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PHOTOINITIATED HYDROGEN ABSTRACTION REACTIONS OF
KETONES AND BEHAVIOR OF BIRADICAL INTERMEDIATES

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Bong Ser Park

has been accepted towards fulfillment
of the requirements for

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Peter Wagner
Major professor

Date June 30, 1992

PHOTOINITIATED HYDROGEN ABSTRACTION REACTIONS OF KETONES AND BEHAVIOR OF BIRADICAL INTERMEDIATES

By

Bong Ser Park

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ABSTRACT

PHOTOINITIATED HYDROGEN ABSTRACTION REACTIONS OF KETONES AND BEHAVIOR OF BIRADICAL INTERMEDIATES

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The photochemistry of several ketones with different structural features was investigated. Intramolecular hydrogen abstraction reactions by excited carbonyl groups results in the formation of biradicals, which then cyclize to give photoproducts. This research concentrated on what determines diastereoselectivities of cyclization of the various biradicals and what determines the rates of biradical formation.

α-Arylacetophenone derivatives show a wide range of diastereoselectivities in their photoproducts depending upon their substitution pattern. The high diastereoselectivity observed in the photocyclization of α-(o-ethylphenyl)acetophenones appears to reflect conformational equilibria in the triplet 1,5-biradical intermediates rather than steric barriers created during cyclization. The low diastereoselectivity observed for α-(o-benzylphenyl)acetophenones is attributed to a benzylic conjugation effect, which reduces the rotational barrier of the bond that determines selectivities. Putting a methyl group at the α position changes reactivity and diastereoselectivity significantly. Changes in ground state geometry appear to be responsible. Most interestingly, α-(2,4,6-triethylphenyl)-propiophenone forms only one out of eight possible stereoisomeric products upon irradiation in methanol and in the solid state.

Photolysis of ortho-alkylphenyl ketones results in formation of benzocyclobutenols. The mechanism for the reaction involves triplet state γ-hydrogen abstraction that generates 1,4 biradicals, which decay to form dienol intermediates. The fact that only the E isomer is formed from o-ethylbenzophenone and 2,4,6-triethylbenzophenone supports the previous suggestion by Matsuura that cyclobutenols are formed by stereospecific conrotatory cyclization of the dienols. The intermediacy of dienols was proven by quenching of the reaction by acids and bases.

Ortho-tert-amylbenzophenone forms two pairs of diastereomeric indanols upon irradiation in solution and in the solid state. Two different reaction sites, ethyl and methyl,

have comparable reactivity even in the solid state. This may reflect upon the insensitivity of the hydrogen abstraction reaction rate to orientational factors.

2,4,6,2',4',6'-hexasubstituted benzils form hydroxyindanones in moderate to good quantum efficiency upon irradiation at 435 nm in both solution and solid state. Based on the least motion principle in solid state, direct 1,6 hydrogen shift is proposed as a mechanism of this reaction, at least in the solid state reaction.

Several examples of remote hydrogen abstraction reaction were also investigated. α-(o-alkylphenyl)acetophenone and β-(o-alkylphenoxy)propiophenone form a six-membered and a seven-membered ring system, respectively. Ortho substituted α-phenoxyacetophenone gives only α-cleavage products and β-(o-alkoxyphenoxy)propiophenone is photostable.

To my father

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The author's sincere thanks are given to Professor Peter J. Wagner. The knowledge he shared with me throughout the course of this research was invaluable. His insight and willingness to discuss any topic made my stay in MSU enjoyable and fruitful.

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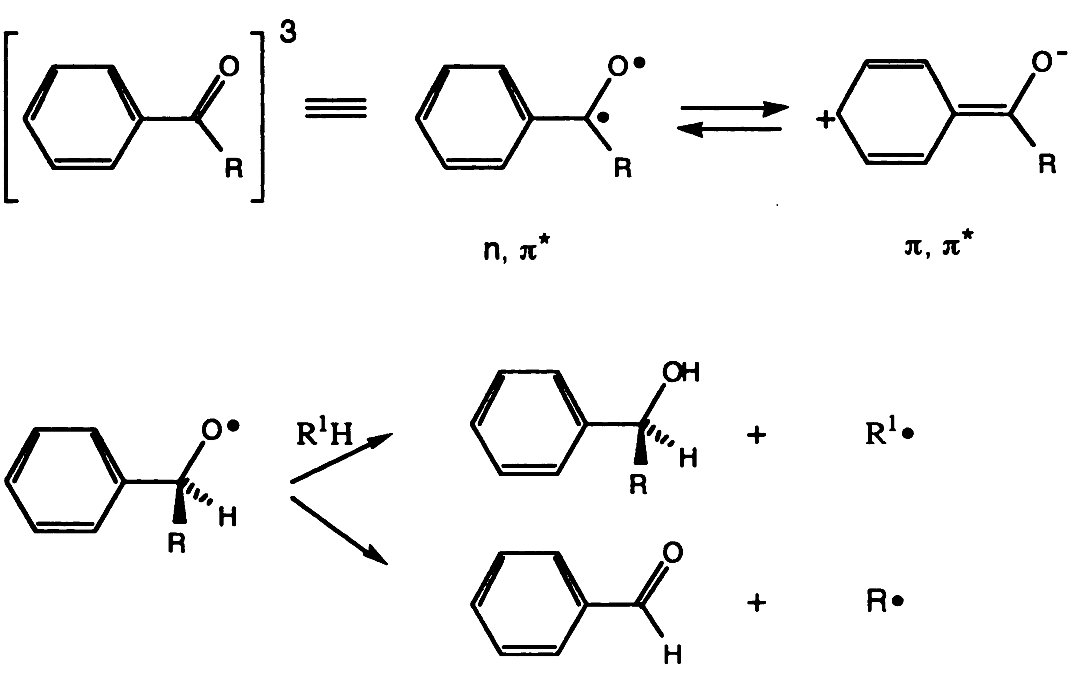
Introduction

Functional groups are an essential part in organic chemistry because they are the sites at which most chemical reactions take place. Among these, the carbonyl group has been considered as the most important, not only because it shows a wide range of interesting chemistry due to its unique electronic structure, but also because carbonyl compounds are abundant in nature. The ground state chemistry of carbonyl compounds has been widely explored since the early stages of chemistry history as evidenced by the lengths of chapters on carbonyl compounds in most organic chemistry textbooks. Thus, it is no surprise to find that the photochemistry of ketones has been a major target for research for many decades. In the early days of ketone photochemistry, various kinds of reactivity of carbonyl compounds were discovered; photoreduction, Norrish type I and type II reactions, Paterno-Buchi reaction, etc. In the 1960's, efforts were shifted toward understanding the mechanisms of these reactions. Instead of a lengthy discussion of the mechanisms of all the reactions that accumulated over the years, the reactions closely related to the research presented in this thesis will be summarized below.

α-Cleavage and hydrogen abstraction reactions are of special interest, not only because they find the most abundant examples in the literature but also because they illustrate the fundamental features of other reactions in organic photochemistry. These two reactions show good similarities to the well known behavior of alkoxy radicals.[1, 2] Depending on the availability of hydrogen donors, alkoxy radicals can either abstract a hydrogen or cleave to give a carbonyl group and a new radical as shown in Scheme 1.[3] The similarity of these two seemingly different reactions can be easily understood in terms of a simplified electronic description of triplet excited states of carbonyl compounds(Scheme 1).



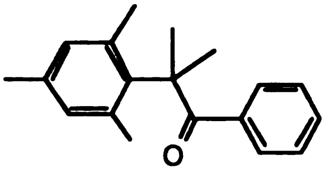
Scheme 1

<u>α-Cleavage reactions</u>

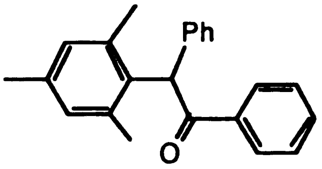
The α-Cleavage reaction, which is better known as the Norrish type I [4] reaction, has been studied extensively and is still actively investigated in studies of magnetic field effects[5] and environmental effects.[6] The reaction is usually followed by disproportionation, coupling or trapping by hydrogen donors. The reaction rate depends on the nature of the excited state, on the relative stability of the resulting radicals and on orbital alignment in the excited state.[7] If the carbonyl group is part of a ring, the cleavage rate can be dependent on the ring size due to differences in strain energy and stereoelectronic factor. These will be discussed with examples below.

Phenyl ketones are known to populate the triplet excited state via very efficient intersystem crossing from initially excited singlet state[8] while aliphatic ketones can react both from singlet and triplet excited state. In the case of aliphatic ketones, it has been shown that the cleavage occurs from the triplet excited state about 100 times faster than from the singlet excited state.[9] [10] It has been generally considered that phenyl ketones undergo the cleavage at much slower rates than aliphatic ketones do.[11,12] This different reactivity between aliphatic ketones and phenyl ketones can be explained by the different triplet energies of the two ketones. The triplet energies of aliphatic ketones and phenyl ketones have been measured to be larger than 79 kcal/mol and 74 kcal/mol, respectively.[13] Thus, the higher triplet energy of aliphatic ketones facilitates cleavage of the relatively strong OC-R bond.(80-90 kcal/mol).[11]

Wagner, Meador and Zhou have studied photochemistry of several substituted α-mesitylacetophenones.[14] Unsubstituted α-mesitylacetophenone undergoes highly efficient photocyclization to a 2-indanol via triplet state δ-hydrogen abstraction(*vida infra*). However, α-mesitylisobutyrophenone, 2-phenyl-1,2-dimesitylethanone and 1,2-dimesitylethanone all undergo only α-cleavage to radicals. [14f]



1



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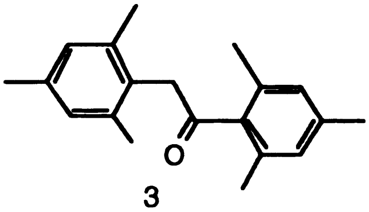
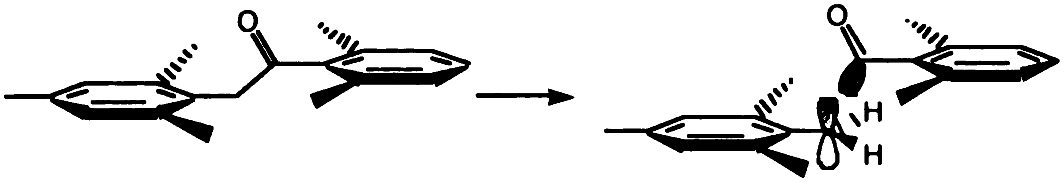


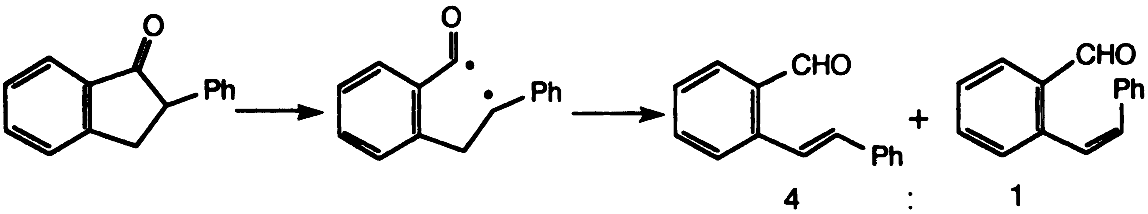
3

The rapid cleavage behavior of compounds 1 and 2 suggests that relief of steric strain in these molecules facilitates α-cleavage. The exclusive cleavage reaction of compound 3 was very interesting not only because this molecule appeared to be relatively uncongested but also because possible competing reactions, δ-hydrogen abstraction and γ-hydrogen abstraction, are known to be very fast. The puzzle was solved by x-ray structure of this compound. The geometry holds the α-mesityl group in a perfect orientation to maximize benzylic conjugation in the developing radical(Scheme 2). Bond rotations are so slow that reaction occurs from the preferred ground state geometries.



Scheme 2.

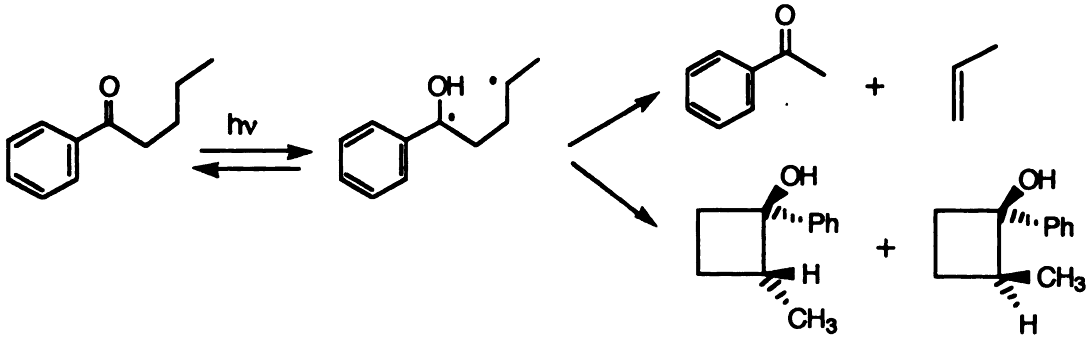
Baum reported that 2-phenylindanone formed cis- and trans-enals in a 4 to 1 ratio via Norrish type I cleavage followed by internal disproportionation of the resulting biradical[15] (Scheme 3). From their studies, they concluded that this reaction is occurring from the n, π* triplet state. The phenyl group at 2 position seemed to be necessary because both 1-indanone and 2-methylindanone were photostable under the same condition. The chemical yield of this reaction was high but the reaction rate was not measured.



Scheme 3

Hydrogen abstraction

Carbonyl compounds can undergo, upon electronic excitation, characteristic hydrogen shift to the carbonyl oxygen from hydrogen donors.[2,7,16 17] If the hydrogen donors are separate molecules, this process is referred to as photoreduction. The photo-initiated reduction of benzophenone by good hydrogen donors such as amines and DABCO has been extensively studied since early part of this century and mechanistic details are still actively being discussed.[18] Intramolecular version of this reaction has also been a highlight in the development of a general picture of how photochemical reactions occur.[2,7] The most classical example of this reaction is shown in Scheme 4.



Scheme 4

The initially formed biradicals can either cleave or cyclize. Both processes have been referred to as "Norrish type II reaction". Recently, Wagner suggested that the latter process be called the "Yang reaction"[17] because Yang was the first person to discover it.[19]

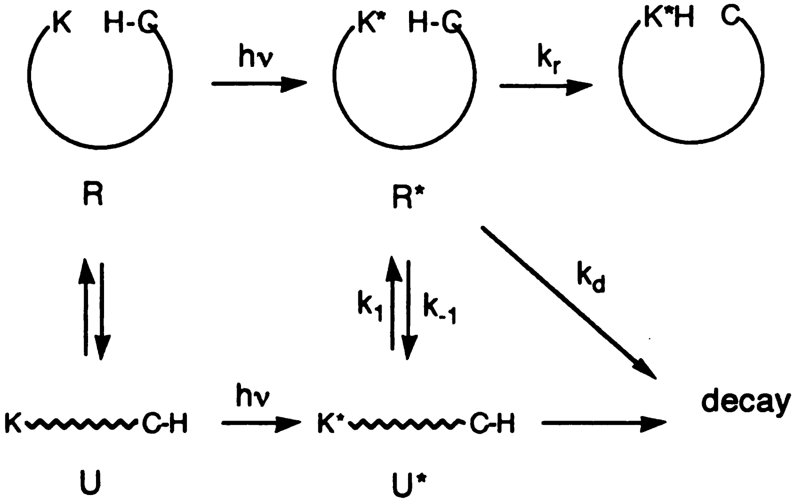
The active excited state that is responsible for the hydrogen abstraction reaction is known to be an n,π* triplet state. If a ketone has a π, π* lowest excited state, the reaction occurs from thermally populated n,π* triplet state[20]. However, it is important to note that the reaction may also occur from the π, π* lowest excited state, but at much slower rate than from n,π* triplet state.[21, 22, 23]

The n,π* triplets, like alkoxy radicals, have such high electron demand that the transition states for hydrogen transfer are stabilized by charge transfer. Therefore, electron withdrawing groups near the hydrogens being abstracted slow down the hydrogen transfer.[20, 24]

Quantum yields of the reaction are determined almost entirely by the extent to which these biradicals revert to starting ketones. Thus, the quantum yield in methanol is much larger than that in benzene because the back hydrogen transfer is prevented by hydrogen bonding to the solvent.[2,25]

A. Conformational effect on photochemical reaction

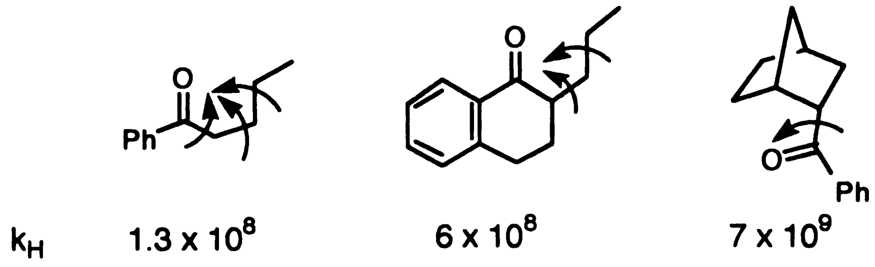
Recently, Wagner has addressed the question of how rates of conformational change affect the course of photochemical reaction.[26] Several possible routes that are derived from competition between conformational change and excited state reaction are shown in Scheme 5, where R and U represent reactive and unreactive conformations, respectively. Three limiting cases could be considered.



Scheme 5.

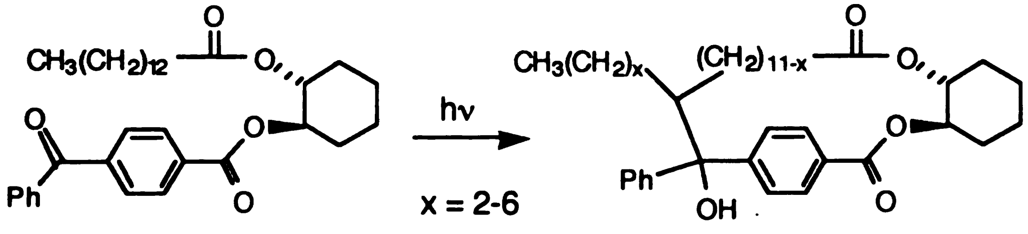
(a) conformational equilibrium; k_1, k_{-1} >> k_r, k_d

Probably, this is the most commonly encountered example in photochemistry especially in flexible acyclic systems. In this dynamic class of excited state reaction, conformational equilibrium is established before reaction. Thus, the reaction rate is dependent upon how much the reactive conformers are populated in excited state. There are many examples showing that incorporation of rings and carbon-carbon multiple bonds between the carbonyl and C-H being broken increase the reaction rate by reducing possible modes of rotation and hence by increasing the population of reactive conformers[27](Scheme 6).



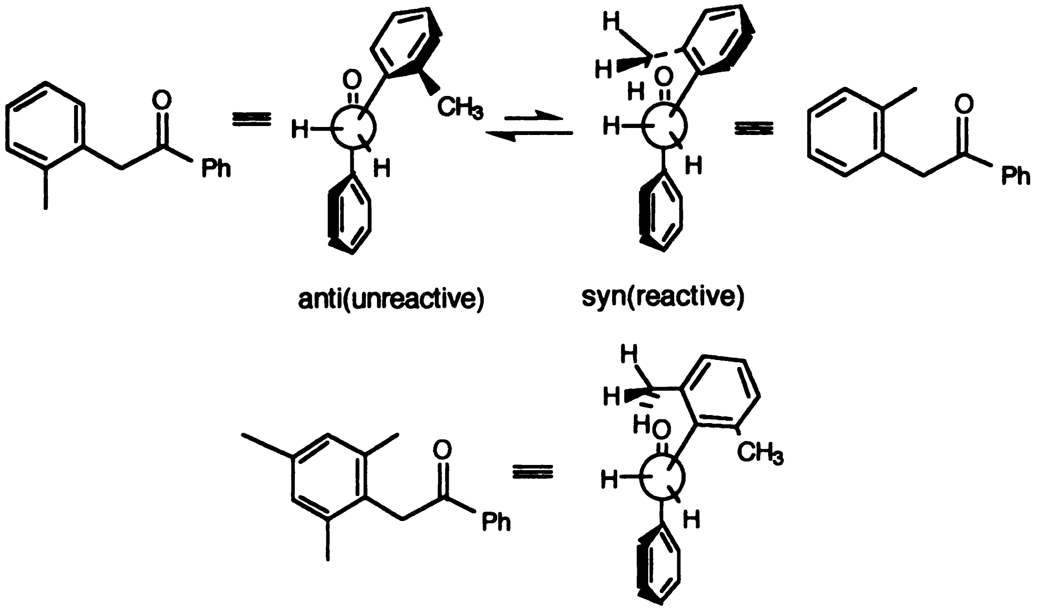
Scheme 6

Another interesting example can be found from remote hydrogen abstraction studied by Breslow[28] and Winnik[29]. They have shown how the rate constants of remote hydrogen abstraction by benzophenones substituted para with long alkyl tails change by varying the chain lengths(Scheme 7). Intuitively, the desired reaction seemed improbable considering the long distance between two reaction sites. Contrary to this prediction, the molecule could react by coiling the chain into proper spatial orientation. This reaction was dubbed a "biomimetic reaction", with reference to enzymatic catalysis.



Scheme 7

Wagner and Meador found that α-(o-alkylphenyl)acetophenones undergo efficient photocyclization to 2-indanols through triplet state δ-hydrogen abstraction.[14] The fact that α-mesitylacetophenone is nearly 7 times more reactive than α-(o-tolyl)acetophenone led the authors to suggest rotational equilibrium between reactive syn conformation and unreactive anti conformation.[14a] According to MMX calculations, this ketone has a minimum energy geometry with Cα-Ar bond eclipsing with the C=O bond. Thus, two conformers shown below were proposed for α-(o-tolyl)acetophenone, whereas no rotation is required for reaction to occur for α-mesitylacetophenone(Scheme 8).

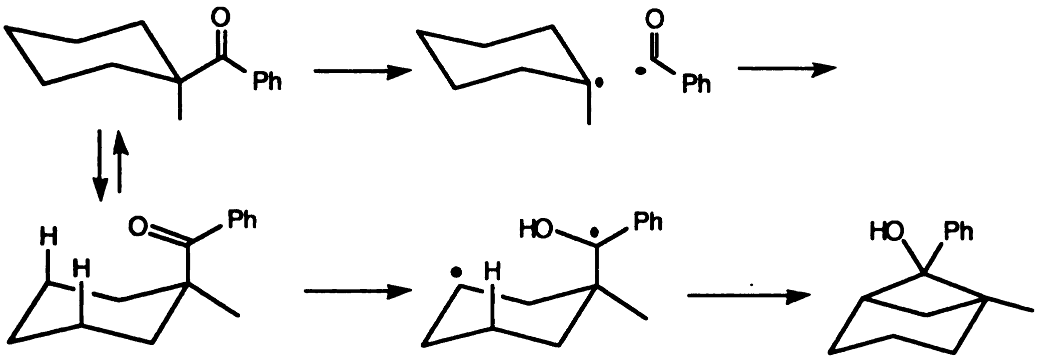


Scheme 8

(b) Ground state control; $k_1, k_{-1} << k_r, k_d$

In this case, conformational interconversions are all slower than decay, such that ground state conformational preferences control photoreactivity. All solid state photoreactions can be classified into this category. For solution phase photochemistry, Lewis' study of the benzoylcyclohexanes represents a good example of ground state control of triplet reactivity.[30] He found that for 1-benzoyl-1-methylcyclohexane, two kinetically distinct triplets are observed , which lead to two different products.(Scheme 9) The author explained that the two different triplets originate from two distinct conformers shown below. When the benzoyl group is in axial position, the reaction proceeds to cyclobutanol formation via γ-H abstraction. In the conformer with benzoyl equatorial, however, both γ-hydrogens are too far away to be abstracted, so α-cleavage reaction takes over. The rate constants for α-cleavage and γ-H abstraction were measured to be 2×10^7 s^{-1} and 6×10^8 s^{-1}, respectively, both of which are much faster than ring inversion rate of cyclohexane, $\sim 10^5$ s^{-1}. For a five membered ring analogue, 1-benzoyl-1-

methylcyclopentane, only one excited triplet was observed, which is consistent with the faster ring inversion rate of cyclopentanone.

