J= 7.8, 1.2 Hz, 2H).

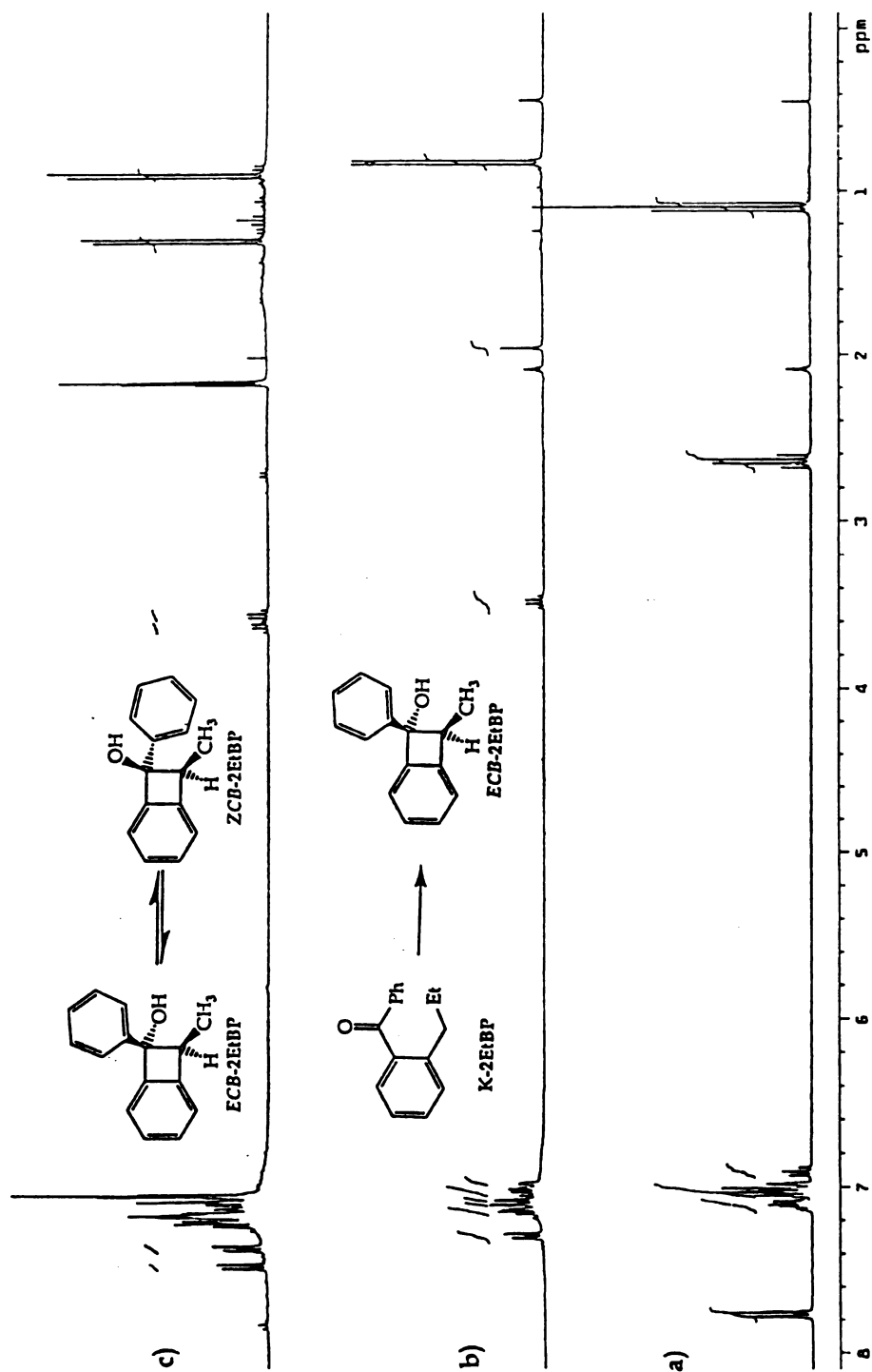
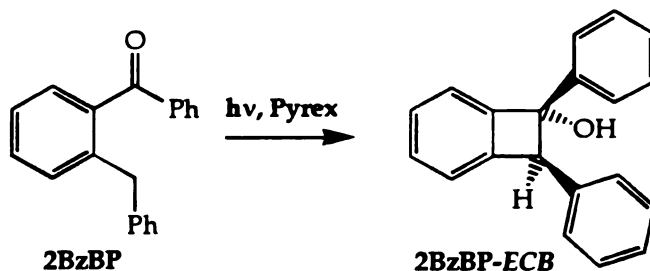


Figure 50. ^1H -NMR Spectra of 2EtBP in $\text{toluene-}d_8$, a) before irradiation b) after 13 hours irradiation c) same sample in (b) after 3 days standing in dark with 2 crystals of pTsOH at RT.

Products from 2-benzylbenzophenone(2BzBP)



NMR experiment 1

This experiment was repeated >20 times and the results could be reproduced if *identical* experimental conditions were used each time. The reaction was sensitive to oxygen, temperature and irradiation time. Also, how the sample was handled after irradiation was complete was extremely important. In a typical experiment a 0.75 ml benzene-*d*₆ solution of 4 mg (0.014 mmols, 0.020 M) of 2BzBP was degassed. Irradiation was conducted with a Pyrex filtered light from a mercury arc lamp submerged in ice water which maintained the temperature between 0-5°C. During the course of the reaction which was followed by ¹H-NMR, the benzylic methylene singlet at 4.02 ppm disappeared at the same rate as the growth of a two singlets at 2.21 and 4.75 ppm in benzene-*d*₆. The broad peak at 2.21 ppm disappeared when washed with deuterium oxide, indicating that it was a hydroxy group. The reaction was complete within 10 minutes at this temperature and the solution had a fluorescent green hue. The product of the reaction is identified as 2BzBP-ECB.

NMR experiment 2

In a separate experiment, 13.0 mg of 2BzBP was dissolved in 0.80 ml acetonitrile- d_4 (from a flame sealed ampoule) and degassed. Irradiation was conducted with a Pyrex filtered light from a mercury arc lamp submerged in ice. The sample was irradiated for 30 minutes and then the sample was placed in a liquid nitrogen. Later the ^1H -NMR and ^{13}C -NMR were acquired at -30°C . The sample was stored in a dewar with liquid nitrogen inside a refrigerator for 36 hours with no appreciable change. Chlorotrimethylsilane (10 μL) was syringed into the same acetonitrile- d_4 solution (which had been frozen after the ^{13}C -NMR was acquired) in an attempt to trap the 2BzBP-ECB. The sample was then warmed to 0°C and maintained at this temperature for 24 hours. ^1H -NMR (at room temperature) analysis revealed that the 2BzBP-ECB had completely reverted to starting ketone.

E-1,2-diphenyl-1,2-benzocyclobuten-1-ol (2BzBP-ECB)

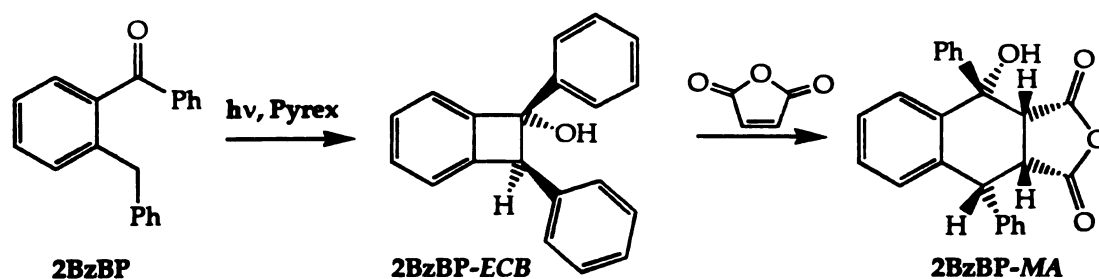
^1H -NMR(Benzene- d_6 , 300 MHz), δ ppm: 2.20(s, 1H, OH), 4.75(s, 1H), 6.75-7.25(m, 14H).

^1H -NMR(acetonitrile- d_4 , 300 MHz, -30°C), δ ppm: 4.81(s, 1H), 4.92(s, 1H), 6.89(distorted dd, $J = 8.1, 1.5$ Hz, 2H), 6.92-7.03(m, 8H), 7.35-7.40(m, 2H), 7.42-7.50(m, 2H).

^1H -NMR(toluene- d_6 , 300 MHz, -80°C), δ ppm: 2.77(broad s, 1H, disappeared with D_2O washing), 4.65(s, 1H), 6.80(distorted d, 2H), 6.83-6.94(m, 6H), 7.09(d, $J = 7.2$ Hz, 2H), 7.16(dd, $J = 7.0, 7.2$ Hz, 2H), 7.22(d, $J = 7.2$ Hz, 2H).

^{13}C -NMR(acetonitrile- d_4 , 75 MHz, -30°C), δ ppm: 66.40, 87.17, 123.50, 125.31, 126.82, 127.40, 127.68, 127.86, 128.34, 128.83, 129.10, 130.34, 139.41, 142.10, 144.25, 149.25.

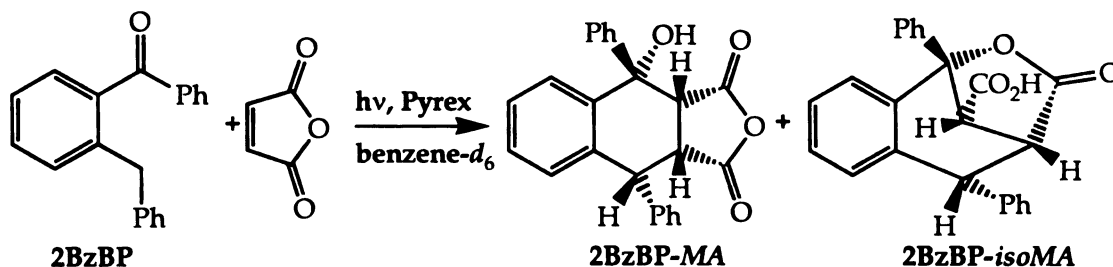
Irradiation of 2BzBP followed by addition of maleic anhydride



This reaction was repeated 7 times with similar results each time. In a typical experiment, 4 mg of 2BzBP was dissolved in 0.75 ml benzene- d_6 in a NMR sample tube and degassed. Irradiation in the Rayonet reactor for 1 hour led to ~25 % conversion (this could be increased to 100 % if the reaction temperature was maintained at 0°C) of the starting ketone and the resulting solution was fluorescent green. 100 μL of an argon purged benzene- d_6 solution of maleic anhydride (10mg/0.5 mL) was added via syringe. Upon addition of the maleic anhydride, the solution lost its fluorescent color and a faint yellow color persisted. Immediately after addition of the maleic anhydride a ^1H -NMR spectrum was acquired and showed a new product consistent with 2BzBP-MA. The spectrum showed three new sets of peaks in the aliphatic region: a doublet of doublets at 2.77 ppm ($J = 9.3, 9.0$ Hz, 1H) and two doublets at 3.14 ($J = 9.3$ Hz, 1H) and 3.72 ppm ($J = 9.0$ Hz, 1H). Continued irradiation of the same sample led

to complete conversion of starting ketone to **2BzBP-MA**, which was the major product.

Irradiation of 2BzBP in the presence of maleic anhydride



A 1.0 mL benzene- d_6 solution of 24.2 mg (0.089 mmol, 0.089 M) of **2BzBP** and 12.8 mg (0.13 mmol, 0.13 M) of maleic anhydride was degassed. The sample tube was irradiated with Pyrex filtered light from a mercury arc lamp submerged in ice water which maintained the temperature between 0-5°C. The reaction was complete within 1 hour. $^1\text{H-NMR}$ analysis showed **2BzBP-MA** as the only product formed with trace (<3 %) amounts of a second product. Purification of **2BzBP-MA** proved difficult because the **2BzBP-MA** apparently reacts with the silica gel. Its decomposition is evident when using TLC analysis to find a suitable solvent system for purification because the spot becomes a long streak as the eluent migrates up the plate. In order to alleviate this problem, separation with neutral Alumina was attempted but the decomposition still occurred.

Irradiation of a similar solution in the Rayonet reactor led to **2BzBP-MA** and a second product **2BzBP-isoMA**. After the complete consumption of the

starting ketone the **2BzBP-MA** was converted thermally to **2BzBP-isoMA** by heating at 75°C for 20 minutes.

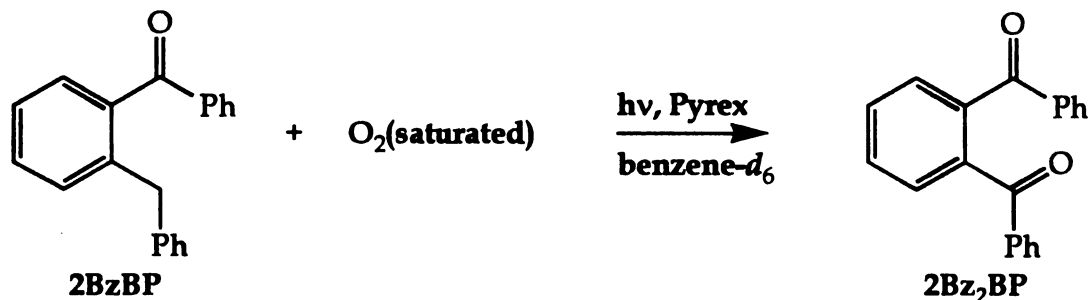
4-hydroxy-4,9-diphenyl-3a,4,9,9a-tetrahydro-naphtho<2,3-c>furan-1,3-dione (2BzBP-MA)

$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 2.80(J= 9.3, 9.0 Hz, 1H), 3.20(d, J= 9.3 Hz, 1H), 3.75(d, J= 9.0 Hz, 1H), 4.85(broad s, 1H).

$^1\text{H-NMR}$ (acetonitrile- d_4 , 300 MHz), δ ppm: 3.96(dd, J= 9.6, 9.3 Hz, 1H), 4.25(d, J= 9.3, 1H), 4.41(d, J= 9.6 Hz, 1H), 6.34(s, 1H), 7.04(distorted d, 1H), 7.18-7.27(m, 2H), 7.27-7.35(m, 8H), 7.37-7.43(m, 3H).

$^{13}\text{C-NMR}$ (acetonitrile- d_4 , 75 MHz), δ ppm: 43.96, 44.35, 53.14, 75.58, 127.6, 127.8, 127.9, 128.2, 128.9, 129.1, 129.2, 129.3, 129.4, 129.7, 130.51, 131.7, 132.6, 167.13, 171.2, 172.3.

Irradiation of 2BzBP in the presence of Oxygen



A 0.75 mL benzene- d_6 solution of 5.5 mg (0.020 mmol, 0.027 M) of **2BzBP** was purged with a continuous stream of pure oxygen for twenty minutes in an NMR sample tube. After 8 hours of irradiation the benzylic hydrogens had

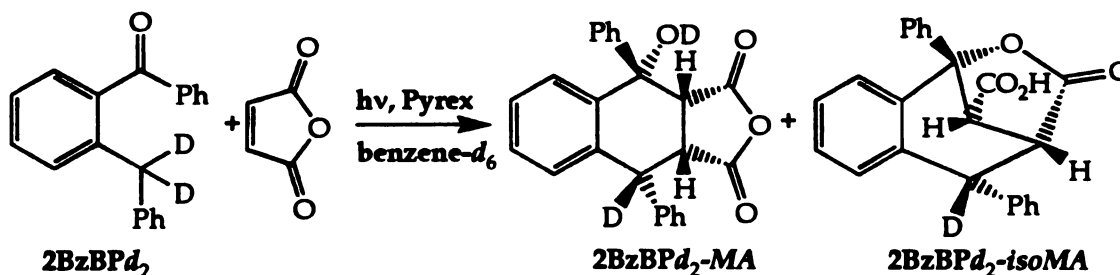
disappeared and the solution remained clear. The NMR sample solution was submitted for mass spectral analysis and the chromatograph indicated only one product and no starting ketone. The ^1H -NMR and mass spectrum are consistent with 2-benzoylbenzophenone(Bz_2BP).¹¹⁵

2-benzoylbenzophenone (Bz_2BP)

^1H -NMR(Benzene- d_6 , 300 MHz), δ ppm: 6.908(dd, $J = 7.8, 6.9$ Hz, 4H), 6.914(dd, 7.8, 6.9 Hz, 1H), 6.96-7.02(m, 3H), 7.27(m, 2H, appears as two doublets with 1:1:1:1 ratio at 7.288, 7.277, 7.269, 7.259 ppm), 7.68(distorted d, $J = 8.4$ Hz, 4H)

LRMS, m/z : 286.1(M^+), 209.0(100%), 105.0, 77.0.

Products from 2'-benzoyl-1,1-dideuteriodiphenylmethane and maleic anhydride



A 0.65 mL benzene- d_6 solution of 9.2 mg (0.034 mmol, 0.052 M) of 2BzBPd_2 and 2.7 mg (0.027 mmol, 0.042 M) of maleic anhydride was degassed. The sample tube was irradiated in a Rayonet reactor (45°C) and was monitored by ^1H -NMR analysis at periodic intervals. The reaction was complete after 5 hours and the ratio of $2\text{BzBPd}_1\text{-MA} : 2\text{BzBPd}_1\text{-isoMA}$ was 9:10. Heating the

mixture at 50°C in the dark resulted in the complete conversion of **2BzBP d_1 -MA** to **2BzBP d_1 -isoMA** after 20 hours.³³

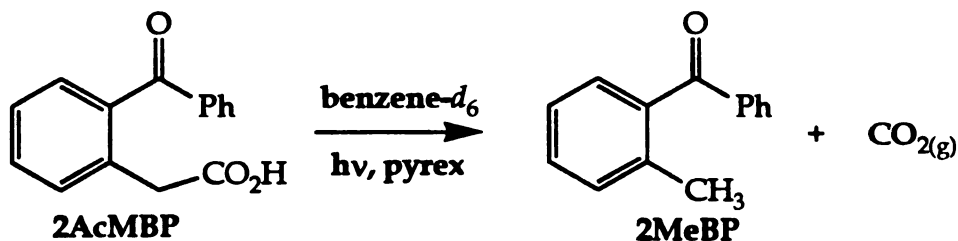
2BzBP d_1 -MA

¹H-NMR(Benzene- d_6 , 300 MHz), δ ppm: 2.74(d, J= 9.3 Hz), 3.12(d, J= 9.3 Hz), 6.70-7.05(m, 12H), 7.82(d, J= 7.0 Hz, 2H).

2BzBP d_1 -isoMA

¹H-NMR(Benzene- d_6 , 300 MHz), δ ppm: 2.90(s, 1H), 3.27(s, 1H), 6.45-6.55(m, 2H), 6.57-6.90(m, 2H), 6.90-7.05(m, 8H), 7.82(d, J= 7.0 Hz, 2H).

Products from (2-benzoylphenyl)acetic acid (2AcMBP)



NMR experiment

A 0.75 mL benzene- d_6 solution of 3.0 mg (0.014 mmol, 0.019 M) of **2AcMBP** was degassed and irradiated in a Rayonet reactor equipped with 300 nm lamps. The reaction was complete after 20 minutes of irradiation. The only product had a ¹H-NMR spectrum consistent with 2-methylbenzophenone. The NMR solution was also injected into the gas chromatograph and gave a peak

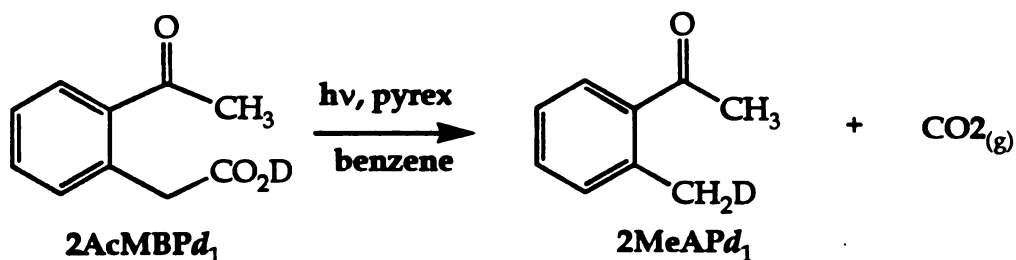
with an identical retention time as 2-methylbenzophenone. Gas chromatographic analysis of the reaction solution with added 2MeBP showed only one peak in the chromatogram confirming the photoproduct's identity.

FTIR experiment

A 1.5 mL benzene solution of 10.8 mg (0.030 M) of 2AcMBP was degassed in a small vial with argon. The solution was then transferred via syringe to a 0.75 mm solution cell. The cell construction consisted of a 0.75 mm teflon disk that had KBr plates on both sides of the disk. One salt plate had two drilled holes, one hole was for adding the sample to the cell, the second hole served as a vent. The transfer of the degassed benzene solution of 2AcMBP to the IR solution cell was conducted in a glove bag within an argon atmosphere. The background spectrum of the instrument was acquired followed by the acquisition of a reference spectrum of the same benzene that was used to prepare the ketone solution. The background and reference spectra were subtracted from the 2AcMBP spectrum that was acquired in benzene. Part of the solution cell body was black in color; in order to keep the cell cool, the cell was wrapped in Aluminum foil. A small rectangular hole was cut in the foil to allow light to reach the KBr window. The solution cell was irradiated for 10 minutes with Pyrex filtered light from a medium pressure Mercury arc lamp. After irradiation a bubble was formed in the capped solution cell and caused a slight decrease in resolution of the FTIR spectrum. The FTIR spectrum (background and solvent

reference subtracted) of the irradiated ketone clearly showed the formation of a new stretches at 2240 and 1663 cm^{-1} with a simultaneous disappearance of the 2AcMBP ketone carboxyl stretch at 1705 and 1709 cm^{-1} . The CO_2 appears to saturate the benzene solution to give only 60 percent transmittance judged by the magnitude of the stretching frequency at 2340 cm^{-1} . In a separate experiment, a 53% saturation limit was observed when CO_2 was bubbled through benzene and the FTIR spectrum acquired. The CO_2 was introduced into the solution by slightly warming dry ice in a Erlenmeyer flask with a 1 hole stopper and tygon tubing with an inline drying tube (Drierite drying agent). A second carbonyl stretching frequency at 1662 cm^{-1} is evident after irradiation which is identical to authentic *o*-methylbenzophenone.

Product from deuterio (2-benzoylphenyl)acetic acid (2AcMBPd₁)

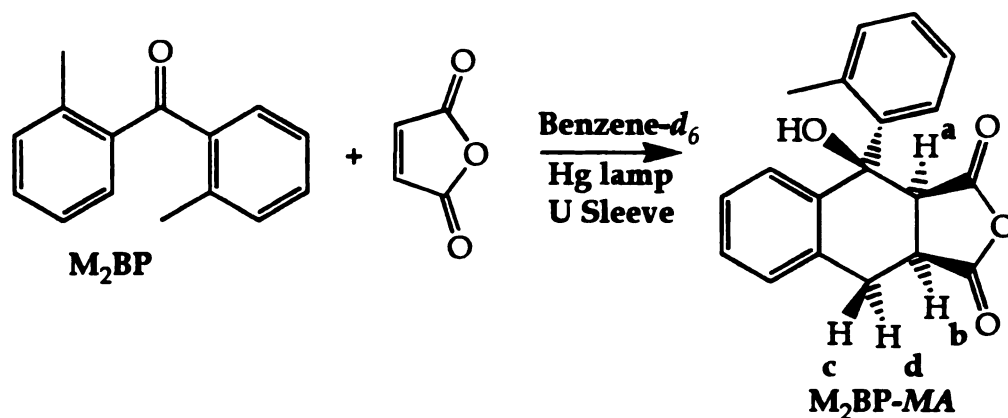


To a 2.0 mL benzene solution of 9.4 mg (0.039 mmol, 0.019 M) of 2AcMBPd₁ was added ~1 mL of 99.9% D₂O, which had been stored under argon in a desiccator. The solution was shaken vigorously and the benzene solution removed and dried with oven dried anhydrous sodium sulfate which had been cooled in a desiccator. The solution was degassed and irradiated in a Rayonet

reactor equipped with 300 nm lamps. The progress of the reaction was monitored by ^2H -NMR and was complete after 20 minutes. ^2H -NMR analysis showed the disappearance of the broad peak at 2.5 ppm with the simultaneous growth of a sharp singlet at 2.25 ppm. This new singlet is consistent with the formation of 2MeBPd_1 .

Products from 2,2'-dimethylbenzophenone (Me_2BP)

Irradiation of Me_2BP in the presence of maleic anhydride



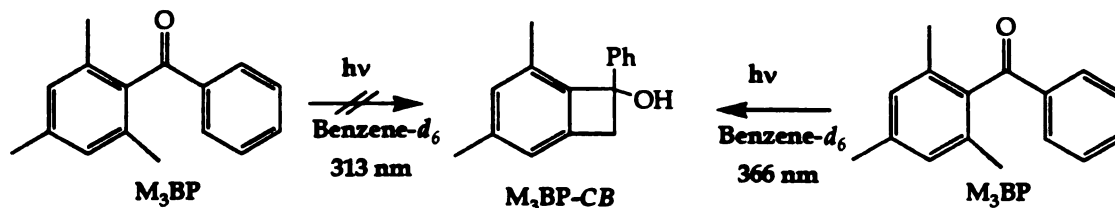
Irradiation of a 0.01 M benzene- d_6 solution of Me_2BP in a NMR tube through a Pyrex filter (medium pressure mercury arc lamp) showed a new methyl singlet at 2.36 ppm after one hour of irradiation. The methyl singlet for Me_2BP at 2.33 ppm disappeared with the simultaneous formation of the new signal. The new signal did not remain and after prolonged irradiation the starting material disappeared with no clean product formation (the spectrum became very complicated with very broad peaks). The characteristic AB quartet (3.4 ppm) for the expected benzocyclobutenol was not observed.¹⁰³

In a separate experiment, a benzene- d_6 solution of Me₂BP (0.032 M) and maleic anhydride (0.15 M) was irradiated in a NMR tube through a Pyrex filter. Within 40 minutes, most of the Me₂BP had disappeared with the formation of a new photostable product. The irradiation was continued for 4 hours and the Me₂BP had reacted completely after this time. The photostable product possessed a ¹H-NMR spectrum consistent with Me₂BP-MA.

Me₂BP-MA

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 3.11(dd, J = 15.9, 9.5 Hz, 1H, c), 3.30(dd, J = 15.9, 5.2 Hz, 1H, d), 3.55(ddd, J = 9.9, 9.6, 4.8 Hz, 1H, b), 4.09(d, J = 9.9 Hz, 1H, a), 7.10-7.50(m, 8H).

Products from 2,4,6-trimethylbenzophenone (M₃BP)

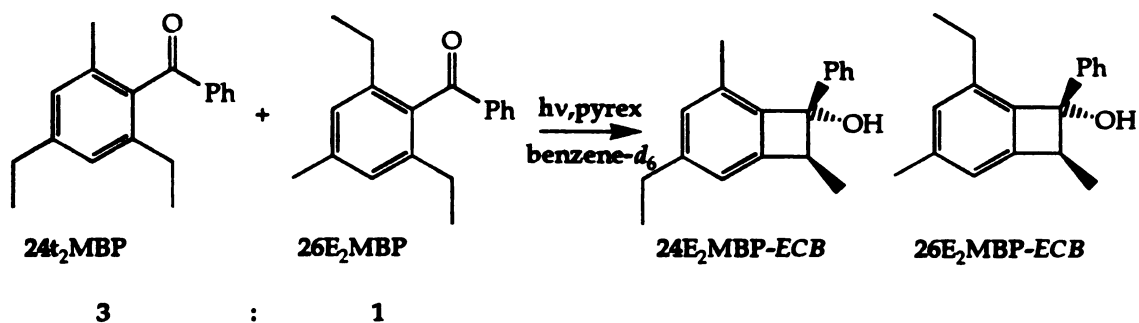


Irradiation of a 0.084 M M₃BP benzene- d_6 solution (methyl benzoate internal standard = 0.013 M) with 313 nm filtered light gave no product formation after 24 hours at 25°C. Three nmr sample tubes were prepared from the same solution. The samples were degassed by three freeze pump thaw cycles with a mechanical pump. The nmr sample tubes were irradiated parrallel to 0.1 M valerophenone. The valerophenone had completely reacted during this time

period indicating that light was reaching the samples. The reaction solution had become pale yellow after the 24 hours of irradiation. After this time, a new valerophenone solution (0.63 M in benzene- d_6) was prepared. The same M_3BP nmr sample tubes were irradiated parallel to the valerophenone solution with 366 nm filtered light. After four hours irradiation (366 nm) at 25°C, 5% of the M_3BP had been converted to M_3BP-CB . Which was observed by the growth of the two doublets at δ 3.10 and 3.29 ppm in the 1H -NMR spectrum. The quantum yield for formation of M_3BP-CB was determined to be 0.022 at 366 nm by integration of these peaks relative to the methyl ester peak of the benzoate internal standard. No attempt was made to isolate the M_3BP-CB product.

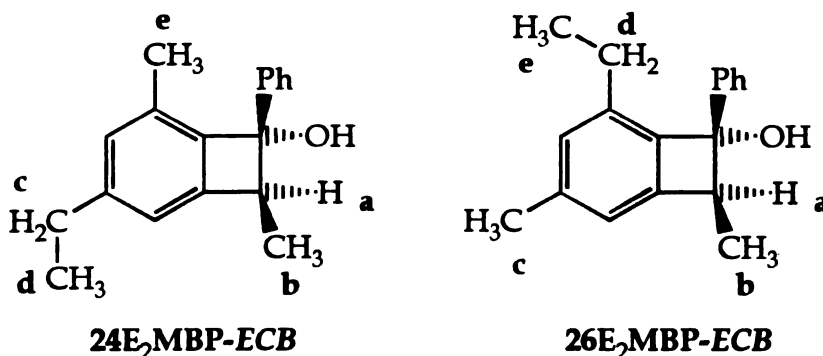
Photochemistry of 2,4-diethyl-6-methylbenzophenone (24E₂MBP) and

2,6-diethyl-4-methylbenzophenone (26E₂MBP)



A 0.75 mL benzene- d_6 solution of 24E₂MBP and 26E₂MBP (5.5 mg, 0.022 mmol, 0.030 M) were prepared in an NMR tube. The ketones 24E₂MBP and 26E₂MBP were irradiated through Pyrex. as a 3:1 mixture (24E₂MBP: 26E₂MBP). The reaction was monitored by 1H -NMR analysis. The two major products had

^1H -NMR spectra consistent with **24E₂MBP-ECB** and **26E₂MBP-ECB**. The ratio of **24E₂MBP-ECB**: **26E₂MBP-ECB** was 3:1 by integration of the aryl methyl signals.



E-2,6-dimethyl-4-ethyl-1-phenyl-1,2-benzocyclobuten-1-ol (**24E₂MBP-ECB**)

from 2,4-diethyl-6-methylbenzophenone(**24E₂MBP**)

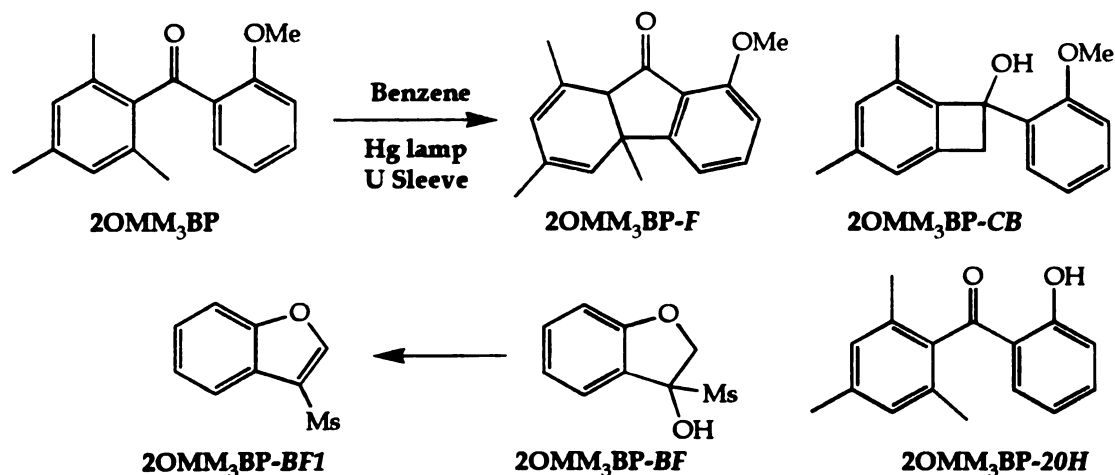
^1H -NMR(benzene-*d*₆, 300 MHz), δ ppm: 0.839(d, J = 7.2 Hz, 3H, b), 1.14(t, J = 7.6 Hz, 3H, d), 2.01(s, 3H, e), 2.49(q, J = 7.7 Hz, 2H, c), 3.40(q, J = 7.4 Hz, 1H, a), 6.74(s, 1H), 6.80(s, 1H), 7.00-7.15(m, 3H), 7.35(dd, J = 9.7, 1.5 Hz, 2H)

E-2,4-dimethyl-6-ethyl-1-phenyl-1,2-benzocyclobuten-1-ol (**26E₂MBP-ECB**)

from 2,6-diethyl-4-methylbenzophenone(**26E₂MBP**)

^1H -NMR(benzene-*d*₆, 300 MHz), δ ppm: 0.829(d, J = 7.3 Hz, 3H, b), 1.04(t, J = 7.7 Hz, 3H, e), 2.20(s, 3H, c), 1.01(q, J = 7.7 Hz, 2H, d), 3.35(q, J = 7.4 Hz, 1H, a), 6.70(s, 1H), 6.84(s, 1H), 7.00-7.15(m, 3H), 7.35(dd, J = 9.7, 1.5 Hz, 2H)

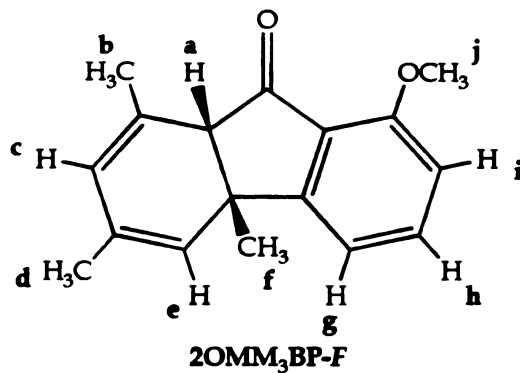
Products from 2'-methoxy-2,4,6-trimethylbenzophenone (2OMM₃BP).



The preparative photolysis of 2OMM₃BP was carried out in 25mm x 250mm pyrex test tubes irradiated with a medium pressure mercury arc lamp with a Uranium glass filter. 0.5 g of 2OMM₃BP was dissolved in 125 mL (0.015 M) of benzene and degassed. The tubes were irradiated for three days and the solvent removed. A ¹H-NMR spectrum of the crude sample revealed a mixture of products. TLC analysis (SiO₂, 85:15, hexane : ethyl acetate) revealed three major products. The photoproducts were isolated using preparative TLC (SiO₂, 85:15, hexane : ethyl acetate). The first compound eluted had spectral data consistent with 1-(2',4',6'-trimethylphenyl)-benzofuran-1-ol, 2OMM₃BP-BF. However, only a ¹H-NMR spectrum could be acquired since the product underwent dehydration overnight to give 1-(2',4',6'-trimethylphenyl)-benzofurene, 2OMM₃BP-BF1. The second compound eluted had spectral data consistent with 2'-hydroxy-2,4,6-trimethylbenzophenone, M₃BP-2OH. The third compound eluted had spectral data consistent with 1-methoxy-5b,6,8-trimethyl-5b,8a-dihydrofluorene-

9-one, 2OMM₃BP-F. The ¹H-NMR spectrum of the crude reaction products shows an AB quartet (3.40, 3.55 ppm, J=14.7 Hz) which is consistent with the benzocyclobutenol product, it decomposed and could not be isolated and characterized.

1-methoxy-5b,6,8-trimethyl-5b,8a-dihydrofluorene-9-one (2OMM₃BP-F)



¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.37(s, 3H, f), 1.63(d, J= 0.9 Hz, 3H, d), 2.02(s, 3H, b), 2.71(s, 1H, a), 3.24(s, 3H, j), 5.13(s, 1H, e), 5.42(q, J= 1.2 Hz, c), 6.17(d, J= 4.8 Hz, 1H, i), 7.08(d, J= 4.8 Hz, 1H, g), 7.53(dd, J= 4.8, 4.8 Hz, 1H, h).

¹H-NMR(benzene-*d*₆, 300 MHz), δ ppm: 1.16(s, 3H, f), 1.46(d, J= 1.2Hz, 3H) , d, 2.17(s, 3H, b), 2.90(s, 1H, a), 3.90(s, 3H, j), 5.22(s, 1H, e), 5.56(q, J= 0.9 Hz, c), 6.71(d, J= 7.8 Hz, 1H, i), 6.78(d, J= 7.5 Hz, 1H, g), 7.11(dd, J= 7.8, 7.5 Hz, 1H, h).

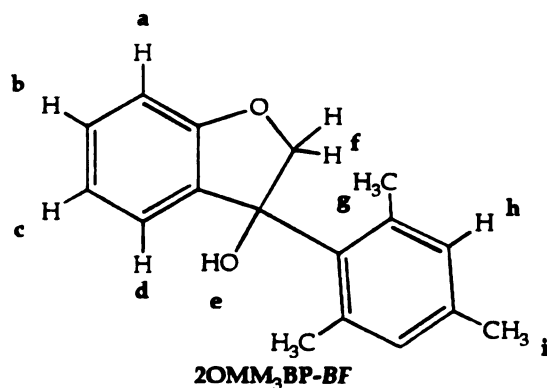
¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 21.44, 22.73, 28.23, 43.65, 55.72, 60.38, 108.45, 115.54, 122.00, 124.06, 125.29, 127.92, 132.78, 136.65, 158.16, 164.49, 202.42.

APT(¹³C-NMR, CDCl₃, 75 MHz): 9 resonances up, 21.44(CH₃), 22.73(CH₃), 28.23(CH₃), 55.72(CH), 60.38 (OCH₃), 108.45(CH), 115.54(CH), 122.00(CH),

125.29(CH); 7 resonances down, 43.65(C(C)₄), 124.06(C(C)₄), 127.92(C(C)₄), 132.78(C(C)₄), 158.16(C(C)₄), 164.49(C(C)₄), 202.42(C=O).

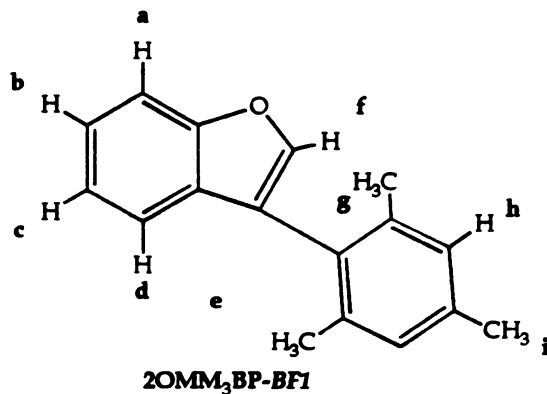
LRMS, m/z: 254(M⁺). 239(100%).

3-(2,4,6-trimethylphenyl)-benzofuran-3-ol (Me₃BP-BF)



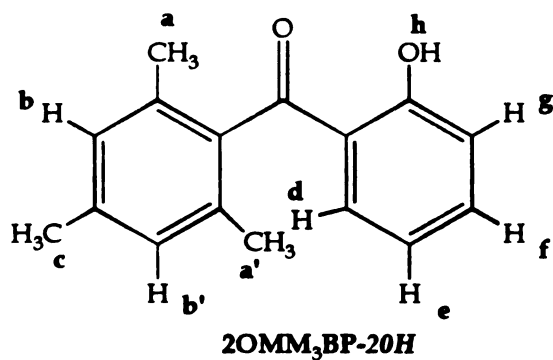
¹H-NMR(CDCl₃, 300 MHz), δ ppm: 2.07(s, 6H), 2.24(s, 3H), 4.57, 4.79 (AB quartet, J= 10.5, 10.2, 2H), 6.82(s, 2H), 6.89(dd, J= 7.5, 7.5 Hz, 1H), 6.92(dd, J= 7.5, 7.5 Hz, 1H), 7.12(distorted d, 1H), 7.27(distorted d, 1H)

3-(2,4,6-trimethylphenyl)-benzofuran (M₃BP-BF1)



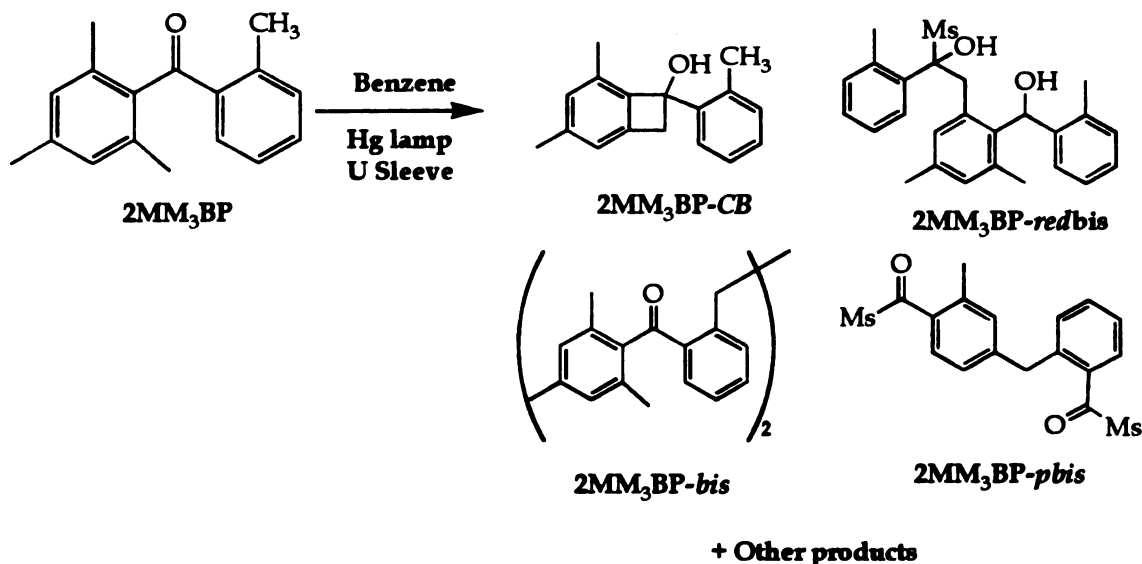
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 2.09(s, 6H, g), 2.36(s, 3H, i), 7.00(s, 2H, h), 7.14-7.24(m, 2H, b & c), 7.33(ddd, J = 8.2, 6.8 Hz, 1H, h), 7.49(s, 1H, f), 7.56(d, J =8.4 Hz, 1H, d).

2'-hydroxy-2,4,6-trimethylbenzophenone (M₃BP-2OH)



$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 2.10(s, 6H, a & a'), 2.32(s, 3H, c), 6.76(ddd, J = 7.2, 7.2, 1.2 Hz, 1H, g), 6.89(s, 2H, b & b'), 7.03(dd, J = 7.2, 1.2 Hz, f), 7.16(dd, J = 7.8, 1.8 Hz, 1H, e), 7.46(ddd, J = 7.2, 7.8, 1.8 Hz, 1H, d), 12.33(s, 1H, h).

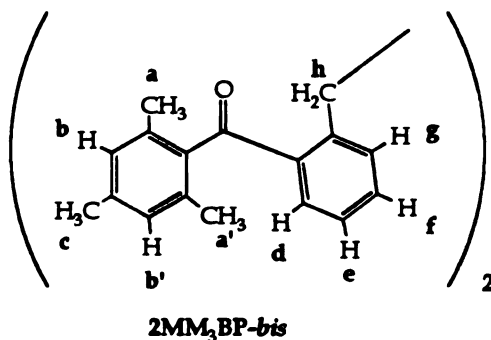
Products from 2'-methyl-2,4,6-trimethylbenzophenone (2MM₃BP).



2'-Methyl-2,4,6-trimethylbenzophenone was dissolved in 125 mL (0.5 g, 0.015 M) of benzene, degassed, and irradiated with uranium glass filtered light from a medium pressure mercury lamp at 17-20°C. The reaction was complete after ~72 hours of irradiation and a yellow color persisted. The solvent from a small fraction of the reaction solution was removed by rotoevaporation; the residue was dissolved in chloroform-*d*₁ and ¹H-NMR analysis revealed a *very* complicated spectrum. The ¹H-NMR sample tube with the crude reaction mixture was left standing and became a very deep green in color. The crude reaction mixture was separated by silica gel column chromatography (95:5 hexane:ethyl acetate) followed by a second purification with PTLC using the same solvent system. Four major products were identified as 2MM₃BP-CB, 2MM₃BP-redbis, 2MM₃BP-bis, and 2MM₃BP-pbis along with three minor products which I could not assign a structure to. However, the unidentified

products were likely dimers since their mass spectra indicated m/e peaks >400 . The **2MM₃BP-*pbis*** eluted first from the column followed by **unknown-1**, **2MM₃BP-*bis***, **unknown-2**, **2MM₃BP-*redbis*** and **unknown-3** being the last. The presumed **2MM₃BP-*CB*** was not isolated due to decomposition during chromatography but was evident in the crude $^1\text{H-NMR}$ spectrum. The characteristic AB quartet for **2MM₃BP-*CB*** was at 3.27, 3.38 ppm but it is not clear if the benzocyclobutenol was formed from hydrogen abstraction from the mesityl ring or the mono substituted ring.

1,2-di-(2'-(2'',4'',6''-trimethylphenyl)carboxy)-ethane (2MM₃BP-*bis*)



$^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ ppm: 2.12(s, 12H, a & a'), 2.32(s, 6H, c), 3.43(s, 4H, h), 6.87(s, 4H), 7.16(ddd, J = 7.5, 7.5, 1.5 Hz, 2H, e or f), 7.37(dd, J = 7.8, 1.5 Hz, 2H, d or g), 7.45(ddd, J = 7.5, 7.5, 1.5 Hz, 2H, e or f), 7.65(dd, J = 7.5, 1.5 Hz, 2H, d or g).

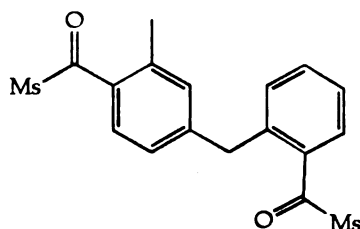
$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 19.52, 21.13, 36.39, 126.12, 128.50, 132.16, 132.25, 132.56, 134.42, 136.55, 138.46, 138.64, 144.27, 202.83.

^{13}C -DEPT(CDCl_3 , 75 MHz), CH carbons 126.12, 128.50, 132.16, 132.25, 132.56;

CH_2 carbons 36.39; CH_3 carbons 19.52, 21.13, 36.39.

LRMS, m/z: 474.4($\text{M}^{+\cdot}$), 456.3, 440.3, 223.2(100%).

2MM₃BP-*pbis*

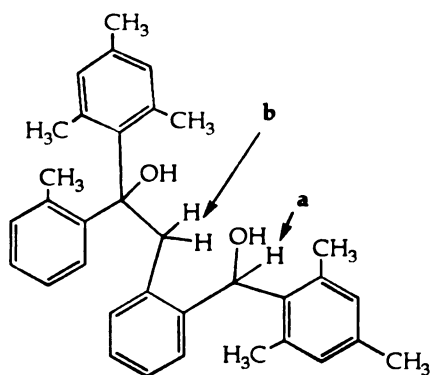


2MM₃BP-*pbis*

^1H -NMR(CDCl_3 , 300 MHz), δ ppm: 1.89(s, 6H), 2.04(s, 6H), 2.28(s, 3H) 2.60(s, 3H), 4.52 ppm (s, 2H), 6.80(s, 2H), 6.82(s, 2H), 6.96 (d, J = 7.8 Hz, 1H), 7.15 (s, 1H), 7.15-7.48 (m, 6H).

^{13}C -NMR(CDCl_3 , 75 MHz), δ ppm: 19.25(2 equivalent carbon atoms), 19.42(3 carbon atoms), 21.12(2 equivalent carbon atoms), 39.60, 126.88, 128.34, 128.47(2 overlapping resonances), 132.30, 132.47, 132.62, 132.78, 133.25, 134.12, 134.38, 134.57, 136.37, 137.97, 138.24, 138.64, 138.67, 140.09, 141.52, 145.56, 202.21 and 202.34

LRMS, m/z: 474.4(3%, $\text{M}^{+\cdot}$) , 456.3(32%), 440.3(75%), 336.3(49%), 321.2(41%), 251.1(45%), 223.2(100%), 147.1(72%), 119.2(58%), 91.1(42%), 77.1(18%).

2MM₃BP-redbis**2MM₃BP-redbis**

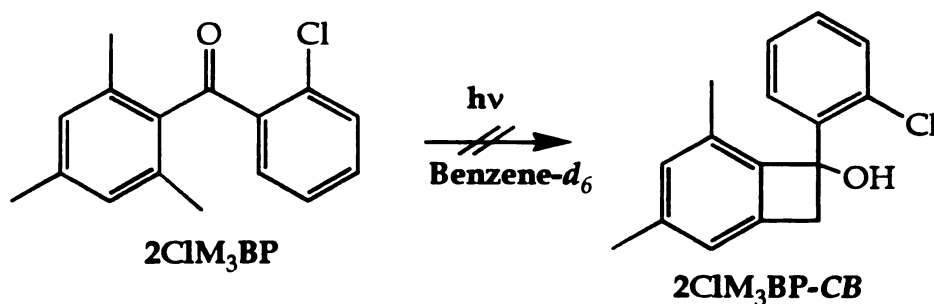
¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.23 (broad s, 1H), 1.94(s, 6H), 1.98(s, 6H), 2.17(s, 3H), 2.26(s, 3H), 2.45(s, 6H), 3.96, 4.12(AB quartet, J= 22.8 Hz, 2H, b), 6.07 (d, J= 3.6 Hz, 1H, a), 6.24 (d, J= 7.8 Hz, 1H), 6.79 (s, 3H), 6.93(s, 1H), 7.00(dd, J= 7.2, 7.2 Hz, 1H), 6.90-6.96(m, 1H), 7.14-7.30(m 4H), 7.52-7.57(m, 1H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 20.70 (2 carbons), 20.75 (2 carbons), 20.80, 20.85 (2 carbons), 20.96, 44.50 (CH₂), 71.48 (2 CH), 120.93, 123.42, 124.82, 126.39, 126.93, 127.04, 127.47, 128.64 (2 carbons), 128.85, 129.86, 130.78, 135.28, 136.63, 136.75, 136.96, 137.09, 137.60, 139.25, 140.30, 142.82, 144.27, 145.85.

¹³C-DEPT(CDCl₃, 75 MHz), δ ppm: CH carbons 71.48, 120.93, 123.42, 124.82, 126.39, 126.93, 127.04, 127.47, 128.64 (2 carbons), 128.85, 129.86, 130.78. CH₂ carbons 44.50. CH₃ carbons 20.70 (2 carbons), 20.75 (2 carbons), 20.80, 20.85 (2 carbons), 20.96.

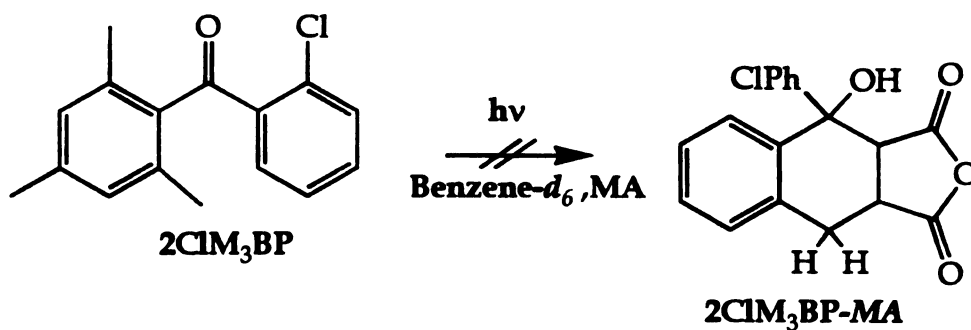
LRMS, m/z: 474.4(M⁺), 456.3, 440.3, 223.2(100%).

Products from 2'-chloro-2,4,6-trimethylbenzophenone (2ClM₃BP)



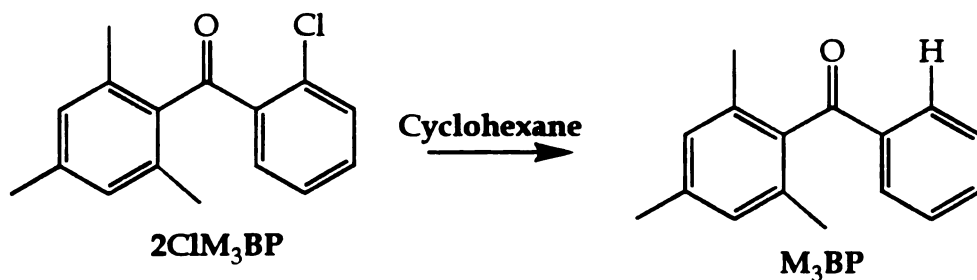
Irradiation of a 0.01 M benzene-*d*₆ solution of 2ClM₃BP did not lead to any products after 72 hours of irradiation. However, the reaction solution had turned yellow/brown. The NMR sample tube was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp at room temperature.

Irradiation of 2ClM₃BP in the presence of excess maleic anhydride.



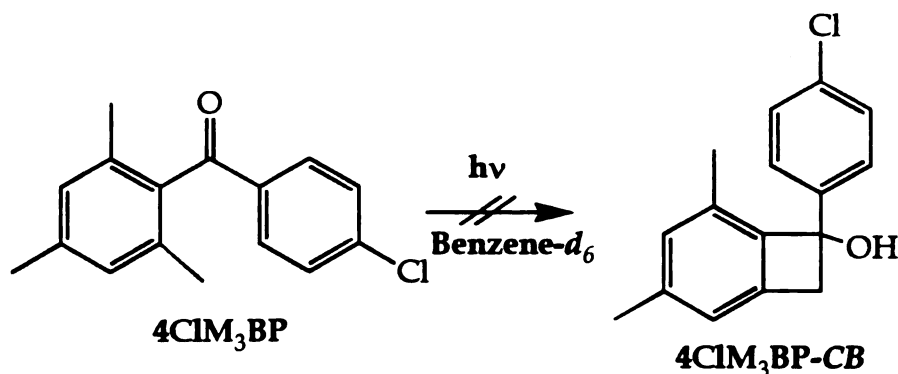
Irradiation of 2ClM₃BP in benzene with excess maleic anhydride (0.10 M MA, 0.01 M ketone) did not give any products after 24 hours of irradiation. The sample was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp at room temperature. The reaction was followed by ¹H-NMR.

Irradiation of 2ClM₃BP in cyclohexane.



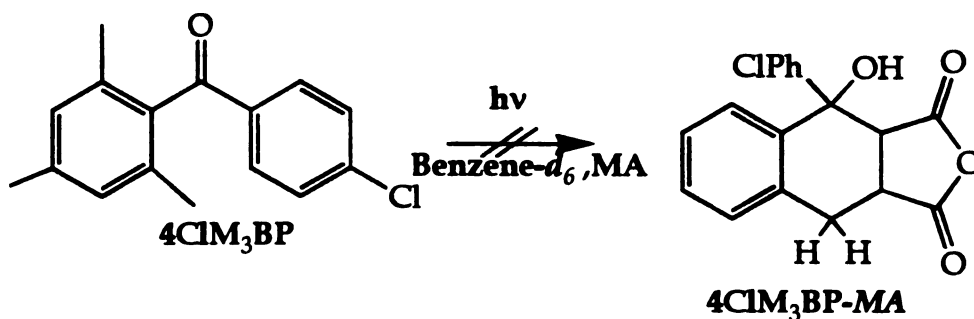
Irradiation of 0.01 M 2ClM₃BP in cyclohexane gave M₃BP after 30 minutes of irradiation (~5% of 2ClM₃BP was consumed during this time). The sample was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp at room temperature. The reaction solution was filtered through a small plug of anhydrous sodium bicarbonate and sodium sulfate and then analyzed by GC. The reaction mixture after irradiation had a stench that was attributed to HCl and also caused the septum to become brittle and turn black. The formation of M₃BP was determined by GC analysis by comparing the chromatogram of the crude reaction mixture with authentic M₃BP. Authentic M₃BP was added to reaction mixture and then injected into the GC. The added M₃BP had the exact same retention time as the unknown product in the reaction solution. This reaction was only conducted as a qualitative experiment not as a quantitative one.