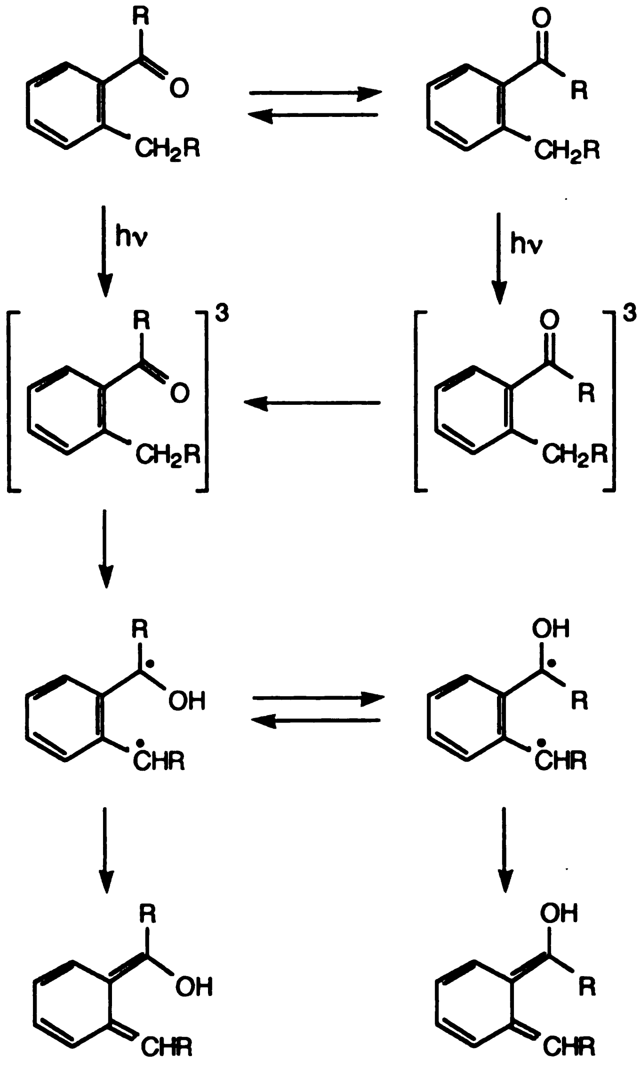


Scheme 9

(c) rotational control; $k_1 \sim k_d$, $k_{-1} < k_r$

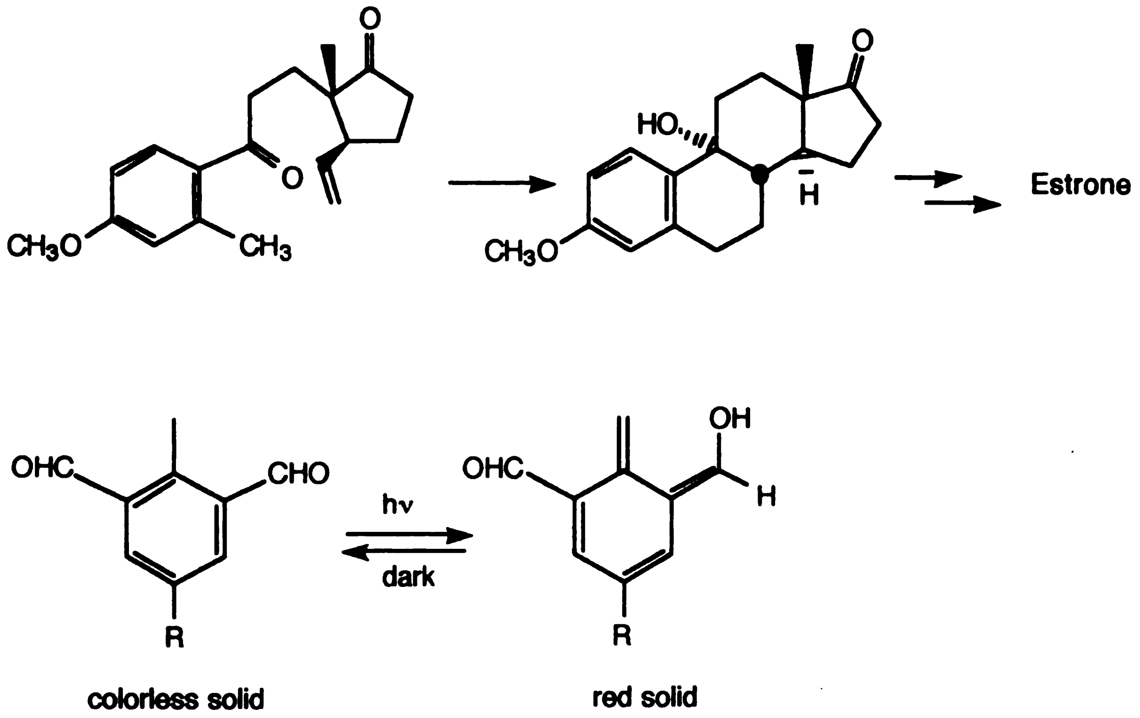
Not many examples are known for rotational control in a photochemical reaction. So far, the best example of this is provided by the photoenolization of o-alkylphenylketones.[31]

Laser flash photolysis of o-alkylphenyl ketones produced several transients of different lifetimes, which led to a mechanistic confusion for many years. Only recently, it was realized that this system formed two kinetically and conformationally distinct triplets, syn and anti rotamers as shown in Scheme 10.[32] This explanation was supported by the behavior of 8-methyl-1-tetralone, which is locked into a syn conformation and which displays only one triplet. The lack of an H/D isotope effect on the rate of decay of the anti triplet led to the conclusion that the rate determining step is not a hydrogen abstraction but bond rotation.



Scheme 10

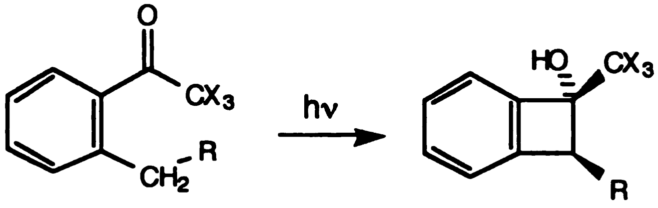
Photoenolization of ortho-alkylphenyl ketones is one of the most widely studied photoreactions in history of ketone photochemistry,[31,32,33] not only because it is mechanistically interesting, but also because it has several practical applications. Excited carbonyl group abstract hydrogen from benzylic position and the resulting biradical decays to dienol. This dienol has been utilized in synthesis of some natural products[34] and the reversibility of the transformation has value a photochromic phenomenon[35](Scheme 11).



Scheme 11

Most early studies of photoenolization were centered around o-alkylbenzophenones. Even though no new products were observed in photolysis of these compounds, formation of dienol intermediate was postulated based on deuterium incorporation into benzylic position in deuterated solvent and trapping the dienol with dienophile[31b]. Later, Matsuura reported that some sterically hindered phenyl ketones such as 2,4,6-trialkylbenzophenones and 2,4,6-trialkylacetophenones gave cyclobutenols as only product.[36]. Soon a question was raised. Why doesn't a simple o-alkylphenylketone cyclize to give benzocyclobutenol while 2,6-dialkylphenyl ketones form benzocyclobutenols efficiently? What factors determine this different photoreactivity?

Recently, Subrahmanyam in our group observed that several acetophenones (shown below) yield benzocyclobutenols as the major or only photoproducts upon irradiation of dilute ketones with wavelength >290 nm[37] (Scheme 12).



1a X = H, R = OCH_3
1b X = H, R = $OCH_2CH{=}CH_2$
1c X = H, R = $OCH_2CH_2CH{=}CH_2$
1d X = F, R = $CH_2CH_2CH{=}CH_2$
1e X = H, R = H

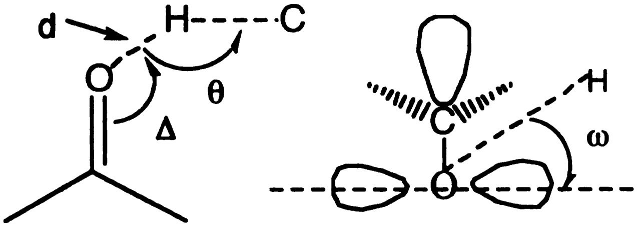
2

Scheme 12

This was a very interesting finding because the cyclization products have rarely been observed from simple ortho-substituted alkylphenylketones. Thus, we decided to investigate several substituted benzophenones and acetophenones in order to find out how general this reaction is.

B. Orientational Requirements of Hydrogen Atom Abstraction

The geometric requirements for hydrogen abstraction by excited carbonyl compounds have been of interest for over 20 years.[38] Scheffer has studied a variety of ketones that undergo γ–hydrogen transfer in their crystalline states.[39] In analyzing their reactivity, he considered the following ground state parameters to be the most important in determining reactivity: d, the distance between O and H; θ, the O-H-C angle; Δ, the C=O-H angle; ω, the dihedral angle that the O-H vector makes with respect to the nodal plane of the carbonyl pi system(Scheme 13). He suggested the theoretically "ideal" values for these parameters shown below; these are based on simple stereoelectronic ideas regarding the directionality of p orbitals and on the known van der Waals radii of oxygen and hydrogen.



Ideal values:

$\Delta = 90\text{-}120°$ $\theta = 180°$

$\omega = 0°$ $d \leq 2.7$ Å

Scheme 13

After comparing triplet reactivity with measured ground state geometries, Scheffer concluded that the distance d is most important in determining reactivity, with values as high as 3.0 Å being okay. However, for those situations in which a hydrogen is within this "reactive" distance of the carbonyl, there still remains the fundamental question as to the proper orientation of atoms, bonds and orbitals.

The value of ω has been of particular interest, with several theoretical studies suggesting that low values are necessary.[40] However, several experimental studies have found that reactivity persists with ω values as high as 60°.[39b,41] Several systems in which ω approaches 90° have been reported to be unreactive.[42] Although rapid competing α–cleavage may reduce hydrogen abstraction efficiency in some polycyclic ketones, it appears that k_H values must be low in such compounds.[43]

Wagner suggested years ago that the rate constant for hydrogen abstraction may be proportional to $\cos^2\omega$, which describes the electron density of a p orbital.[2,7] This concept accommodates all the experimental observations.

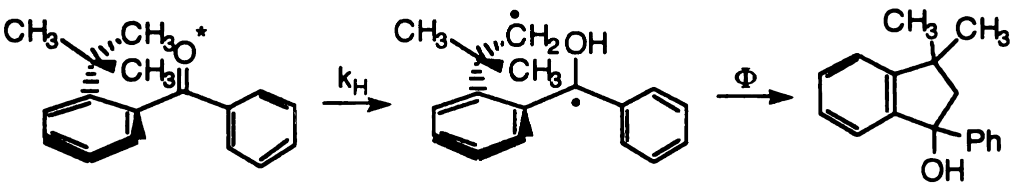
C. δ hydrogen abstraction

Early investigation of hydrogen abstraction reaction focused mainly on γ hydrogen abstraction, which generates 1,4 biradicals. The ease of this transformation can be attributed to the formation of a favorable six membered ring transition state. Later, hydrogen abstraction from δ position was also studied extensively by Wagner. The intrinsic γ/δ selectivity in triplet ketones was shown to be 20/1 from Wagner's study of δmethoxyvalerophenone.[44] Recently, Houk reproduced the preference by his theoretical studies of intramolecular hydrogen transfer. The calculation showed that much of the preference is entropic, but that there is little enthalpy difference between the two modes. [45]

If γ-hydrogens are not available either by substitution at γ-position or by conformational factors, the reaction can occur predominatly from δ-position. Among many examples of δ-H abstraction known up to now, two different systems which are closely related to the research of this thesis, will be briefly reviewed below.

(a) o-tert-butylbenzophenone

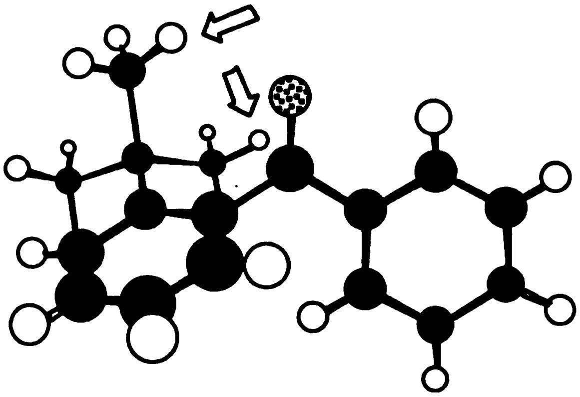
Some time ago, photochemistry of ortho-tert-butylbenzophenone was studied in depth in our lab.[46] Irradiation of o-*tert*--butylbenzophenone (OTBBP) as a solid or in solution from 77 °K to room temperature results in its quantitative cyclization to 1-phenyl-3,3-dimethyl-1-indanol. The quantum efficiency of this process and the lifetime of the resulting 1,5-biradical show a much larger solvent effect than do typical 1,4-biradicals.



$k_H \geq 10^9\ M^{-1}\ s^{-1}$ at 25° ; E_a = 2.5 kcal/mole ; log A = 10.6

biradical lifetime = 43 ns in methanol , 4 ns in toluene

$\Phi_{benzene} = 0.04$ $\Phi_{methanol} = 1.00$



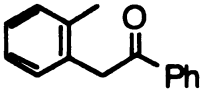
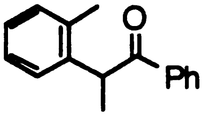
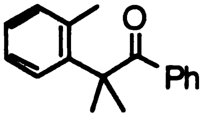
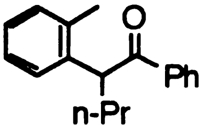
The unusually large value of k_H for OTBBP has been attributed to the ketone existing exclusively in a conformation ideal for internal hydrogen abstraction. The X-ray structure shows that one of the *tert*-butyl hydrogens is held 2.46 Å from the carbonyl oxygen and 40° above the nodal plane of the carbonyl π system while another is held 2.67 Å from the oxygen but perpendicular to the same nodal plane.

It would be very interesting to know which hydrogen is preferentially attacked. But, it was impossible to get the information from OTBBP because of the symmetry of the molecule. Since this system reacts efficiently in solid state, where position of atoms is pretty much fixed, knowing which hydrogen has more reactivity would provide an important information on orientational requirement of hydrogen abstraction reaction. Thus, an unsymmetrical analogue, o-tert-amylbenzophenone, was prepared and the photochemistry of this compound was investigated by Wagner and Pabon.[47] The continuation of this project will be described in this thesis.

(b) α-(o-alkylphenyl)acetophenones

As mentioned above, α-(o-alkylphenyl)acetophenones undergo very efficient photocyclization to 2-indanols via triplet state δ-hydrogen abstraction. The reaction rate for α-(o-tolyl)acetophenone is $>10^8$ s^{-1} and the biradical lifetime is 20-50 nsec.[80] This system shows an interesting α-substituent effect. When additional α-substituents are present, the quantum yield of indanol formation drops significantly and α-cleavage takes over instead.[75]

Table 1. α-substituent effect on o-tolylacetophenone derivatives.

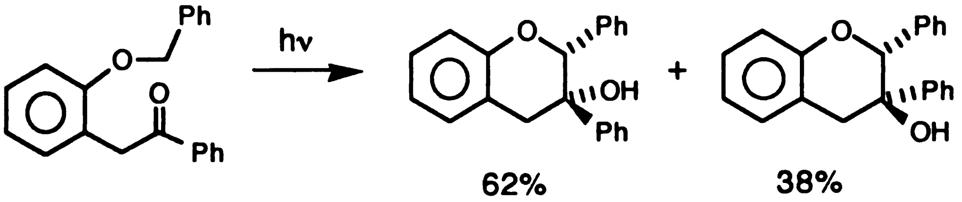
	Φ_{cyc}	Φ_{cleav}	$k_q\tau$, M^{-1}
	1.0	0	50
	0.05	0.28	98
	0	0.38	121
	0.014	0.03	28

This interesting phenomenon was soon rationalized based on the result from X-ray structure, NMR analysis as well as MMX calculation. For α-(o-tolyl)acetophenone, the most stable conformation has α-aryl group eclipsing with C=O group, which is very close to "reactive" geometry. For the substituted ones, however, an additional α-substituent makes the tolyl group twist away from the carbonyl The eclipsed geometries become too high in energy to be populated within the short triplet lifetimes and reaction has to occur from the highly twisted geometry. In this "poor" geometry for hydrogen abstraction, the reaction rate drops and other reactions such as α-cleavage, start to compete. In solid state, however, cyclization predominates despite the "poor" geometry, probably due to reversibility of α-cleavage in the solid.[14e]

D. More remote systems than δ hydrogen abstraction

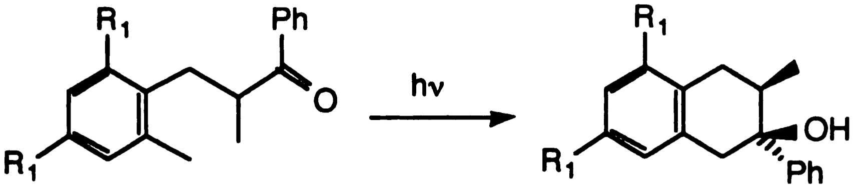
There have been scattered reports on H-abstraction more remote than δ-hydrogen abstraction.[48] Carbonyl compounds which lack suitably aligned γ- and δ- hydrogens by reason of conformation or substitution have the possibility of more remote hydrogen abstraction. This remote H-abstraction require 8 or larger membered ring transition state and the resulting cyclization products are 6 or larger membered rings. There have been great demand for efficient synthetic methodology to form larger than six membered ring in organic syntheses.

Wagner and Meador studied photocyclization of α-(o-benzyloxyphenyl)acetophenone[49]. Irradiation of this ketone in cyclohexane formed two isomeric diphenylbenzodihydropyranols in high chemical yield(Scheme 14). The ratio of two isomers was 1.6 to 1 favoring the more stable Z isomer. It would be interesting to see how general this reaction is and how reactivity changes depend on structural variation.



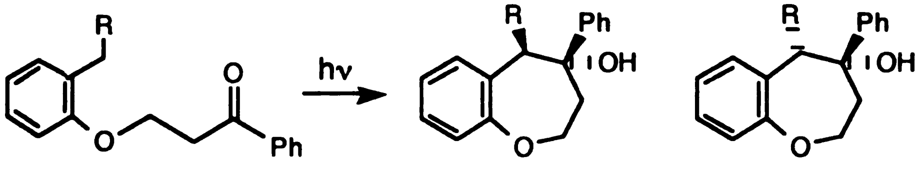
Scheme 14

Wagner and Zhou also studied the photochemistry of β-(o-tolyl)propiophenone, which form 2-tetralols via ε-hydrogen abstractions(Scheme 15)[50]. As expected, quantum yield and rate constants were quite low, 0.001-0.002 and 10^5-10^6 s^{-1}, respectively, but the chemical yield was reasonably good. The low quantum efficiency was explained by competing, rapid CT quenching by the β-aryl group, which is a well known process for this type of system. In a minimized geometry by MMPMI calculation, the carbonyl group was too far away to reach the benzylic hydrogens, which may explain the low reactivity of this molecule. Interestingly, methyl substitution at α-carbon increase k_H significantly, which led author to suggest that the methyl group at α-position increase the population of reactive geometry.



Scheme 15

Recently, Carless and coworkers studied photochemistry of three different β-(o-alkylphenoxy)propiophenones as shown in Scheme 16.[51] From this reaction, they observed formation of 7 membered ring , tetrahydrobenzoxepinol via 1,7 biradicals.



R = allyl, phenyl

2

1

Scheme 16

This was a very interesting finding because this presumably occurs via a most unusual nine-membered transition state for hydrogen abstaction by the triplet excited carbonyl group. No efforts were made to obtain quantum efficiency and triplet lifetime of these compounds. It would be interesting to know these values in order to understand photochemistry and photophysics of this conformationally flexible system better.

E. The fate of biradical intermediate.

(a) Biradical lifetime

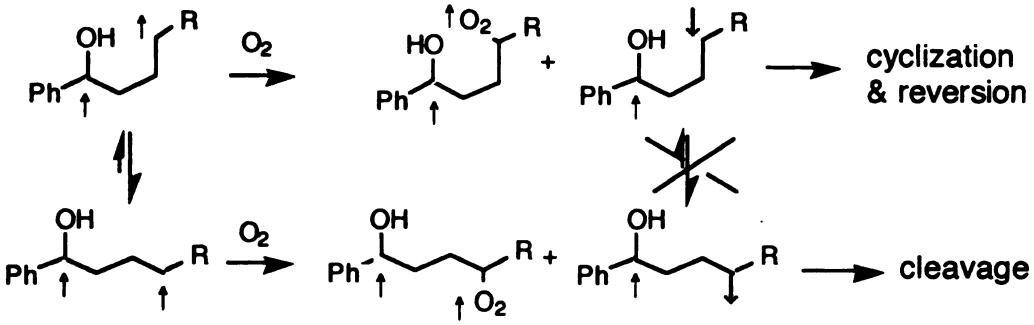
The biradical intermediate in the Norrish type II reaction was first demonstrated by racemization of ketones with asymmetric γ-carbons[52] and by trapping with thiols.[53] Since then, the biradicals have been generally accepted as intermediates for most hydrogen abstraction reactions of excited carbonyl group.[54] These reactions are known to occur from triplet excited states, so the resulting biradicals are triplets. For the formation of photoproducts, intersystem crossing (ISC) into the singlet manifold is therefore necessary.

Now, several interesting questions can be raised. What causes ISC? When does this ISC occur? Is ISC solely responsible for biradical lifetime? In fact, all of these subjects have been heavily discussed for last two decades.[55]

Scaiano proposed[55a] that biradical lifetimes are simply a measure of how fast they convert irreversibly to the singlet biradical that then yields products in a fast process. He also added that if the reaction forms several products, the product ratio can be controlled by interactions at the triplet manifold level. The latter is better known as "conformational memory in singlet biradical". Scaiano explained this concept using the following experimental observations; [56]

Photolysis of γ-methylvalerophenone produces several different photoproducts via elimination and cyclization. Cisoid conformation of the 1,4 biradical result in cyclization and reversion while anti conformation is responsible for cleavage reaction due to stereoelectronic necessity for overlap of the breaking bond with both singly occupied p orbitals.