Products from 4'-chloro-2,4,6-trimethylbenzophenone (4ClM₃BP)



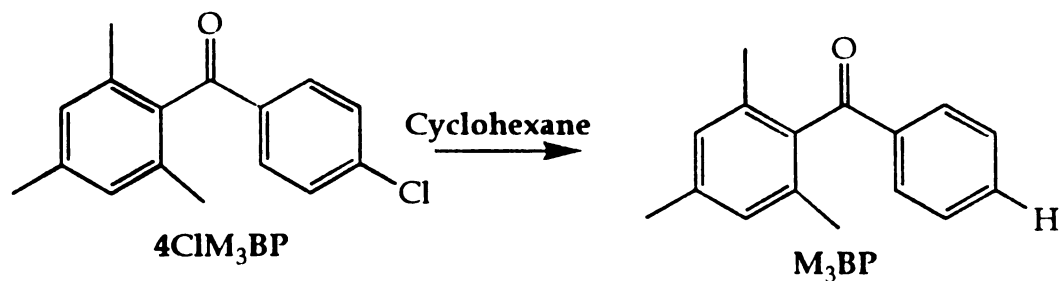
Irradiation of a 0.01 M benzene-*d*₆ solution of 4ClM₃BP did not lead to any products after 72 hours of irradiation. However, the reaction solution had turned yellow/brown. The NMR sample tube was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp at room temperature.

Irradiation of 4ClM₃BP in the presence of excess maleic anhydride.



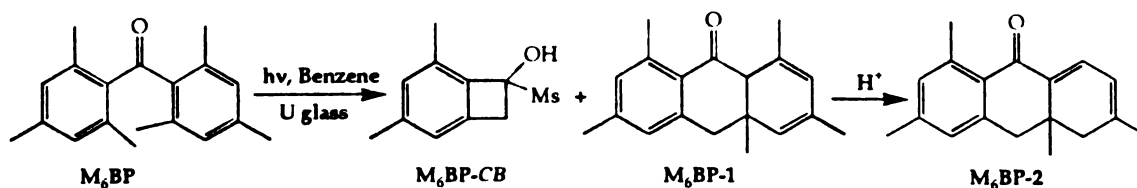
Irradiation of 4ClM₃BP in benzene with excess maleic anhydride (0.10 M MA, 0.01 M ketone) did not give any products after 48 hours of irradiation. The sample was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp at room temperature. The reaction was followed by ¹H-NMR.

Irradiation of 4ClM₃BP in cyclohexane.



This reaction was conducted in the same manner as 2ClM₃BP with similar results. The only difference with the 2' isomer was that the 4ClM₃BP reacted slower. The 4ClM₃BP reached ~5% after 1 hour irradiation whereas 2ClM₃BP reached the same conversion in 30 minutes. This reaction was only conducted as a qualitative experiment not as a quantitative one.

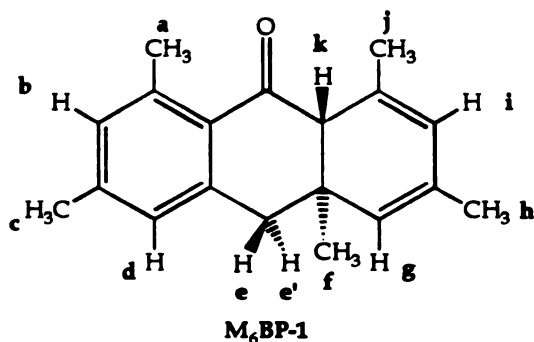
Products from 2,4,6,2'4',6'-hexamethylbenzophenone (M₆BP).



The preparative photolysis of M₆BP was carried out in 25mm x 250mm Pyrex test tubes with a medium pressure mercury arc lamp with a uranium glass filter (17-20°C). 0.5 g of Me₆BP was dissolved in 125 mL (0.015 M) of benzene and degassed. The tubes were irradiated for 36 hours and the solvent removed. A ¹H-NMR spectrum of the crude sample revealed a mixture of two products. The products were first separated by a dry flash column with TLC grade SiO₂, 1:1, CHCl₃: CCl₄, followed by PTLC with a 1:1 mixture of CHCl₃: CCl₄ as an eluent.

The first product that eluted from the column had a ^1H -NMR spectrum was consistent with the structure of *1,3,4a,7,9-pentamethyl-1a,4a-dihydroanthracene-10-one*, **M₆BP-1**. The presumed **M₆BP-1** was then subjected to prep. TLC (benzene) to remove minor impurities. After elution, two distinct bands with R_f values of 0.46 (yellow in color) and 0.69 were found. The band with $R_f=0.69$ had a ^1H -NMR spectrum consistent with the previously assigned **M₆BP-1**. The ^1H -NMR spectrum of this second product was consistent with the structure of *1,3,4a,7,9-pentamethyl-4a-dihydroanthracene-10-one*, **M₆BP-2**. The ^1H -NMR spectrum of the crude reaction products shows an AB quartet (at 3.4 ppm) which is consistent with the benzocyclobutenol product, *4,6-dimethyl-1-(2',4',6'-trimethylphenyl)-benzocyclobutenol*, **M₆BP-CB**, but decomposed and could not be isolated and characterized.

1,3,4a,7,9-pentamethyl-1a,4a-dihydroanthracene-10-one (M₆BP-1)

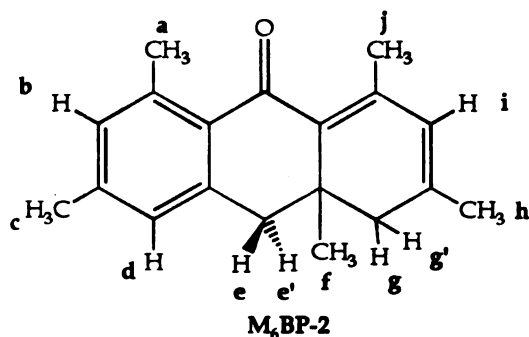


^1H -NMR(benzene- d_6 , 300 MHz), δ ppm: 0.90(s, 3H, f), 1.56(d, $J=1.8$ Hz, 3H, j or h), 1.96(s, 3H, j or h), 2.32(s, 3H, a or c), 2.44(d, $J=17$ Hz, 1H, e'), 2.63(s, 3H, a or h),

c), 2.95(d, $J = 17$ Hz, 1H, e), 3.27(s, 1H, k), 5.02(s, 1H, g or i), 5.49(q, $J = 1.8$ Hz, 1H, g or i), 6.53(s, 1H, b or d), 6.59(s, 1H, b or d).

^{13}C -NMR(benzene- d_6 , 75 MHz), δ ppm: 17.82, 21.20, 22.28, 22.82, 33.84, 44.68, 58.16, 126.18, 128.00, 128.99, 129.68, 131.11, 131.15, 134.82, 139.80, 140.95, 141.83, 199.66.

1,3,4a,7,9-pentamethyl-4,4a-dihydroanthracene-10-one ($M_6\text{BP-2}$)



^1H -NMR(CDCl_3 , 300 MHz), δ ppm: 0.81(s, 3H, f), 1.90(s, 3H), 1.97(d, $J = 17$ Hz, 1H), 2.30(s, 3H), 2.349(s, 3H), 2.35(d, $J = 17$ Hz, 1H, h or h'), 2.50(d, $J = 15$ Hz, 1H, e or e'), 2.56(s, 3H), 2.81(d, $J = 15$ Hz, 1H, e or e'), 5.81(q, $J = 1.6$ Hz), 6.82(s, 1H), 6.92(s, 1H).

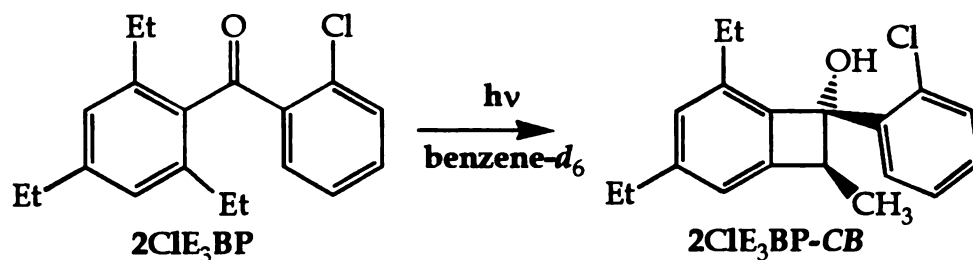
^1H -NMR(benzene- d_6 , 300 MHz), δ ppm: 0.763(s, 3H), 1.49(dd, $J = 1.5, 0.6$ Hz, 3H), 1.50(d, $J = 17$ Hz, 1H), 1.90(qd, $J = 17, 0.6$ Hz, 1H), 2.00(s, 3H), 2.16(d, $J = 14$ Hz, 1H), 2.51(s, 3H), 2.54(d, $J = 16$ Hz, 1H), 2.77(s, 3H), 5.49(q, $J = 1.5$ Hz, 1H), 6.59(s, 1H), 6.71(s, 1H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 21.38, 21.95, 22.13, 22.29, 23.90, 34.31, 43.48, 44.89, 126.66, 127.75, 131.30, 131.72, 132.24, 139.66, 141.03, 141.27, 142.57, 144.31, 190.58.

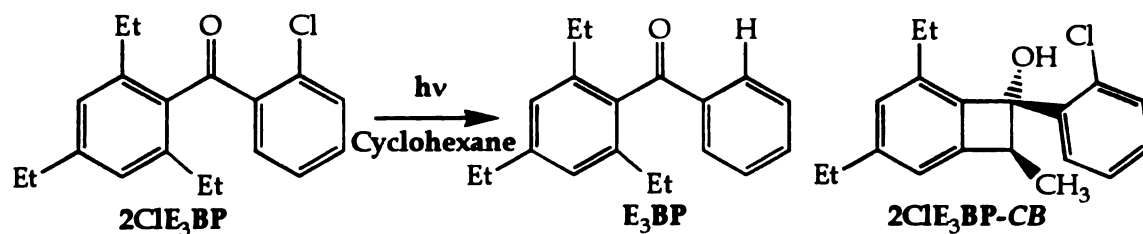
FTIR(0.025mm CCl_4 , cm^{-1}) 875.79(m), 908.59(m), 1255.82(s), 1543.25(m), 1610.77(s), 1635.84(m), 1655.13(vs), 2850.00(w), 2924.46(m), 2950.00(m).

UV-VIS Cyclohexane, yellow solution, λ_{max} =214, 277, 333 nm.

Products from 2'-chloro-2,4,6-triethylbenzophenone (2ClE₃BP)



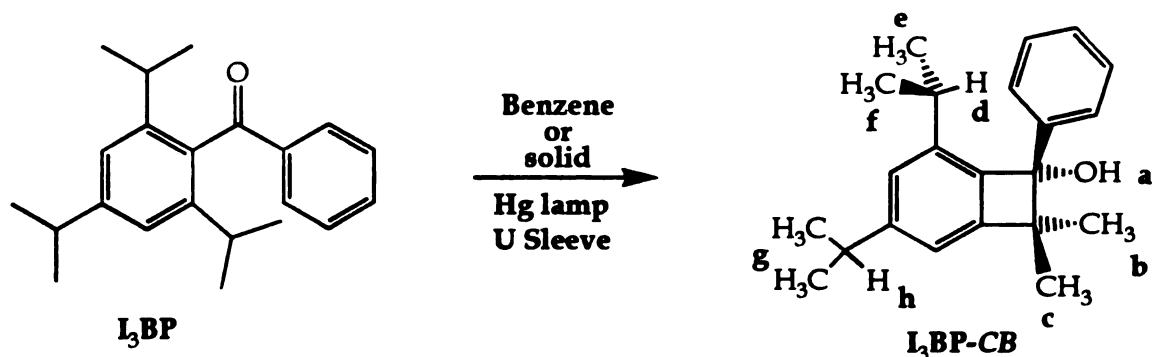
Irradiation of a 0.01 M benzene- d_6 solution of 2ClE₃BP gave a complex mixture of products. The NMR sample tube was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp. The reaction was complete after 11 hours. The major product of the crude mixture possessed a quartet at 3.72 ppm with $J = 6.9$ Hz coupling, it also contained a doublet at 1.04 ppm with a $J = 6.9$ Hz coupling. The chemical shift of the methyl doublet is in agreement with the chemical shift of the methyl cis to the 2-chlorophenyl ring in 2ClE₃BP-CB which is 1.06 ppm thus the benzocyclobutenol 2ClE₃BP-ECB is assigned the *E* configuration. No attempt was made to isolate the products.

Irradiation of 2ClE₃BP in cyclohexane.

Irradiation of a 0.01M cyclohexane solution of 2ClE₃BP gave primarily two products, E₃BP and 2ClE₃BP-CB. The sample was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp at room temperature. Periodically a small aliquot of the reaction solution was filtered through a small plug of anhydrous sodium bicarbonate and sodium sulfate and then analyzed by GC. The reaction mixture after irradiation had a stench that was attributed to HCl and also caused the septum to become brittle and turn black. The chromatogram gave a peak (~4%) with a retention time of 5.45 minutes after 30 minutes irradiation, the peak grew to ~20% of total area after 4 hours but decreased to 16% of total area after 25 hours. A standard solution of 2,4,6-triethylbenzophenone (E₃BP) gave a retention time of 5.56 minutes while the starting ketone 2ClE₃BP had a retention time of 11.65 minutes. A second peak was also visible after 30 minutes irradiation with a retention time of 15.11 minutes and ~6% of total area. This peak grew to 15% of the total area after 4 hours irradiation but decreased to 11% of the total area after irradiating the sample 25 hours. Authentic E₃BP was added to reaction mixture and then injected into the GC. The added E₃BP had the exact same retention time as the unknown product (at ~5.45 min) in the reaction solution. ¹H-NMR analysis

confirmed that 2ClE₃BP-CB was formed. The same solution that was analyzed by GC was also analyzed by ¹H-NMR after removal of the cyclohexane by evaporation. No attempt was made to isolated any of the photoproducts

Product from 2,4,6-triisopropylbenzophenone (I₃BP).



A 0.75 mL benzene-*d*₆ solution containing 7.7 mg (0.025 mmol, 0.033 M) of I₃BP was degassed and irradiated through a uranium glass filter sleeve. The sample was hung outside the immersion well setup and the reaction was complete after 45 minutes giving only one major product. A preparative scale reaction was carried out in the solid state by placing 340 mg (1.10 mmol) of finely powdered I₃BP between two 1" x 3" glass slides that were held together by clear tape. A small amount of solid was washed from the glass plates with chloroform-*d*₁ and analyzed by ¹H-NMR periodically. The reaction was complete after 5 hours of irradiation with uranium glass filtered light; no precautionary measure was taken to exclude air from the sample. The slides were rinsed with methylene chloride. The solvent was removed by rotoevaporation and a clear viscous liquid remained. The crude product was purified by

PTLC with 97:3 hexane:ethyl acetate as the eluent and gave 240 mg (73%) of a pure white solid which had spectral data consistent with I₃BP-CB. The I₃BP-CB eluted from the HPLC (flow= 1.0 mL/min., 92:8, hexane:ethyl acetate, Microsorb Si80-125-CS silica gel column) with a retention time of 4.56 minutes while the ketone eluted in 3.01 minutes. For ¹H-NMR spectral data of the NMR experiment see Figure 51

4,6-diisopropyl-1-phenyl-2,2-dimethylbenzocyclobutenol (I₃BP-CB)

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 0.85(s, 3H, c), 1.16(d, J= 6.9 Hz, 3H, f), 1.26(d, J= 6.9 Hz, 3H, e), 1.31(d, J=6.9 Hz, 6H, g), 1.49(s, 3H, b), 2.58(s, 1H, a), 2.94(septet, J= 6.9 Hz, 1H, d), 2.95(septet, J= 6.9 Hz, 1H, h), 6.92(s, 1H), 7.10(s, 1H), 7.31(m, 5H).

¹H-NMR(Benzene-*d*₆, 300 MHz), δ ppm: 0.886(s, 3H, c), 1.14(d, J= 6.9 Hz, 3H, f), 1.17(d, J= 6.9 Hz, 3H, e), 1.203(d, J= 6.9 Hz, 6H, g), 1.33(s, 3H, b), 2.18(s, 1H, a), 2.79(septet, J= 6.9 Hz, 1H, d), 2.87(septet, J= 6.9 Hz, h), 6.87(d, J=1.2 Hz, 1H), 7.0-7.1(m, 4H), 7.34(d, J= 8.0 Hz, 2H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 22.64, 24.00, 24.29, 24.36, 24.54, 24.71, 30.36, 35.03, 54.54, 85.86, 116.07, 123.82, 126.64, 127.02, 127.68, 139.93, 142.53, 145.06, 151.27, 152.86.

FTIR(0.025mm CCl₄, cm⁻¹) 871.94(m), 1610.77(w), 2870.44(m), 2928.32(m), 2963.04(vs), 3028.63(w), 3615.06(m, OH, sharp).

UV-VIS Cyclohexane, $\epsilon_{227} = 16,000 \text{ M}^{-1}$ ($\lambda_{\text{max}} = 227 \text{ nm}$), $\epsilon_{267} = 2,840 \text{ M}^{-1}$ ($\lambda_{\text{max}} = 267 \text{ nm}$), $\epsilon_{275} = 2,550 \text{ M}^{-1}$ ($\lambda_{\text{max}} = 275 \text{ nm}$), $\epsilon_{313} = 42.3 \text{ M}^{-1}$.

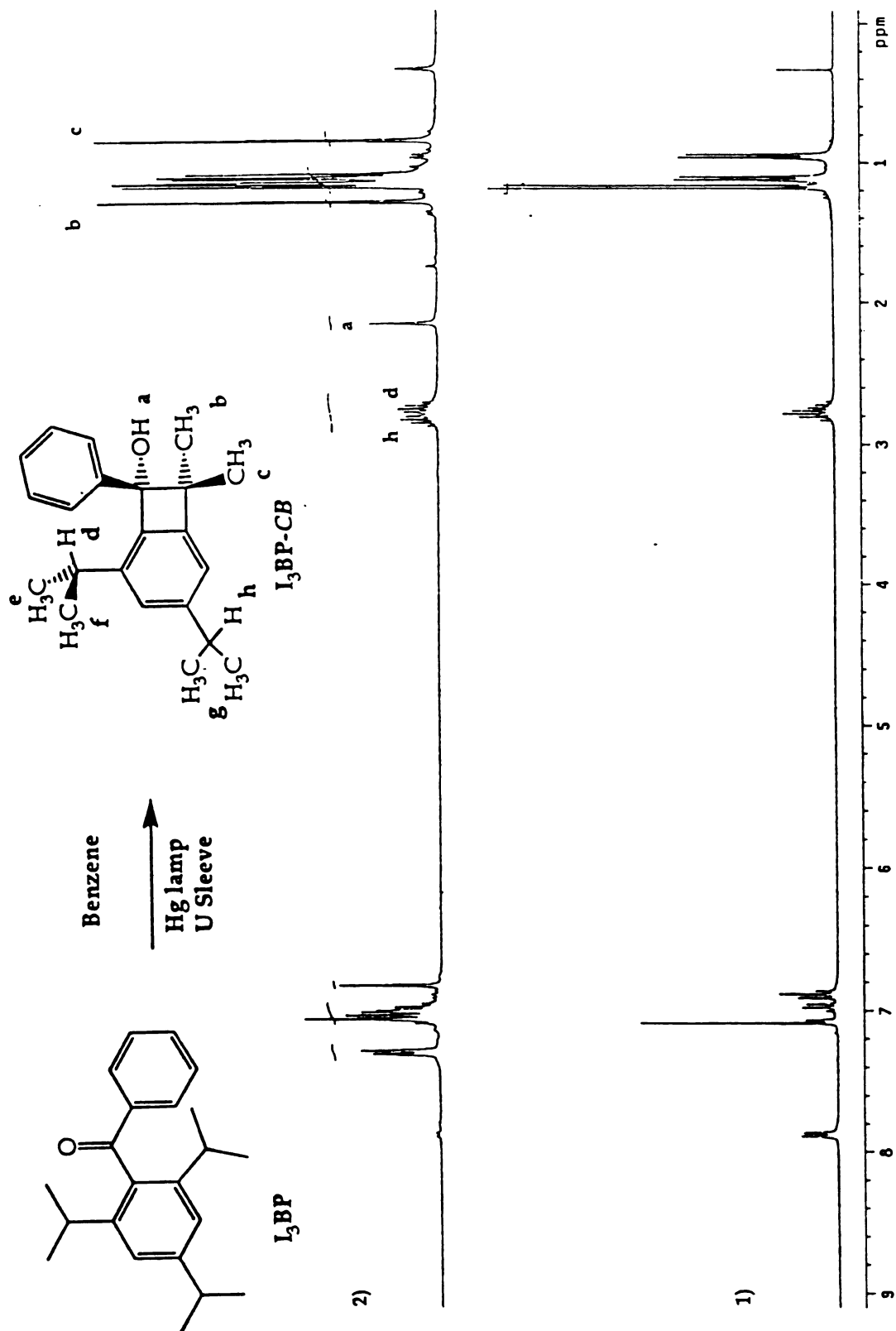
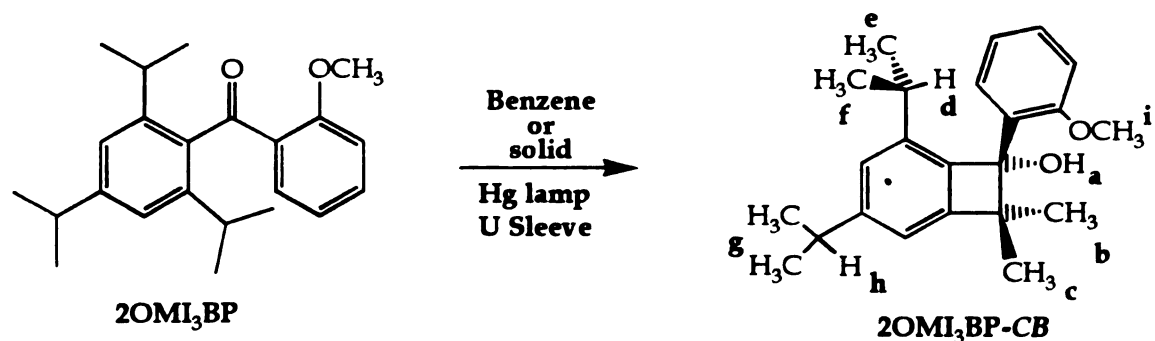


Figure 51. ¹H-NMR Spectra of I₃BP in benzene-*d*₆ 1) before irradiation 2) after 15 minutes irradiation.

Product from 2'-methoxy-2,4,6-triisopropylbenzophenone (2OMI₃BP).

The solution photochemistry of 2OMI₃BP was carried out by the same procedure as used for I₃BP and gave only one product after 25 minutes of irradiation. The solid state photochemistry was also carried out by the same procedure as used for I₃BP. The crude product was purified by PTLC with 97:3, hexane:ethyl acetate as the eluent and gave 154 mg (62%) of a pure white solid which had spectral data consistent with 2OMI₃BP-CB. The 2OMI₃BP-CB eluted from the HPLC (flow= 1.0 mL/min., 96:4, hexane:ethyl acetate, Microsorb Si80-125-CS silica gel column) with a retention time of 10.54 minutes while the ketone eluted in 11.52 minutes. For ¹H-NMR spectral data of the NMR experiment see Figure 52.

4,6-diisopropyl-1-(2'-methoxyphenyl)-2,2-dimethylbenzocyclobutenol (2OMI₃BP-CB).

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 0.88(s, 3H, c), 1.29(d, J= 6.9 Hz, 3H, f), 1.30(d, J= 6.9 Hz, 6H, g), 1.38(d, J= 6.9 Hz, 3H, e), 1.53(s, 3H, b), 2.94(septet, J= 6.9 Hz, 1H, d), 3.09(septet, J= 6.9 Hz, 1H, h), 3.96(s, 3H, i), 4.58(s, 1H, a), 6.88(s, 1H), 6.90(dd, J= 7.7, 7.7 Hz, 1H), 6.97(d, J= 8.1 Hz, 1H), 7.01(dd, J=7.4, 1.7 Hz, 1H), 7.11(s, 1H), 7.27(ddd, J= 8.1, 7.7, 1.7 Hz, 1H).

¹H-NMR(benzene-*d*₆, 300 MHz), δ ppm: 0.96(s, 3H, c), 1.21(d, J= 6.9 Hz, 3H, f), 1.22(d, J=6.9 Hz, 3H, e), 1.34(d, J=6.9 Hz, 3H, g), 1.37(d, J= 6.9 Hz, 3H, g), 1.65(s, 3H, b), 2.82(septet, J=6.9 Hz, 1H, d), 3.05(s, 3H, i), 3.28(septet, J= 6.9 Hz, 1H, h), 4.62(s, 1H, a), 6.41(d, J=8.2 Hz, 1H), 6.63(dd, J= 7.5, 7.4 Hz, 1H), 6.94(ddd, J= 8.1, 7.5, 1.8 Hz, 1H), 7.09(dd, J= 7.4, 1.6 Hz, 1H), 7.20(s, 3H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 22.22, 23.44, 24.05, 24.31, 24.37, 25.17, 30.18, 35.05, 53.69, 55.21, 86.81, 110.34, 116.04, 120.52, 122.94, 128.31, 129.04, 130.81, 137.67, 145.29, 150.99, 152.25, 157.01.

FTIR(0.025mm CCl₄, cm⁻¹) 870.01,(w), 941.38(w), 1230.74(vs), 1593.40(w), 2800.00(w), 2850.00(m), 2900.00(m), 2961.11(vs), 3555.26(m, sharp).

UV-VIS Cyclohexane, ϵ_{226} = 4,870 M⁻¹ (λ_{max} =226 nm), ϵ_{270} = 2,250 M⁻¹, (λ_{max} =270 nm), ϵ_{313} =74.6 M⁻¹.