When the same compound was irradiated in the presence of paramagnetic quenchers such as oxygen, nitroxide etc, product ratio of elimination/cyclization changed and the biradical lifetime shortened. The latter is often described as paramagnetic catalysis of ISC. Once again, this observation was explained such that ISC is product determining and that the conformation from which ISC occurs is probably different when the process involves interaction with a paramagnetic quencher. This idea suggests that different conformer of biradicals may have different intrinsic rates of ISC. Scheme 17 describes Scaiano's hypothesis.



Scheme 17

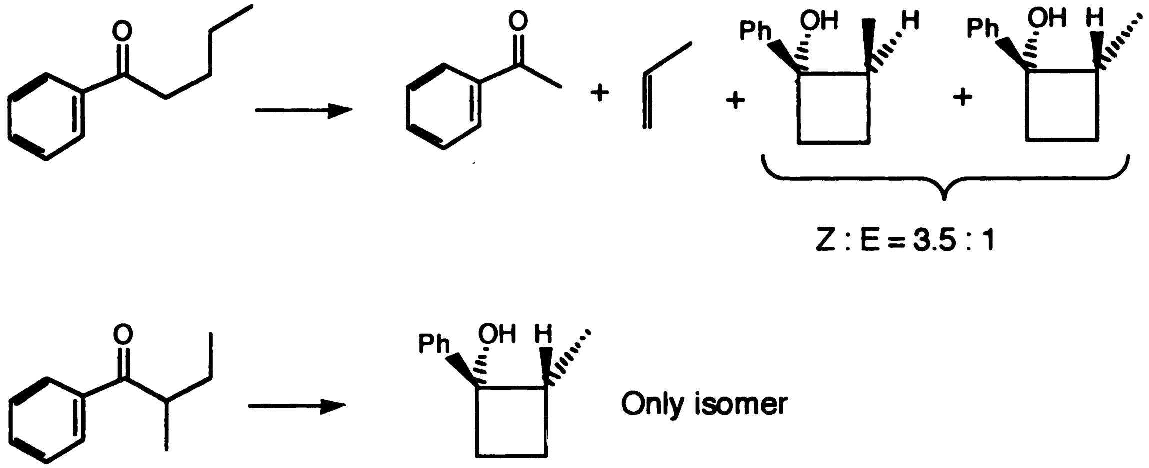
Scaiano explained that paramagnetic quenching produces a different distribution of conformers of singlet biradicals than does simple ISC of triplet biradicals. The reactions of singlet biradicals are so fast that no equilibration of different conformers occurs, so the singlet biradical can effectively "remember" the conformation of the triplet biradical when ISC occurs.

Scaiano also discussed solvent effects on biradicals.[54a] For above reaction, addition of Lewis base increased quantum yields of product formation and biradical lifetime was increased by comparable factors. Originally, this was explained by the suppression of the major chemical reaction, disproportionation back to starting ketone, by hydrogen bonding. Scaiano suggested that the lengthening of biradical lifetime is due to change in the conformational distribution in the triplet biradicals, which lead to different rate of ISC.

Scaiano's hypothesis has been widely accepted, although firm experimental support for other type of biradicals has been lacking. But, several fundamental questions were still unanswered. What really induces ISC? How do ISC rates change with biradical structure and solvent? Are rate determining ISC and chemical reaction of the biradicals separate, consecutive steps as Scaiano stated? Wagner recently tackled these questions and suggested a modified explanation of these subjects[17,54b]. This will be discussed in detail later in the discussion section.

(b) Diastereoselectivity

Another interesting aspect of Norrish type II reaction (Yang reaction) is the diastereoselectivity displayed when two prochiral sites are connected to give cyclization products. In 1972, Lewis reported an interesting difference in diastereoselectivity of valerophenone and α-methylbutyrophenone.[57] They both form the same photoproduct, 1-phenyl-2-methylcyclobutanol, but the former gives a 3.5:1 Z:E ratio while the latter gives only the Z isomer(Scheme 18).

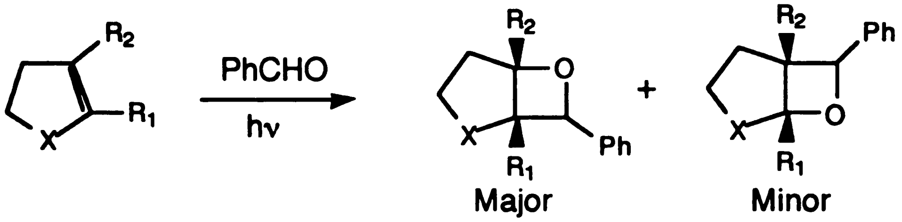


Scheme 18

The factors controlling the stereochemistry of photoreactions via triplet states are not well understood. In contrast to the corresponding transformations via singlet excited states, pure steric arguments alone could not explain or predict the stereoselectivity. Major difference between singlet and triplet reactions comes from the fact that triplets have to go through singlet energy surface to form the final products via intersystem crossing. Thus, timing of ISC becomes very important in determining the stereoselectivity.

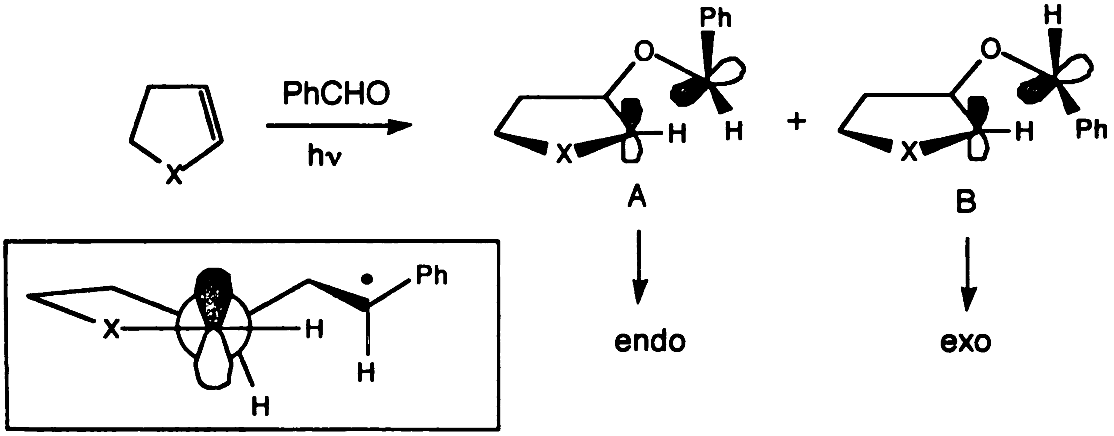
Not many examples to address this subject are found in the literature. Griesbeck recently studied stereoselectivity in 2+2 photocycloaddition of benzaldehyde to cyclic olefins and suggested electronic control of endo stereoselectivity of this reaction.[58] As shown in Table 2, a good endo selectivity was observed in the reaction between aromatic aldehydes and unsubstituted cycloalkenes while methyl groups at either position 1 or 2 on the cycloalkene moiety lower the amount of endo oxetane.

Table 2. Diastereoselectivity in photocycloaddition of benzaldehyde to cycloalkenes

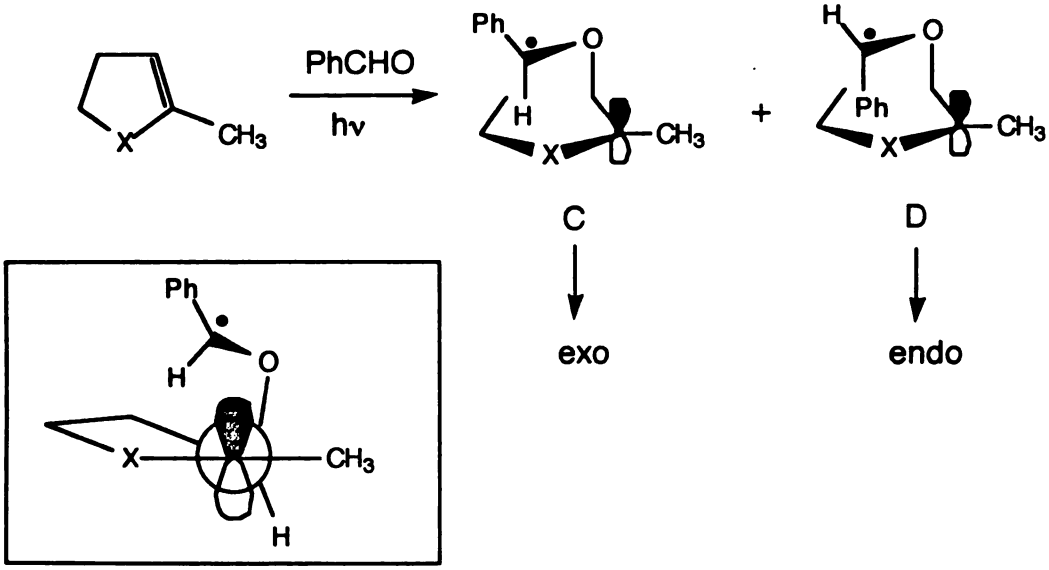


X	R_1	R_2	endo/exo[a]
CH_2	H	H	61:39
CH_2	CH_3	H	16:94
O	H	H	88:12
O	CH_3	H	65:35

a. endo/exo ratio of major product.



Scheme 19



Scheme 20

The author explained that the stereoselectivity of this reaction was controlled by reactive 1,4-biradical conformations of appropriate orbital alignment for rapid ISC. For the reaction between aromatic aldehydes and unsubstituted cycloalkenes, the two biradical conformers A and B were considered, with the alkyloxy substituent in a pseudoequatorial position. Among these two conformers, conformer A was responsible for the high endo selectivity, for being more populated due to fewer steric interactions(Scheme 19). For the substituted cycloalkenes, the increasing gauche interactions between methyl and β-alkyloxy substituent make other conformers, C and D, populated, and again conformer C is preferred due to fewer steric interactions(Scheme 20).

The author also emphasized that these biradical conformations are not real minima on the triplet potential energy surface, instead these are favorable geometry for rapid ISC, with two p orbitals at the radical centers orthogonal to each other. Adam and Wilson[59] have proposed that the ISC rates of various biradicals increase as their singly occupied p orbitals approach orthogonality, in agreement with earlier proposals of Salem[60] and of Shaik and Epiotis.[61]

The most important discussion in Griesbeck's paper maybe is the fact that he interpreted these conformations as transient points through which stable 1,4-biradicals have to pass in order to invert the spin and overcome the spin barrier for bond formation. This interpretation will be elaborated in the discussion section of this thesis, in connection with recently modified proposal by Wagner on importance of timing of ISC for the product forming processes..

In order to determine the factors that control the stereochemistry of photoreactions via triplet states in more systematic fashion, we decided to investigate the diastereoselectivity of several compounds having various substituents at different positions. Two types of substitution are of special interest Since there are many examples in which a methyl and a phenyl on adjacent carbons in a cyclization product show widely varying Z/E selectivity, biradical cyclizations that have not been examined for this steric interaction were chosen as targets. There are also several examples of restricted rotations about benzylic bonds affecting biradical reactions, More examples of the benzylic conjugation effect on photochemical reactions will be illustrated later in this thesis.

F. Measurements of excited state lifetimes

(a) Stern Volmer analysis

If several decay pathways of a given excited state are competing, the liftetime of the excited state is the inverse of the sum of all the rate constants for decay as shown below.

$$1/\tau = \Sigma k_d \qquad (1)$$

It means that all the rate constants for decay of the excited states should be known in order to calculate the lifetime of the excited state. Since this is obviously not an easy task, another indirect way to estimate the excited state lifetime is required.

In the presence of an external quencher, equation (1) becomes

$$1/\tau = \Sigma k_d + k_q[Q] \qquad (2)$$

where k_q is the bimolecular quenching rate constant and [Q] is the concentration of quencher. A mathematical relationship, referred to as the Stern-Volmer equation[62], can be derived between the ratio of photoproduct in the absence and presence of quencher and [Q],

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \qquad (3)$$

A plot of Φ_0/Φ versus [Q] then should give a straight line with an intercept of 1 and a slope of $k_q\tau$. Thus, if k_q is known, the lifetime of the excited state can be calculated from the slope of this plot. It is known that the rate of triplet energy transfer quenching by dienes or naphthalene is 5-6 x 10^9 $M^{-1}s^{-1}$ in benzene at room temperature.[63] All the kinetic measurements in this thesis were measured by the Stern-Volmer analysis.

(b) Flash kinetics

The emergence of nanosecond and picosecond laser spectroscopy has allowed the direct detection of the biradical intermediates that are generated from hydrogen abstraction reactions, which confirmed the previous studies by Wagner. Since then, this technique has made a great contribution to understanding mechanisms of hydrogen abstraction reactions *via* direct studies of reactive intermediates such as triplet excites states and biradicals.

The kinetic studies using laser flash photolysis are good complementary tools to the steady state kinetic studies using Stern-Volmer plots, assuming that the transients give strong and unique UV absorptions. It can also measure the quenching rate constant, k_q, using the expression shown below.

$$k_{obs} = k_o + k_q\,[Q]$$

where k_{obs}, k_o, k_q and [Q] are the observed decay rate constant of the transient absorption, the decay rate constant without quencher, the quenching rate constant and the quencher concentration, respectively.

Numerous kinetic data for hydrogen abstraction reactions have been accumulated using this laser flash technique over the years. Table 3 shows a collection of kinetic data for some representative ketones, which are closely related to the research that are presented in this thesis.

Table 3. kinetic data of some representative ketones.[a]

ketones	$\tau_{triplet}$, ns	τ_{BR}, ns	k_H, s-1
valerophenone[54]	10	100	1×10^8
o-methoxybenzophenone[74]	1080	<5	5×10^5
o-benzyloxybenzophenone[74]	53	<5	2×10^7
o-*tert*--butylbenzophenone[46c]	<1	4(43)[b]	$>10^9$
α-(p-xylyl)acetophenone[80]	4	23(38)[b]	1.9×10^8
α-mesitylacetophenone[80]	<1	18(23)[b]	5.5×10^8

[a] All the measurements were made in nonpolar solvents such as benzene, hexane or toluene unless otherwise stated.

[b] The measurements in methanol were given in parenthesis.

The plot of transient decay rates at several different temperature can give Arrhenius parameters, which can provide additional information about reaction mechanism. Some experimental data are shown in Table 4.

Table 4. Arrhenius parameters of some representative ketones.

ketones	E_a, kcal/mol	$\log(A/s^{-1})$
valerophenone[64]	4.0	11.2
o-methoxybenzophenone[74]	4.2	9.2
o-benzyloxybenzophenone[74]	2.8	9.2
o-*tert*--butylbenzophenone[46c]	2.3	10.6

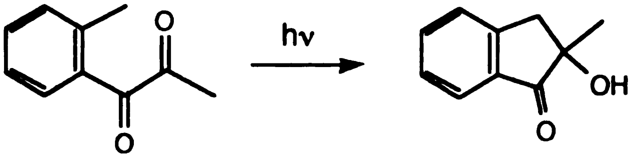
The result of o-tert-butylbenzophenone was quite surprising because the high reactivity of this compound was expected to be due to already built-in structure for hydrogen abstraction of this molecule, which would be reflected as higher A factor than the values for flexible ketones. Instead, the A factor stayed normal, but the activation energy decreased. Wagner explained that this phenomena may be due to relief of strain energy in transition state. Steric strain by the nonbonding interaction between tert-butyl group and lone pair electrons of carbonyl oxygen can be somewhat relieved by OH bond formation. The possibility of a tunneling mechanism was ruled out by the author because this molecule showed a classical H/D isotope effect[46c].

G. Benzil derivatives.

For some time, the excited state behavior of 1,2 diketones has drawn much attention from photochemists and spectroscopists.[65,66] The most interesting feature of this system has been due to existence of two carbonyl groups, which led to many speculations on the nature of its excited states. Unlike monoketones, there are two carbonyl groups which can be potentially active reaction sites.

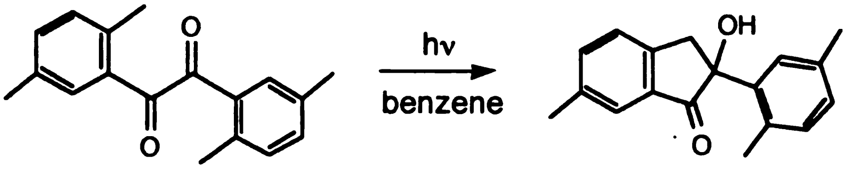
Benzil and other 1,2-diketones have been known to be inert to conventional one-photon photolysis in solvent that acts as a hydrogen donor.[67] Later Scaiano reported[68] that type I cleavage occurred readily upon biphotonic laser irradiation, but the resulting benzoyl radicals usually recoupled to yield the parent material, which made the photocleavage an "invisible" reaction. Scaiano explained that the photocleavage of benzil was a two photon process instead of conventional one photon process, because the triplet energy of benzil, 60 kcal/mol, was not enough to cleave the carbon carbon bond, whose bond energy is above 70 kcal/mol. Reexcitation of the excited benzil, which can be readily performed using laser flash photolysis, gives sufficient energy to undergo bond cleavage. He called this process "reluctant" Norrish type I reaction, where the term "reluctant" referred to the relatively inert one-photon behavior of this compound.

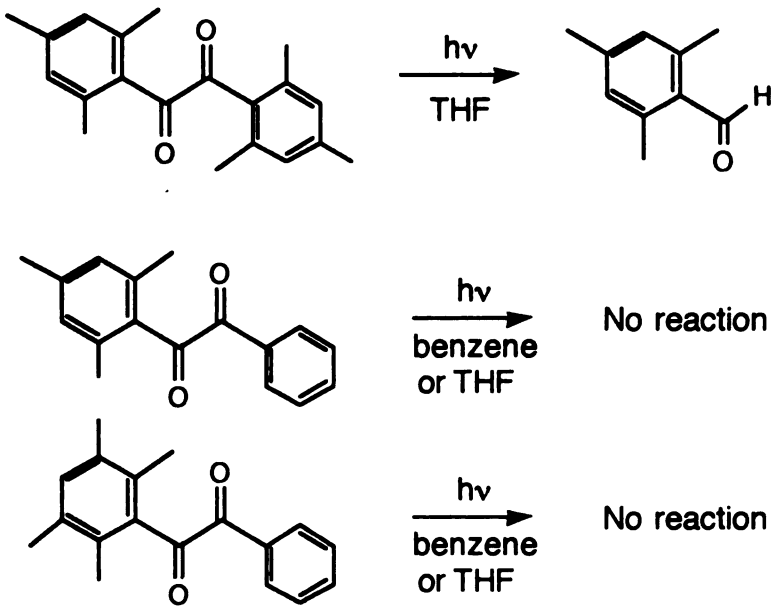
For ortho substituted benzil and other 1,2-diketones, more channels to dissipate their triplet excited energy are available. About 20 years ago, Hamer and Bishop reported that irradiation of 1-(o-tolyl)-1,2-propandione formed 2-hydroxy-2-methylindanone· shown below·[69]



Scheme 21.

Later, Maruyama studied photoreactivities of several substituted benzil derivatives and he observed that 2,5,2',5'-tetramethylbenzil in benzene photocyclized to give the corresponding indanol as a sole product very efficiently, whereas 2,4,6,2',4',6'-hexamethylbenzil in THF gave only photocleavage product.[70] The latter compound was also irradiated in benzene and it was reported to be much less reactive than in THF, but he failed to point out what the product was in benzene. Interestingly, he observed that neither 2,4,6-trimethylbenzil nor 2,3,5,6-tetramethylbenzil reacted under the same photolysus condition in all the solvents invesitigated. The nonreactivity of two substituted benzils were attributed to the low efficiency of intersystem crossing of the two diketones, based on the fact that the two benzils phosphoresce very weakly, unlike benzil and 2,5,2',5'-tetramethylbenzil.





Scheme 22.

Mechanism of the photocyclization of ortho-substituted 1,2-diketones has been heavily discussed for last 20 years.[71] Hamer proposed a benzocyclobutenol as an intermediate for this reaction[72] whereas others[71a] have argued in favor of the E-enol as an intermediate. Despite this disagreement over an intermediate, they seemed to agree upon 1,5 H transfer as the first step rather than 1,6 H transfer. At that time, the direct 1,6-H shift seemed to be limited to carbonyl systems which have no γ-hydrogens or have a δ-hydrogen atom activated by alkoxy or other groups Another reason that they ruled out the direct 1,6-H shift for this system was that a monoketone analog, α-(o-tolyl)acetone, did not photocyclize to the corresponding indanol, instead it gave α-cleavage products.[71a]

For benzil system, however, a monoketone analog is α-(o-alkylphenyl)acetophenone., which we know gives efficient photocyclization. Furthermore, examples of δ-hydrgen abstraction are abundant now in the literature.[55b.]

Ortho-substituted benzils can be related to either o-alkylphenyl ketones or α-(o-alkylphenyl)acetophenones in terms of structure and reactivity. Since both of these systems have been discussed in this thesis, it would be interesting to see how this combined system behaves photochemically.

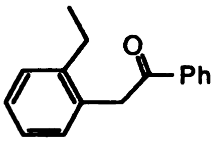
In collaboration with Prof. Zvi Rappoport of Jerusalem, an effort was made to solve the old mechanistic puzzle on the photochemistry of 1,2 diketones.

Results

A. α-Arylacetophenones and derivatives

General preparation of the ketones. α-(o-alkylphenyl)acetophenones were prepared by carboxylation of o-bromoethylbenzene, reduction with lithium aluminum hydride, chlorination with thionyl chloride, cyanation with sodium cyanide and coupling with phenyl Grignard reagent.

α-(2,4,6-Triethylphenyl)acetophenone was prepared by chloromethylation of 2,4,6-triethylbenzene, cyanation with sodium cyanide and coupling with phenyl Grignard reagent. The corresponding propiophenones were prepared by methylation of the acetophenones with lithium diisopropylamide (LDA) and methyl iodide. As a result, the following compounds were prepared.



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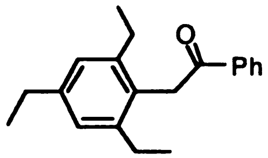

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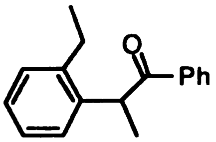

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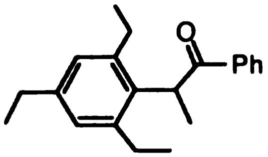

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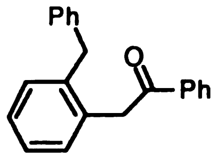

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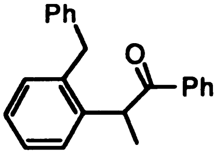

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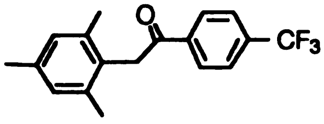

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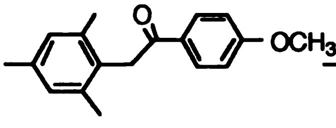

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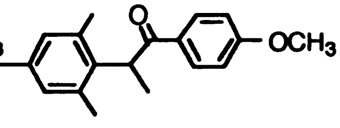
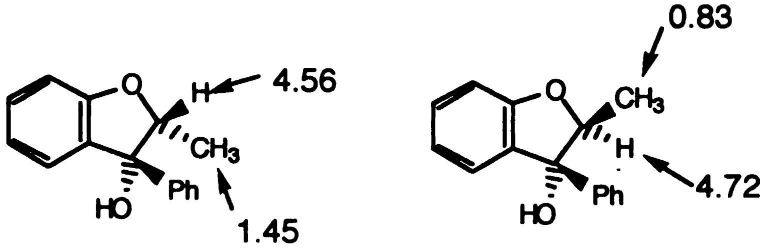


9

Identification of photoproducts. 0.01 M of ketones in deuterated benzene, methanol or acetonitrile were irradiated in NMR tubes with a Pyrex filter. All the starting ketones disappeared after 30-40 minutes' irradiation and diastereomeric mixtures of 2-phenyl-2-indanols were formed. In cases of compound 3 and 6, type I cleavage compounds were also formed. In all cases, chemical yield was within experimental error of 100 %.

For identification of photoproducts, large scale irradiation was performed with 0.1-0.2 g of ketones in benzene or methanol. The products were usually isolated by column chromatography or preparative TLC using hexane/ethyl acetate as eluent.

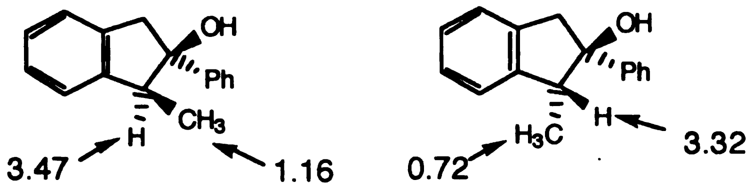
For assigning structures of photoproducts, methyl doublets at 0.6-1.5 ppm were particularly useful because it has been generally accepted that a methyl cis to the phenyl is significantly shielded relative to one trans, as previously observed in a number of such products[73]. For example, in photoproducts from o-ethoxybenzophenone, the chemical shift of methyl group of E isomer was shifted much more upfield than that of Z isomer, as shown in Scheme 23.[74]



EBP-Z EBP-E

Scheme 23.

When compound 1 (0.01M) was irradiated in benzene-d_6 and methanol-d_4, two isomeric products(1Z and 1E) were formed in 20 to 1 and 2 to 1 ratios, respectively. The product with the methyl doublet at higher field was assigned as E isomer.



1Z 1E

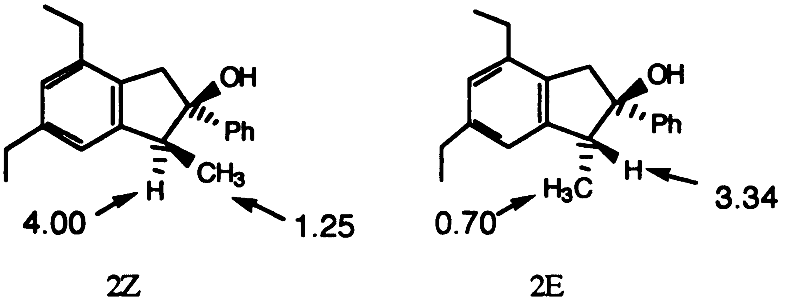
Scheme 24.

Even though this assignment seemed to be reasonable, two more experiments were performed to ensure this assignment. In NMR experiment using shift reagent such as $Eu(dpm)_3$, E isomer of the two photoproducts from α-(o-ethylphenyl)acetophenone, with only hydrogens cis to the OH, complexed more strongly with $Eu(dpm)_3$; its methine cis to the OH and the more upfield of its two methylene protons were shifted much more than the methyl and the other methylene. In the Z isomer, the methyl cis to the OH and the upfield methylene undergo the largest shifts. The more upfield of the methylene proton signals in both isomers must be cis to the OH.

In the Nuclear Overhauser Enhancement (NOE) experiment, doublets at 7.4 (E isomer) and 7.6 ppm(Z isomer) that correspond to the two ortho hydrogens on the 2-phenyl group were irradiated. Unfortunately, both methyl and methine resonances were enhanced in both isomers, which is probably due to rapid ring puckering of five membered ring systems. However, relative magnitude of enhancement was different in two isomers. The intensity ratio of methyl to methine NOE was larger for E isomer than for Z isomer. This is consistent with our original assignment

TEMPO is known to catalyze intersystem crossings of biradical species externally.[54, 40c] If the product ratios can be varied by "rate determining" ISC, the addition of TEMPO would change the product ratios. However, the product ratio from α-(o-ethylphenyl)acetophenone did not change upon irradiation in the presence of up to 0.02 M of TEMPO or 4-OH TEMPO in benzene and methanol. Over this concentration range, all the peaks in ^1H NMR became too broadened to get any information due to paramagnetic nature of this additive.

Compound 2 formed two isomeric products, 2Z and 2E, after irradiation in benzene or methanol. The product ratios in several different reaction media are shown in Table 5. Once again, the product with methyl doublet at higher field was assigned as E isomer.

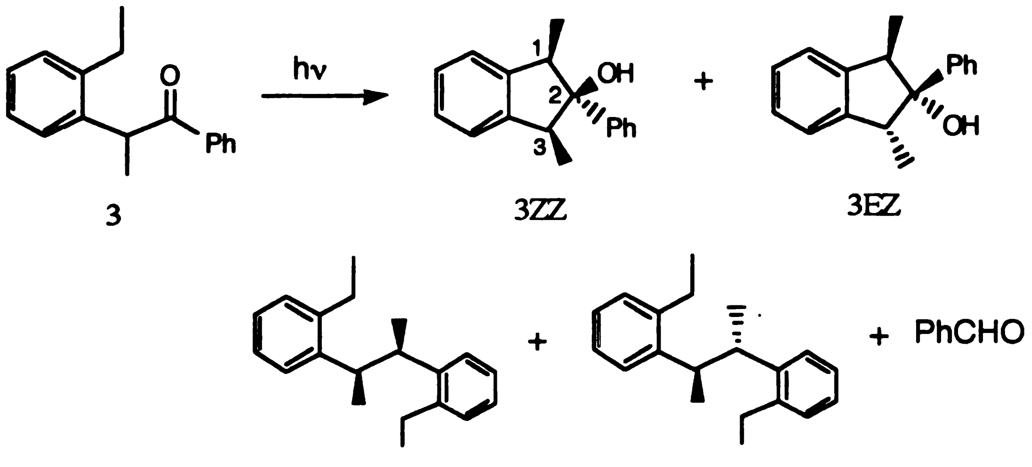


2Z

2E

Scheme 25

After compound 3 (0.01 M) was irradiated in benzene, several photoproducts were isolated. These products were two isomeric indanols (3ZZ and 3ZE) and two isomeric 2,3-di-(o-ethylphenyl)butane (3Bu1 and 3Bu2). The latter compounds were Norrish type I cleavage products. ^{1}H NMR spectrum of crude mixture of photoproducts showed also presence of benzaldehyde, another Type I cleavage product.



3

3ZZ

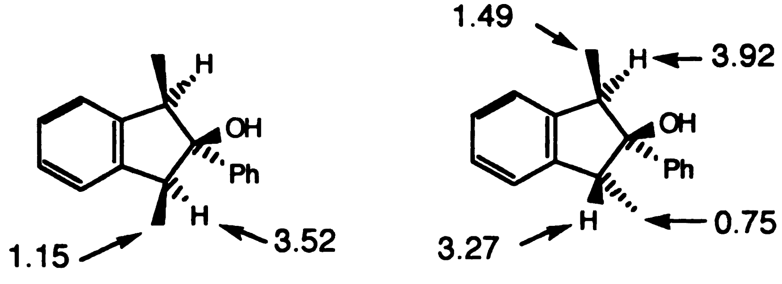
3EZ

3Bu1

3Bu2

Scheme 26.

It was easy to assign the structure of two isomeric indanols from compound 3 because of the symmetry of the molecule. The product with only one set of doublet and quartet was assigned as Z,Z isomer and the product with two sets of doublet and quartet was assigned as Z,E isomer.(Scheme 27)

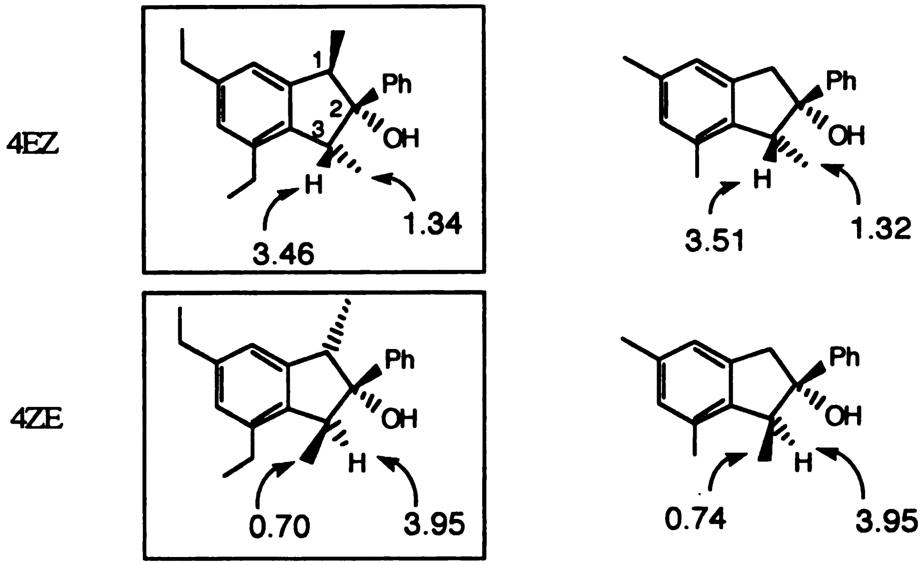


3ZZ 3ZE

Scheme 27

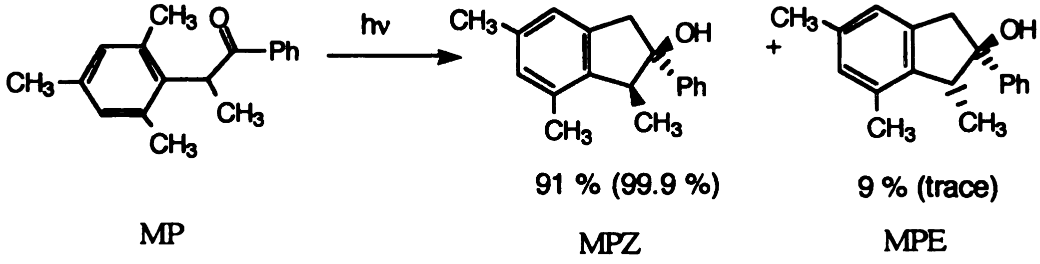
After compound 4 was irradiated in benzene-d_6, two isomeric indanol products were shown in almost an equal amount in ^{1}H NMR spectrum of the crude reaction mixture. No other products were shown in the spectrum.

The structure of photoproducts from compound 4 was assigned based on the following information. Both isomers had one of two doublets at high field region (below 1.0 ppm), which is indicative of cis orientation between methyl and phenyl group. This would narrow down to two diastereomers, which are E, Z- and Z, E- isomers. The structure of these two isomers can be compared to those of photoproducts from α-mesitylpropiophenone as shown below.[75] The extra methyl group at 1 position should not change the geometry much. If this is true, the chemical shifts of methyl and hydrogen at 3-position should be similar in both compounds. In fact, the values match each other very well as shown in Scheme 28.



Scheme 28

When the compound 4 was irradiated in methanol-d_4, the ratio of two isomeric photoproducts was changed to 95:5 in favor of 4EZ. The dramatic increase in diastereoselectivity of photoproducts in methanol was quite surprising not only because of the magnitude of the change but also because of the direction of the change. For other ketones that were investigated so far, it had been shown that the solvation of OH group by hydrogen bonding in methanol made the OH group comparable in size to the neighboring phenyl group, so the diastereoselectivity decreased. In order to see whether this is a general phenomena for this kind of system, the photochemistry of α-mesitylpropiophenone (MP)[14g] was reinvestigated.

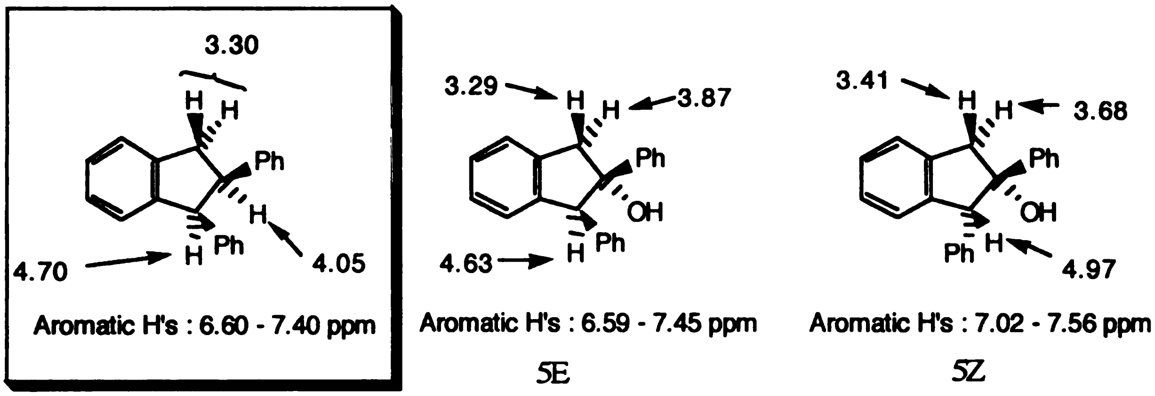


Scheme 29.

When α-mesitylpropiophenone(0.01M) was irradiated in benzene-d_6, two isomeric indanols were formed in 10 to 1 ratio and no other products were observed. This was consistent with previous observation by Zhou.[80] But, when this compound was irradiated in methanol-d_4, only one isomer was formed, whose methyl doublet appeared at 1.32 ppm. This isomer was assign to be Z isomer. Indeed, this compound showed the same type of solvent effect as compound 4.

Compound 5 also gave two isomeric indanols as photoproducts in benzene-d_6 or methanol-d_4. The ratios in two different solvents were not much different.

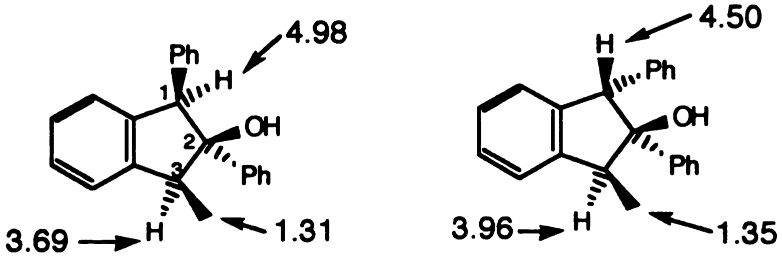
For assigning the structure of these two photoproducts, recent study by Iglesias was very helpful[76]. They synthesized several mono- and di-substituted indanes and assigned the structure using NMR spectroscopy. 1,2-diphenylindane was prepared by stereospecific hydrogenation of 1,2-diphenylindene with platinum dioxide as catalyst. Only one isomer was formed and this was assigned to be the cis isomer based on well known reaction mechanism of the hydrogenation.



Scheme 30.

After comparing spectroscopic data of the two isomeric photoproducts with that of 1,2-diphenylindane, the slightly major isomer in 6 to 5 ratio was assigned to be the Z isomer. A peak at around 6.6 ppm, which is one of aromatic hydrogens, was particularly informative to assign the structure because the unusually upfield shifted peaks must originate from cis orentation of two phenyl groups.

This also helped to assign the structure of two isomeric photoproducts from α-(o-benzylphenyl)propiophenone, compound 6. One isomer that showed doublet at 6.5 ppm was assumed to have cis orientation between two phenyl groups using the same idea as above.



Aromatic H's : 7.0 - 7.55 ppm

6ZZ

Aromatic H's : 6.5 - 7.4 ppm

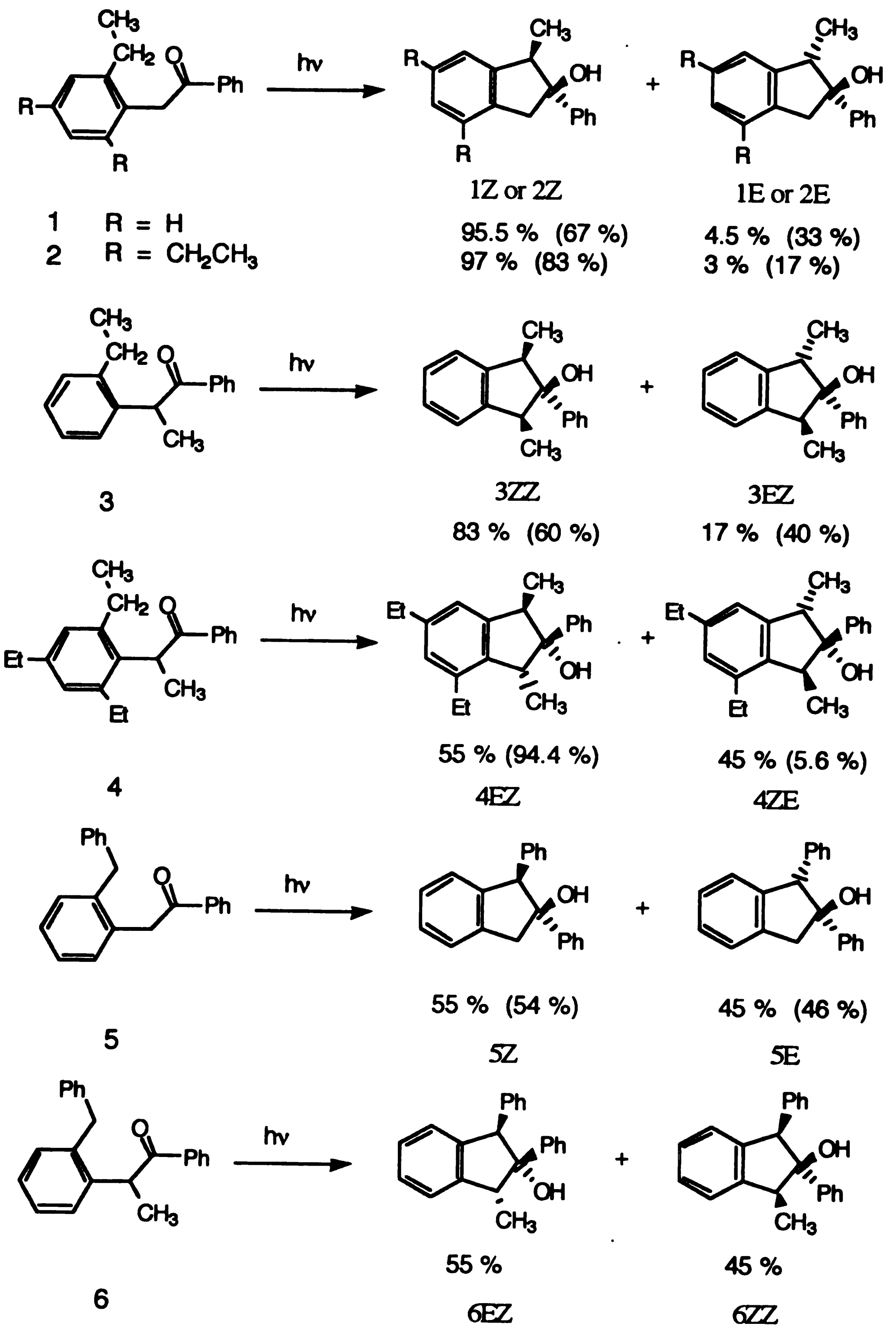
6EZ

Scheme 31.

The ratios of stereoisomers were determined by ^{1}H NMR spectra because most photoproducts dehydrated completely under the GC condition. Especially, most unhindered indanols seemed to dehydrate readily. The observed ratios of photoproducts from several ketones are shown in Table 5.

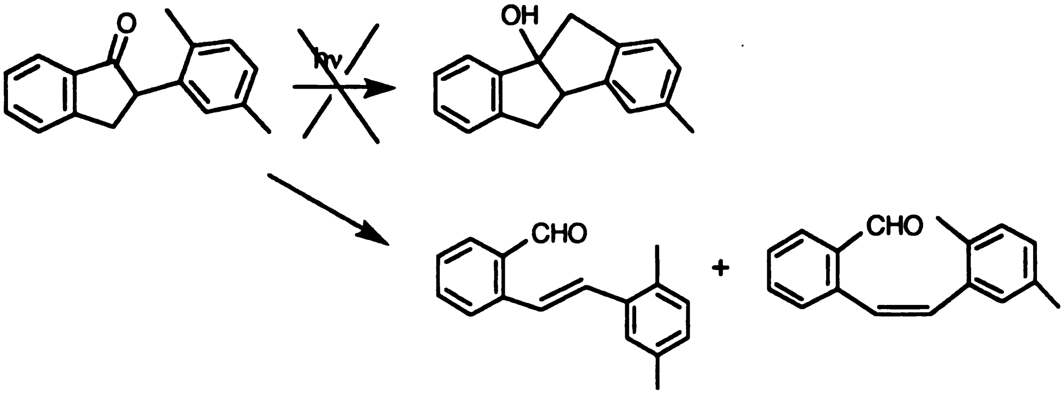
Table 5..Ratios of photoproducts in benzene and methanol(in parentheses).

Ketones	Reaction Media	Ratio(Percentage)	
		Z isomer	E isomer
1	Benzene	95.5	4.5
	Methanol	67	33
	Dioxane	82	18
	Solid State (at low conversion)	92	8
	Solid State (at high conversion)	83	17
2	Benzene	97	3
	Methanol	83	17
	Dioxane	91	9
	Solid State	>99	trace


hν
1 R = H
2 R = CH₂CH₃
1Z or 2Z
95.5 % (67 %)
97 % (83 %)
1E or 2E
4.5 % (33 %)
3 % (17 %)
3
3ZZ
83 % (60 %)
3EZ
17 % (40 %)
4
55 % (94.4 %)
4EZ
45 % (5.6 %)
4ZE
5
55 % (54 %)
5Z
45 % (46 %)
5E
6
55 %
6EZ
45 %
6ZZ

Scheme 32.

Photochemistry of α-(2,5-dimethylphenyl)indanone was investigated for the study of conformational effect of hydrogen abstraction of α-(o-alkylphenyl)propiophenone system. Irradiation of 0.01 M of α-(2,5-dimethylphenyl)indanone in benzene-d_6 resulted in formation of two isomeric enals in 3 to 1 ratio, as was previously observed in the photolysis of α-phenylindananone by Baum[15].



Scheme 33.

Steady state photokinetics. Degassed benzene solution 0.025-0.05 M in ketone and containing varying amounts of quencher (2,5-dimethyl-2,4-hexadiene, ethyl sorbate or naphthalene) and a fixed amount of inert internal standard were irradiated at 313 nm or 366 nm. Detailed condition for irradiation and data analysis are given in Appendix of this thesis.