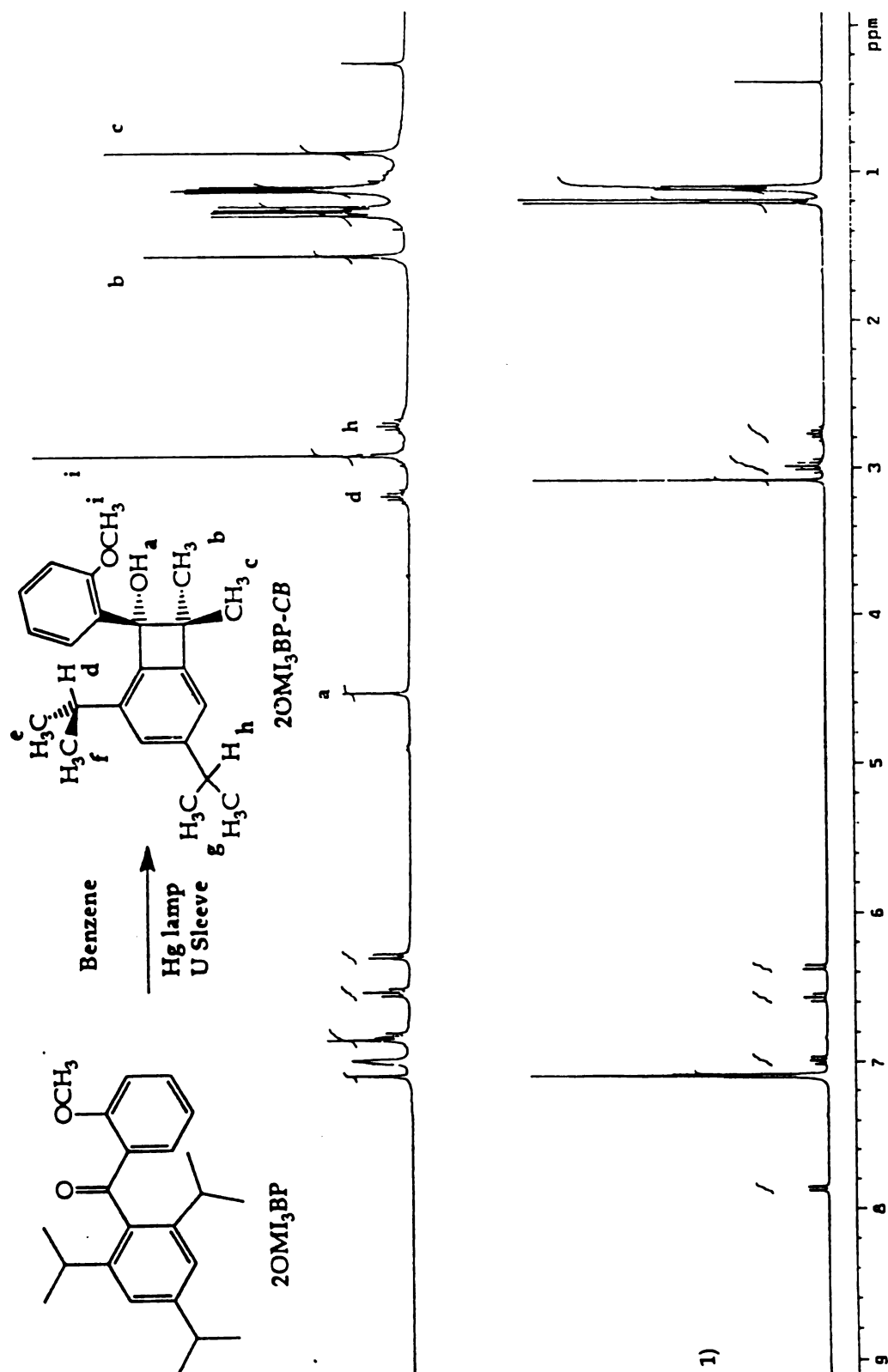
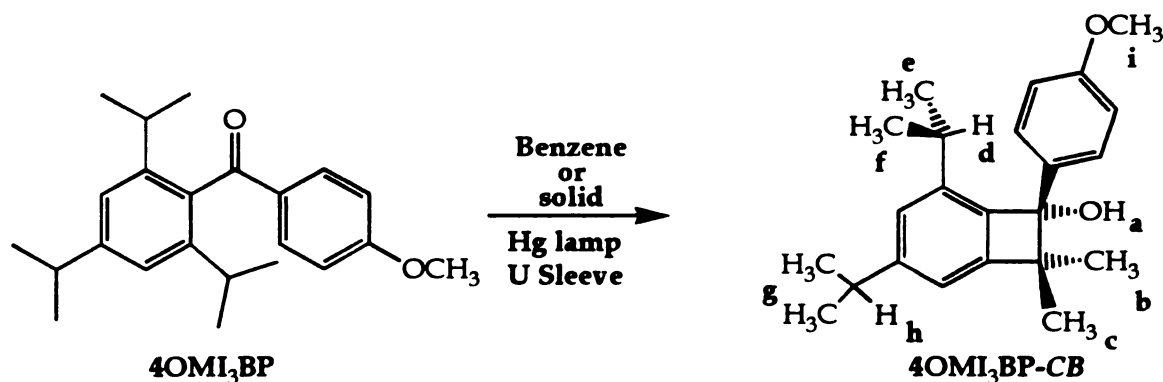


Figure 53. ^1H -NMR Spectra of 2OMI₃BP in benzene- d_6 1) before irradiation 2) after 25 minutes irradiation.

Product from 4'-methoxy-2,4,6-triisopropylbenzophenone (4OMI₃BP).



The solution photochemistry of 4OMI₃BP was carried out by the same procedure as used for I₃BP and gave only one product after 25 minutes of irradiation. The solid state photochemistry was also carried out by the same procedure as used for I₃BP. The crude product was purified by PTLC with 97:3, hexane:ethyl acetate as the eluent and gave 88 mg (57%) of a pure white solid which had spectral data consistent with 4OMI₃BP-CB. The 4OMI₃BP-CB eluted from the HPLC (flow= 1.0 mL/mL, 92:8, hexane:ethyl acetate, Microsorb Si80-125-CS silica gel column) with a retention time of 6.86 minutes while the starting ketone eluted in 5.40 minutes. For ¹H-NMR spectral data of the NMR experiment see Figure 53.

4,6-diisopropyl-1-(4'-methoxyphenyl)-2,2-dimethylbenzocyclobutenol (4OMI₃BP-CB).

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 0.84(s, 3H, c), 1.19(d, J=6.9 Hz, 3H, f), 1.25(d, J=6.9 Hz, 3H, e), 1.29(d, J=6.9 Hz, 6H, g), 1.46(s, 3H, b), 2.56(broad s, 1H, a), 2.887(septet, J= 6.9 Hz, 1H), 2.896(septet, J= 6.9 Hz, 1H), 3.79(s, 3H, i), 6.84(d, J= 8.9 Hz, 2H), 6.90(s, 1H), 7.07(s, 1H), 7.20(d, J=8.6 Hz, 2H).

¹H-NMR(benzene-*d*₆, 300 MHz), δ ppm: 0.923(s, 3H, c), 1.15(d, J= 6.9 Hz, 3H, f), 1.197(d, J= 6.9Hz, 6H, g, e), 1.202(d, J= 6.9 Hz, 3H, g), 1.34(s, 3H, b), 2.18(s, 1H, a), 2.79(septet, J= 6.9 Hz, 1H, d), 2.90(septet, J= 6.9 Hz, 1H, h), 3.21(s, 3H, i), 6.68(d, J= 9.0 Hz, 2H), 6.87(d, J= 1.5 Hz, 1H), 7.10(d, J= 1.5 Hz, 1H), 7.25(d, J= 8.7 Hz, 2H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 22.62, 23.94, 24.28, 24.35, 24.61, 24.72, 30.35, 35.00, 54.57, 55.09, 85.57, 112.98, 116.06, 123.74, 127.79, 134.85, 140.19, 144.99, 151.18, 152.88, 158.57.

FTIR(0.025mm CCl₄, cm⁻¹) 831.43(w), 871.94(m), 1240.10(vs), 1512.38(s), 1585.69(w), 1612.70(m), 2835.72(w), 2870.44(m), 2930.24(m), 2961.11(vs), 3615.06(m, OH, sharp).

UV-VIS Cyclohexane, ε₂₂₇= 16,000 M⁻¹ (λ_{max}=227 nm), ε₂₆₇= 2,840 M⁻¹(λ_{max}=267 nm), ε₂₇₅= 2,550 M⁻¹(λ_{max}=275 nm), ε₃₁₃=42.3 M⁻¹.

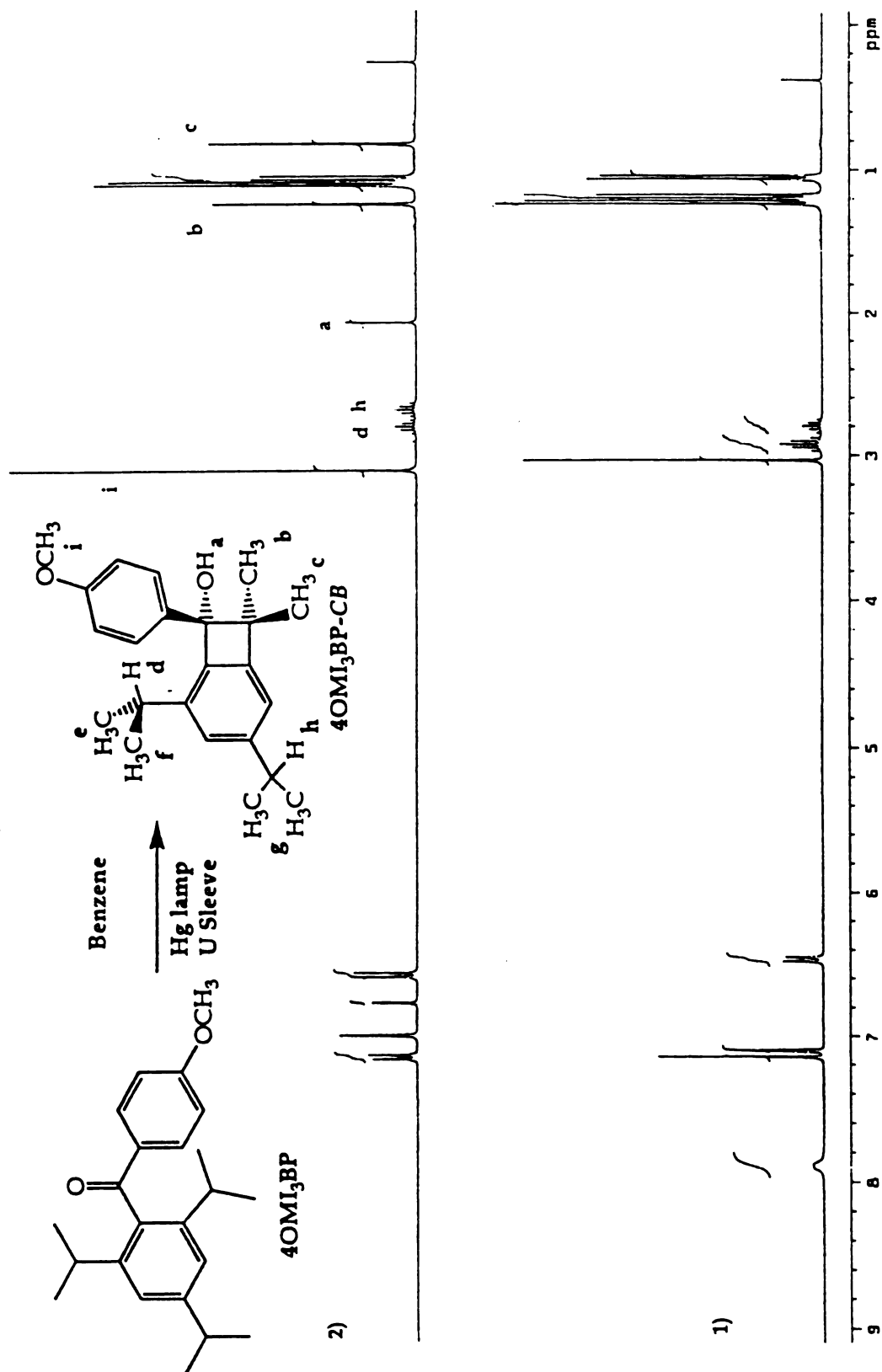
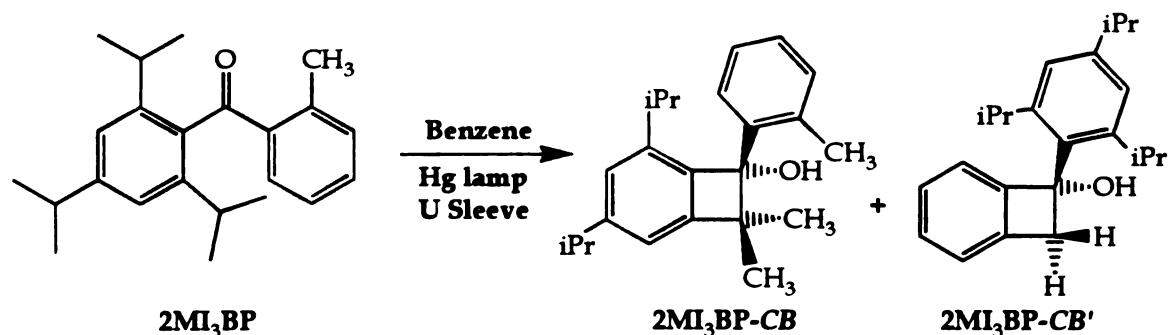


Figure 53. ¹H-NMR Spectra of 4OMI₃BP in benzene-*d*₆ 1) before irradiation 2) after 45 minutes irradiation.

Product from 2'-methyl-2,4,6-triisopropylbenzophenone (2MI₃BP).



The solution photochemistry of 2MI₃BP was carried out by the same procedure as used for I₃BP. The reaction was complete after 19 hours and gave two major product, 2MI₃BP-CB and 2MI₃BP-CB' in a 1:2.7 ratio. The solid state photochemistry was also carried out by the same procedure as used for I₃BP. The ketone did not react after 17 hours of continuous irradiation in the solid. For ¹H-NMR spectral data of the NMR experiment see Figure 54. The products were not isolated because they decomposed on the PTLC plate.

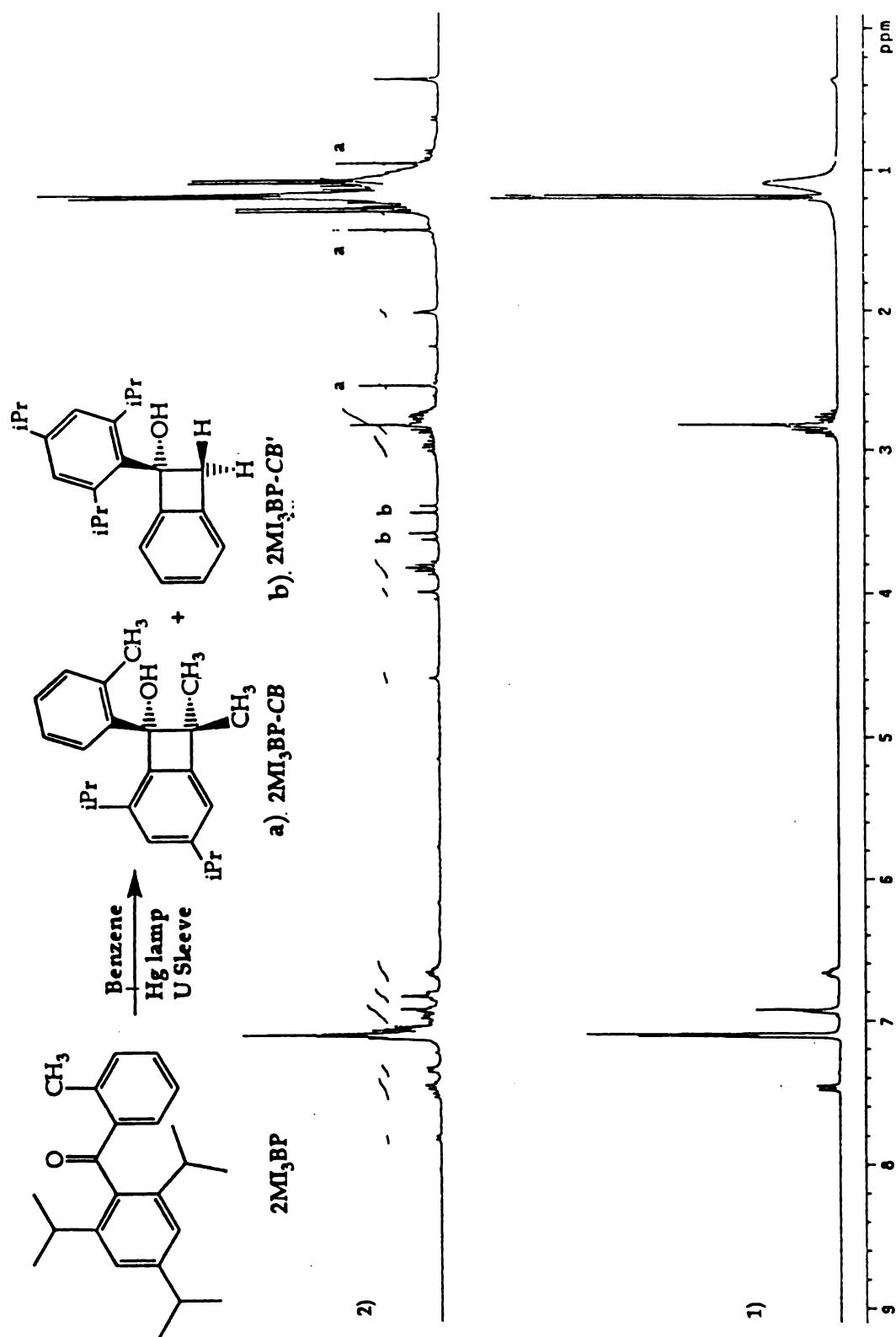
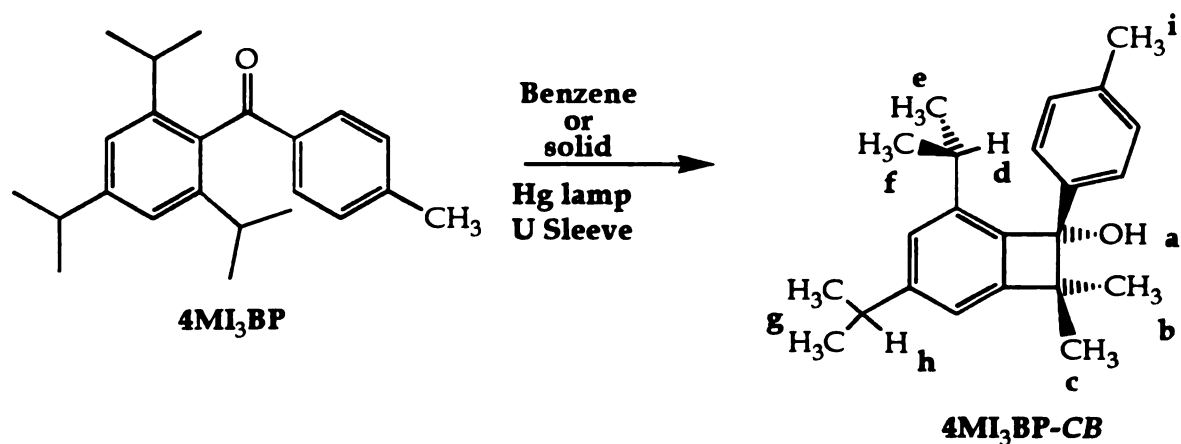


Figure 54. ^1H -NMR Spectra of $2\text{MI}_3\text{BP}$ in $\text{benzene-}d_6$ 1) before irradiation 2) after 19 hours irradiation.

Product from 4'-methyl-2,4,6-triisopropylbenzophenone (4MI₃BP).



The solution photochemistry of 4MI₃BP was carried out by the same procedure as used for I₃BP and gave only one product after 25 minutes of irradiation. The solid state photochemistry was also carried out by the same procedure as used for I₃BP. The crude product was purified by PTLC with 97:3, hexane:ethyl acetate as the eluent and gave 154 mg (62%) of a pure white solid which had spectral data consistent with 4MI₃BP-CB. The 4MI₃BP-CB eluted from the HPLC (flow = 1.0 mL, 95:5, hexane:ethyl acetate, Microsorb Si80-125-CS silica gel column) with a retention time of 6.70 minutes while the starting ketone eluted in 4.51 minutes. For ¹H-NMR spectral data of the NMR experiment see Figure 55.

4,6-diisopropyl-1-(4'-methylphenyl)-2,2-dimethylbenzocyclobutenol (4MI₃BP-CB)

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 0.807(s, 3H, c), 1.16(d, J= 7.0 Hz, 3H, f), 1.22(d, J= 6.9 Hz, 3H, e), 1.27(d, J= 6.9 Hz, 6H, g), 1.44(s, 3H, b), 2.32(s, 3H, i),

2.89(septet, $J = 6.9$ Hz, 1H, **d**), 2.91(septet, $J = 6.9$ Hz, 1H, **h**), 6.87(s, 1H), 7.05(s, 1H), 7.10(distorted d, $J = 8.2$ Hz, 2H), 7.15(distorted d, $J = 8.3$ Hz, 2H).

$^1\text{H-NMR}$ (benzene- d_6 , 300 MHz), δ ppm: 0.922(s, 3H, **c**), 1.15(d, $J = 6.9$ Hz, 3H, **f**), 1.188(d, $J = 6.9$ Hz, 3H, **e**), 1.193(d, $J = 6.9$ Hz, 6H, **g**), 1.34(s, 3H, **b**), 2.03(s, 3H, **i**), 2.20(s, 1H, **a**), 2.78(septet, $J = 6.8$ Hz, 1H, **d**), 2.89(septet, $J = 6.9$ Hz, 1H, **h**), 6.87(s, 2H), 6.91(d, $J = 8.1$ Hz, 2H), 7.27(d, $J = 8.0$ Hz, 2H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 21.11, 22.58, 23.95, 24.27, 24.34, 24.62, 24.74, 30.35, 35.01, 54.47, 85.79, 116.03, 123.73, 126.56, 128.40, 136.55, 139.58, 140.13, 145.02, 151.18, 152.91.

FTIR(0.025mm CCl_4 , cm^{-1}) 871.94(m), 912.45(w), 1057.13(m), 1161.29(w), 1192.16(w), 1363.85(m), 1462.23(m), 1514.31(w), 2870.44(m), 2928.32(m), 2961.11(vs), 3615.06(w),

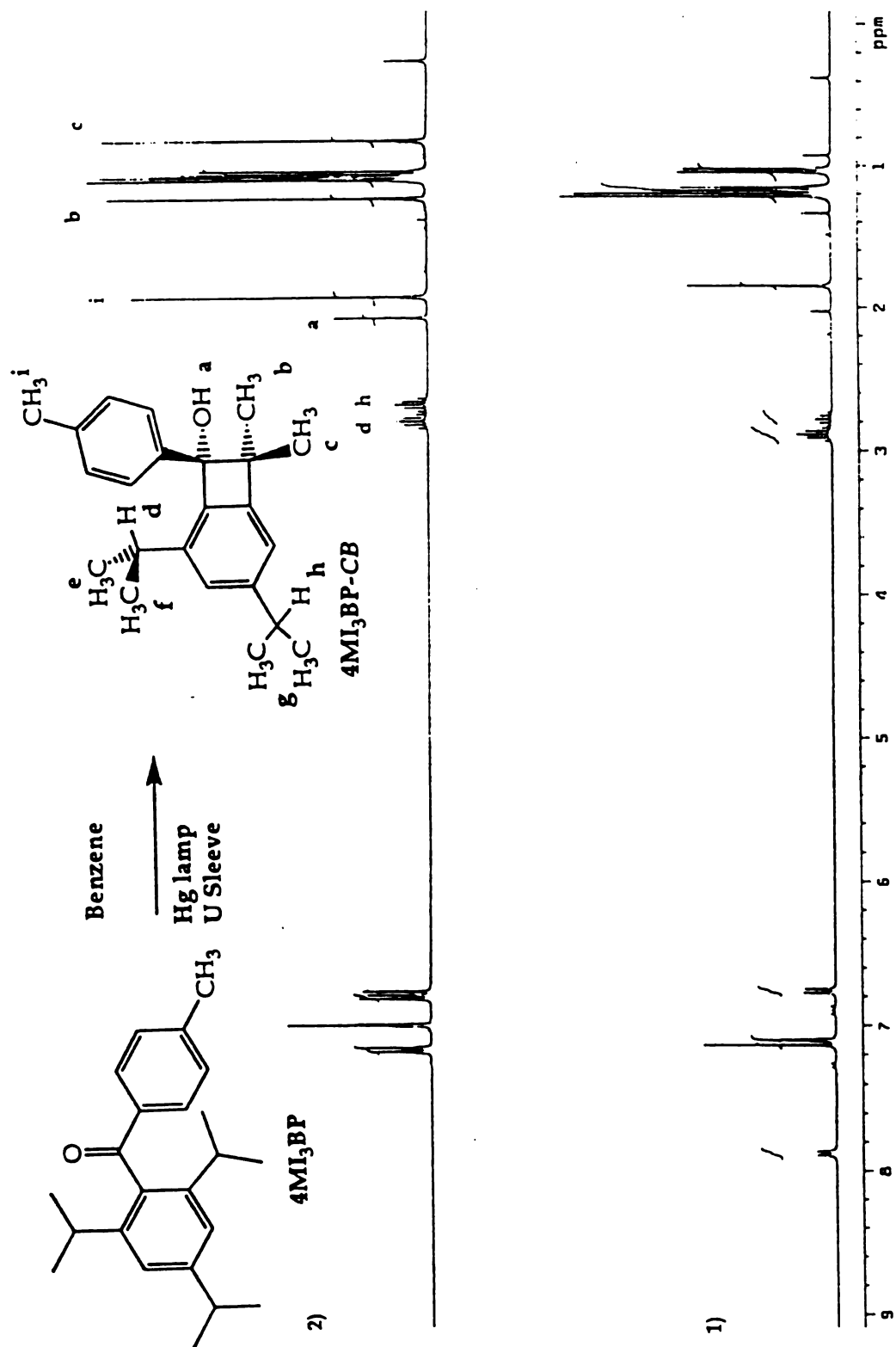
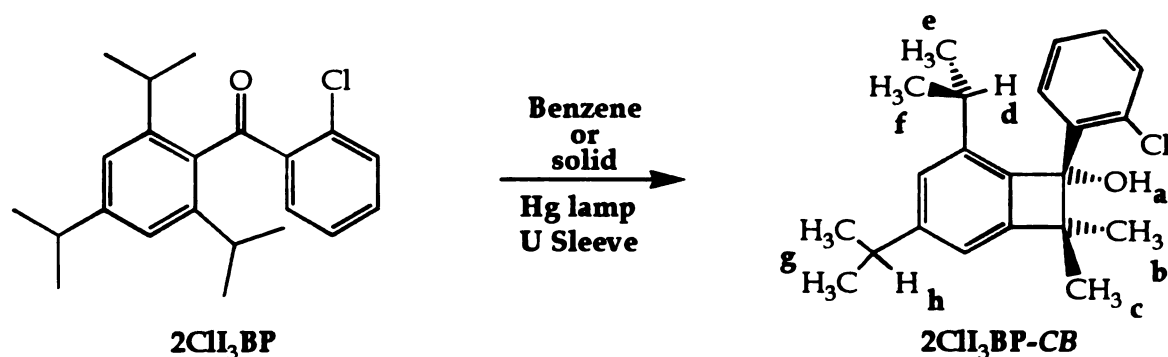


Figure 55. ^1H -NMR Spectra of $4\text{MI}_3\text{BP}$ in $\text{benzene-}d_6$ 1) before irradiation 2) after 25 minutes irradiation.

Product from 2'-chloro-2,4,6-triisopropylbenzophenone (2ClI₃BP).



The solution photochemistry of 2ClI₃BP was carried out by the same procedure as used for I₃BP and gave only one product after 45 minutes of irradiation. The solid state photochemistry was also carried out by the same procedure as used for I₃BP. The crude product was purified by PTLC with 95:5, hexane:ethyl acetate as the eluent and gave 154 mg (62%) of a pure white solid which had spectral data consistent with 2ClI₃BP-CB. The 2ClI₃BP-CB eluted from the HPLC (flow= 1.0 mL/min., 97:3, hexane:ethyl acetate, Microsorb Si80-125-CS silica gel column) with a retention time of 4.93 minutes while the starting ketone eluted in 4.62 minutes. For ¹H-NMR spectral data of the NMR experiment see Figure 56.

4,6-diisopropyl-1-(2'-chlorophenyl)-2,2-dimethylbenzocyclobutenol (2ClI₃BP-CB)

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.07(s, 3H, c), 1.31(d, J= 6.9 Hz, 3H, f), 1.33(d, J= 6.9 Hz, 6H, g), 1.42(d, J= 6.9 Hz, 3H, e), 1.65(s, 3H, b), 2.98(septet, J= 6.9 Hz, 1H, d), 3.11(septet, J= 6.9 Hz, 1H, h), 3.73(s, 1H, a), 6.94(s, 1H), 7.16(s, 1H), 7.21-7.30(m, 3H), 7.48(d, J= 6.8 Hz, 1H).

$^1\text{H-NMR}$ (benzene- d_6 , 300 MHz), δ ppm: 1.06(s, 3H, c), 1.17(d, J = 6.9 Hz, 3H), 1.19(d, J =6.9 Hz, 3H), 1.27(d, J = 6.9 Hz, 3H), 1.28(d, J = 6.9 Hz, 3H), 1.59(s, 3H, b), 2.77(septet, J = 7.0 Hz, 1H, d), 3.10(septet, J = 7.0 Hz, 1H, h), 3.69(broad s, 1H, a), 6.62-6.65(m, 2H), 6.86(d, J = 0.6 Hz 1H), 7.05-7.13(m, 2H), 7.16(d, J = 0.6 Hz, 1H)

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 22.14, 23.51, 23.97, 24.33, 25.25, 30.09, 35.07, 54.36, 87.44, 116.07, 123.22, 126.38, 128.62, 130.67, 132.29, 137.59, 139.78, 145.06, 151.45, 151.90.

FTIR(0.025mm CCl_4 , cm^{-1}): 871.94(m), 941.38(w), 1591.48(w), 1616.55(w), 2870.44(m), 2900.00(m), 2928.32(m), 2961.11(vs), 3576.48(m, OH, sharp).

UV-VIS Cyclohexane, ϵ_{232} = 5,600 M^{-1} (λ_{max} =232 nm), ϵ_{267} = 1,440 M^{-1} (λ_{max} =267 nm), ϵ_{275} = 1,350 M^{-1} (λ_{max} =275 nm), ϵ_{313} =15.8 M^{-1} .