Product yields at 5-10 % conversion were measured by gas chromatography or HPLC and converted to quantum yields by anaysis of valerophenone actinometers that had been irradiated in parallel with the samples. Stern-Volmer plots were linear, with slopes equal to $k_q\tau$. The kinetic data and the quantum yields are listed in Table 6 and 7. Triplet lifetimes, based on a k_q value of $6 \times 10^9\ M^{-1}s^{-1}$, are also listed.

Table 6. Lifetimes of Triplet Ketones.in Benzene

Ketones	$k_q\tau$, M^{-1}	$\tau^{-1} \times 10^{-9}$ [d]
1	5.5 ± 0.5, 3.8[a]	1.12, 1.37[a]
2	1.0 ± 0.3[a]	5.88[a]
3	12[c]	0.66[c]
4	6.5 ± 0.5[a]	0.89[a]
5	4.9 ± 0.3, 2.8[a]	1.36, 1.94[a]
6	6.12[c]	0.98[c]
7	1.26, 0.63[c]	4.76, 9.52[c]
8	950[b]	0.006
9	8750 ± 350	0.0007

Measured at 313 nm using 2,5-dimethyl-2,4-hexadiene as a quencher unless otherwise stated. a. measured at 365 nm using naphthalene as a quencher. b. Measured at 313 nm using ethyl sorbate as a quencher c. Measured at 313 nm using piperylene as a quencher. d. Triplet lifetimes, based on a k_q value of 5×10^9 $M^{-1}s^{-1}$

Table7. Quantum Yield of Photoproducts

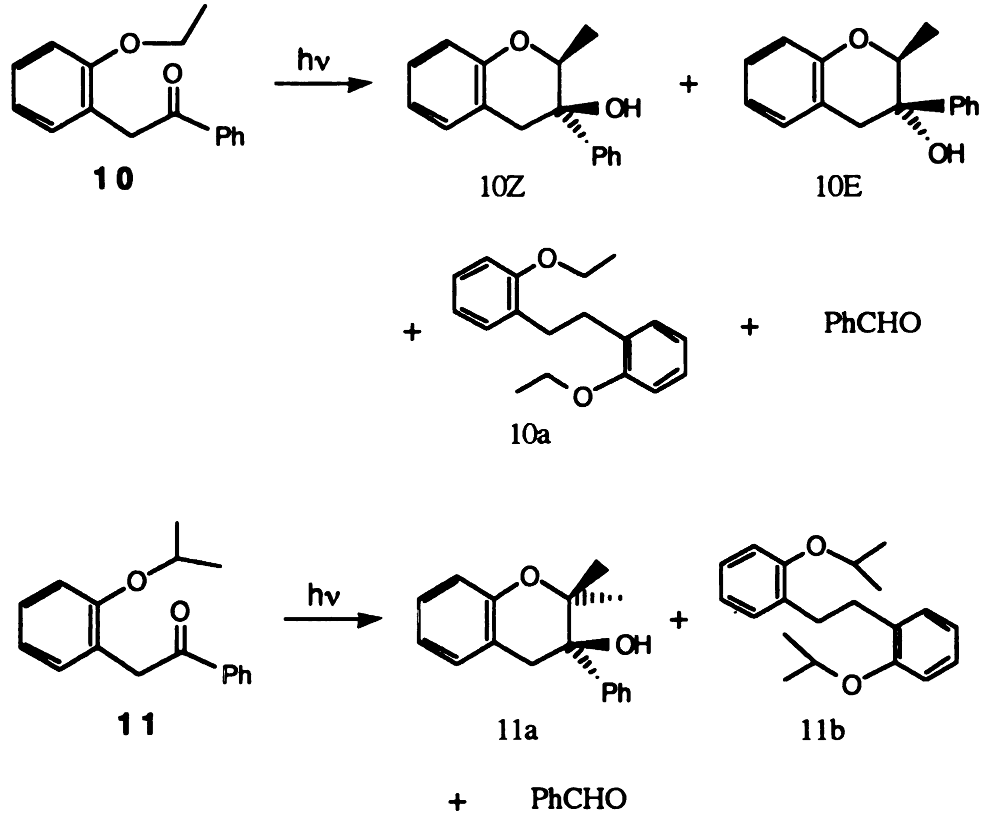
Ketones	Φ_{Cyc}	$\Phi_{Cleavage}$
1	0.73 ± 0.07	
2	0.52 ± 0.01	
3	0.066 ± 0.007	0.071 ± 0.007
4	0.24	
5	0.36(0.45)[a]	
6	0.051 ± 0.005	0.061 ± 0.005
7	0.30(0.49)[a]	
8	0.18(0.42)[a]	
9	0.14 ± 0.05	

Measured in benzene unless otherwise stated a. measured in 5 % ethanol in methanol. Φ_{Cyc} = sum of quantum yield of formation of all the isomeric indanols $\Phi_{Cleavage}$ = sum of quantum yield of formation of all the products which originated from Norrish type I cleavage.

B. More Remote Hydrohen abstraction

(1) α-(o-alkoxyphenyl)acetophenone

General preparation of the ketones. Both α-(o-ethoxyphenyl)acetophenone and α-(o-isopropoxyphenyl)acetophen-one were prepared by alkylation of o-cyanophenol, hydrolysis of the nitrile with KOH/ethylene glycol, reduction of the acid with lithium aluminum hydride, chlorination with thionyl chloride, cyanation with NaCN and coupling with phenyl Grignard reagent.



Scheme 34

Identification of photoproducts. The ketones(typically 0.01-0.02 M) in benzene or methanol were irradiated with pyrex filter. The starting material disappeared completely in less than an hour in NMR scale irradiation. The photoproducts were separated by either preparative TLC or column chromatography with hexane/ethyl acetate as eluent.

For α-(o-ethoxyphenyl)acetophenone, several photoproducts were isolated. Based on spectroscopic data, these were assigned to be the two isomeric 1-methyl-2-phenylbenzodihydropyranols (75 %), di-(o-ethoxy-phenyl)ethane (18.2 %) and benzaldehyde (6.8 %).. Z and E isomer were formed in 2.5 to 1 ratio in benzene and 2.3 to 1 ratio in methanol. The assignment of two isomers could not be made based on chemical shifts of methyl doublets. The difference in chemical shifts in the two isomers was too small. NMR experiment using shift reagents did not differentiate two isomers.

For α-(o-isopropoxyphenyl)acetophenone, similar photoproducts as those from α-(o-ethoxyphenyl)acetophenone were formed. The photoproducts in benzene consist of 1,1-dimethyl-2-phenylbenzodihydropyranol (71 %), di-(o-isopropoxyphenyl)ethane (21 %) and benzaldehyde (8 %)..

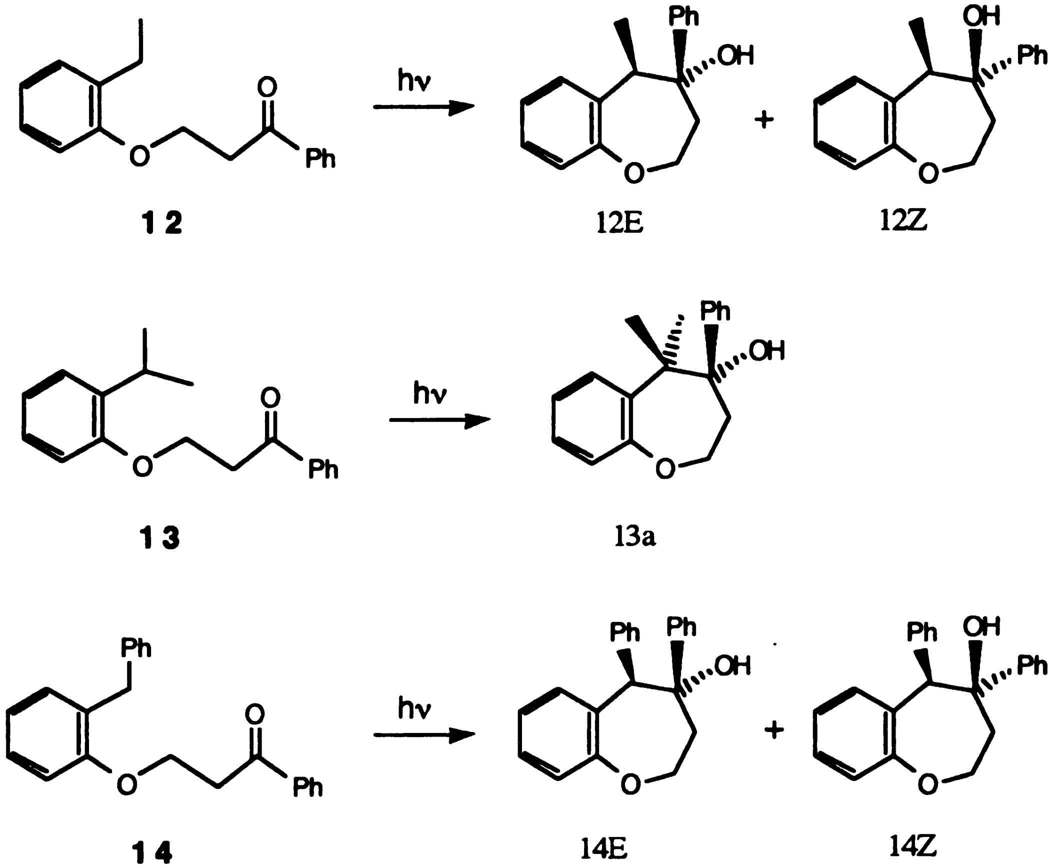
Steady state photokinetics. Degassed benzene solution 0.025 M in ketone and containing varying amounts of 2,5-dimethyl-2,4-hexadiene and a fixed amount of inert internal standard were irradiated at 313 nm.

Product yields at 5-10 % conversion were measured by gas chromatography and converted to quantum yields by analysis of valerophenone actinometers that had been irradiated in parallel with the samples. Stern-Volmer plots were linear, with slopes equal to $k_q\tau$.

For α-(o-isopropoxyphenyl)acetophenone, quantum yield of benzodihydropyranol formation was 0.015 in benzene and $k_q\tau$ of 69 M^{-1} was obtained.

(2) β-(o-alkylphenoxy)propiophenone

General preparation of the ketones. β-(o-ethylphenoxy)propiophenone, β-(o-isoproylphenoxy)propiophenone and β-(o-benzylphenoxy)propiophenone were prepared by Michael addition of o-alkylphenoxide to in-situ generated acrylophenone.



Scheme 35

Identification of photoproducts. The ketones(typically 0.01-0.02 M) in benzene were irradiated with pyrex filter for 1 week. Even after this long irradiation, starting material still remained. The photoproducts were separated by preparative TLC with hexane/ethyl acetate as eluent.

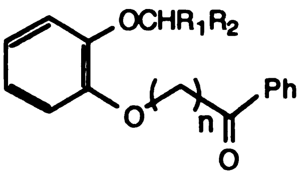
For β-(o-ethylphenoxy)propiophenone and β-(o-benzylphenoxy)propiophenone, two isomeric photoproducts were formed and these were assigned to be the tetrahydrobenzoxepinol on the basis of spectroscopic evidence and comparison to reported spectroscopic data[77]. The ratios of Z and E in benzene were 1 to 1 for β-(o-benzylphenoxy)propiophenone and 2.4 to 1 for β-(o-ethylphenoxy)propiophenone.

Steady state photokinetics. Degassed benzene solution 0.04 M in ketone and containing varying amounts of 2,5-dimethyl-2,4-hexadiene and a fixed amount of inert internal standard(C24) were irradiated at 313 nm.

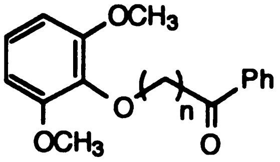
Product yields at 5-10 % conversion were measured by gas chromatography and converted to quantum yields by analysis of o-methylvalerophenone actinometers that had been irradiated in parallel with the samples. Stern-Volmer plots were linear, with slopes equal to $k_q\tau$. For β-(o-benzylphenoxy)propiophenone, quantum yield of tetrahydrobenzoxepinol formation in benzene was 0.0018 and 0.0020 for E and Z isomer, repectively and $k_q\tau$ of 152 M^{-1} was obtained.

(3) α-(o-alkoxyphenoxy)acetophenones, α-(o-alkylphenoxy)acetophenones, β-(o-alkoxyphenoxy)propiophenones and α-(2,4-di-tert-butylphenyl)acetophenone.

General preparation of the ketones. All the ketones except α-(2,4-di-tert-butylphenyl)acetophenone were prepared by coupling reaction between the corresponding phenoxides and α-chloroacetophenone or β-chloropropiophenone. α-(2,4-di-tert-butylphenyl)acetophenone was prepared by Friedel Craft tert-butylation of benzene, bromination using $Br_2/AgNO_3$, carboxylation with dry ice under Grignard condition, reduction with $LiAlH_4$, chlorination with thionyl chloride, cyanation with NaCN/DMSO and coupling with phenyl Grignard reagent.

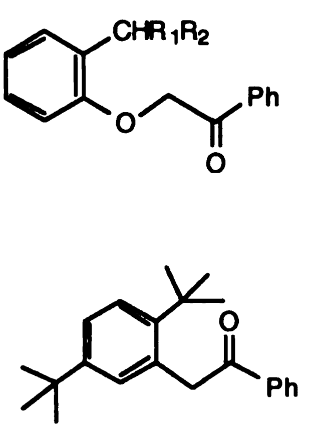


15 $n = 1, R_1 = H, R_2 = H$
16 $n = 1, R_1 = CH_3, R_2 = CH_3$
17 $n = 1, R_1 = H, R_2 = Ph$
18 $n = 2, R_1 = H, R_2 = H$
19 $n = 2, R_1 = CH_3, R_2 = CH_3$
20 $n = 2, R_1 = H, R_2 = Ph$



21 $n = 1$

22 $n = 2$



23 $R_1 = H, R_2 = H$
24 $R_1 = H, R_2 = CH_3$
25 $R_1 = CH_3, R_2 = CH_3$
26 $R_1 = H, R_2 = Ph$

27

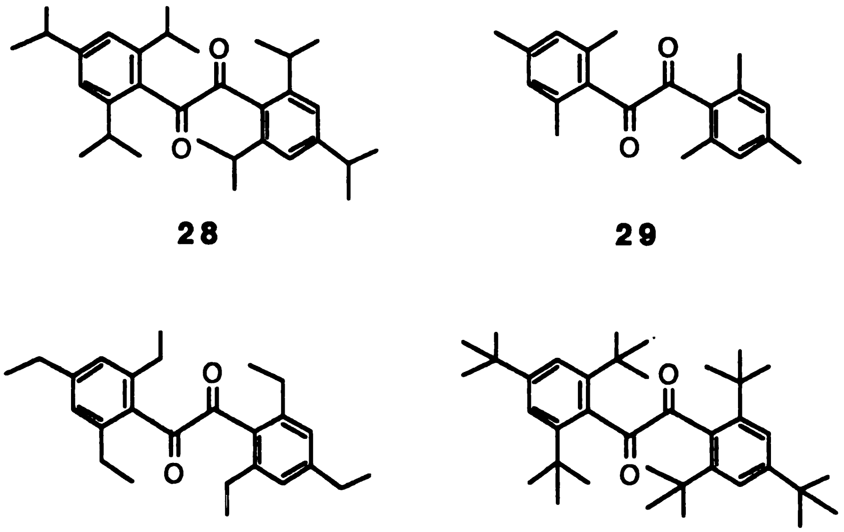
Scheme 36

Identification of photoproducts. 0.01 M of ketones in deuterated benzene, methanol or acetonitrile were irradiated in NMR tubes with a pyrex filter. All the photoproducts from α-(o-alkoxyphenoxy)acetophenones and α-(o-alkylphenoxy)acetophenones turned out to be radical cleavage products; acetophenone, ortho-substituted phenols and 1,2-dibenzoylethane. The photoproducts were identified by comparing with spectroscopic data of authentic samples or by comparing with reported NMR data. No evidence of cyclization via hydrogen abstraction was found. β-(o-alkoxyphenoxy)propiophenones did not give any photoproducts even after prolonged irradiation.

α-(2,5-di-tert-butylphenyl)acetophenone was another candidate for ε- hydrogen abstraction. But, the irradiation of this compound for several hours did not show any significant amount of product formation. After prolonged irradiation, α-cleavage products including benzaldehyde started to appear, but no sign of cyclization product was shown judging from the absence of unique AB quartet of the cyclization product in ^{1}H NMR.

C. Sterically Congested Benzil Derivatives.

General preparation of the ketones. 2,4,6,2',4',6'-hexamethylbenzils, 2,4,6,2',4',6'-hexaethylbenzils, 2,4,6,2',4',6'-hexaisopropylbenzils and 2,4,6,2',4',6'-hexa-tert-butylbenzils were gifts from Prof.- Zvi. Rappoport of Hebrew University in Jerusalem.



28

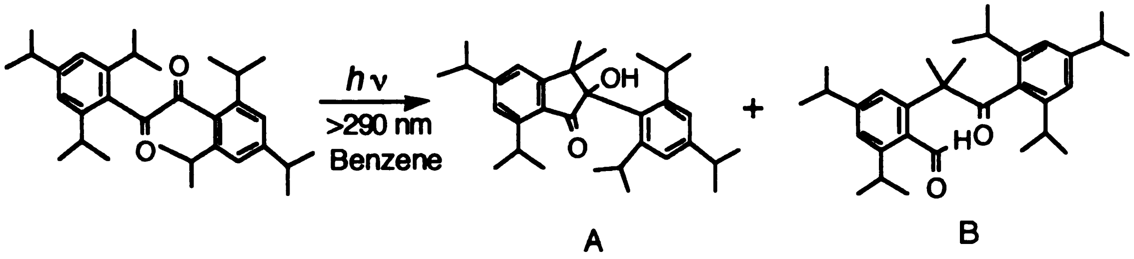
29

30

31

Scheme 37

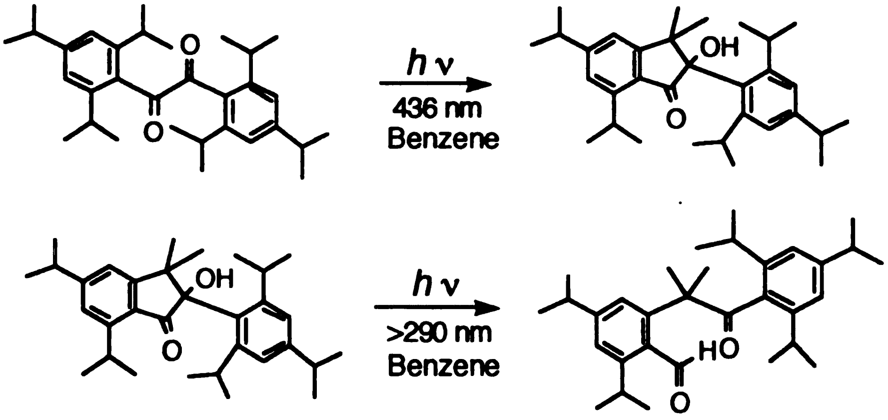
Identification of photoproducts. Under argon atmosphere, the compound 28 (0.01 M) was irradiated in benzene with 450 W medium pressure mercury lamp through pyrex filter(l>290 nm) until 100 % disappearance of diketone. After irradiation, orange colored starting solution became colorless. Crude photoproducts showed several spots on TLC plate. This mixture was chromatographed through silica gel column, followed by preparative TLC with 98 % hexane in ethylacetate. Two major products were identified.



Scheme 38

Assignment of each proton in ^{1}H NMR was made with help of NOE and 2D COSY experiment. It is worthy of note that five cleanly separated septets, nine set of doublets and four separated peaks in aromatic region were shown in proton NMR of product A,

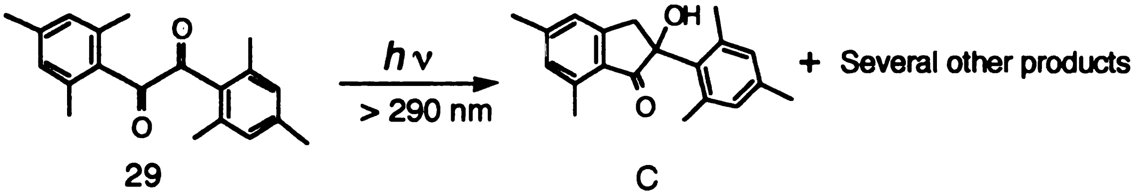
Product A was irradiated separately under the same conditions and product B was formed as the sole product, which confirmed product B was a secondary photoproduct of product A. To avoid this secondary photoprocess, a longer wavelength(436 nm) was chosen, where only compound 28 would absorb the light. 436 nm emission was obtained by a uranium glass filter sleeve and a 1 cm thickness of the following solution: 20 g of $CuSO_4$, 25 g of $NaNO_2$ and 34 ml of concentrated ammonium hydroxide diluted into 500 ml. Under this condition, only product A was formed as expected.



Scheme 39

Compound 28 was also irradiated in solid state. It was packed into melting point capillary tube up to 1 cm length and this was put into a streched test tube. This tube was degassed and sealed under vacuum. This sample was irradiated at either 313 nm or 436 nm. After photolysis, the sample was dissolved into $CDCl_3$ and ^1H NMR was taken. Product A was the only noticeable product with unreacted starting diketone.

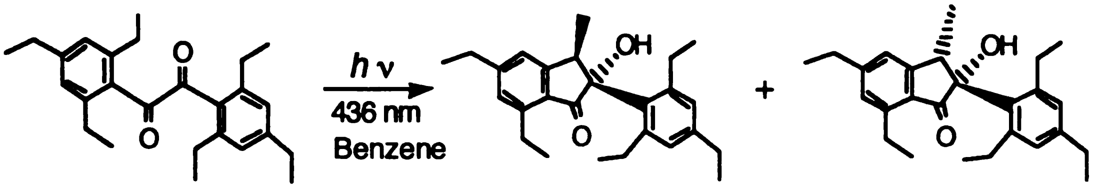
When compound 28 was irradiated in methanol, the quantum efficiency of the diketone disappearance was reduced significantly. The optical density at irradiating wavelength was essentially same for both in benzene and in methanol according to UV spectra. Acidic impurities in methanol were suspected to be responsible for the observed retardation of the reaction. In order to test this possibility, parallel irradiation was performed on NMR samples in benzene-d_6 with and without a few crystal of p-toluenesulfonic acid and the ^1H NMR spectra of two samples were taken at regular intervals. Until completion of the reaction, the NMR spectra of the samples were essentially same.



Scheme 40

Compound 29 was irradiated in the same way as described above. After photolysis, ^1H NMR of crude product showed that there were several other products in addition to product C. Appearance of product C could be easily spotted by distinctive AB quartet between 3 and 4 ppm. Once again, irradiation at 435 nm simplified the spectra a lot and product C was predominant Solid state irradiation of this compound also led to a formation of product C as only noticeable product. At this point, it should be noted that compound 29 required a lot longer irradiation time than compound 1 to get the same amount of conversion.

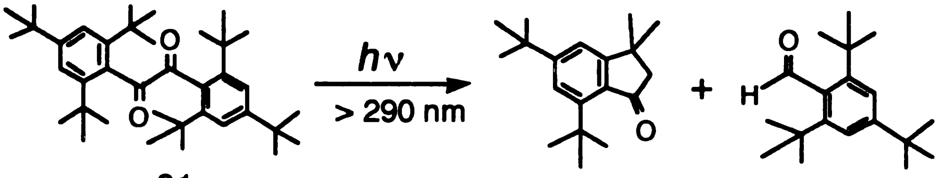
Compound 30 (0.01 M) was irradiated in deuterated benzene at 436 nm and it produced two isomeric indanones in the ratio of 2.5 to 1. It was also irradiated in solid state under the same condition and the ratio of two isomers slightly increased to 5 to 1.



30

Scheme 41

Under argon atmosphere, compound 31 (0.01 M) was irradiated in benzene with 450 W medium pressure mercury lamp through pyrex filter(>290 nm) until 100 % disappearance of diketone. Crude photoproducts showed several spots on TLC plate. This mixture was chromatographed through silica gel column, followed by preparative TLC with 98 % hexane in ethylacetate. Two major products were identified as shown below. These are probably secondary photoproducts which are given by initial product. This initaial product could not be found, which maybe means that secondary photoprocess is very fast under the reaction condition. In order to prevent this secondary photoprocess, this compound was irradiated at 436 nm. However, the reaction was too slow to isolate any identifiable products.



31

Scheme 42

o-tert-Butylbenzophenone reacts in methanol 20 times more efficiently than in benzene. Hoping that this solvent effect applies here, compound 31 was irradiated in methanol. However, the reaction seemed to slow down more in methanol than in benzene and no reaction was evident even at 290 nm for same period of time as before. After extended period of irradiation, complex mixtures were formed, which could not be identified.

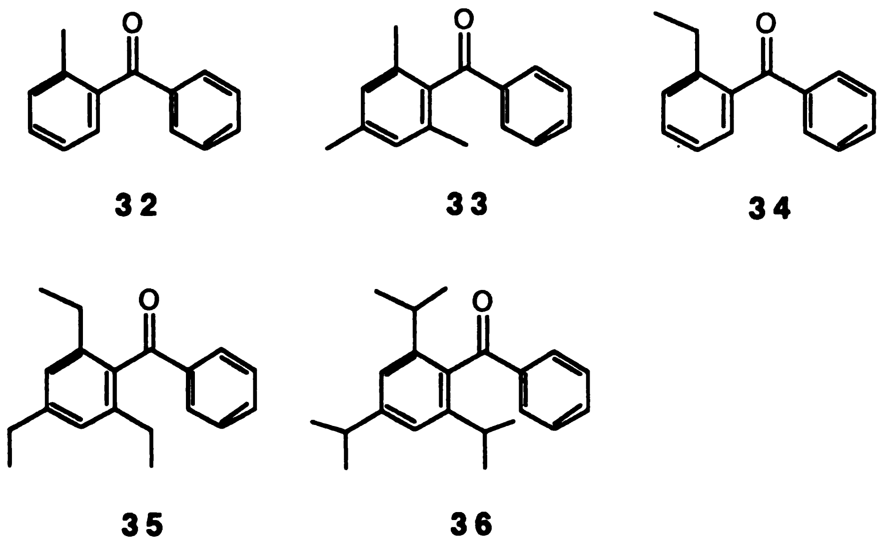
Steady state photokinetics. Degassed 0.01 M solution of compound 1 in benzene and containing varying amounts of pyrene and a fixed amount of inert internal standard(C20) were irradiated at 365 nm. Parallel irradiation with actinometer at 435 nm was discouraged because extinction coefficient of the ketone at this wavelength was very low, so large amount of the ketone was required to get an accurate number for quantum yield.

The ratios of the photoproduct to internal standard were obtained from GC analysis. Stern-Volmer plots were linear, with slopes of $k_q\tau = 686\ M^{-1}$. Since pyrene also absorbed a small amount of light at the wavelength, the obtained value had to be corrected using Beer-Lambert law. The corrected value turned out to be 485 for $k_q\tau$, which could be converted into triplet lifetime of 97 ns, assuming that kq is $5 \times 10^9\ s^{-1}$.

D. Ortho-alkylphenyl ketones:

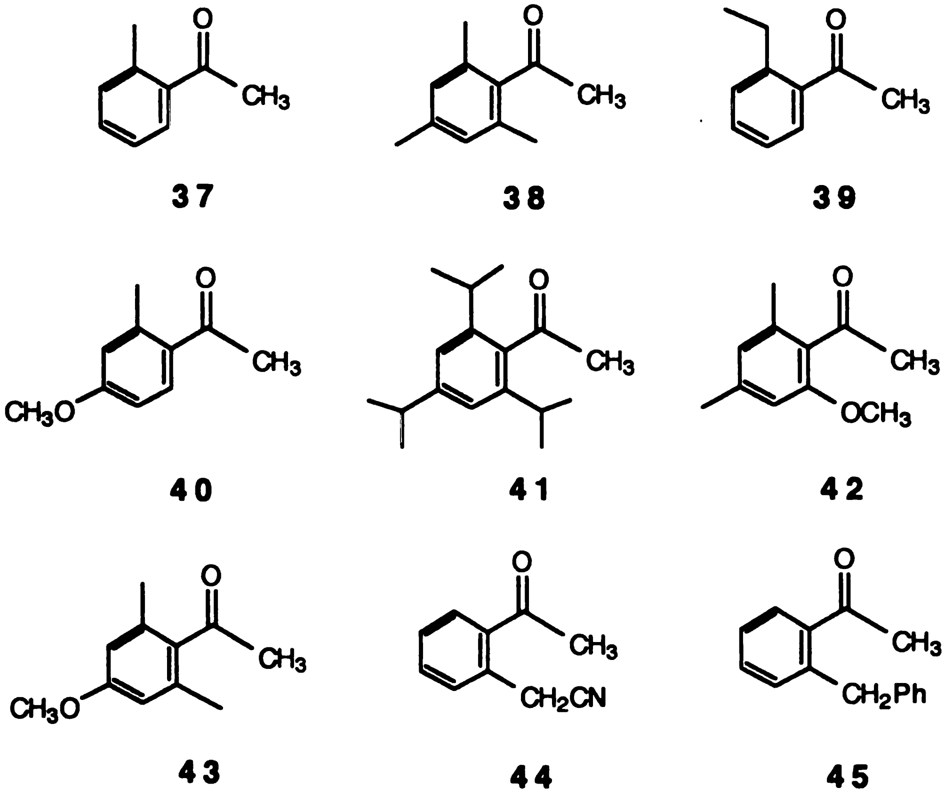
General preparation of ketones ortho-alkylbenzophenones were prepared by coupling of ortho-alkylphenyl Grignard reagents and benzonitrile. 2,4,6-trialkylbenzophenones and 2,4,6-trialkylacetophenones are made by Friedel-Crafts acylation of 2,4,6-trialkylbenzene using benzoyl chloride or acetic anhydride. Ortho-alkylacetophenones were prepared by Lithium halogen exchange of o-bromoalkylbenzene using either lithium wire or n-butyllithium, followed by coupling with acetic anhydride. The following compounds were investigated.

Benzophenones



Scheme 43

Acetophenones

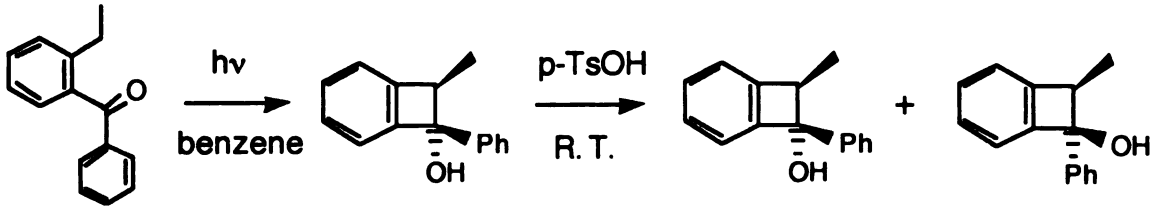


Scheme 44

Irradiation of ketones 0.01 M of ketones in deuterated benzene, methanol or acetonitrile were irradiated in NMR tubes with a pyrex filter. o-Methylbenzophenone formed cyclobutenol cleanly after 45 minutes' irradiation. There was no evidence for the other products reported by Wilson.[84]

2,4,6-trimethylbenzophenone also formed cyclobutenol efficiently in benzene. When a single crystal of p-toluenesulfonic acid was added into the solution prior to irradiation, no product was formed after irradiation for 1 hour. For the same time period, the reaction was completed without the acid.

o-Ethylbenzophenone in benzene formed E-cyclobutenol quantitatively with no trace of the Z isomer. The same single isomer was formed in acetonitrile solvent. If NMR of the photoproduct was taken after the solvent was changed from benzene-d_6 to $CDCl_3$, trace amount of the Z isomer could be detected in the NMR, indicating that E to Z isomerization occurred in small extent in the process of changing solvents. When o-ethylbenzophenone was irradiated in deuterated methanol, a methyl triplet at 1.1 ppm turned into a broad singlet and a methylene quartet at 2.6 ppm disappeared, indicating that deuterium exchange was occurring at the dienol intermediate. This was the only change observed even after twice the irradiation time required to convert 100 % of the ketone to cyclobutenol in benzene. After extended period of irradiation, a new, broad singlet appeared at 0.8 ppm representing the deuterium-broadened CH_3 group of the product cyclobutenol. Solvent was removed and ^1H NMR was taken in deuterated benzene in order to compare with result of photolysis in benzene. Every peak was the same except that a methine quartet diappeared and a methyl doublet was replaced by a broad singlet, confirming these are same products.



Scheme 45

benzene-d_6 solution containing o-ethylbenzophenone and one crystal of p-toluenesulfonic acid produced no benzocyclobutenol after hours of irradiation. Addition of the same amount of acid to solutions containing only benzocyclobutenol caused a new set of doublet and quartet to appear in ^{1}H NMR, indicating E/Z interconversion. The Z/E ratio changed to 1:2 after 24 hrs at room temperature. After 48 hrs, it changed to 2 to 1 and this ratio remained same up to 4 days.

benzene-d_6 solution of valerophenone with a few crystals of p-toluenesulfonic acid was irradiated under the same condition and the reaction was complete in 15 minutes, indicating that the ketones' intrinsic reactivity was not affected by the added acid.

Addition of one drop of pyridine to solutions containing only benzocyclobutenol caused slow growth of the other isomer and starting ketone. The ratio between E isomer, Z isomer and o-ethylbenzophenone was 3:1:1 after 3 days at room temperature. The ratio changed to 6:3:2 after 7 days.

Methanol-d4 solution containing o-ethylbenzophenone and one drop of concentrated HCl formed only deuterium incorporated starting material after extended period of irradiation.

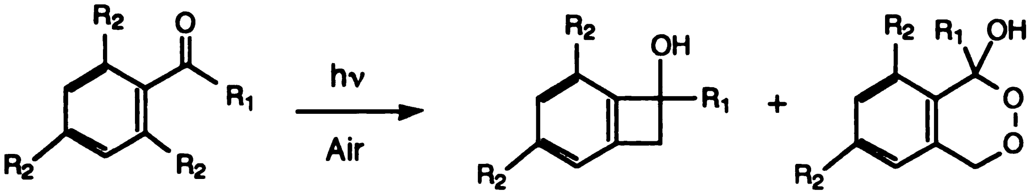
Structural assignment of each isomer was made based on ^{1}H NMR, NOE experiment and isomerization in the presence of p-toluenesulfonic acid. The chemical shift of methyl doublet in E isomer was more upfield than that of Z isomer due to anisotropy of neighboring phenyl group.(0.8 vs. 1.2 ppm in benzene-d_6) In NOE experiment of E isomer, when methyl doublet was irradiated, enhancement was observed for the peaks for a methine hydrogen and two ortho hydrogens of phenyl group which is attached to the carbon containing OH group. Acid catalyzed isomerization to the more stable product supported this assignment.

When o-ethylbenzophenone was irradiated in the presence of maleic anhydride in benzene, a single isomer of trapped products was formed as reported by Pfau.[78] When the same ketone was irradiated in the presence of premixed D_2O and $SOCl_2$ in methanol, only one isomer of SO_2 trapped products was formed. Both reactions were so efficient that all the starting ketones disappeared after 10 minutes' irradiation.

2,4,6-triethylbenzophenone in benzene-d_6 also formed only E isomer of benzocyclobutenol quantitatively. When the same compound was irradiated in methanol-d_4, a significant amount of nondeuterated benzocyclobutenol was formed with deuterated ones. Again, only E isomer was formed. In case of o-ethylbenzophenone, benzocyclobutenol was formed only after nondeuterated starting ketone was converted completely into deuterated starting material

When 2,4,6-triethylbenzophenone in benzene-d_6 was irradiated in the presence of a single crystal of p-toluenesulfonic acid, the reaction was complete in 20 min., which seemed to be as efficient as the reaction without the acid. But, when the same compound in methanol-d_4 was irradiated in the presence of two drops of HCl, the reaction was much slower than the one without HCl. For example, the reaction without HCl was complete in 20 min whereas the reaction with HCl was only ca. 10 % done after 1 hour irradiation.

Acetophenones took much longer time than benzophenones in converting same percentage of ketones into products. While most benzophenones reacted completely in 30 minutes, acetophenones required several hours. Since acetophenones reacted slowly, degassing became more important than in case of benzophenones. If air leaked into NMR tubes during irradiation, oxygen trapping products were always observed.



Scheme 46

When o-methylacetophenone and 2,4,6-trimethylacetophenone were irradiated in NMR tubes, benzocyclobutenol and oxygen trapping products were formed in comparable amounts. For example, when 0.01 M of o-methylacetophenone in benzene-d_6 was irradiated, the reaction was complete after 3 hours and the ratio between benzocyclobutenol and oxygen trapped product was 3 to 1.

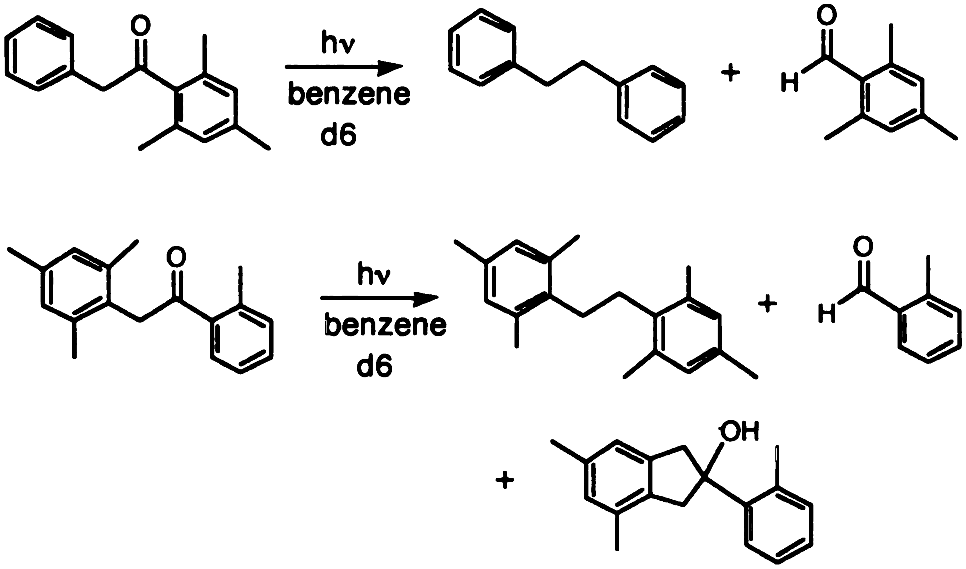
The appearance of the oxygen trapped products could be easily spotted from the ^1H NMR spectra. They have exactly same pattern as benzocyclobutenols in their ^1H NMR spectra. except their chemical shifts. As an example, the benzocyclobutenol product from o-methylacetophenone showed a methyl singlet at 1.49 ppm, a AB quartet at 2.91, 3.07 ppm in benzene-d_6, whereas the corresponding oxygen trapped product showed a methyl singlet at 1.52 ppm, a AB quartet at 4.32, 5.06 ppm.

When these compounds were irradiated in large scale under argon atmosphere, reaction was very clean and only benzocyclobutenol was formed quantitavely. 1-Methylbenzocyclobutenol was one of a few stable, isolable products, which was separated as colorless solid.

2,4-Dimethyl-6-methoxyacetophenone in benzene-d_6 formed benzocyclobutenol very cleanly after two hours' irradiation.

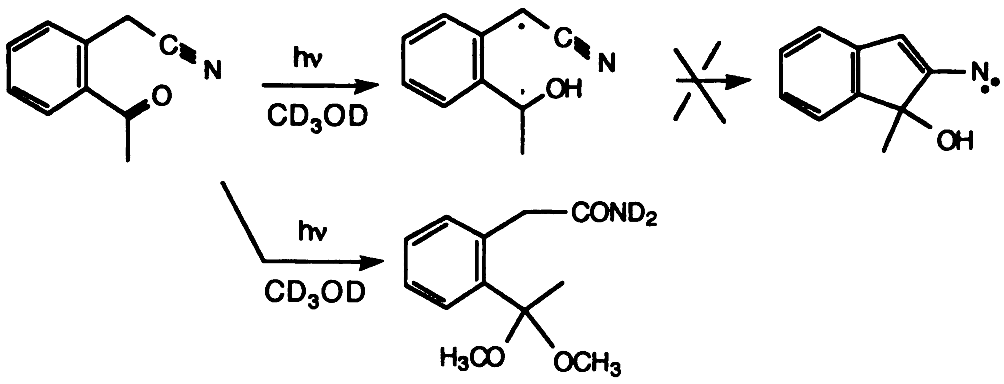
2-Ethylacetophenone took much longer time to form benzocyclobutanol than most other acetophenones. Two isomeric products were formed in 2 to 1 ratio. It was difficult to assign the structure because there was no neighboring phenyl group to give shielding effect to methyl group unlike product from 2-ethylbenzophenone. When NMR shift reagent was added into $CDCl_3$ solution containing both isomers, one of the methyl doublet shifted slightly more down field than other methyl doublet. Based on this result, the compound, whose methyl doublet shifted more, was assigned as Z isomer.

Photochemistry of α-phenyl-2',4',6'-trimethylacetophenone and α-mesityl-2'-methylacetophenone has been studied by Wagner and Zhou. We decided to reinvestigate these compounds to see if cyclobutenol formation could be detected by NMR. benzene-d$_6$ solutions of these compounds(0.01 M) were prepared separately and the reaction was monitored by NMR. In both cases, no benzocyclobutenols could be detected, but the previous observation by Zhou was reproduced as shown below.



Scheme 47

When o-cyanomethylacetophenone was irradiated in deuterated methanol, only reaction observed was ketalization by solvent and hydrolysis of the nitrile to amide as shown below. Solvent incorporation in the photoproduct was proved by comparing NMR spectra of the photproducts of the compound in methanol and deuterated methanol. The ketalization did not occur in the dark, indicating that the carbonyl carbon became more electrophilic under the photolysis conditions. The hydrolysis of the nitrile was caused presumably by water, which was released in ketalization. Neither cyclobutenol nor nitrene trapping products were observed. When the same compound was irradiated in benzene, not much change was observed in ^1H NMR spectra even after prolonged irradiation.



Scheme 48

Steady state photokinetics. Some photoproducts were unstable under the analysis condition. Especially, photoproducts from benzophenones were partially isomerized and rearranged to starting ketones even in HPLC condition. Thus, the quantum yields of some benzophenones were measured by parallel irradiation of samples in NMR tubes with 2,4,6-triisopropylbenzophenone whose quantum yield has been measured by Matsuura.[36c]

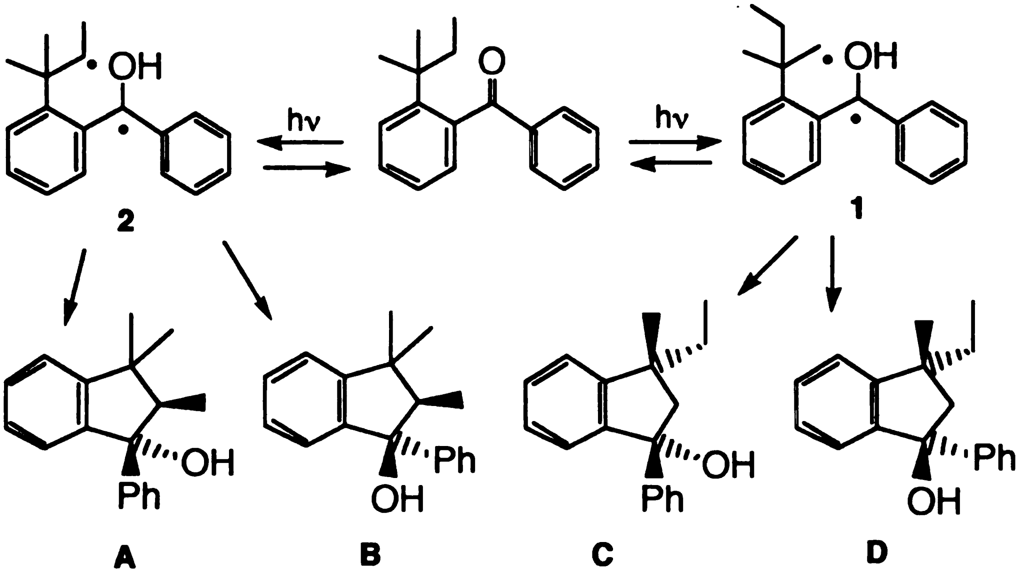
On the other hand, photoproducts from acetophenones were quite stable under the HPLC analysis condition. The results are shown below.

Table 8. Quantum yields of benzocyclobutenol formation from some o-alkylphenyl ketones.

Ketones	Φ_{Cyc}
o-methylacetophenone	0.005
2,4,6-trimethylacetophenone	0.013
o-ethylbenzophenone	0.09
2,4,6-triethylbenzophenone	0.13

E. o-tert-amylbenzophenone

Identification of photoproducts 0.01 M of o-tert-amylbenzophenone (OTABP) in 0.75 ml of deuterated benzene was irradiated with pyrex filtered UV light. After 2 hrs' irradiation, all the starting ketone diappeared and two pairs of isomers were formed.(Scheme 49) A and B measure abstraction of a secondary ethyl hydrogen; C and D, a primary methyl hydrogen. This reaction was repeated in several different solvents. Product ratios were determined at low conversion by HPLC and comparison with NMR spectra of reaction mixtures.



Scheme 49

The reaction mixture had to be analyzed immediately after irradiation because the photoproducts seemed to dehydrate readily, especially in methanol. As with o-tert-butylbenzophenone, reaction proceeded in the solid as well as in solution and also at 77° K. A large single crystal was irradiated in a test tube briefly and it was washed quickly with a few drops of solvent three times in succession. The product ratio was almost identical in all three washings, although the second and the third washings gave much lower yields of products.

0.2 g of OTABP in 50 ml of benzene was irradiated with pyrex filtered UV light under argon atmosphere overnight. Photoproducts were separated by preparative HPLC using 3 % ethyl acetate in hexane. Product A was significantly dehydrated after evaporating solvent at reduced pressure and room temperature. On the other hand, product B was quite stable under the same condition. Product C and D were also readily dehydrated after evaporating solvent. If this dehydration was catalyzed by glass surface, syn elimination was probably operating in this process. The fact that product A was dehydrated more readily than product B was helpful to assign product A to be Z isomer. This assignment was further confirmed by ^{1}H NMR, which showed that methyl group was more shielded by neighboring phenyl group in product A than product B. Assigning product C and D was not easy. A NMR shift reagent, Eu(dpm)3, was added to the mixture of C and D. Unfortunately, both isomers were converted to dehydrated product, which was apparently catalyzed by the shift reagent.