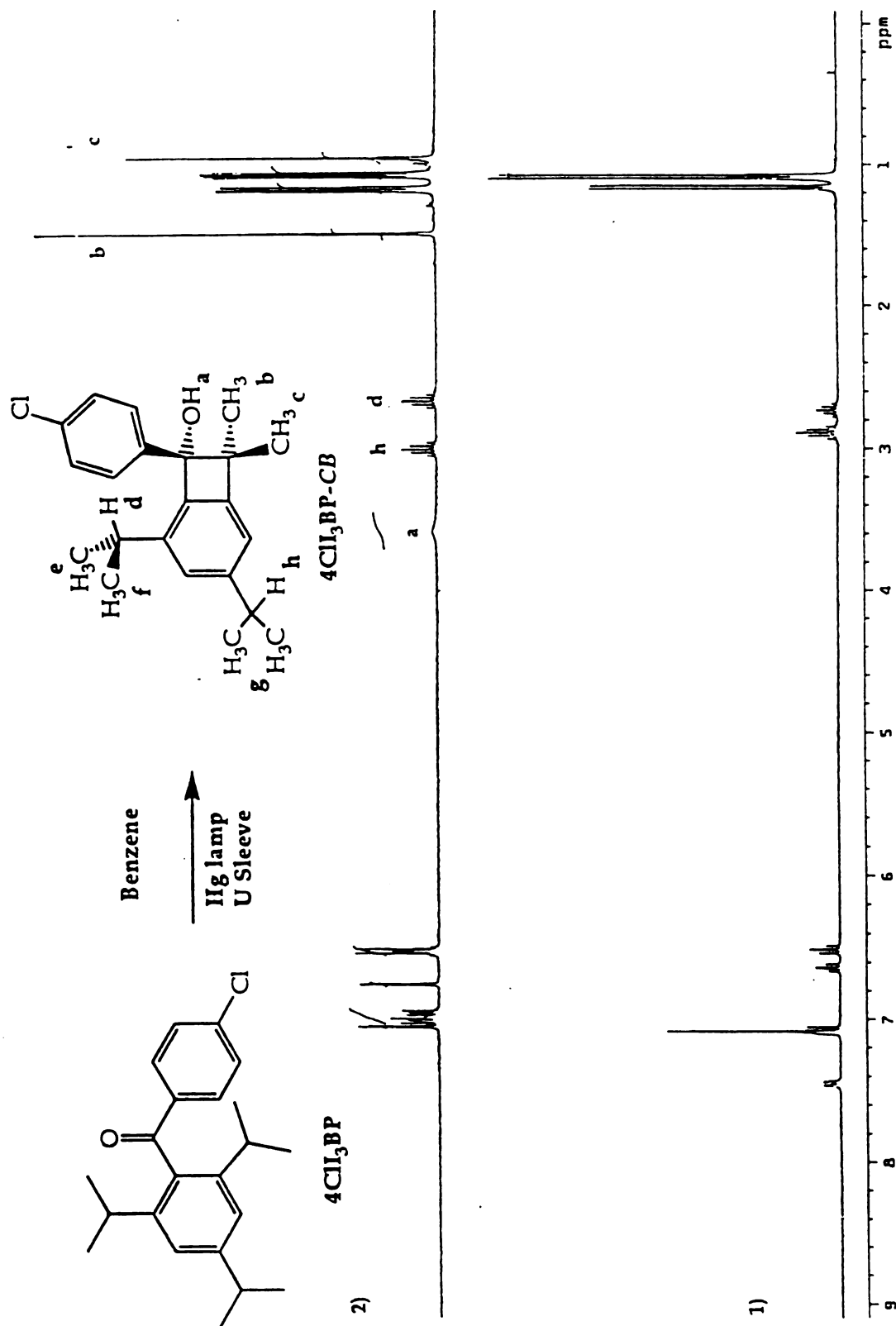
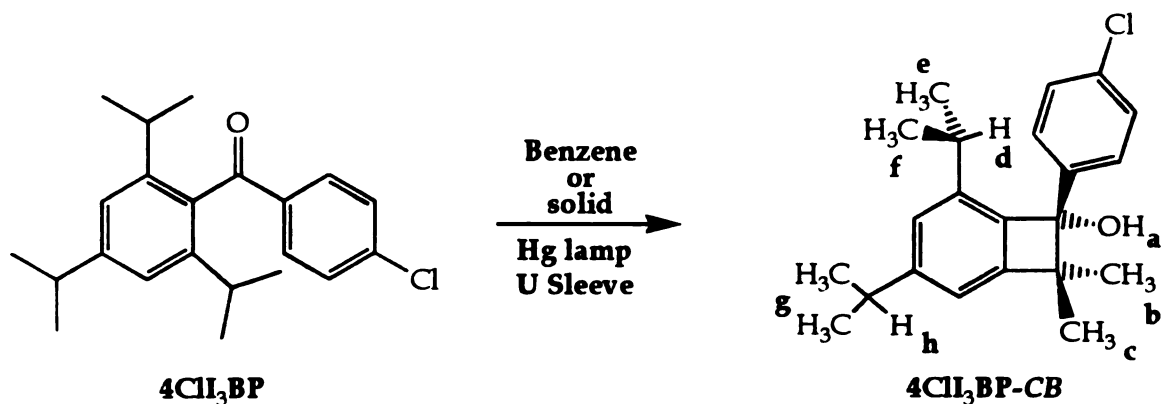


Figure 56. ^1H -NMR Spectra of $2\text{ClI}_3\text{BP}$ in $\text{benzene-}d_6$ 1) before irradiation 2) after 1 hour irradiation.

Product from 4'-chloro-2,4,6-triisopropylbenzophenone (4ClI₃BP).



The solution photochemistry of 4ClI₃BP was carried out by the same procedure as used for I₃BP and gave only one product after 45 minutes of irradiation. The solid state photochemistry was also carried out by the same procedure as used for I₃BP. The crude product was purified by PTLC with 97:3, hexane:ethyl acetate as the eluent and gave 110 mg (39%) of a pure white solid which had spectral data consistent with 4ClI₃BP-CB. The 4ClI₃BP-CB eluted from the HPLC (flow= 1.0 mL/min, 97:3, hexane:ethyl acetate, Microsorb Si80-125-CS silica gel column) with a retention time of 4.59 minutes while the starting ketone eluted in 7.87 minutes. For ¹H-NMR spectral data of the NMR experiment see Figure 57.

4,6-diisopropyl-1-(4'-chlorophenyl)-2,2-dimethylbenzocyclobutenol (4ClI₃BP-CB).

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 0.800(s, 3H, c), 1.15(d, J= 7.0 Hz, 3H, f), 1.20(d, J=7.0 Hz, 3H, e), 1.26(d, J= 6.9 Hz, 6H, g), 1.43(s, 3H, b), 2.52(s, 1H, a),

2.84(septet, $J=6.9$ Hz, 1H, d), 2.91(septet, $J= 6.9$ Hz, 1H, h), 6.87(s, 1H,), 7.04(s, 1H), 7.18(d, $J= 8.6$ Hz, 2H), 7.26(d, $J=8.6$ Hz, 2H).

$^1\text{H-NMR}$ (benzene- d_6 , 300 MHz), δ ppm: 0.780(s, 3H, c), 1.09(d, $J= 6.9$ Hz, 3H, f), 1.11(d, $J=6.9$ Hz, 3H, e), 1.18(d, $J= 6.9$ Hz, 6H, g), 1.22(s, 3H, b), 2.10(broad s, 1H, a), 2.76(septet, $J=6.9$ Hz, 2H, d & h), 6.82(s, 1H), 7.01(d, $J= 8.8$ Hz, 2H), 7.06(s, 1H), 7.08(d, $J= 8.8$ Hz, 2H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 22.71, 24.04, 24.26, 24.34, 24.45, 24.62, 30.47, 35.03, 54.62, 85.38, 116.18, 124.10, 127.82, 128.11, 132.76, 139.52, 141.5, 145.04, 151.59, 152.76.

FTIR(0.025mm CCl_4 , cm^{-1}) 871.94(w), 910.52(w), 2872.37(w), 2928.32(m), 2963.04(vs), 3616.99(w, sharp).

UV-VIS Cyclohexane, $\epsilon_{226}= 11,400 \text{ M}^{-1}$ ($\lambda_{\text{max}}=226 \text{ nm}$), $\epsilon_{268}= 1,320 \text{ M}^{-1}$ ($\lambda_{\text{max}}=268 \text{ nm}$), $\epsilon_{276}= 1,150 \text{ M}^{-1}$ ($\lambda_{\text{max}}=276 \text{ nm}$), $\epsilon_{313}=15.8 \text{ M}^{-1}$.

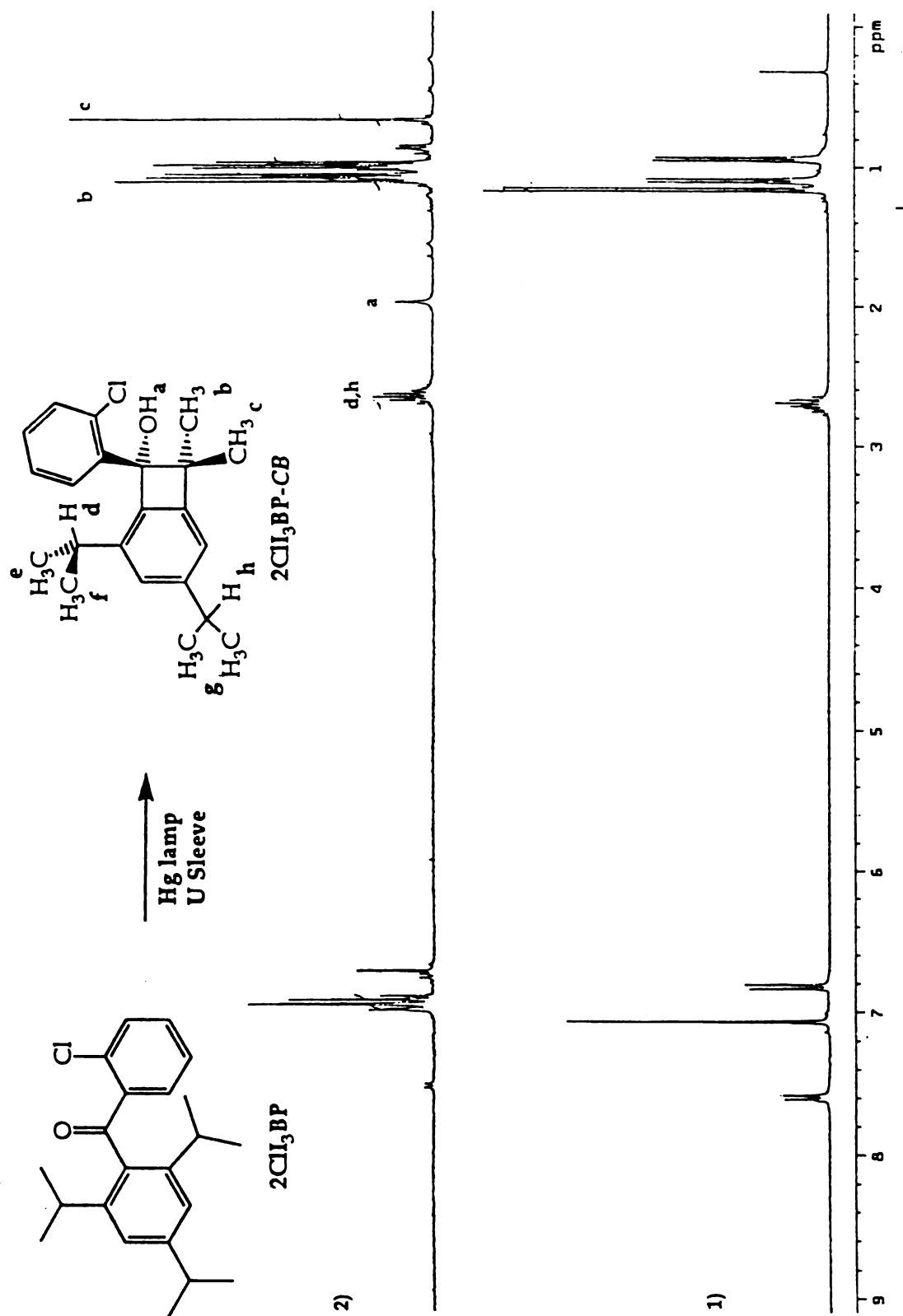
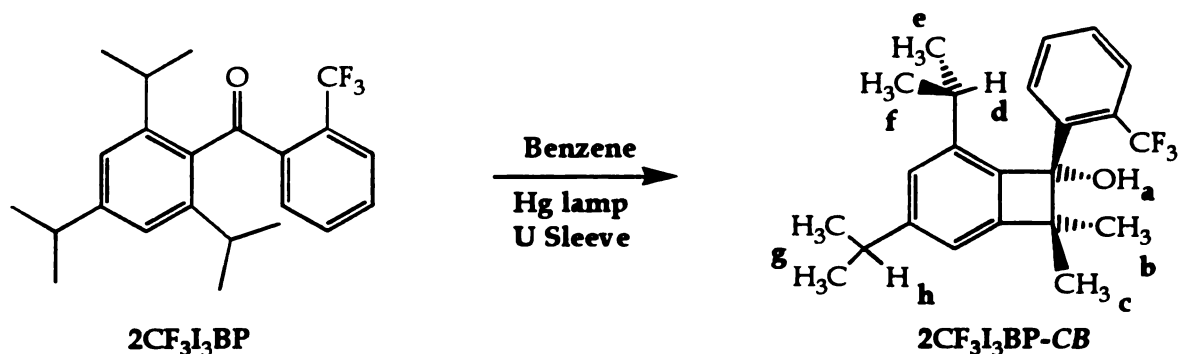


Figure 57. ^1H -NMR Spectra of $4\text{ClI}_3\text{BP}$ in $\text{benzene-}d_6$ 1) before irradiation 2) after 1 hour irradiation.

Product from 2'-(α,α,α -trifluoromethyl)-2,4,6-triisopropylbenzophenone ($2\text{CF}_3\text{I}_3\text{BP}$).



The solution photochemistry of $2\text{CF}_3\text{I}_3\text{BP}$ was carried out by the same procedure as used for I_3BP and gave only one product after 20 hours of irradiation. The solid state photochemistry was also carried out by the same procedure as used for I_3BP but gave no products after 24 hours of irradiation. The preparative photolysis was carried out in 25mm x 250mm Pyrex test tubes, 100 mg (0.27 mmol, 0.018 M) of $2\text{CF}_3\text{I}_3\text{BP}$ was dissolved in 15 mL of benzene and degassed. The tube was irradiated for 24 hours after which the starting ketone had reacted completely. The solvent was removed and the ^1H -NMR spectrum of the crude sample revealed one product. The crude product was purified by PTLC with 97:3, hexane:ethyl acetate as the eluent and gave 45 mg (45%) of a pure white solid which had spectral data consistent with $2\text{CF}_3\text{I}_3\text{BP-CB}$. The $2\text{CF}_3\text{I}_3\text{BP-CB}$ eluted from the HPLC (flow= 1.0 mL/min, 97:3, hexane:ethyl acetate, Microsorb Si80-125-CS silica gel column) with a retention time of 5.44 minutes while the starting ketone eluted in 5.11 minutes. The reaction of $2\text{CF}_3\text{I}_3\text{BP}$ in the solid state gave no products after 26 hours of irradiation with

uranium glass filtered light from a medium pressure mercury arc lamp. For ^1H -NMR spectral data of the NMR experiment see Figure 58.

4,6-diisopropyl-1-(2'-(α,α,α -trifluoromethyl)-phenyl)-2,2-dimethyl-1,2-benzocyclobuten-1-ol (2CF₃I₃BP-CB)

^1H -NMR(CDCl_3 , 300 MHz), δ : 0.91(s, 3H, c), 1.21(d, J = 6.9 Hz, 3H, f), 1.27(d, J = 6.9 Hz, 3H, e), 1.30(d, J =6.9 Hz, 6H, g), 1.50(s, 3H, b), 2.68(s, 1H, a), 2.89(septet, J = 6.9, d Hz, 1H), 2.94(septet, J = 6.9 Hz, 1H, h), 6.91(s, 1H), 7.12(s, 1H), 7.10(m, 1H), 7.37(m, 2H), 7.80(m, 1H).

^1H -NMR(benzene- d_6 , 300 MHz), δ ppm: 0.915(s, 3H, c), 1.07(d, J = 6.9 Hz, 3H, f), 1.14(d, J = 6.9 Hz, 3H, e), 1.16(d, J = 6.9 Hz, 3H, g), 1.17(d, J = 6.9 Hz, 3H, g), 1.33(s, 3H, b), 2.43(broad s, 1H, a), 2.75(septet, J = 6.9 Hz, 1H, d), 2.78(septet, J = 6.9 Hz, 1H, h), 6.70-6.80(m, 2H), 6.80(d, J =1.2 Hz, 1H), 7.1(d, masked by solvent, J =1.2 Hz, 1H), 6.99(dd, J = 7.2 Hz, 1.5 Hz, 1H), 7.58(dd, J = 7.8 Hz, 1.5 Hz, 1H).

^{13}C -NMR(CDCl_3 , 75 MHz), δ ppm: 22.43, 23.06, 23.09, 24.27, 24.32, 24.92, 29.85, 35.04, 55.42, 87.69, 116.1, 123.7, 124.4(q, $J_{\text{C-F}}$ = 272 Hz), 125.2, 127.9(q, $J_{\text{C-F}}$ = 27.3 Hz), 130.7, 130.8, 139.7, 144.8, 151.7, 152.2.

FTIR(0.025mm CCl_4 , cm^{-1}) 871.94(w), 1037.83(m), 1066.77(w), 1140.08(m), 1273.18(w), 1309.83(vs), 2870.44(w), 2930.24(w), 2963.04(m), 3620.85(w, sharp).

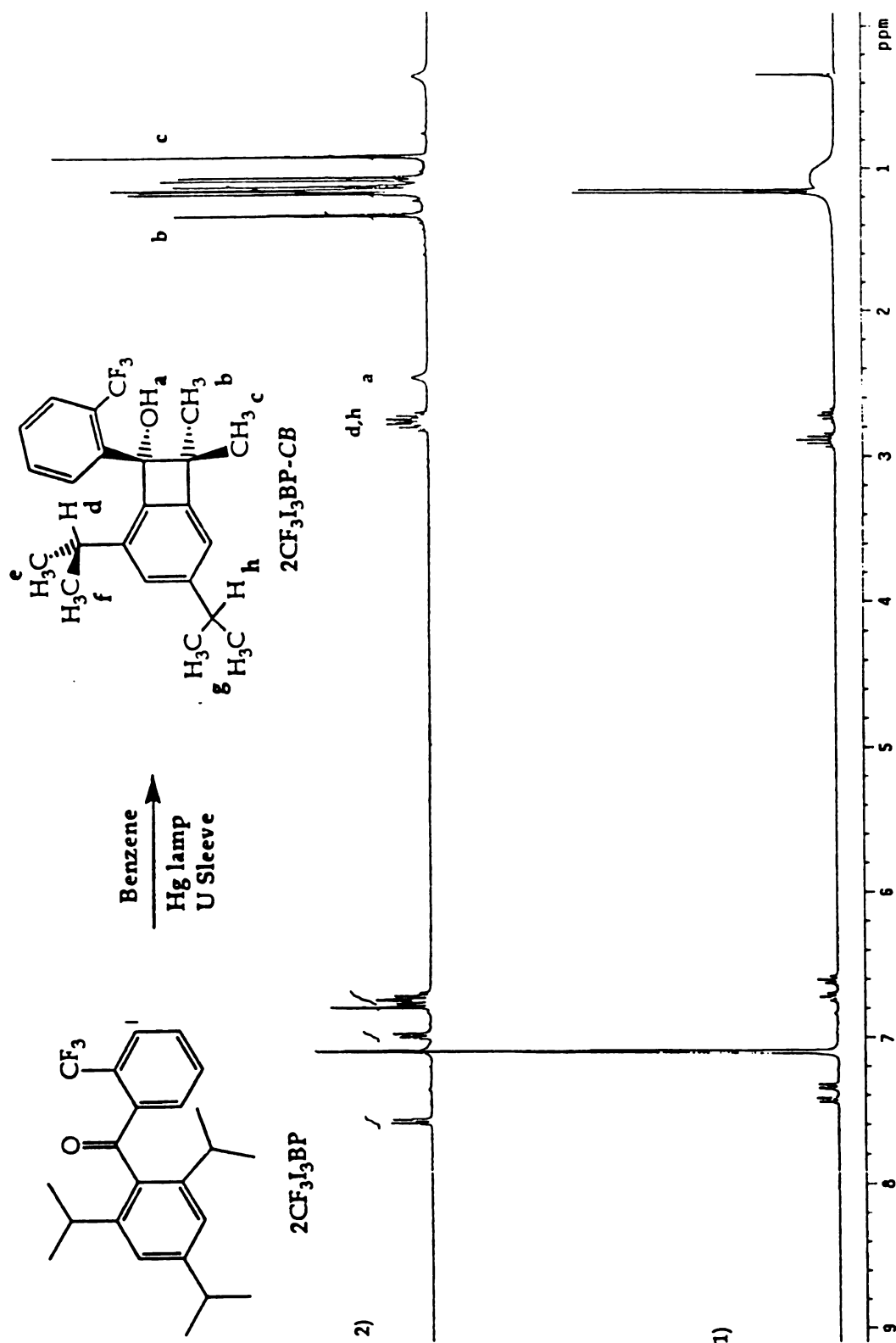
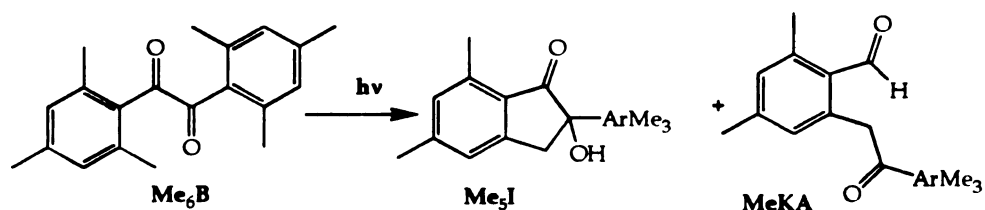


Figure 59. ^1H -NMR Spectra of $2\text{CF}_3\text{I}_3\text{BP}$ in benzene- d_6 1) before irradiation 2) after 19 hours irradiation.

Products from 2,4,6,2',4',6'-hexamethylbenzil (Me₆B)

The reaction was carried out in the solid state by placing 250 mg of finely powdered Me₆B between two 1" x 3" glass slides that were held together by clear tape. The samples were hung outside the immersion well setup and irradiated with ~438 nm filtered light; emission at 438 nm was achieved with a uranium glass filter sleeve and filter solution of 20 g CuSO₄, 25g of NaNO₂ and 34 mL of concentrated ammonium hydroxide diluted to 500 mL. No precautionary measure was taken to exclude air from the samples. A small amount of solid was washed from the glass plates with chloroform-*d*₁ and analyzed by ¹H-NMR periodically. The reaction was complete after 8 days of irradiation. The slides were rinsed with methylene chloride. The solvent was removed by rotoevaporation and a pale yellow solid remained. The crude product was purified by PTLC with 95:5, hexane:ethyl acetate as the eluent. One major product was isolated which had a ¹H-NMR spectrum consistent with Me₃I. The PTLC plate was eluted several times to obtain adequate separation from minor products but this made it difficult to calculate a R_f value for the Me₃I. The Me₃I was furthered purified by PTLC with 97:3, hexane:ethyl acetate gave 52 mg (25% yield) of a white solid. The following spectral data are consistent with Park's

findings.¹⁰³ MeKA was not isolated but was apparent in the ¹H-NMR reaction mixture.

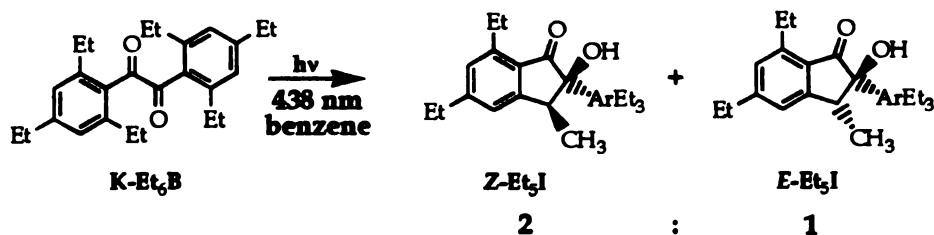
2-hydroxy-2-(2',4',6'-trimethylphenyl)-5,7-dimethyl-1-indanone (Me₃I)

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 2.21(s, 3H), 2.24(s, 6H), 2.38(s, 3H), 2.63(s, 3H), 2.75(broad singlet, 1H), 3.33(¹/₂ AB quartet, J=17.9 Hz, 1H), 3.54(¹/₂ AB quartet, J=17.8 Hz, 1H), 6.81(s, 2H), 6.98(s, 1H), 7.02(s, 1H).

¹H-NMR(benzene-*d*₆, 300 MHz), δ ppm: 2.19(s, 3H), 2.29(s, 3H), 2.34(s, 6H), 2.51(s, 3H), 3.09(¹/₂ AB quartet, J= 17.9 Hz, 1H), 3.44(¹/₂ AB quartet, J= 17.9 Hz, 1H), 6.52(s, 1H), 6.59(s, 1H), 6.72(s, 1H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 18.35, 20.50, 21.99, 23.34, 42.57, 82.04, 124.44, 130.04, 130.90, 136.38, 136.49, 137.46, 139.89, 146.26, 206.57.

Products from 2,4,6,2',4',6'-hexaethylbenzil(Et₆B).

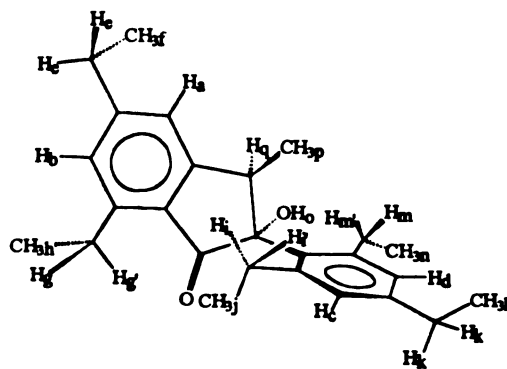


2,4,6,2',4',6'-hexaethylbenzil was irradiated on NMR and preparative scales. The NMR tube reaction was carried out by irradiating a degassed 0.01 M benzene-*d*₆ solution with ~438 nm light at room temperature. The progress of the reaction was monitored by ¹H-NMR analysis. The reaction was approximately

90% complete after 24 hours, but took an additional 36 hours for the reaction to reach completion. The NMR spectrum of the crude reaction sample was virtually uninterpretable due to overlapping peaks.

The preparative reaction sample was prepared using the same technique that was applied to the NMR scale sample except with 40mg of Et₆B. Two isomeric products were separated by PTLC using silica gel as a stationary phase and benzene as the eluent. After the spectrum for each purified isomer was obtained in benzene-*d*₆, the product ratio was determined from the crude NMR scale spectra. Integration of the methyl doublets gave a Z:E ratio of 2:1.

***E*-2-hydroxy-2-(2'4'6'-triethylphenyl)-3-methyl-5,7-diethyl-1-indanone (E-Et5I)**



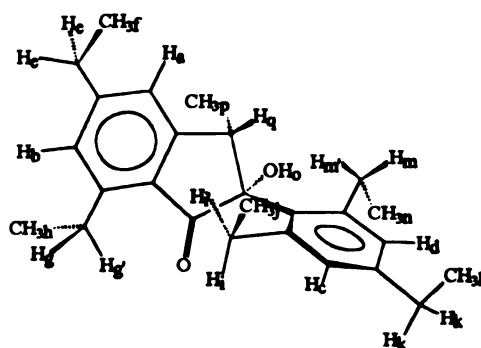
¹H-NMR(500MHz, CDCl₃) δ ppm: 0.986(**p**, *d*, J=7.5 Hz; 3H), 1.09(**j**, *t*, J=7.0 Hz; 3H), 1.22(**l**, *t*, J=7.5Hz; 3H), 1.25(**h**, *t*, J=7.5Hz; 3H), 1.28(**f**, *t*, J=7.5 Hz; 3H), 1.31(**n**, *t*, J=7.5 Hz; 3H), 2.07(**i** & **i'**, *q*, J=7.0Hz; 2H), 2.58(**k**, *q*, J=7.5Hz; 2H), 2.67(**m**, *q* of *d*, J=21.5, 6.5; 2H), 2.71(**e**, *q*, J=7.5 Hz, 2H), 3.06(**g** & **g'**, AB *quartet* of *quar*, J=14 Hz, 6.5Hz; 2H), 3.10(**m'**, *q* of *d*, J=21.5, 6.5; 2H), 3.60(**q**, *q*, J=7.5 Hz; 1H), 6.83(**c**, *d*, J=1.5 Hz; 1H), 6.96(**d**, *d*, J=1.5 Hz; 1H), 7.04(**b**, *s*; 1H), 7.11(**a**, *s*, 1H).

$^1\text{H-NMR}$ (500MHz, benzene- d_6) δ ppm: 0.885(p, d, $J=8.0$ Hz; 3H), 0.960(t, $J=7.5$ Hz; 3H), 1.09(t, $J=7.5$ Hz; 3H), 1.14(t, $J=7.5$ Hz; 3H), 1.24(t, $J=7.5$ Hz; 3H), 1.26(t, $J=7.5$ Hz; 3H), 2.05(i, q of d, $J=15$ Hz, 7.5 Hz; 1H), 2.20(i', q of d, $J=15$ Hz, 7.5 Hz; 1H), 2.31(q, $J=7.5$ Hz; 2H), 2.42(q, $J=7.5$ Hz; 2H), 2.64(o, s; 1H), 2.71(m, q of d, $J=14$ Hz, 7.5 Hz; 1H), 3.18(g&g', AB quartet of quar, $J=14$ Hz,6.5Hz; 2H), 3.17(m', q of d, $J=14$ Hz, 7.5 Hz; 1H), 3.571(q, q, $J=7.5$ Hz, 1H) 6.75(b?, s; 1H), 6.78(c&d, broad s; 2H), 6.95(a?, d, $J=1$ Hz; 1H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ ppm: 14.84, 15.12, 15.19, 15.28, 17.30, 18.71, 24.96, 28.25, 28.54, 29.46, 29.70, 45.27, 85.07, 122.68, 126.13, 128.10, 128.43, 128.45, 135.07, 141.02, 142.68, 145.80, 146.26, 152.58, 157.79, 204.58.

FTIR (0.025 mm, CDCl_3 , cm^{-1}) 3560, 2970, 2936, 2876, 1707, 1605, 1460, 1210, 876.

Z-2-hydroxy-2-(2'4'6'-triethylphenyl)-3-methyl-5,7-diethyl-1-indanone (*Z*-Et₃I)



$^1\text{H-NMR}$ (500MHz, CDCl_3) δ ppm: 1.13(j&n, very broad t, $J=7.5$ Hz; 6H), 1.21(l?, t, $J=7.5$ Hz; 3H), 1.26(t, $J=7.5$ Hz; 3H), 1.28(f, t, $J=7.5$ Hz; 3H), 1.46(p, d, $J=7$ Hz; 3H), 2.42(i&m or i&m', very broad singlet, line width at $\frac{1}{2}$ height = 225Hz; 2H), 2.57(k, q, $J=7.5$ Hz; 2H), 2.61(o, broad s; 1H), 2.71(e, q, 7.5 Hz; 2H), 2.76(i&m or

i'&m', *very broad singlet*, line width at $\frac{1}{2}$ height = $\sim 300\text{Hz}$; 2H), 3.05 and 3.12(**g&g'**, *AB quartet of quar*, $J=14\text{ Hz}$, 7.5 Hz ; 2H), 3.44(**q**, *q*, $J=7\text{Hz}$; 1H), 6.88(**c&d**, *broad s*; 2H), 7.05(**b**, *s*, 1H), 7.08(**a**, *s*, 1H).

$^1\text{H-NMR}$ (500MHz, benzene- d_6) δ ppm: 0.936(**l**, *t*, $J=7.5\text{ Hz}$; 3H), 1.06(**f**, *t*, $J=7.5\text{ Hz}$; 3H), 1.09(**j&n**, *broad triplet*, $J=7.5\text{ Hz}$; 6H), 1.26(**h**, *t*, $J=7.5\text{ Hz}$; 3H), 1.40(**p**, *d*, $H=7\text{ Hz}$; 3H), 2.30(**e**, *q*, $J=7.5\text{Hz}$; 2H), 2.39(**k**, *q*, 7.5 Hz ; 2H), 2.46(**i&m** or **i'&m'**, *very broad singlet*, line width at $\frac{1}{2}$ height = 180Hz ; 2H), 2.63(**o**, *s*; 1H), 2.79(**i&m** or **i&m'**, *very broad singlet*, line width at $\frac{1}{2}$ height = 300Hz ; 2H), 3.12 and 3.21(**g&g'**, *AB quartet of quar*, $J=13\text{ Hz}$, 7.5 Hz ; 2H), 3.38(**q**, *q*, $J=7\text{Hz}$; 1H), 6.76(**b**, *s*; 1H), 6.77(**a**, *s*, 1H), 6.81(**c&d**, *broad s*; 2H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ ppm: 13.94, 14.83,, 15.13, 15.18, 16.96(*broad*, 2 C's), 25.0, 27.93(2), 28.14, 29.48, 46.66, 84.54, 121.76, 128.04, 128.12(*broad*), 128.49, 135.68, 142.68, 142.68, 146.10, 152.33, 156.66, 294.64.

FTIR (0.025 mm, CDCl_3 , cm^{-1}) 3570, 1707, 1604, 1460, 1210, 875.

Temperature dependence $^1\text{H-NMR}$ of **Z-Et₃I**.

Z-Et₃I was subjected to $^1\text{H-NMR}$ temperature studies from -77 to $105\text{ }^\circ\text{C}$ in toluene- d_8 . A Varian VXR 500 spectrometer with a variable temperature probe was used. The temperature of the probe was allowed to stabilize for 15 minutes before the sample was shimmed and the spectrum acquired. The first spectrum was acquired at -77 the last at $105\text{ }^\circ\text{C}$. The results are given in Figure 59, Figure 60, Table 27.

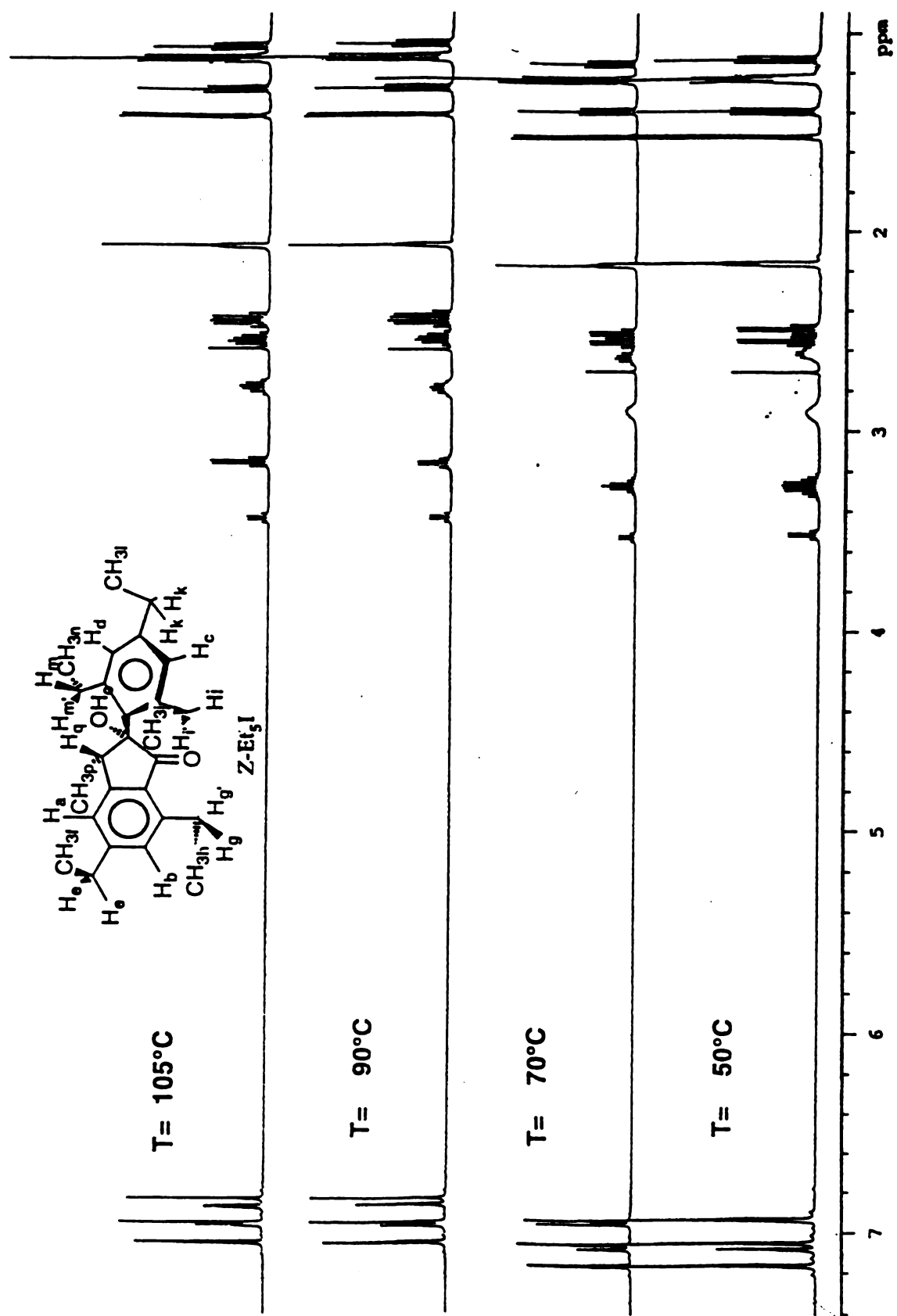


Figure 59. Temperature dependence ¹H-NMR of Z-Et₅I in toluene-*d*₆.

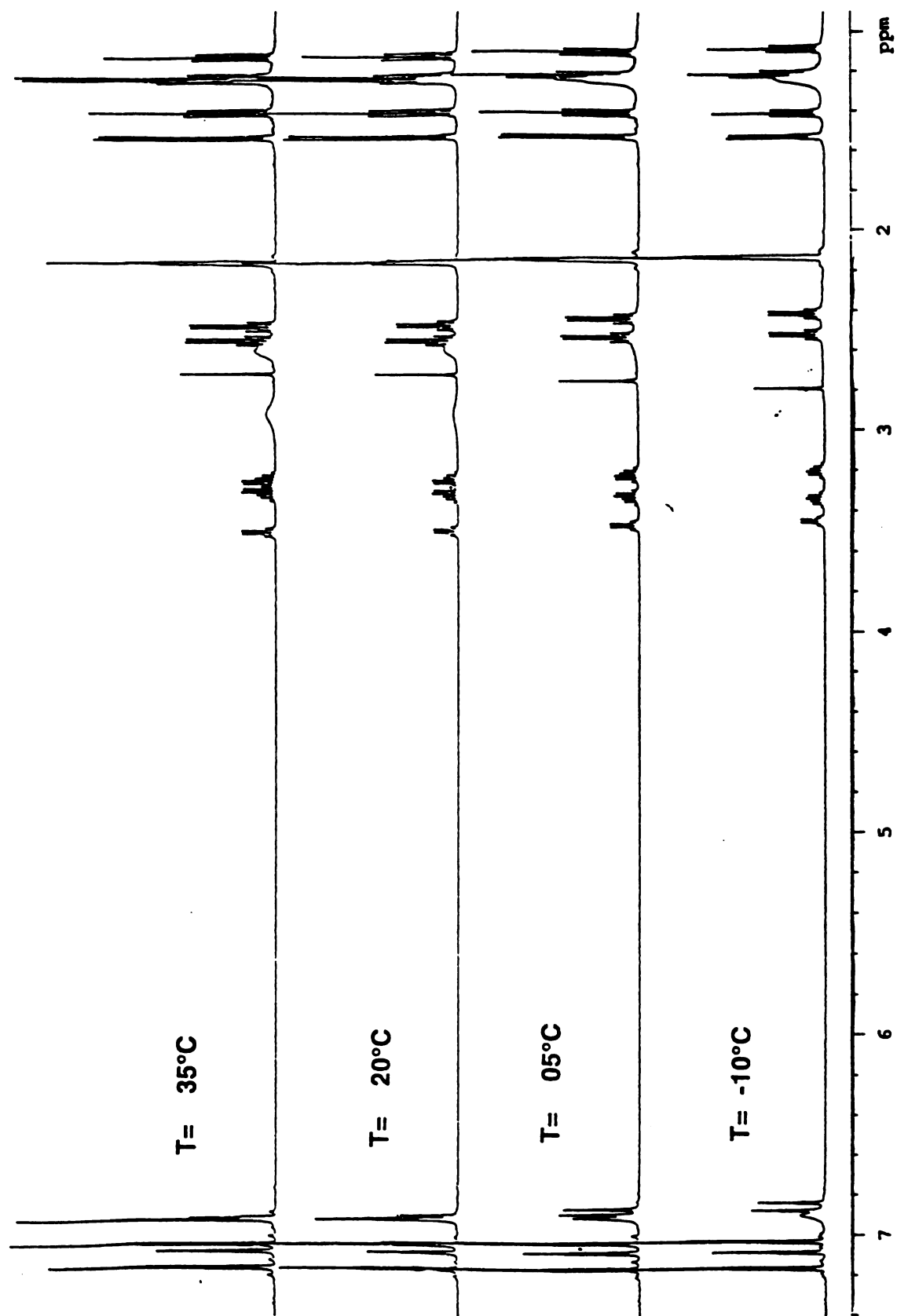


Figure 60. Temperature dependence ^1H -NMR of $\text{Z-Et}_3\text{I}$ in $\text{toluene-}d_6$ (continued).

Table 27. ^1H -NMR (500MHz; toluene- d_8) Temperature studies for Z-isomer. Chemical Shifts are in ppm.*

peak/T °C	-77	-60	-40	-25	-10	05	20	35	50	70	90	105
a(AR-H)	6.76	6.78	6.80	6.82	6.83	6.84	6.86	6.86	6.85	6.87	6.88	6.93
b(AR-H)	6.34	6.69	6.74	6.77	6.79	6.81	6.84	6.84	6.85	6.85	6.85	6.84
c(AR-H)	6.85	6.88	6.90(b)	6.86(vb)	6.855(b)	6.86	6.86	6.86	6.85	6.85	6.85	6.84
d(AR-H)	6.73	6.76	6.78(b)	6.86(vb)	6.855(b)	6.86	6.86	6.86	6.85	6.85	6.85	6.84
e(-CH ₂ -)	2.29	2.31	2.34	2.35	2.37	2.38	2.40	2.41	2.42	2.43	2.44	2.45
f(-CH ₃)	1.19	1.19	1.17	1.165	1.16	1.16	1.15	1.15	1.15	1.14	1.14	1.14
g(-CH ₂ H-)	3.40	3.38	3.37	3.32	3.29	3.27	3.24	3.23	3.21	3.19	3.18	3.18
g'(-CH ₂ H-)	3.02	3.09	3.12	3.15	3.20	3.17	3.18	3.18	3.18	3.18	3.18	3.18
h(-CH ₃)	1.38	1.40	1.39	1.37	1.36	1.35	1.33	1.33	1.32	1.31	1.30	1.29
i(-CH ₂ H-)	2.05	2.07	2.17(vb)	2.20(vb)	2.52(vb)	2.52(vb)	2.53(vb)	2.53(b)	2.54	2.55	2.56	2.56
i'(-CH ₂ H-)	2.13	2.15	2.17(vb)	2.20(vb)	?	2.85(vb)	2.84(vb)	2.84(vb)	2.83(vb)	2.815	2.80	2.80
j(-CH ₃)	1.19	1.21	1.17(vb)	1.19(vb)	1.19(vb)	1.18(b)	1.17	1.17	1.16	1.15	1.14	1.13
k(-CH ₂ -)	2.47	2.48	2.47	2.47	2.47	2.475	2.48	2.48	2.47	2.48	2.48	2.48
l(-CH ₃)	0.99	1.01	1.02	1.03	1.035	1.04	1.05	1.05	1.055	1.06	1.07	1.07
m(-CH ₂ H-)	2.69	2.71	2.73	2.73	2.52(vb)	2.52(vb)	2.53(vb)	2.53(b)	2.54	2.55	2.56	2.56
m'(-CH ₂ H-)	3.71	3.66	3.62	3.58	?	2.85(vb)	2.84(vb)	2.84(vb)	2.83(vb)	2.815	2.80	2.80
n(-CH ₃)	1.25	1.21	1.23(vb)	1.19(vb)	1.19(vb)	1.18(b)	1.17	1.17	1.16	1.15	1.14	1.13
o(-OH)	3.26	2.99	2.81	2.76	2.74	2.69	2.65	2.64	2.63	2.62	2.61	2.61
p(-CH ₃)	1.52	1.51	1.50	1.49	1.48	1.47	1.46	1.46	1.45	1.44	1.43	1.43
q(-CH)	3.32	3.34	3.34	3.39	3.40	3.415	3.43	3.43	3.44	3.44	3.45	3.45

* b= broad, vb= very broad.

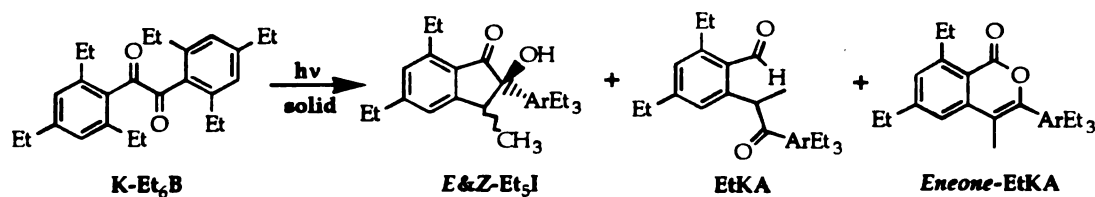
Table 28. ^1H -nOe (500MHz; CDCl_3 for E isomer, benzene- d_6 for Z isomer).

E-isomer				Z-isomer			
Hx irrad enhanced	$\Rightarrow$ Hy NOE enhancement	%	mm2 minimized distance(A)	Hx irrad enhanced	$\Rightarrow$ Hy NOE enhancement	%	mm2 minimized distance(A)
a $\Rightarrow$ e	-(12.13)		3.77	a $\Rightarrow$ e	-4.00		2.56
b $\Rightarrow$ e	-(7.35)		2.46	b $\Rightarrow$ e	-4.00		2.45
c $\Rightarrow$ i'&i	-(3.60)		2.49	c $\Rightarrow$ i'&i	—		3.48
c $\Rightarrow$ k	-5.30		2.55	c $\Rightarrow$ k	-5.10		2.54
d $\Rightarrow$ k	-(4.6)		2.43	d $\Rightarrow$ k	-5.10		2.46
g $\Rightarrow$ g'	-(23)		1.77	g $\Rightarrow$ g'	—		—
g $\Rightarrow$ b	-6.47		2.53	g $\Rightarrow$ b	-6.19		2.46
g' $\Rightarrow$ g	-7.0		1.77	g' $\Rightarrow$ g	—		—
g' $\Rightarrow$ b	-8.22		3.74	g' $\Rightarrow$ b	-5.87		3.69
i&i' $\Rightarrow$ p	-5.03		2.55&3.10	i&i' $\Rightarrow$ p	—		—
i&i' $\Rightarrow$ q	—		—	i&i' $\Rightarrow$ q	-4.08		2.81
k $\Rightarrow$ c	-5.1		2.55	k $\Rightarrow$ c	-(~7)		2.54
k $\Rightarrow$ d	-6.0		2.43	k $\Rightarrow$ d	-(~7)		2.46
m $\Rightarrow$ m'	-18.0		1.78	m $\Rightarrow$ m'	—		—
m' $\Rightarrow$ m	-22.0		1.78	m' $\Rightarrow$ m	—		—
m' $\Rightarrow$ q	-(9.0)		2.42	m' $\Rightarrow$ q	—		—
m&m' $\Rightarrow$ q	—		—	m&m' $\Rightarrow$ q	-2.00		2.91
q $\Rightarrow$ a	-5.14		2.87	q $\Rightarrow$ a	—		—
q $\Rightarrow$ i&i'	-4.17		2.55&3.10	q $\Rightarrow$ i&i'	—		—
q $\Rightarrow$ m'	-4.23		2.42	q $\Rightarrow$ m'	—		—
p $\Rightarrow$ q	—		—	p $\Rightarrow$ q	-5.42		2.20
p $\Rightarrow$ a	—		—	p $\Rightarrow$ a	-3.62		2.56

Table 29. ^1H -NMR (500 MHz; CDCl_3) selective decoupling.

E-isomer				Z-isomer			
Hx irradiated	⇌Hy decoupled	decoupler frequency(ppm)	frequency decoupled(ppm)	HHx irradiated	⇌Hy decoupled	decoupler frequency(ppm)	frequency decoupled(ppm)
i&i' ⇌ j		2.07(q,2H)	1.09(t,3H)	i&m or i'&m' ⇌ i&n		2.42(very broad s,2H)	1.13(t,6H)
j ⇌ i&i'		1.09(t,3H)	2.07(q,2H)	i&n ⇌ i&m or i'&m'		1.13(t,6H)	————
k ⇌ l		2.56(q,2H)	1.22(t,3H)	k? ⇌ l?		2.57(q,2H)	1.21(t,3H)
l ⇌ k		1.22(t,3H)	2.56(q,2H)	l? ⇌ k?		1.21(t,3H)	2.57(q,2H)
m ⇌ n		2.68(q ABq,1H)	of 1.31(t,3H)	e? ⇌ f?		2.71(q,3H)	1.28(t,3H)
n ⇌ m		1.31(t,3H)	2.68(q ABq,1H) of	f? ⇌ e?		~1.28(t,3H)	2.71(q,3H)&3.08(q of ABq,1H)
e ⇌ f		2.71(q,2H)	1.28(t,3H)	g&g' ⇌ h		3.08(q ABq,2H) of	1.26(t,3H)
f ⇌ e		1.28(t,3H)	2.71(q,2H)	h ⇌ g&g'		1.26(t,3H)	3.08(q ABq,2H) of
g' ⇌ h		3.02(ABq of q, 1H)	1.25(t,3H)	p ⇌ q		3.44(q,1H)	1.46(d,3H)
h ⇌ g'		1.25(t,3H)	3.02(ABq of q, 1H)	q ⇌ p		1.46(d,3H)	3.44(q,1H)
m' ⇌ n		3.10(ABq of q, 1H)	1.31(t,3H)				
n ⇌ m'		1.31(t,3H)	3.10(ABq of q, 1H)				
g ⇌ h		3.20(ABq of q, 1H)	1.25(t,3H)				
h ⇌ g		1.25(t,3H)	3.20(ABq of q, 1H)				
q ⇌ p		3.60(ABq of q, 1H)	0.986(d,3H)				
p ⇌ q		0.986(d,3H)	3.60(ABq of q, 1H)				

Products from solid state photochemistry of Et₆B



This solid state photochemistry of Et₆B was carried out by the same procedure as used for Me₆B. Irradiation of Et₆B with ~438 nm filtered light gave two isomeric indanols (Et₅I) in a 6:1 E/Z ratio after 5 days of irradiation. The crude product was purified by PTLC with 95:5, hexane:ethyl acetate as the eluent. One major band (R_f =0.29) was isolated and contained both isomeric indanols. The E and Z isomers were separated by PTLC with benzene and gave 150 mg (60% yield) of Et₅I-E and 40 mg (16% yield) of Et₅I-Z, both as white solids. The product *eneone*-EtKA was isolated when *Pyrex* filtered light was used instead of ~438 nm light. The *eneone*-EtKA was separated from the indanols by PTLC using eluted with 95:5, hexane:ethyl acetate as the eluent. The *eneone*-EtKA eluted on the PTLC plate with a R_f value of 0.32.

***eneone*-EtKA**

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.12(t, J= 7.5 Hz, 6H), 1.26(t, J=7.5 Hz, 3H), 1.31(t, J=7.5 Hz, 3H), 1.32(t, J=7.5 Hz, 3H), 1.95(s, 3H), 2.47(q, J= 7.5 Hz, 2H), 2.50(q, J= 7.5 Hz, 2H), 2.65(q, J= 7.5 Hz, 2H), 2.77(q, J= 7.5 Hz, 2H), 3.30(q, J=7.5 Hz, 2H), 6.97(s, 2H), 7.22(s, 1H), 7.24(s, 1H).

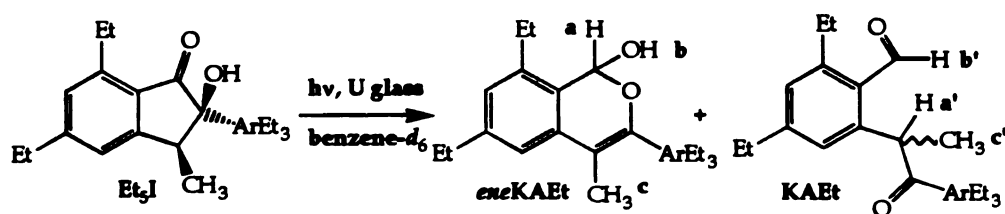
$^1\text{H-NMR}$ (Benzene- d_6 , 300 MHz), δ ppm: 1.128(t, J = 7.5 Hz, 3H), 1.133(t, J =7.5 Hz, 6H), 1.26(t, J =7.5 Hz, 3H), 1.47(t, J =7.5 Hz, 3H), 1.81(s, 3H), 2.48(q, J = 7.5 Hz, 2H), 2.52(q, J =7.5 Hz, 2H), 2.55(q, J = 7.5 Hz, 2H), 2.60(q, J = 7.5 Hz, 2H), 3.53(q, J =7.5 Hz, 2H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ ppm: 13.57, 15.21, 15.28(2 CH_3), 15.43, 15.61, 26.40(2 CH_3), 28.85, 28.89, 29.37, 110.55, 120.20, 123.95, 125.30(2 Ar- C^{H}), 128.99, 129.38, 129.56, 140.17, 143.25, 149.91, 150.32, 150.92, 161.53.

FTIR(0.025mm CCl_4 , cm^{-1}) 873.86(w), 1041.69(m), 1462.23(m), 1604.98(m), 1650.00(w, C=C), 1728.44(vs, C=O), 2874.49(w), 2935.16(m), 2968.83(s).

Mass Spec, m/z : 376(M^+), 348, 329, 305, 188(100%).

Photochemistry of Z- or E-2-hydroxy-2-(2'4'6'-triethylphenyl)-3-methyl-5,7-diethyl-1-indanone (Et₅I).



A degassed 0.01 M benzene solution of Z-Et₅I (100 mg) was irradiated with uranium glass filtered light from a medium pressure mercury arc lamp at room temperature. After two hours of irradiation 40% of the Z-Et₅I had been consumed and gave a 1:1 KAEt:eneKAEt product ratio. After five hours of irradiation 95% of the Z-Et₅I had been consumed and gave a 1:3 KAEt:eneKAEt

product ratio. The products were separated using PTLC with 97:3 hexane:ethyl acetate as the eluent which gave two bands with R_f values of 0.21 and 0.13. The first band (R_f = 0.21) contained two compounds Z-Et₃I and KAEt, the second band (R_f = 0.13) consisted of *ene*KAEt. The mixture of Z-Et₃I and KAEt was rechromatographed using benzene as the eluent. Two bands were isolated with R_f values of 0.26 and 0.22. The first band (R_f = 0.26) contained KAEt while the second band (R_f = 0.26) consisted of only Z-Et₃I. The ketoaldehyde (KAEt) and *ene*KAEt were also isolated from the irradiation of Et₃B and E-Et₃I.

α -(2-formyl-3,5-diethylphenyl)-2',4',6'-triethylpropioiphenone (EtKA)

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 1.00(broad triplet, J= 7.2 Hz, 6H), 1.13(t, J=7.2 Hz, 3H), 1.18(t, J=7.2 Hz, 3H), 1.22(t, J=7.2 Hz, 3H), 1.57(d, J= 7.2 Hz, 3H, b), 2.09(broad doublet of triplet, J= 7.2 Hz, ?, 2H), 2.20(broad doublet of triplet, J= 7.2 Hz, 2H), 2.55(q, J= 7.5 Hz, 2H), 2.63(q, J= 7.5 Hz, 2H), 2.77(q, J= 7.5 Hz, 2H), 5.35(q, J= 6.9 Hz, 1H, c), 6.79(s, 2H), 6.932(d, J= 1.2 Hz, 1H), 7.234(d, J= 1.2 Hz, 1H), 10.01(s, 1H).