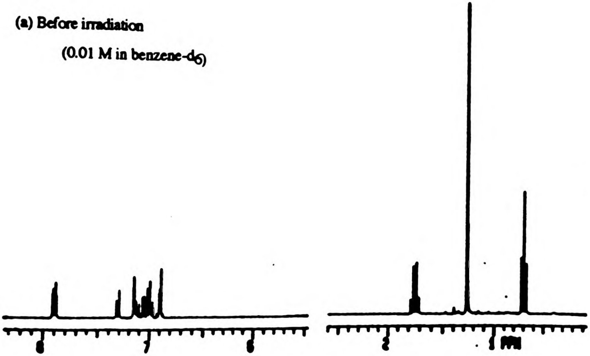
Table 9. Product ratios from photoreaction of o-tert-amylbenzophenone

Reaction Media	Irradiation Temperature	Product Ratio (Percentage) A	B	C(D)	D(C)
Benzene	R.T.	20	20	30	30
Toluene	-78 ^{o}C	10	10	40	40
Methanol	R.T.	34	28	14	23
Methanol[a]	-78 ^{o}C	35	28	13	24
Methanol[a]	70 ^{o}C	35	28	13	24
Methanol[b]	77 K	12	48	7	33
CH_3CN	R.T.	27	25	23	25
Crystal	R.T.	17	54	8	21
Silica Gel	R.T.	26	52	11	11

[a] 10 % ethanol [b] 50 % ethanol

(a) Before irradiation

(0.01 M in benzene-d_6)



(b) After irradiation for 30 min

(Pyrex filter)

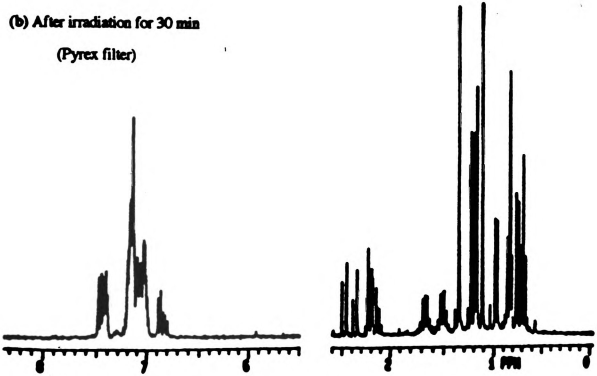
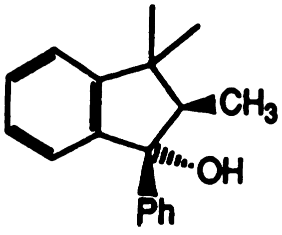
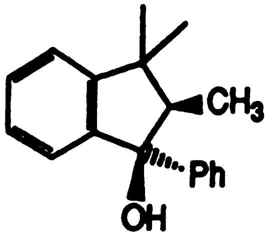


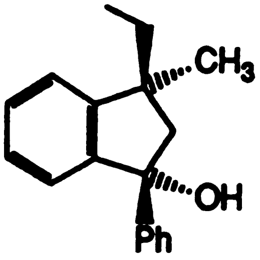
Figure.1. ^{1}H-NMR of o-tert-Amylbenzophenone



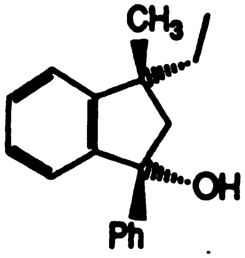
A



B



C



D

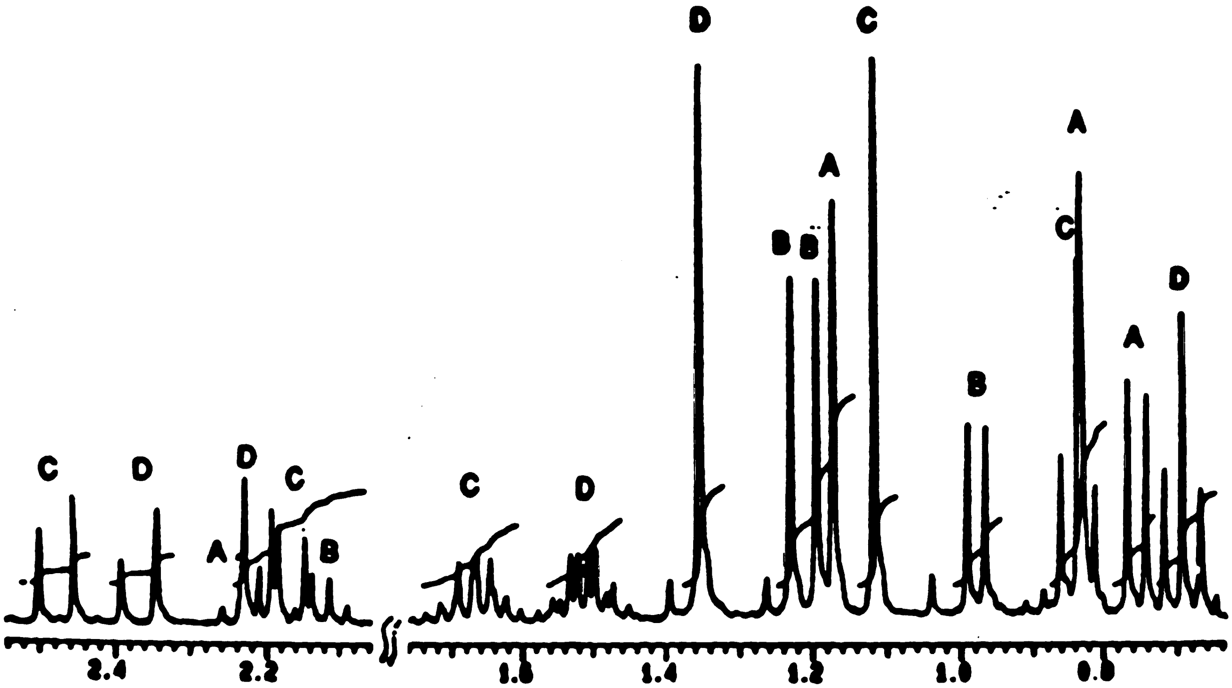
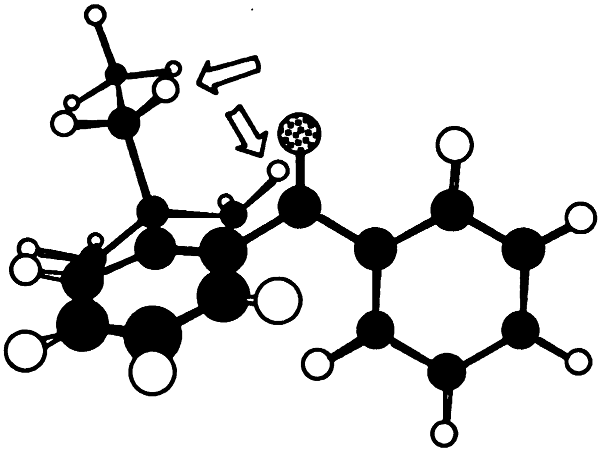


Figure 2. Expanded ^{1}H NMR of o-tert-amylbenzophenone at 0.6-2.6 ppm



The X-ray structure of OTABP is very similar to that of OTBBP, with the ethyl group pointed up and out. There are two hydrogens less than 2.7 Å from the carbonyl oxygen but at much different angles with respect to the n-orbital. An ethyl C-H bond is lined up nicely (d = 2.63 Å, w=45 °) while a methyl hydrogen is closer but lies perpendicular to the n orbital (d = 2.53 Å, w = 95°).

MMX calculations were performed with a dihedral driver (10° increments) for rotation around the benzene–*t*-amyl bond to ascertain the likelihood of conformations with a methyl group better aligned for reaction (lower w) than in the crystal geometry. The calculations revealed two energy minima, separated by 2.5-3.0 kcal/mole, in both of which the ethyl group is held perpendicular to the benzene ring, as expected for the largest benzylic substituent. One of these conformers (R270) closely resembles the crystal structure; the other (R90) is related by a 180° rotation of the *t*-amyl group. R90 is calculated to be 0.3 kcal/mole more stable than R270. Structure R90 has no ethyl but two methyl hydrogens within 2.8 Å of the oxygen; they make ω values of 65° and 99°. The distances, but not the angles, are very sensitive; a 10° change in either direction moves one hydrogen to 3 Å.

Low temperature NMR confirmed a low barrier to rotation of the *t*-amyl group. Rotation around the carbonyl–benzene bonds freezes out at -70°. The methylene proton signals also decoalesce and separate into two. However, their nonequivalence is caused by the rest of the molecule freezing into an asymmetric shape. The same effect also is observed in CH_2Cl_2, where the two methyl groups also become nonequivalent below -80°

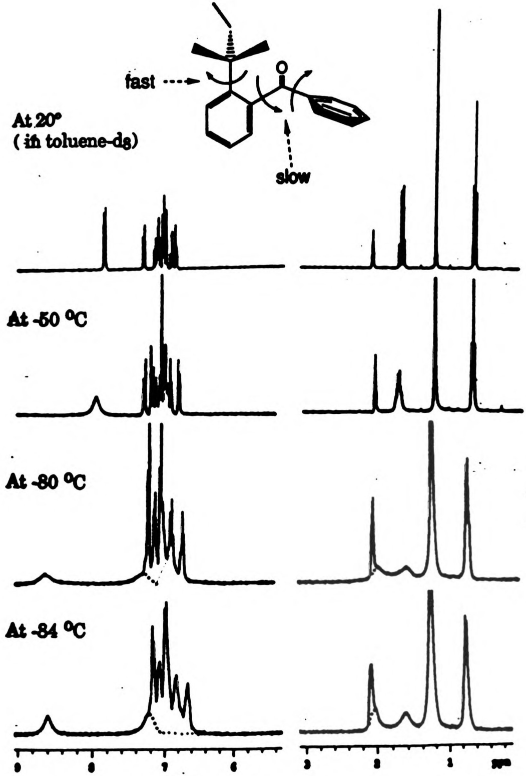


Figure 3. Variable Temperature ^1H-NMR of o-tert-Amylbenzophenone.

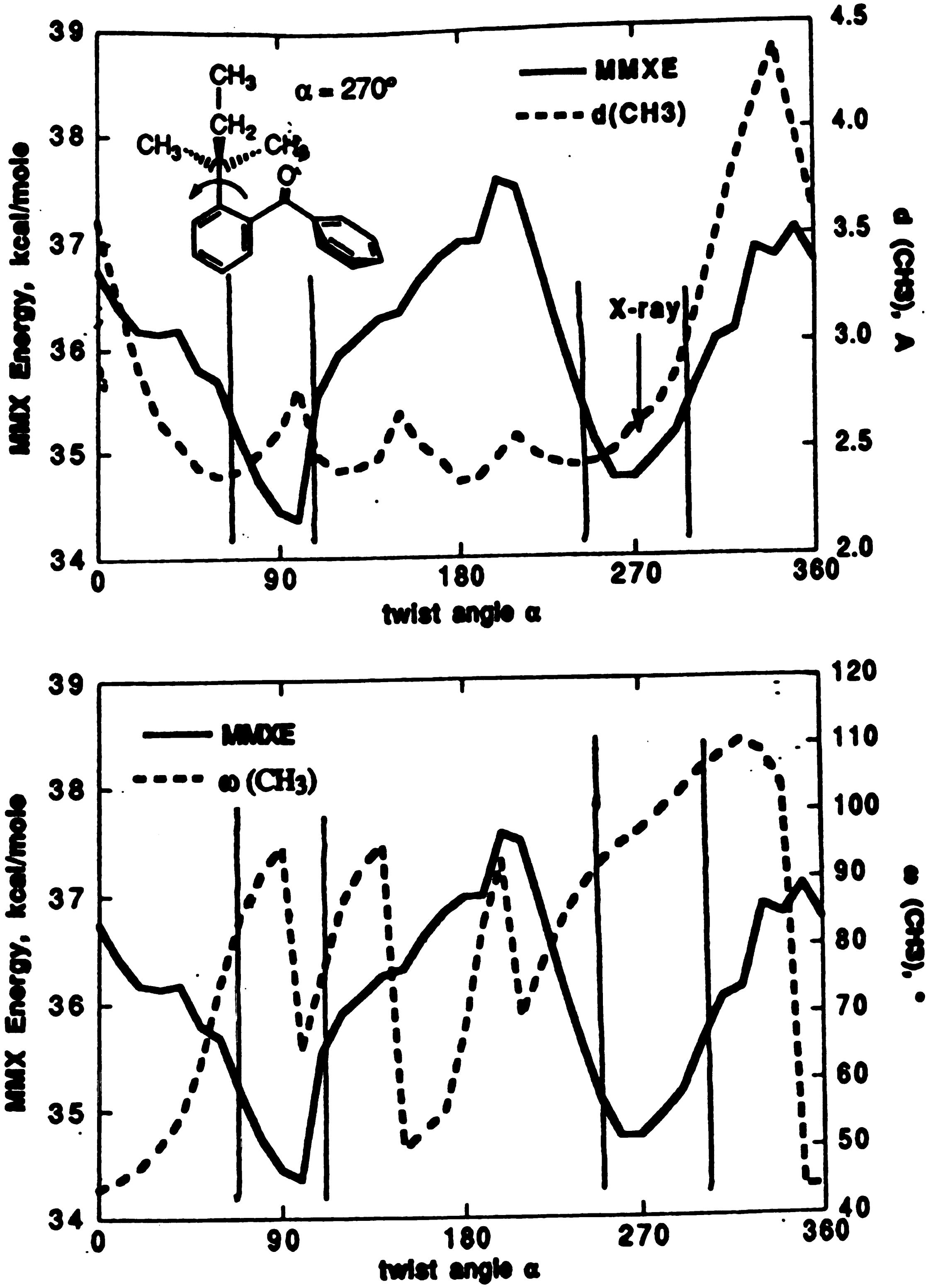
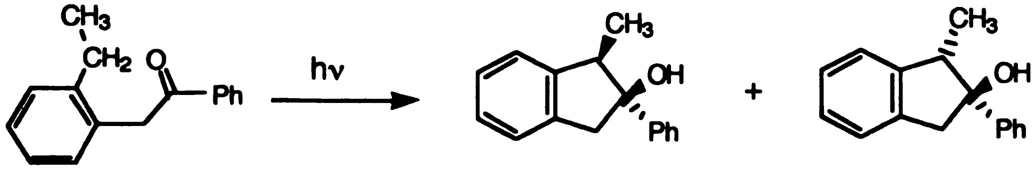


Figure 4. MMX Calculation on Rotation around t-Amyl-benzene Ring Bond

Discussion

A. Diastereoselectivity

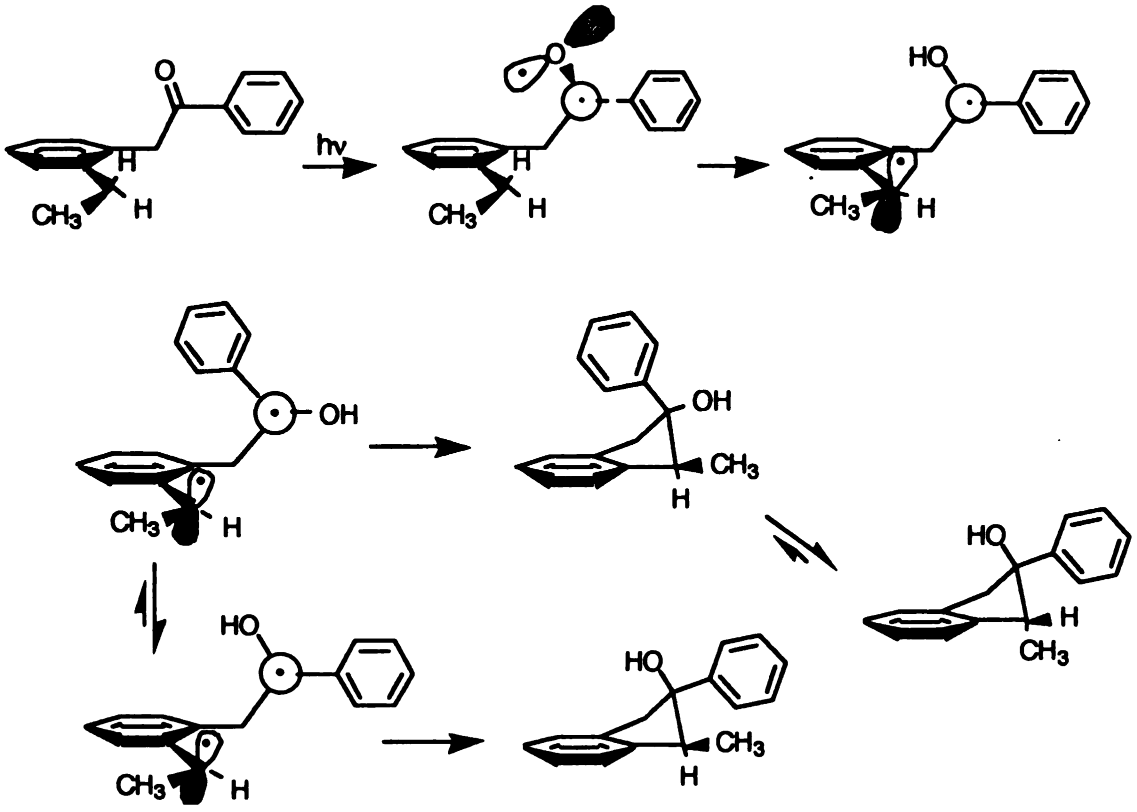


benzene	95 %	5 %
MeOH	67 %	33 %

Scheme 50

The high diastereoselectivity observed in the photocyclization of α-(o-ethylphenyl)acetophenones[79] was quite surprising because the thermodynamic energy difference between the Z and E products did not seem to be that large. Since the value was not available from the literature, we decided to calculate it using molecular mechanics program. The result of this calculation indicated that puckering of the five membered ring reduced the energy difference to near zero. Based on this, the possibility that such selectivity was created during cyclization as the methyl and phenyl groups on the biradical ends approach each other can be ruled out. Therefore, the discrimination between the two modes of cyclization probably reflects pre-existing energy differences that persist during cyclization.

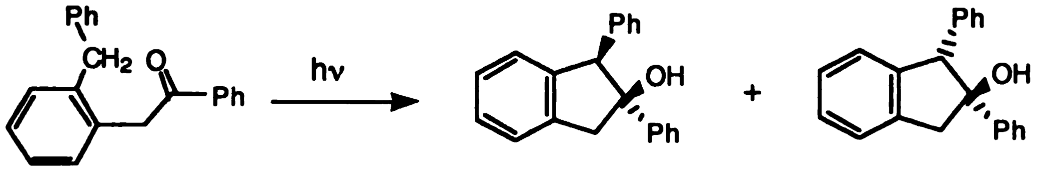
This idea was tested by performing MMX calculations on the biradical from α-(o-ethylphenyl)acetophenones. After minimization with respect to rotation about all acyclic C-C bonds, the two minimum energy geometries shown in Scheme 51 were calculated to differ in energy by 1.6 kcal/mol.



Scheme 51.

The minimized geometries of biradicals seemed to be reasonable because both methyl radical and hydroxy radical sites want to stay conjugated to the corresponding phenyl groups. The only bond rotation that could occur freely would be the one around bond connecting the hydroxy carbon and the α-carbon to it. Given the 30-50 ns lifetimes of such 1,5-biradicals[80], two rotamers shown above have plenty of time to establish such a conformational equilibrium. If the two biradical rotamers indeed differ by 1.6 kcal, most of the observed selectivity simply reflects this conformational equilibrium in the biradical before cyclization, provided that cyclization of both rotamers involves the same motion. This assumption seems reasonable here, since a simple disrotaion around the two ortho C-C bonds is all that is required for coupling. When the OH group is solvated by hydrogen bonding in methanol, it is comparable in size to the phenyl group, such that the two rotamers are nearly equal in energy and selectivity is lost.

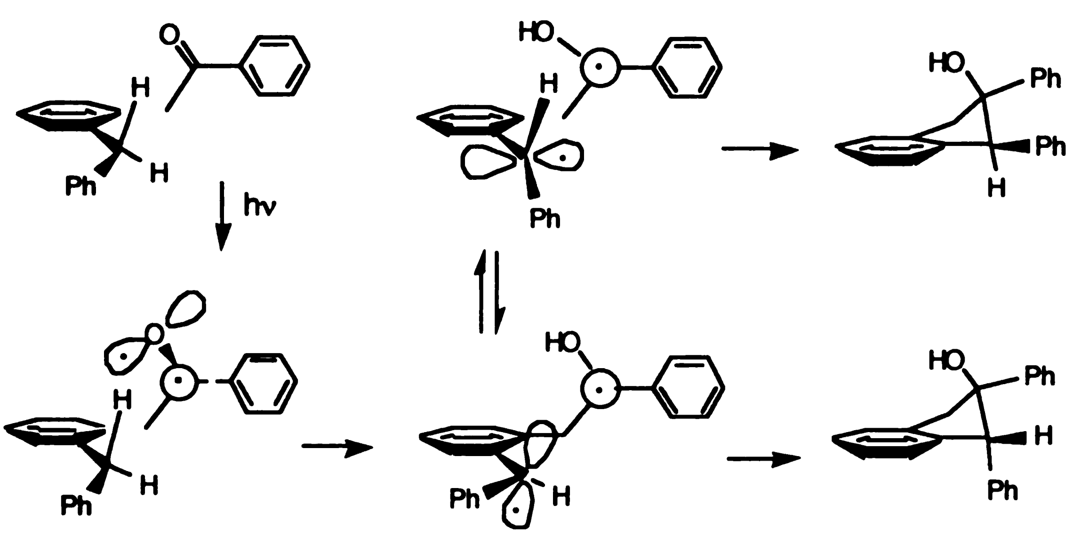
This photoreaction was also very efficient in solid state. The solid turned into liquid when it was irradiated to high conversion. The selectivity was reduced at higher conversion, implying that this environment behaves much like weak hydrogen bonding accepter.



benzene	55 %	45 %
MeOH	53 %	47 %

Scheme 52

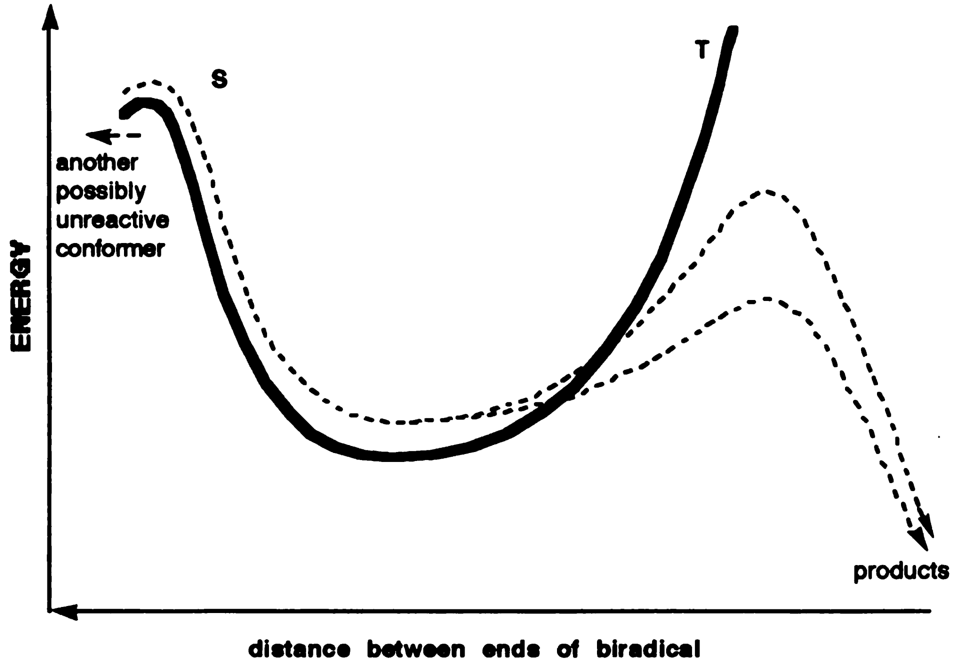
The result of α-(o-benzylphenyl)acetophenone was also quite surprising because the size difference between methyl and phenyl group did not seem to be large enough to cause such a big change in diastereoselectivity. Soon it was realized that this could be another benzylic conjugation effect. A possible pathway of this reaction is shown in Scheme 53. An initially formed biradical would have geometry such that phenyl group is held away from the rest of the molecule and the hydroxy radical site stays conjugated. Unlike α-(o-ethylphenyl)acetophenone, the rotation around the bond connecting diphenylcarbinyl radical site and disubstituted phenyl group would be less hindered because the extra phenyl group can stabilize the radical site in twisted conformation. Thus, this conformational equilibrium in the biradical before cyclization can be estabilished during the time scale of the biradicals' lifetime. The solvation by methanol did not change selectivity much because the conformational preference between OH and phenyl group is not a deciding factor any more in product formation.