¹H-NMR(Benzene-*d*₆, 300 MHz), δ ppm: 0.865(t, J= 7.5 Hz, 3H), 0.970(t, J= 7.5 Hz, 3H), 1.01(t, J= 7.5 Hz, 6H), 1.04(t, J= 7.5 Hz, 3H), 1.65(d, J= 6.9 Hz, 3H, b), 2.18-2.28(broad m, 4H), 2.27(q, J= 7.5 Hz, 2H), 2.35(q, J= 7.5 Hz, 2H), 2.41(q, J= 7.5 Hz, 2H), 5.62(q, J= 7.2 Hz, 1H, c), 6.59(d, J= 1.5 Hz, 1H), 6.71(s, 2H), 7.36(d, J= 1.5 Hz, 1H), 9.99(s, 1H, a).

^{13}C -NMR(CDCl_3 , 75 MHz), δ ppm: 15.19, 15.37, 15.42, 16.74, 17.10, 25.94, 26.41, 28.79, 29.03, 47.50, 125.20, 126.53, 128.63, 130.78, 137.61, 139.58, 139.95, 145.00, 147.37, 149.49, 193.30, 209.57.

(EneEtKA)

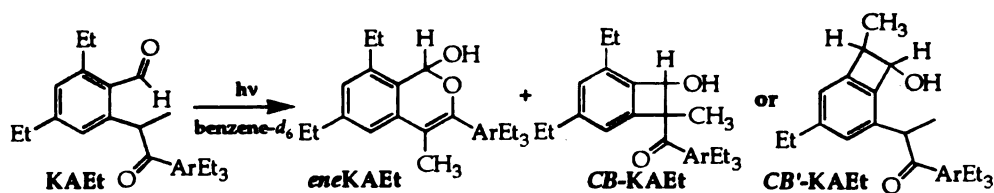
R_f = 0.13, 97:3, hexane:ethyl acetate.

^1H -NMR(CDCl_3 , 300 MHz), δ ppm: 1.09(t, J = 7.5 Hz, 3H), 1.18 t, J = 7.5 Hz, 3H), 1.24(t, J = 7.5 Hz, 3H), 1.27(t, J = 7.5 Hz, 3H), 1.30(t, J = 7.5 Hz, 3H), 1.81(s, 3H, **b**), 2.40-2.55(m, 2H), 2.56-2.80(m, 8H), 2.94(d, J = 6.9 Hz, 1H, **c**), 6.56(d, J = 7.2 Hz, 1H, **a**), 6.95(s, 1H), 6.97(s, 1H), 7.02(s, 2H).

^{13}C -NMR(CDCl_3 , 75 MHz), δ ppm: 13.31, 15.37, 15.46, 15.53, 15.56, 15.66, 24.49, 25.62, 26.12, 28.83, 29.12, 89.96, 107.37, 118.87, 125.18, 125.35, 126.65, 130.74, 126.65, 130.74, 140.54, 143.16, 143.59, 144.82, 145.20, 145.38.

FTIR(0.025mm CCl_4 , cm^{-1}) 870.01(m), 929.81(w), 997.32(m), 1030.12(w), 1103.42(w), 1464.16(m), 1577.97(w), 1604.98(m), 1653.21(m), 2874.30(m), 2936.03(s), 2966.90(vs), 3586.13(w, sharp).

Photochemistry of α -(2-formyl-3,5-diethylphenyl)-2',4',6'-triethylpropiophenone (EtKA)



A degassed 0.01 M benzene- d_6 solution of KAet (10 mg) was irradiated with uranium glass filtered light from a medium pressure mercury arc lamp at room temperature. After two hours of irradiation ~50% of the KAet had been consumed and gave two products, >95% was consumed after 11 hours. One product had the identical ^1H -NMR spectrum to *ene*KAet while the second appeared to be benzocyclobutenol, possibly CB-KAet or CB'-KAet. The benzocyclobutenol assignment was based on the growth of a quartet (~4.1 ppm) which may represent the benzylic methine proton of CB'-KAet. Several other minor products were apparent in the ^1H -NMR spectrum of the crude reaction mixture but no attempt was made to isolate them. See Figure 61 for details.

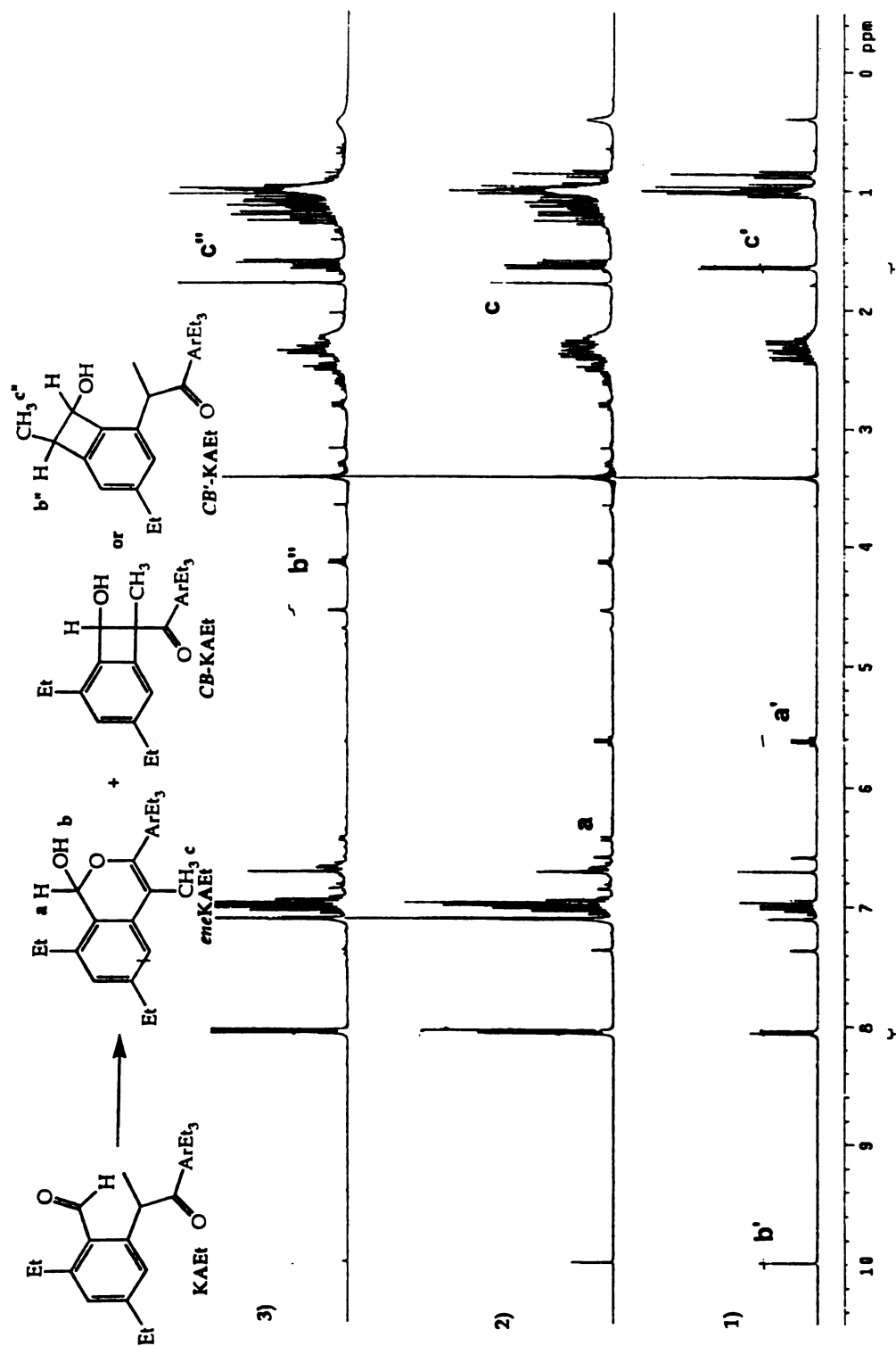
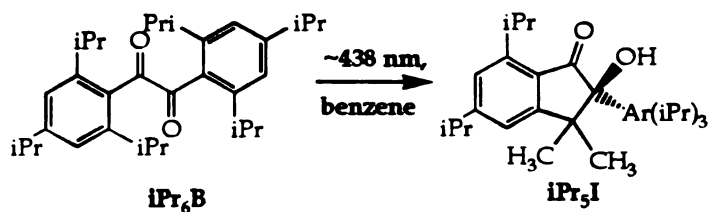


Figure 61. ^1H -NMR Spectra of KAEt in benzene- d_6 1) before irradiation 2) after 2 hours irradiation 3) after 11 hours irradiation.

Products from 2,4,6,2',4',6'-hexaisopropylbenzil (iPr₆B)

This solid state photochemistry of iPr₆B was carried out by the same procedure as used for Me₆B. The crude product was purified by PTLC with 95:5, hexane:ethyl acetate as the eluent. One major product was isolated that had a ¹H-NMR spectrum identical with iPr₃I which had previously been reported by Park.¹⁰³

2-hydroxy-2-(2',4',6')-triisopropylphenyl)-3,3-dimethyl-5,7-diisopropyl-1-indanone
(iPr₃I)

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 0.860(d, J= 6.8Hz, 3H), 1.14(d, J= 6.8 Hz, 3H), 1.15(s, 3H), 1.21(d, J= 6.8 Hz, 3H), 1.22(d, J= 6.8 Hz, 3H), 1.23(d, J= 6.8 Hz, 3H), 1.25(d, J= 6.8 Hz, 3H), 1.27(d, J=6.8 Hz, 3H), 1.30(d, J= 6.8 Hz, 6H), 1.33(d, J=6.8 Hz, 3H), 1.59(s, 3H), 2.19(septet, J= 6.8 Hz, 1H), 2.69(broad s, 1H), 2.83(septet, J= 6.8 Hz, 1H), 2.99(septet, J= 6.8 Hz, 1H), 4.02(septet, J= 6.8 Hz, 1H), 4.21(septet, J= 6.8 Hz, 1H), 6.86(d, J= 2 Hz, 1H), 7.09(d, J= 2 Hz, 1H), 7.14(d, J= 1 Hz, 1H), 7.18(d, J= 1 Hz, 1H).

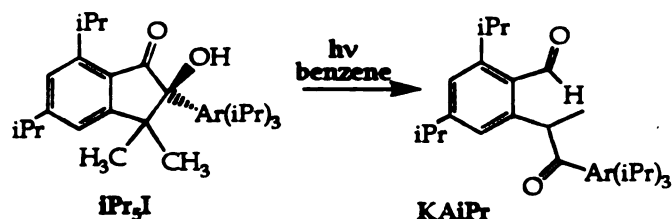
¹H-NMR(benzene-*d*₆, 300 MHz), δ ppm: 0.825(d, J= 6.8Hz, 3H), 1.05(d, J= 6.8 Hz, 6H), 1.153(d, J= 6.8 Hz, 3H), 1.156(d, J= 6.8 Hz, 3H), 1.24(s, 3H), 1.27(d, J= 6.8 Hz, 3H), 1.30(d, J= 6.8 Hz, 3H), 1.31(d, J=6.8 Hz, 3H), 1.33(d, J= 6.8 Hz, 6H),

1.43(d, $J=6.8$ Hz, 3H), 1.72(s, 3H), 2.51(septet, $J= 6.8$ Hz, 1H), 2.66(septet, $J= 6.8$ Hz, 1H), 2.72(septet, $J= 6.8$ Hz, 1H), 2.85(s, OH, 1H), 4.25(septet, $J= 6.8$ Hz, 1H), 4.60(septet, $J= 6.8$ Hz, 1H), 6.86(d, $J= 2$ Hz, 1H), 7.00(d, $J= 2$ Hz, 1H), 7.17(d, $J= 1$ Hz, 1H), 7.23(d, $J= 1$ Hz, 1H).

^{13}C -NMR(CDCl_3 , 75 MHz), δ ppm: 23.37, 23.43, 23.74, 23.78, 23.84, 25.42, 25.55, 25.96, 26.22, 27.18, 28.97, 30.46, 33.34, 33.60, 35.00, 86.20, 119.10, 122.20, 123.20, 124.06, 126.84, 135.76, 146.08, 146.98, 150.58, 150.80, 157.16, 162.47, 205.3.

FTIR(0.025mm CCl_4 , cm^{-1}) 1461, 1604, 1704, 2870, 2966, 3551.

Products from 2-hydroxy-2-(2'4'6'-triisopropylphenyl)-3,3-dimethyl-5,7-diisopropyl-1-indanone (iPr₅I).



A degassed 0.01 M benzene- d_6 solution of iPr_5I (100 mg) was irradiated with uranium glass filtered light from a medium pressure mercury arc lamp at room temperature. After nine hours of irradiation the iPr_5I had been consumed and gave a new product with an aldehydic peak at 9.99 ppm. The product was assigned to KAlPr based on spectral data that was identical to that reported by Park.¹⁰³ The crude product was purified by PTLC with 95:5, hexane:ethyl acetate as the eluent.

α -(2-formyl-3,5-diisopropylphenyl)-2',4',6'-triisopropylisobutyrophenone (KAiPr)

¹H-NMR(CDCl₃, 300 MHz), δ ppm: 0.940(d, J= 6.8Hz, 6H), 1.02(d, J= 6.8Hz, 6H), 1.19(d, J= 6.8Hz, 6H), 1.198(d, J= 6.8Hz, 6H), 1.20(d, J= 6.8Hz, 6H), 1.63(s, 6H), 2.21(septet, J= 6.8 Hz, 1H), 2.82(septet, J= 6.8 Hz, 1H), 2.84(septet, J= 6.8 Hz, 1H), 3.13(septet, J= 6.8 Hz, 1H), 6.88(s, 2H), 7.12d, J= 1 Hz, 1H), 7.13d, J= 1 Hz, 1H), 10.71(s, 1H).

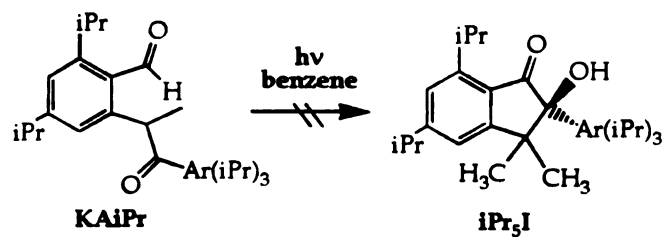
¹H-NMR(benzene-*d*₆, 300 MHz), δ ppm: 1.025(d, J= 6.8Hz, 6H), 1.03(d, J= 6.8Hz, 6H), 1.06(d, J= 6.8Hz, 6H), 1.09(d, J= 6.8Hz, 6H), 1.13(d, J= 6.8Hz, 6H), 1.58(s, 6H), 2.43(septet, J= 6.8 Hz, 1H), 2.59(septet, J= 6.8 Hz, 1H), 2.68(septet, J= 6.8 Hz, 1H), 3.17(septet, J= 6.8 Hz, 1H), 6.98(s, 2H), 7.12d, J= 1 Hz, 1H), 7.09 d, J= 1 Hz, 1H), 10.98(s, 1H).

¹³C-NMR(CDCl₃, 75 MHz), δ ppm: 22.30, 23.80, 23.92, 24.11, 25.95, 29.49, 29.86, 31.89, 34.11, 34.48, 53.77, 120.75, 122.74, 123.78, 136.09, 136.50, 141.33, 144.00, 147.71, 149.15, 150.19, 199.81, 215.54.

FTIR(0.025mm CCl₄, cm⁻¹) 1462, 1605, 1688, 1701, 2870, 2930, 2985.

Photochemistry of α -(2-formyl-3,5-diisopropylphenyl)-2',4',6'-triisopropylpropiophenone

(iPrKA)



A degassed 0.01 M benzene- d_6 solution of KAiPr (10 mg) was irradiated with uranium glass filtered light from a medium pressure mercury arc lamp at room temperature. After 50 hours of irradiation no iPr₅I had formed which was determined by ¹H-NMR.

A. Measurement of Quantum Yields

Solvents

Benzene- Analytical reagent grade benzene was purified by stirring 3.5 L with 500 mL concentrated sulfuric acid. The sulfuric acid washing was discarded and a new portion added until the acid layer remained colorless. The benzene was then stirred over 10% aqueous sodium hydroxide for 24 hours, washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. The benzene was distilled from 100 g phosphorous pentoxide through a 1 meter column packed with glass helices. A high reflux ratio was maintained and the initial 10% was discarded. The middle cut (~80%) was collected for use leaving ~10% in the distillation pot. The boiling point remained constant at 79.8 ± 0.2 °C.

Benzene- d_6 - The benzene- d_6 was purchased from Aldrich chemical in 50 mL quantities. The purity used was 99+ atom %D and was used without purification.

Internal standards

methylbenzoate (MB)- Methyl benzoate was purified by fractional distillation by Dr. Kung-Lung Cheng and used without further purification.

Di-n-butyl phthalate(DBP)- Di-n-butyl phthalate (Fischer Chemical) was washed dissolved in diethyl ether, washed with aqueous saturated sodium bicarbonate and fractionally distilled through a 35 mm vigreux column.

n-Butyl 4-methoxybenzoate (BMB)- n-Butyl 4-methoxybenzoate was purified by Dr. Peter J. Wagner and used without further purification.

n-octyl benzoate (OB)- n-Butyl 4-methoxybenzoate was purified by Dr. Peter J. Wagner and used without further purification.

Actinometers

Valerophenone (VP)- Valerophenone (Aldrich Chemical) was purified by fractional distillation by Dr. Wilfred Wiegel.

o-methylvalerophenone (2MVP)- was synthesized and purified by Dr. Peter J. Wagner.

Glassware

All new glassware (syringes, volumetric flasks and pipettes) used in quantitative measurements were rinsed with reagent grade acetone, deionized water and boiled in an Alconox (laboratory detergent) and deionized water solution for 24 hours. The glassware was rinsed and boiled in deionized for 24 hours, this cycle was repeated 3 times. After the final rinse with deionized water, the glassware dried at 140°C in a dedicated oven for photolysis glassware and cooled to room temperature prior to use. If the glassware was previously used,

the glassware was rinsed thoroughly with HPLC grade acetone and oven dried, this cleaning (rinsing) procedure limits the inaccuracy due to glass degradation with constant Alconox washings.

Ampoules used for the irradiation were made from alconox washed 13 x 100 mm Pyrex culture tubes by flame heating approximately 2.5 cm from the top with an oxygen-natural gas torch and drawing them to a uniform 15 cm length.

The nmr sample tubes were prepared by the Michigan State University Glass Shop. High resolution model 535pp (pyrex, ID= 4.000 mm $\pm \leq 0.005''$) from Wilmad Glass were fused to a 2 inch Pyrex extension and attached to a 10/30 ground glass joint. The tubes were cleaned by rinsing thoroughly with HPLC grade acetone and then oven dried. The tubes were recycled by scoring and breaking the Pyrex extension and reattaching the ground glass joint.

Preparation of samples

Solution Preparation

The solutions were prepared by weighing the desired material directly into a volumetric flask. Dilutions were made with the minimum number of transfers by volumetric pipettes. The ketone/internal standard solutions were divided equally into four 2.8 mL portions by a 5.0 mL Hamilton syringe with 20 gauge luer lock needle and placed into the pre-drawn ampoules.

In the case for NMR solutions, four 0.7 mL portions were syringed by a 1.0 mL Hamilton syringe with 20 gauge, 10 in. luer lock needle which limited the

ketone solution beading to the wall of the NMR tube. To limit the waste of benzene- d_6 and still weigh out accurate masses of actinometer and internal standard, excess actinometer solution was prepared (usually 10.0 mL volumes). However, only 2.8 mL (4×0.70 mL) is necessary for a single experiment, thus the excess actinometer solution was flame sealed in pre-scored 5 mL ampoules to ensure no change in concentration and wrapped with aluminum foil and stored in the dark. In a typical experiment, a 5.00 mL standard stock solution methyl benzoate (~ 0.05 M) in benzene- d_6 was prepared, 1.00 mL was transferred via volumetric pipette to a 4.0 mL volumetric flask with the pre-weighed ketone (usually 0.01 M, but varied with ϵ_{313}) and diluted to 4.0 mL to give a final methyl benzoate concentration of ~ 0.005 M. In order to obtain accurate results we adapted our merry-go-round method, which was constructed for standardized test tubes.

Degassing Procedure

Previously filled irradiation ampoules were attached to a vacuum line that was evacuated for at least one hour. These tubes were arranged on a circular manifold equipped with twelve vacuum stopcocks each fitted with size 00 one hole rubber stoppers. The sample tubes were frozen in liquid nitrogen and evacuated for at least twenty minutes. The stopcocks were closed and the tubes were allowed to warm to room temperature. The freeze-pump-thaw cycle was conducted four times and the tubes sealed with an oxygen-natural gas torch while

still under vacuum. In the degassing of NMR samples, it was necessary to facilitate the thawing procedure with by rinsing the tube with 95% EtOH from the top of the sample level to the bottom of the tube. If this was not done the thawing solution would expand and crack the thin walled NMR sample tubes.

Photochemical Reaction Setup

The quantum yield measurements were conducted at 313 and 366 nm with filtered light. The 366 nm band was isolated from a medium pressure 450 W Hanovia mercury arc lamp by filtration with Corning 7-83 filters, the 313 nm light was isolated using a solution of alkaline potassium chromate (0.002 M K_2CrO_4 in 1% aqueous potassium carbonate). Irradiation was conducted with the light source mounted in the center of a merry-go-round setup. For NMR tubes, the 14 mm merry-go-round hole size was adapted with Teflon disk adapters (1 mm x 12 Teflon wafer with a 5 mm centered bore) to ensure the NMR tube fit snug inside of the standardized test tube. The portion of the NMR tube above the merry-go-round was wrapped with black electrical tape since the 0.7 mL volume was above this level and would have absorbed reflected light. The use of the Teflon adapter ensured the NMR sample tubes were equal distance from the light source which was mounted in the center.

Actinometry

The quantum yields for product formation were measured by irradiating ketone solutions parallel to valerophenone as an actinometer. The quantum yields were calculated using Equation 2,

$$\text{Equation 2. } \Phi = [\text{PP}] / I$$

where [PP] is the concentration of photoproduct and I is the intensity of light absorbed by the sample. The value of I was determined by parallel irradiation to valerophenone which forms acetophenone with a quantum yield of $\Phi_{\text{AP}}=0.33$ at 313 nm. The acetophenone concentration was determined from Equation 3,

$$\text{Equation 3. } [\text{AP}] = R_f * [\text{IS}] * A_{\text{AP}} / A_{\text{IS}}$$

where,

[AP] is the concentration of acetophenone.

[IS] is the concentration of internal standard.

R_f is the instrument response factor.

A_{AP} is the integrated area of acetophenone.

A_{IS} is the integrated area of the internal standard.

The instrumental response factor was determined by measuring various concentrations of product versus a single concentration of internal standard. The response factors were determined from Equation 4,

Equation 4. $R_{IX} = ([X] / [IS]) * (A_{IS} / A_X) = (1 / m_{\text{slope}}) * (1 / [IS])$

where,

R_I is the instrument response factor for analyte X.

$[X]$ is the concentration of analyte X.

$[IS]$ is the concentration of internal standard.

A_X is the integrated area of analyte X.

A_{IS} is the integrated area of the internal standard.

m_{slope} is the slope of the standard curve.

Thus, the intensity of light, I , is determined from Equation 5 since $[AP]$ is known.

Equation 5. $I = [AP] / 0.33$

The concentration of photoproduct, $[PP]$ is calculated from Equation 6 .

Equation 6. $[PP] = R_{IPP} * [IS] * (A_{PP} / A_{IS})$

where:

$[PP]$ is the concentration of photoproduct.

$[IS]$ is the concentration of internal standard.

R_{IPP} is the instrument response factor.

A_{PP} is the integrated area of product.

A_{IS} is the integrated area of the internal standard.

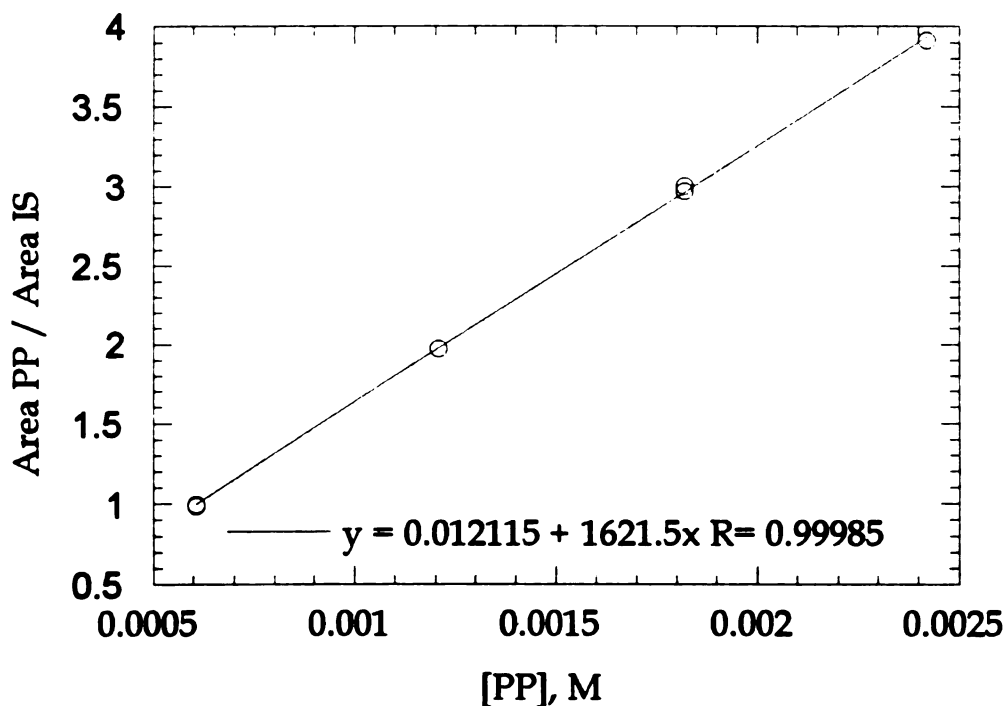


Figure 62. Calibration curve for CB-4Cl₃BP

Figure 62 is an example of a calibration curve for the benzocyclobutenol from 4'-chloro-2,4,6-triisopropylbenzophenone where the internal standard used was 4-methoxybenzoate (2.60×10^{-4} M). Substituting the slope from the plot into Equation 4 gives a value of $R_{4Cl} = 2.37$.

$$R_{4Cl} = (1 / m_{\text{slope}}) * (1 / [IS]) = (1 / 1621.5 \text{ M}^{-1}) * (1 / 2.60 \times 10^{-4} \text{ M}) = 2.37$$

In cases where product formation was faster than acetophenone formation from valerophenone, a standard curve was established. This was done by turning the lamp on 30 minutes prior to the addition of samples (actinometer or sample ketones) to the merry-go-round apparatus. While the lamp was on

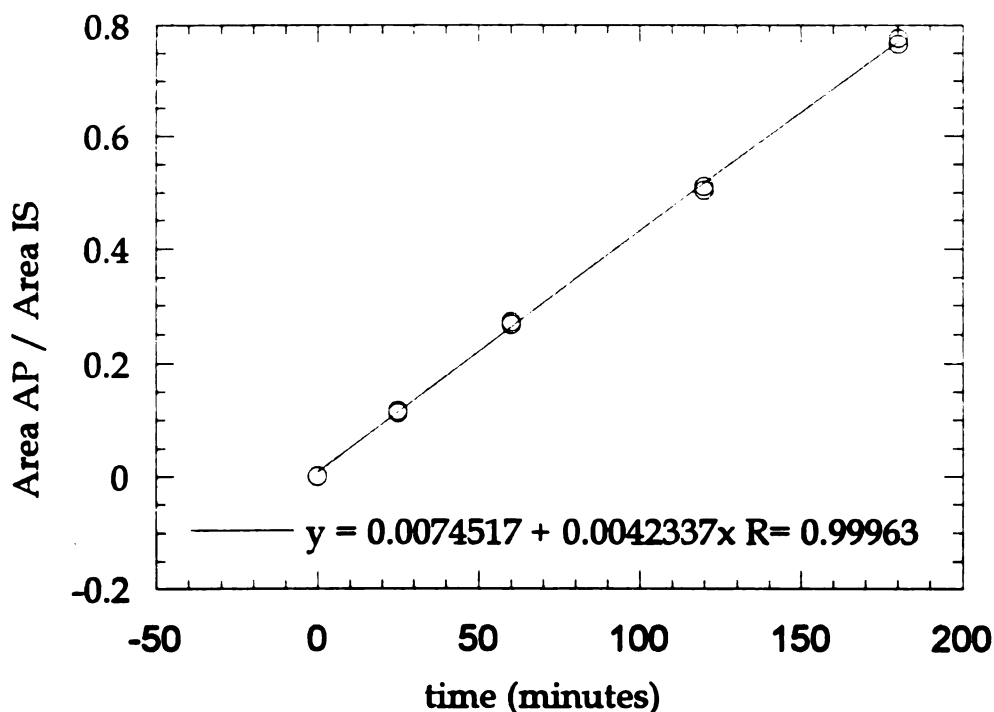


Figure 63. Calibration Curve for Acetophenone formation vs. time

the actinometer and sample ketones were introduced and the carousel started. Generally, eight actinometer tubes were irradiated and two tubes were removed at periodic time intervals monitored by a stop watch (± 1 minute), the samples were removed at 20 minute, 2 hour, 4 hour, 8 hour. The time versus area of actinometer divided by the area of internal standard were plotted and gave a straight line. The samples ketones were removed at the appropriate time to maintain conversions less than 10 percent, the time the ketone samples were irradiated were then correlated to the actinometer standard curve.

Quenching studies

Stern-Volmer quenching studies were performed with the appropriate triplet quencher. The Stern-Volmer expression (Equation 7) is:

$$\text{Equation 7. } \phi_0/\phi = 1 + k_q[Q]\tau_0$$

where:

ϕ_0 is the quantum yield in the absence of quencher.

ϕ is the quantum yield in the presence of quencher.

$[Q]$ is the concentration of quencher.

k_q is the bimolecular rate constant for quenching.

τ_0 is the life time of the excited state being quenched.

There is a linear relation between ϕ_0/ϕ and the quencher concentration. When ϕ_0/ϕ is plotted versus $[Q]$, the slope is $k_q\tau_0$. The quenching is assumed to be diffusion controlled with a rate constant of $6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.

Quantum yield measurement for 2'-methyl-2,2,2-trifluoroacetophenone¹H-NMR analysis: Varian VXR-300

Relaxation time (D1) = 15 sec

Table 30. Data for quantum yield measurement of 2'-methyl-2,2,2-trifluoroacetophenone

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	2MeTFA-CB	3.93	6.49	0.00702	0.076
2	2MeTFA-CB	3.72	6.45	0.00669	0.073
3	2MeTFA-CB	3.81	6.65	0.00665	0.072
Average	2MeTFA-CB	3.82	6.53	0.00679	0.074

ACT = VP, [VP] = 0.102 M; IS_{ACT} = MB, [IS_{ACT}] = 0.054 M; [ketone] = 0.069 M, IS_{KET} = MB, [IS_{KET}] = 0.012. photon count = 0.092 $\xi \cdot L^{-1}$. Irradiation time 19 hours. Conversion = 10 %. Irradiation wave length = 313 nm.

Quantum yield measurement for 2'-ethylbenzophenone¹H-NMR analysis: Varian VXR-300

Relaxation time (D1) = 10 sec

Table 31. Data for quantum yield measurement of 2'-ethylbenzophenone

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	2EtBP-CB	2.81	3.20	0.8781	0.033
2	2EtBP-CB	2.89	3.16	0.9146	0.035
3	2EtBP-CB	4.06	3.28	1.2378	0.047
Average	2EtBP-CB	2.82	3.20	0.8790	0.039

ACT = VP, [VP] = 0.63 M; IS_{ACT} = MB, [IS_{ACT}] = 0.062 M; [ketone] = 0.083 M, IS_{KET} = MB, [IS_{KET}] = 0.013. photon count = 0.340 $\xi \cdot L^{-1}$. Irradiation time 19 hours. Conversion = 14 %. Irradiation wave length = 366 nm.

Quantum yield measurement for 2-benzylbenzophenone¹H-NMR analysis: Varian VXR-300

Relaxation time (D1) = 10 sec.

Table 32. Data for quantum yield measurement of 2-benzylbenzophenone.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	BzBP-ECB	0.030	0.110	0.00491	0.09
2	BzBP-ECB	0.030	0.100	0.00540	0.10
Average	BzBP-ECB	0.030	0.105	0.00515	0.095

ACT = VP, [VP] = 0.112 M; IS_{ACT} = MB, [IS_{ACT}] = 0.033 M; [ketone] = 0.0406 M, IS_{KET} = MB, [IS_{KET}] = 0.018. photon count = 0.0557 ξ .L⁻¹. Irradiation time = 6 min. Conversion = 13 %. Irradiation wave length = > 300 nm..

Quantum yield measurement for 2,4,6-trimethylbenzophenone¹H-NMR analysis: Varian VXR-300

Relaxation time = 10 sec.

Table 33. Data for quantum yield measurement of 2,4,6-trimethylbenzophenone.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	M ₃ BP-CB	0.930	3.340	0.00362	0.021
2	M ₃ BP-CB	0.780	3.190	0.00318	0.019
3	M ₃ BP-CB	0.990	3.360	0.00383	0.023
4	M ₃ BP-CB	0.960	3.080	0.00405	0.024
Average	M ₃ BP-CB	0.915	3.243	0.00367	0.022

ACT = VP, [VP] = 0.63 M; IS_{ACT} = MB, [IS_{ACT}] = 0.062 M; [ketone] = 0.084 M, IS_{KET} = MB, [IS_{KET}] = 0.013. photon count = ξ .L⁻¹. Irradiation time 4 hours. Conversion = 5 %. Irradiation wave length = 366 nm.

Quantum yield measurement for 2'-methoxy-2,4,6-trimethylbenzophenone¹H-NMR analysis: Varian VXR-300

Relaxation time = 10 sec.

Table 34. Data for quantum yield measurement of 2OMM₃BP.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	2OMM ₃ BP-F	0.735	2.05	0.00416	0.020
2	2OMM ₃ BP-F	0.68	1.97	0.00397	0.019
3	2OMM ₃ BP-F	0.56	1.94	0.00332	0.016
Average	2OMM ₃ BP-F	0.66	1.99	0.00382	0.019

ACT = VP, [VP] = 0.102 M; IS_{ACT} = MB, [IS_{ACT}] = 0.054 M; [ketone] = 0.111 M, IS_{KET} = MB, [IS_{KET}] = 0.0116. photon count = 0.0205 ξ .L⁻¹. Irradiation time 43 hours. Conversion = 27 %. Irradiation wave length = 313 nm..

Quantum yield measurement for 2,4,6-triisopropylbenzophenone

HPLC analysis: Rainin with Dynamax
 Column: Rainin SiO₂ normal phase
 Solvent system: Hexane : Ethyl Acetate
 Solvent ratio: 92:8
 Flow rate: 1.0 mL/min., Loop: 20 μ l
 Detection wave length: 270 nm

Table 35. Data for quantum yield measurement of I₃BP by HPLC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	I ₃ BP-CB	85436	231891	0.00083	0.68
2	I ₃ BP-CB	92460	234798	0.00089	0.73
3	I ₃ BP-CB	94402	234898	0.00090	0.75
Average	I ₃ BP-CB	90766	233345	0.00086	0.71

ACT = VP, [VP] = 0.102 M; IS_{ACT} = BMB, [IS_{ACT}] = 0.00220 M; [ketone] = 0.0100 M, IS_{KET} = DBP, [IS_{KET}] = 0.00250 M. R_f(PP) = 0.90. Photon count = 0.00164 ξ .L⁻¹. Irradiation time = 25 minutes. Conversion = 9 %. Irradiation wave length = 313 nm.

Quantum yield measurement for 2,4,6-triisopropylbenzophenone

¹H-NMR analysis: Varian VXR-300
 Relaxation time (D1) = 15 sec

Table 36. Data for quantum yield measurement of I₃BP by ¹H-NMR.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	I ₃ BP-CB	4.590	0.940	0.0566	0.62
2	I ₃ BP-CB	4.380	0.970	0.0524	0.57
3	I ₃ BP-CB	4.490	0.955	0.0545	0.59
Average	I ₃ BP-CB	4.487	0.955	0.0545	0.59

ACT = VP, [VP] = 0.102 M; IS_{ACT} = MB, [IS_{ACT}] = 0.054 M; [ketone] = 0.111 M, IS_{KET} = MB, [IS_{KET}] = 0.0116. photon count = 0.0920 ξ .L⁻¹. Irradiation time 19 hours. Conversion = 49 %. Irradiation wave length = 313 nm.

Quantum yield measurement for 2'-methoxy-2,4,6-triisopropylbenzophenone

HPLC analysis: Rainin with Dynamax
 Column: Rainin SiO₂ normal phase
 Solvent system: Hexane : Ethyl Acetate
 Solvent ratio: 96:4
 Flow rate: 1.0 mL/min.
 Loop: 20 μ l
 Detection wave length: 270 nm

Table 37. Data for quantum yield measurement of 2OMI₃BP by HPLC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	2OMI ₃ BP-CB	196860	895789	0.00085	0.52
2	2OMI ₃ BP-CB	182833	886032	0.00080	0.49
3	2OMI ₃ BP-CB	194453	893721	0.00084	0.51
4	2OMI ₃ BP-CB	202563	890520	0.00088	0.54
Average	2OMI ₃ BP-CB	194177	891516	0.00084	0.51

ACT = VP, [VP] = 0.102 M; IS_{ACT} = BMB, [IS_{ACT}] = 0.00220 M; [ketone] = 0.0104 M, IS_{KET} = BMB, [IS_{KET}] = 0.00340 M. R_f(PP) = 1.14. Photon count = 0.00164 ξ .L⁻¹. Irradiation time = 25 minutes. Conversion = 8 %. Irradiation wave length = 313 nm.

Quantum yield measurement for 4'-methoxy-2,4,6triisopropylbenzo-phenone

HPLC analysis: Rainin with Dynamax
 Column: Rainin SiO₂ normal phase
 Solvent system: Hexane : Ethyl Acetate
 Solvent ratio: 92:8
 Flow rate: 1.0 mL/min.
 Loop: 20 μ l
 Detection wave length: 270 nm

Table 38. Data for quantum yield measurement of 4'-methoxy-2,4,6triisopropylbenzo-phenone by HPLC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	4OMI ₃ BP-CB	215444	105166	0.00110	0.78
2	4OMI ₃ BP-CB	204303	102020	0.00107	0.77
3	4OMI ₃ BP-CB	204735	105212	0.00104	0.74
4	4OMI ₃ BP-CB	213990	105547	0.00108	0.77
Average	4OMI ₃ BP-CB	209618	104486	0.00107	0.77

ACT = VP, [VP] = 0.102 M; IS_{ACT} = BMB, [IS_{ACT}] = 0.00220 M; [ketone] = 0.0986 M, IS_{KET} = DBP, [IS_{KET}] = 0.00107 M. R_f(PP) = 0.50. Photon count = 0.00164 ξ .L⁻¹. Irradiation time = 25 minutes. Conversion = 11 %. Irradiation wave length = 313 nm.

Quantum yield measurement for 4'-methyl-2,4,6-triisopropylbenzophenone

HPLC analysis: Rainin with Dynamax
 Column: Rainin SiO₂ normal phase
 Solvent system: Hexane : Ethyl Acetate
 Solvent ratio: 95:5
 Flow rate: 1.0 mL/min.
 Loop: 20 μ l
 Detection wave length: 270 nm

Table 39. Data for quantum yield measurement of 4'-methyl-2,4,6-triisopropylbenzo-phenone by HPLC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	4MI ₃ BP-CB	115897	291004	0.00099	0.65
2	4MI ₃ BP-CB	111421	289711	0.00095	0.63
3	4MI ₃ BP-CB	114274	289091	0.00098	0.65
4	4MI ₃ BP-CB	114779	289779	0.00098	0.65
Average	4MI ₃ BP-CB	114093	289896	0.00097	0.64

ACT = VP, [VP] = 0.102 M; IS_{ACT} = BMB, [IS_{ACT}] = 0.00220 M; [ketone] = 0.0960 M, IS_{KET} = BMB, [IS_{KET}] = 0.00090 M. R_f(PP) = 2.5. Photon count = 0.00164 ξ .L⁻¹. Irradiation time = 25 minutes. Conversion = 10 %. Irradiation wave length = 313 nm.

Quantum yield measurement for 2'-(α,α,α -trifluoromethyl)-2,4,6-triisopropylbenzophenone

HPLC analysis: Rainin with Dynamax
 Column: Rainin SiO₂ normal phase
 Solvent system: Hexane : Ethyl Acetate
 Solvent ratio: 97:3
 Flow rate: 1.0 mL/min.
 Loop: 20 μ l
 Detection wave length: 270 nm

Table 40. Data for quantum yield measurement of 2'-(α,α,α -trifluoromethyl)-2,4,6-triisopropylbenzophenone by HPLC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	2CF ₃ I ₃ BP-CB	82456	272583	0.00049	0.013
2	2CF ₃ I ₃ BP-CB	84200	273837	0.00049	0.013
3	2CF ₃ I ₃ BP-CB	80100	273967	0.00047	0.012
4	2CF ₃ I ₃ BP-CB	84356	273344	0.00050	0.013
Average	2CF ₃ I ₃ BP-CB	82778	273433	0.00049	0.013

ACT = VP, [VP] = 0.102 M; IS_{ACT} = BMB, [IS_{ACT}] = 0.00220 M; [ketone] = 0.0100 M, IS_{KET} = BMB, [IS_{KET}] = 0.00136 M. R_f(PP) = 1.18. Photon count = 0.00164 x. ξ .L⁻¹. Irradiation time = 615 minutes. Conversion = 5 %. Irradiation wave length = 313 nm.

Quantum yield measurement for 2,4,6,2',4',6'-hexamethylbenzil at 313 nm

GC analysis: Varian 3400
 Column: DB 210
 Initial temperature: 125°C
 Hold time: 5 min.
 Final temperature: 200°C
 Rate: 15°C/min.
 Injector temperature: 250°C
 Detector temperature: 225°C
 Detector Range: 10⁻¹²

Table 41. Data for quantum yield measurement for 2,4,6,2',4',6'-hexamethylbenzil by GC at 313 nm.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	Me ₃ I	37,400	160,902	0.214	0.0061
2	Me ₃ I	42,182	165,795	0.234	0.0067
3	Me ₃ I	40,870	165,458	0.227	0.0065
4	Me ₃ I	41,386	166,587	0.229	0.0065
Average	Me ₃ I	40459.5	164685.5	0.226	0.0064

ACT = VP, [VP] = 0.103 M; IS_{ACT} = OB, [IS_{ACT}] = 0.0254 M, R_f(AP) = 1.9; [ketone] = 0.0020M, IS_{KET} = DBP, [IS_{KET}] = 0.00052 M. R_f(PP) = 0.92. Photon count = 0. ξ .L⁻¹. Conversion = 6 %. Irradiation wave length = 313 nm. Irradiation time = 6 hr.

Quantum yield measurement for 2,4,6,2',4',6'-hexamethylbenzil at 366 nm

GC analysis: Varian 3400
 Column: DB 210
 Initial temperature: 125°C
 Hold time: 5 min.
 Final temperature: 200°C
 Rate: 15°C/min.
 Injector temperature: 250°C
 Detector temperature: 225°C
 Detector Range: 10⁻¹²

Table 42. Data for quantum yield measurement for 2,4,6,2',4',6'-hexamethylbenzil at 366 nm by GC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	MesI	42,809	65,374	0.000133	0.0087
2	MesI	45,469	66,469	0.000138	0.0091
3	MesI	45,820	67,312	0.000138	0.0090
4	MesI	43,727	69,440	0.000127	0.0083
Average	MesI	44,456	67,149	0.000134	0.0088

ACT = VP, [VP] = 0.249 M; IS_{ACT} = OB, [IS_{ACT}] = 0.0567 M, R_f(AP) = 1.9; [ketone] = 0.00166M, IS_{KET} = DBP, [IS_{KET}] = 0.00022 M. R_f(PP) = 0.92. Photon count = 0.0871 ξ .L⁻¹. Conversion = 6 %. Irradiation wave length = 366 nm. Irradiation time = 1.5 hr.

Quantum yield measurement for 2,4,6,2',4',6'-hexaethylbenzil at 313 nm

GC analysis: Varian 3400
 Column: DB 210
 Initial temperature: 125°C
 Hold time: 5 min.
 Final temperature: 200°C
 Rate: 15°C/min.
 Injector temperature: 250°C
 Detector temperature: 225°C
 Detector Range: 10⁻¹²

Table 43. Data for quantum yield measurement for 2,4,6,2',4',6'-hexaethylbenzil at 313 nm by GC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP], M	ϕ
1	Z-Et ₆ I	202,919	193532	0.765	0.026
2	Z-Et ₆ I	180,788	211,852	0.623	0.021
3	Z-Et ₆ I	303,336	275,996	0.802	0.027
4	Z-Et ₆ I	233,319	208,596	0.817	0.028
Average	Z-Et ₆ I	230090	222494	0.755	0.026
1	E-Et ₆ I	89,905	193532	0.353	0.012
2	E-Et ₆ I	63,709	138,480	0.350	0.012
3	E-Et ₆ I	64,352	128,249	0.381	0.013
4	E-Et ₆ I	103,451	208596	0.377	0.013
Average	E-Et ₆ I	80354	167214	0.365	0.012

ACT = VP, [VP] = 0.103 M; IS_{ACT} = OB, [IS_{ACT}] = 0.0254 M, R_f(AP) = 1.9; [ketone] = 0.0032 M, IS_{KET} = DBP, [IS_{KET}] = 0.00062 M. R_f(PP) = 0.73. Photon count = 0.0183 $\xi \cdot L^{-1}$. Conversion = 7 %. Irradiation wave length = 313 nm. Irradiation time = 6 hr.

Quantum yield measurement for 2,4,6,2',4',6'-hexaethylbenzil at 366 nm

GC analysis: Varian 3400
 Column: DB 210
 Initial temperature: 125°C
 Hold time: 5 min.
 Final temperature: 200°C
 Rate: 15°C/min.
 Injector temperature: 250°C
 Detector temperature: 225°C
 Detector Range: 10⁻¹²

Table 44. Data for quantum yield measurement for 2,4,6,2',4',6'-hexaethylbenzil at 366 nm by GC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP], M	ϕ
1	Z-Et ₃ I	132,814	64,332	0.000345	0.0212
2	Z-Et ₃ I	137,532	68,443	0.000336	0.0206
3	Z-Et ₃ I	197,284	103,923	0.000317	0.0195
4	Z-Et ₃ I	210,856	98,569	0.000358	0.0219
Average	Z-Et ₃ I	169,622	83,817	0.000338	0.0208
1	E-Et ₃ I	38,917	42,637	0.000147	0.0090
2	E-Et ₃ I	56,960	68,443	0.000134	0.0082
3	E-Et ₃ I	48,878	52,273	0.000189	0.0116
4	E-Et ₃ I	69,096	77,808	0.000143	0.0087
Average	E-Et ₃ I	53,463	60,290	0.000142	0.0087

ACT = VP, [VP] = 0.249 M; IS_{ACT} = OB, [IS_{ACT}] = 0.0567 M, R_f(AP) = 1.9; [ketone] = 0.0026 M, IS_{KET} = DBP, [IS_{KET}] = 0.00022 M. R_f(PP) = 0.73. Photon count = 0.0174 ξ .L⁻¹. Conversion = 18 %. Irradiation wave length = 366 nm. Irradiation time = 1.5 hr.

Quantum yield measurement for 2,4,6,2',4',6'-hexaethylbenzil at 313 nm¹H-NMR analysis: Varian VXR-300

Relaxation time (D1) = 10 sec

Table 45. Data for quantum yield measurement for 2,4,6,2',4',6'-hexaethylbenzil at 366 nm by ¹H-NMR.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	<i>Z</i> -Et ₃ I	0.290	1.300	0.00091	0.029
2	<i>Z</i> -Et ₃ I	0.180	0.880	0.00084	0.026
Average	<i>Z</i> -Et ₃ I	0.235	1.090	0.00088	0.028
1	<i>E</i> -Et ₃ I	0.150	1.300	0.00047	0.015
2	<i>E</i> -Et ₃ I	0.090	0.880	0.00042	0.013
Average	<i>E</i> -Et ₃ I	0.120	1.090	0.00045	0.014

ACT = VP, [VP] = 0.010 M; IS_{ACT} = MB, [IS_{ACT}] = 0.065 M; [ketone] = 0.0075 M, IS_{KET} = MB, [IS_{KET}] = 0.041. photon count = 0.0211 ξ .L⁻¹. Irradiation time 17 hours. Conversion = 17 %. Irradiation wave length = 313 nm.

Quantum yield measurement for 2,4,6,2',4',6' hexaisopropylbenzil at 313 nm

GC analysis: Varian 3400
 Column: DB 210
 Initial temperature: 125°C
 Hold time: 5 min.
 Final temperature: 200°C
 Rate: 15°C/min.
 Injector temperature: 250°C
 Detector temperature: 225°C
 Detector Range: 10⁻¹²

Table 46. Data for quantum yield measurement of 2,4,6,2',4',6'-hexaisopropylbenzil at 313 nm by GC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	iPr ₃ I	483,820	313,570	0.802	0.044
2	iPr ₃ I	466,955	321,140	0.756	0.041
3	iPr ₃ I	460,937	307,320	0.780	0.043
4	iPr ₃ I	487,455	324,455	0.781	0.043
Average	iPr ₃ I	474,792	316,621	0.780	0.043

ACT = VP, [VP] = 0.103 M; IS_{ACT} = OB, [IS_{ACT}] = 0.0254 M, R_f(AP) = 1.9; [ketone] = 0.0032M, IS_{KET} = DBP, [IS_{KET}] = 0.00062 M. R_f(PP) = 0.73. Photon count = 0.0183 ξ .L⁻¹. Conversion = 7 %. Irradiation wave length = 313 nm. Irradiation time = 6 hr.

Quantum yield measurement for 2,4,6,2',4',6' hexaisopropylbenzil at 366 nm

GC analysis: Varian 3400
 Column: DB 210
 Initial temperature: 125°C
 Hold time: 5 min.
 Final temperature: 200°C
 Rate: 15°C/min.
 Injector temperature: 250°C
 Detector temperature: 225°C
 Detector Range: 10⁻¹²

Table 47. Data for quantum yield measurement of 2,4,6,2',4',6'-hexaisopropylbenzil at 366 nm by GC.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	iPr ₃ I	227,052	218,246	0.01050	0.041
2	iPr ₃ I	236,002	205,536	0.01050	0.045
3	iPr ₃ I	236,450	209,527	0.01050	0.044
Average	iPr ₃ I	233,168	211,103	0.01050	0.043

ACT = VP, [VP] = 0.103 M; IS_{ACT} = OB, [IS_{ACT}] = 0.0254 M, R_f(AP) = 1.9; [ketone] = 0.0036 M, IS_{KET} = DBP, [IS_{KET}] = 0.00079 M. R_f(PP) = 0.51. Photon count = 0.0105 $\xi \cdot L^{-1}$. Conversion = 13 %. Irradiation wave length = 366 nm. Irradiation time = 45 min.

Quantum yield measurement for 2,4,6,2',4',6'-hexaisopropylbenzil at 313 nm¹H-NMR analysis: Varian VXR-300

Relaxation time (D1) = 10 sec

Table 48. Data for quantum yield measurement of 2,4,6,2',4',6'-hexaisopropylbenzil at 366 nm by ¹H-NMR.

sample #	Photoproduct(PP)	Area(PP)	Area (IS)	[PP]	φ
1	iPr ₃ I	0.240	0.650	0.00151	0.048
2	iPr ₃ I	0.230	0.660	0.00143	0.045
3	iPr ₃ I	0.210	0.660	0.00130	0.041
Average	iPr ₃ I	0.220	0.660	0.00137	0.043

ACT = VP,[VP]= 0.010 M; IS_{ACT} = MB, [IS_{ACT}]= 0.065 M; [ketone]= 0.0091 M, IS_{KET}= MB, [IS_{KET}]= 0.041. photon count = 0.0211 ξ.L⁻¹. Irradiation time 17 hours. Conversion = 16 %. Irradiation wave length = 313 nm.

Quantum yield measurement for α-(2-formyl-3,5-dimethylphenyl)-2',4',6'-trimethylpropiophenone from 2-hydroxy-2-(2'4'6'-trimethylphenyl)-5,7-dimethyl-1-indanone¹H-NMR analysis: Varian VXR-300

Relaxation time (D1) = 10 sec

Table 49. Quantum yield measurement of KAMe from Me₃I by ¹H-NMR.

sample #	Photoproduct (PP)	Area(PP)	Area (IS)	[PP]	φ
1	KAMe	0.14	0.72	0.0010	0.049
2	KAMe	0.10	0.73	0.0007	0.035
3	KAMe	0.22	0.83	0.0013	0.067
Average	KAMe	0.15	0.76	0.0010	0.051

ACT = VP,[VP]= 0.106 M; IS_{ACT} = MB, [IS_{ACT}]= 0.0529 M; [ketone]= 0.0193 M, IS_{KET}= MB, [IS_{KET}]= 0.0049. photon count = 0.0193 ξ.L⁻¹. Irradiation time 4 hours. Conversion = 5 %. Irradiation wave length = 313 nm.

Quantum yield measurement for α -(2-formyl-3,5-diethylphenyl)-2',4',6'-triethylpropiophenone from Z-2-hydroxy-2-(2'4'6'-triethylphenyl)-3-methyl-5,7-diethyl-1-indanone

¹H-NMR analysis: Varian VXR-300
Relaxation time (D1) = 10 sec

Table 50. Quantum yield measurement of KAet from Z-Et₃I by ¹H-NMR.

sample #	Photoproduct (PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	KAet	0.14	0.63	0.0014	0.070
2	KAet	0.12	0.50	0.0015	0.076
3	KAet	0.10	0.49	0.0012	0.065
4	KAet	0.08	0.46	0.0011	0.055
Average	KAet	0.11	0.52	0.0013	0.067

ACT = VP, [VP] = 0.106 M; IS_{ACT} = MB, [IS_{ACT}] = 0.0529 M; [ketone] = 0.0150 M, IS_{KET} = MB, [IS_{KET}] = 0.0061. photon count = 0.0193 ξ .L⁻¹. Irradiation time 4 hours. Conversion = 12 %. Irradiation wave length = 313 nm.

Quantum yield measurement for α -(2-formyl-3,5-diethylphenyl)-2',4',6'-triethylpropiophenone from E-2-hydroxy-2-(2'4'6'-triethylphenyl)-3-methyl-5,7-diethyl-1-indanone

¹H-NMR analysis: Varian VXR-300
Relaxation time (D1) = 10 sec

Table 51. Quantum yield measurement of KAet from E-Et₃I by ¹H-NMR.

sample #	Photoproduct (PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	KAet	0.22	0.67	0.0020	0.104
2	KAet	0.26	0.98	0.0016	0.083
3	KAet	0.22	0.66	0.0020	0.105
Average	KAet	0.23	0.77	0.0018	0.096

ACT = VP, [VP] = 0.106 M; IS_{ACT} = MB, [IS_{ACT}] = 0.0529 M; [ketone] = 0.0194 M, IS_{KET} = MB, [IS_{KET}] = 0.0061. photon count = 0.0193 ξ .L⁻¹. Irradiation time 4 hours. Conversion = 7 %. Irradiation wave length = 313 nm.

Quantum yield measurement for α -(2-formyl-3,5-diisopropylphenyl)-2',4',6'-triisopropylpropiophenone from 2-hydroxy-2-(2'4'6'-triisopropylphenyl)-3,3-dimethyl-5,7-diisopropyl-1-indanone

¹H-NMR analysis: Varian VXR-300

Relaxation time (D1) = 10 sec

Table 52. Quantum yield measurement of KAiPr from iPr₃I by ¹H-NMR.

sample #	Photoproduct (PP)	Area(PP)	Area (IS)	[PP]	ϕ
1	KAiPr	0.18	0.40	0.00257	0.098

ACT = VP, [VP] = 0.106 M; IS_{ACT} = MB, [IS_{ACT}] = 0.0536 M; [ketone] = 0.0097 M, IS_{KET} = MB, [IS_{KET}] = 0.0057. photon count = 0.0437 ξ .L⁻¹. Irradiation time 311 min. Conversion = 26 %. Irradiation wave length = 366 nm.

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