Scheme 53

As mentioned in introduction of this thesis, Scaiano postulated that rate determining ISC and chemical reaction of the biradicals are separate and consecutive steps. He also suggested that paramagnetic species and solvent induced changes in product ratio were caused by variations in ISC rates of various biradical conformations. But, he failed to point out how ISC rates vary with biradical structure.

There are several known mechanisms for ISC of biradicals.[81] In short biradicals, ISC is mainly driven by spin-orbit coupling, which is known to be very much dependent upon the distance between radical centers[82]. This means that ISC occurs most fast when the biradical ends are proximate, which is most likely to be at the moment of biradical coupling. Wagner recently proposed the notion of coupled ISC and reaction.[55b, 80] The concept can be best explained by Scheme 54.

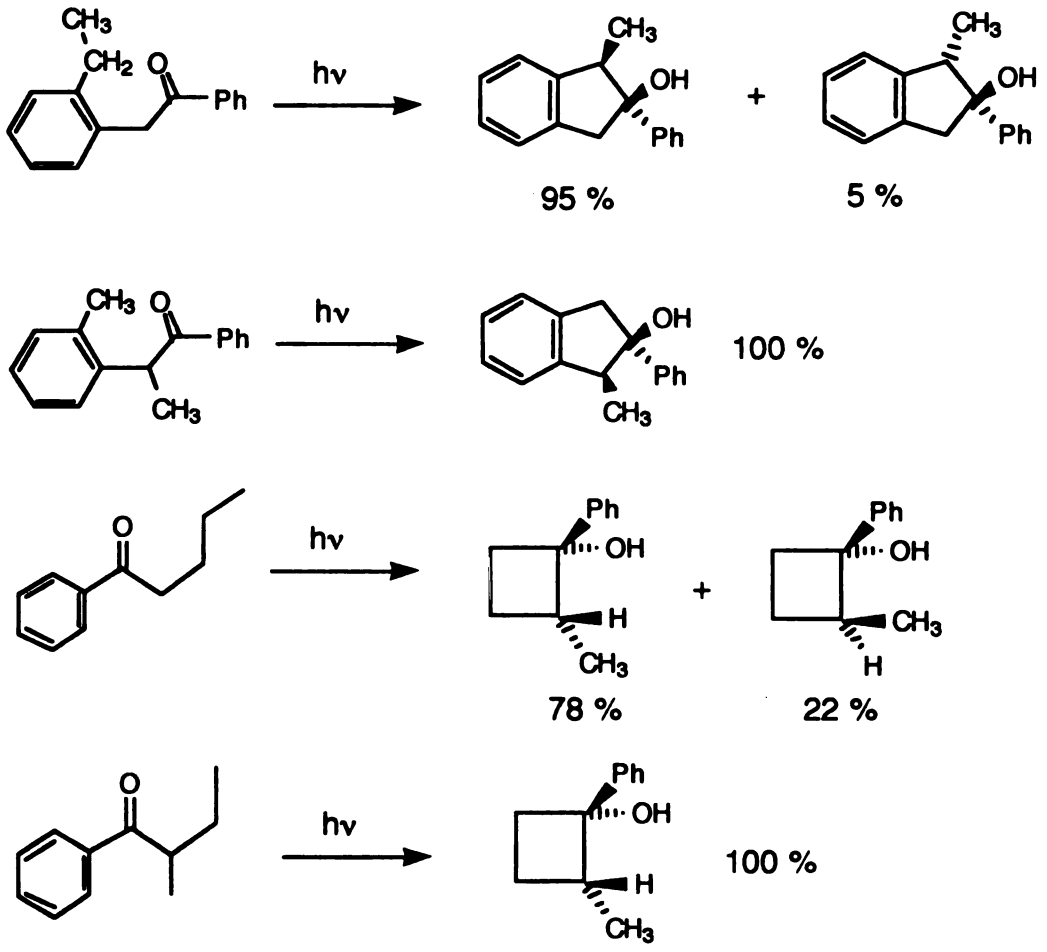


Scheme 54

Both the singlet and triplet surfaces rise in energy with movement along the reaction coordinate, but the singlet surface is soon stablized by the developing bond, such that the two surfaces cross at points that represent very low observed activation enrgies. If the biradicals experience some steric or electonic strain along the reaction coordinate, this will be reflected as activation energy of the triplet biradical decay. Therefore, one would expect more barrier for cyclization reaction than for cleavage or disproportionation reaction. In fact, activation energies for 1,5-biradical cyclization and decay of 1,4-biradicals were 1 kcal and zero kcal, respectively, which indicate that cleavage and disproportionation are the major reactions for the 1,4-biradicals.

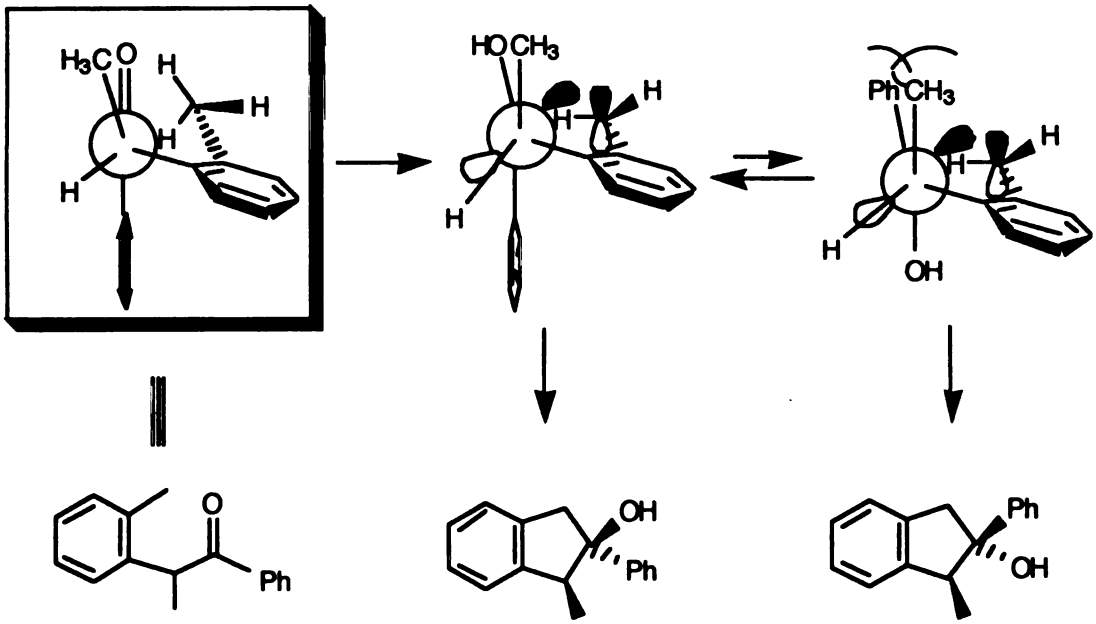
The concept of reaction induced ISC has also been implied by Griesbeck's explanation on stereoselectivity in 2+2 photocycloaddition of benzaldehyde to cyclic olefins.[57] He suggested that the observed stereoselectivity is caused by relative energy difference of two different conformers, which he interpreted as transient points through which stable 1,4-biradicals have to pass in order to invert the spin and overcome the spin barrier for bond formation. This is consistent with Wagner's new proposal in that ISC and product formation are induced by molecular motion along reaction coordinate. Even though this concept are getting attention from more and more people, more definite experimental evidence are still remained to be explored.

The Scheme also shows that products partitioning can occur after ISC. Otherwise, no diastereoselectivity could develop during cyclization as discussed above. This is contrary to Scaiano's postulate saying that singlet biradicals will couple without any barrier immediately after ISC. However, it seems resonable to assume that there will be certain steric repulsion when two biradical ends containing sizeable substituents approach to bonding distance.



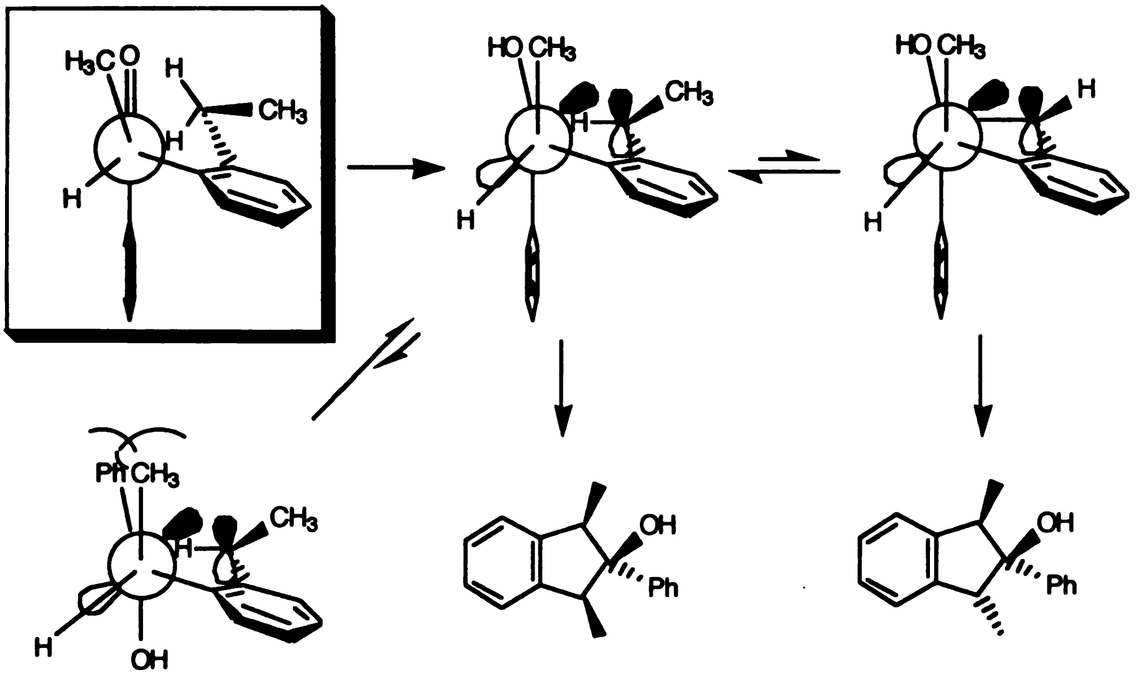
Scheme 55

Addition of extra α-substituents caused an interesting change in product composition. For example, Wagner and Zhou have reported that α-(o-tolyl)propiophenone forms only Z-isomer upon irradiation in benzene.[83] This was reminiscent to Lewis' work on α-methylbutyrophenone, which formed Z-isomer exclusively(Scheme 55). These selectivities were rationalized by pre-existing nonbonded interactions of methyl and phenyl group. Molecular mechanics calculation of α-(o-tolyl)propiophenone indicated that the minimum energy geometry has the methyl group eclipsed with the carbonyl group. Therefore, the initially formed biradical has a perfect geometry to form the Z-isomer. The other geometry, which may have given the E-isomer, suffers from severe repulsion between methyl and phenyl group(Scheme 56).



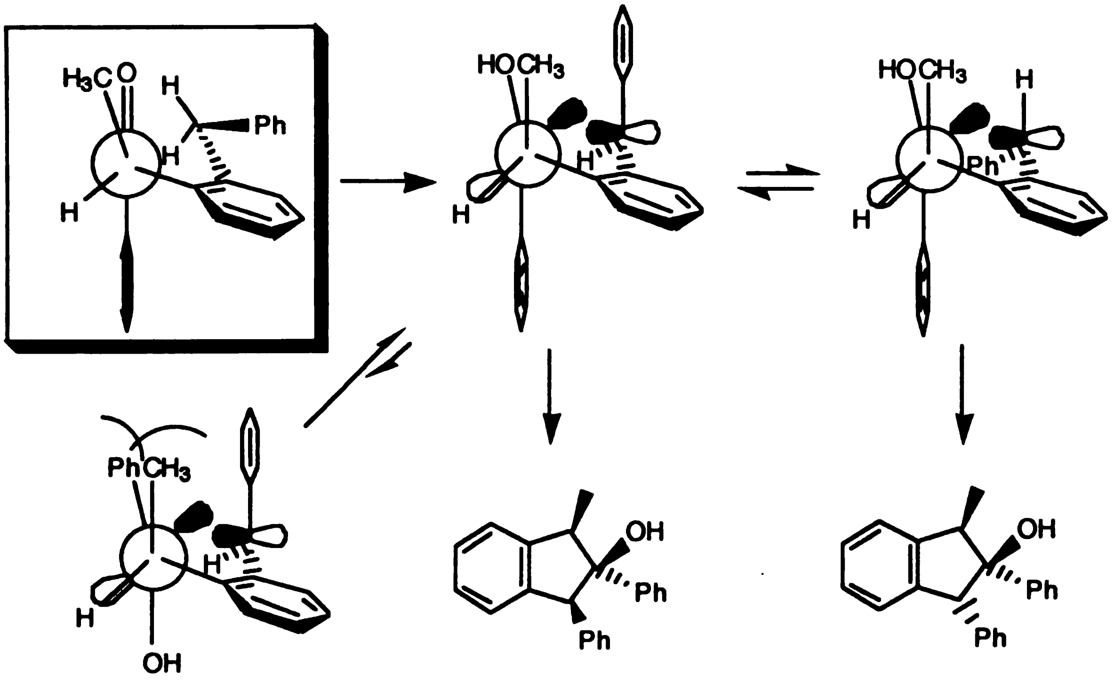
Scheme 56

Similar rationale can be applied to the observed product ratio from α-(o-ethylphenyl)propiophenone. The Z/E ratio was reduced to 5 to 1 from 20 to 1 for α-(o-ethylphenyl)acetophenone. There are two bond rotations determining the diastereoselectivity. One of them stays at one conformation for the same reason as mentioned above. The other benzylic radical site wants to stay conjugated with the disubstituted benzene. Thus, two conformers of the biradical shown in Scheme 57 will probably determine the diastereoselectivity. The first conformation, which puts a methyl group away from the rest of the molecule, is preferred over the other conformation.



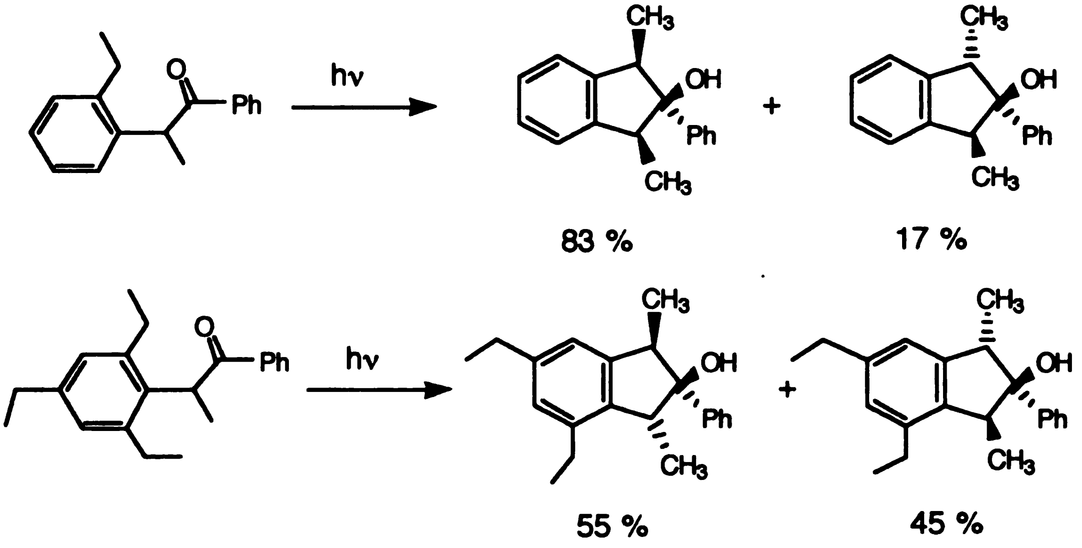
Scheme 57

This idea can be tested by studying the behavior of α-(o-benzylphenyl)-propiophenone. In this case, the benzylic radical site does not have to stay conjugated with the disubstituted benzene ring because of the extra benzene ring. Therefore, the two conformers of biradical from α-(o-benzylphenyl)propiophenone, which lead to products, will be different from the ones of biradical from α-(o-ethylphenyl)propiophenone (Scheme 58). The energy difference of the former appeared to be less than that of the latter because putting the benzene ring up or down relative to the disubstituted benzene does not cause serious repulsion with the rest of the molecule. In fact, the product ratio of α-(o-benzylphenyl)propiophenone was only 1.2 to 1, consistent with the behavior of α-(o-benzylphenyl)acetophenone and α-(o-tolyl)propiophenone..



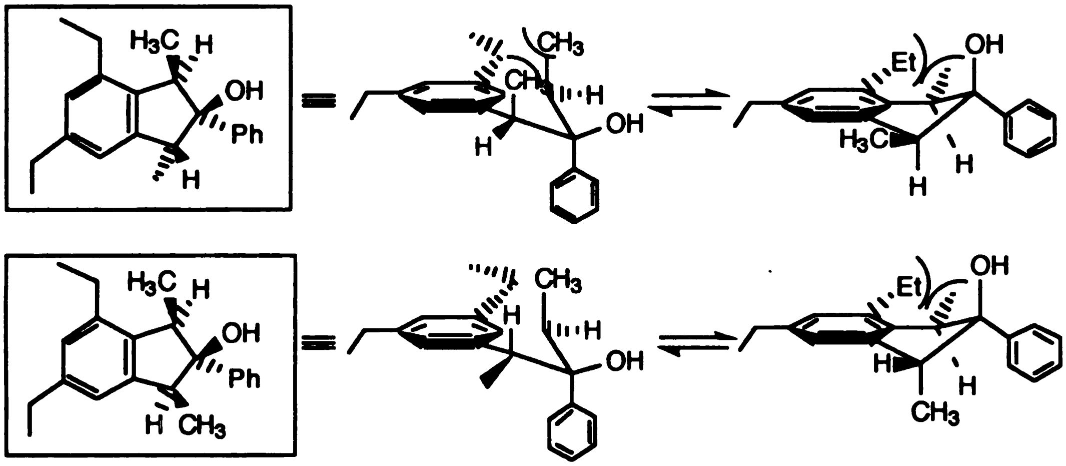
Scheme 58

α-(2,4,6-trialkylphenyl)propiophenones showed an interesting trend in diastereoselectivity, compared to the α-(2-alkyl-phenyl)propiophenones. In the case of α-(2,4,6-triethylphenyl)propiophenones, the product selectivity is completely lost.



Scheme 59

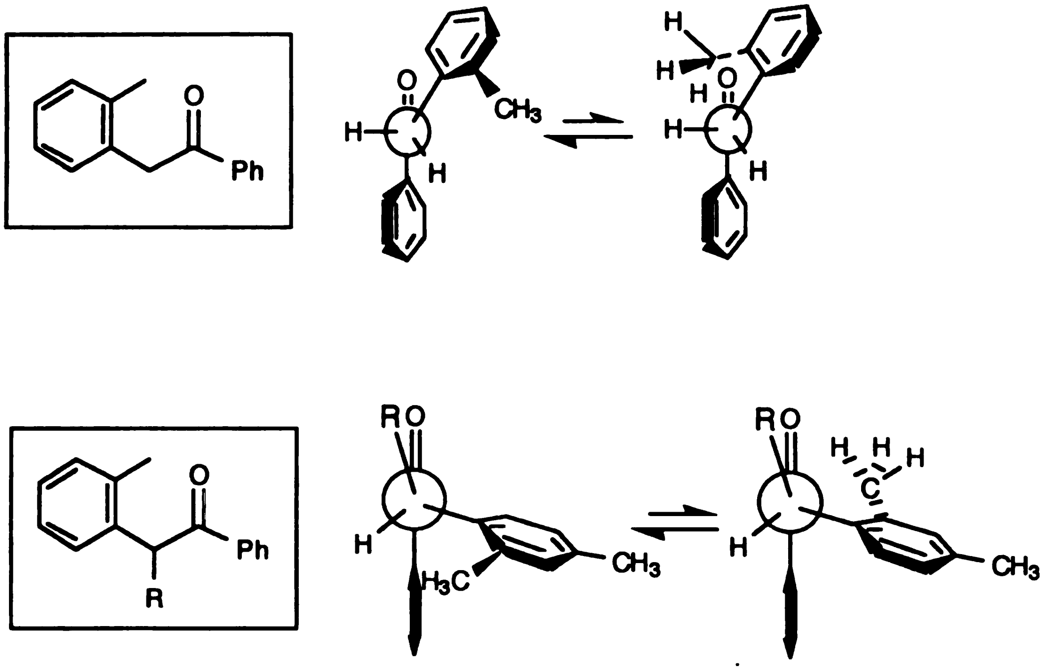
If we look at the geometry of biradicals leading to two isomeric products, the extra ethyl group at 6-position does not seem to change the relative energy of two conformers much. However, if we look at the several conformations of two products, it can be realized that the extra substituents at 6-position destabilized the isomer corresponding to the major product of α-(2-alkylphenyl)propiophenones. Both conformations, with a phenyl group at pseudo axial and equatorial position of five membered ring, suffered from steric repulsion as shown below (Scheme 60). This means that the reduced selectivity is determined at late stage of product forming step because this kind of interaction can happen only when the transition state geometry resemble the product geometry. This then reminds us that product forming step after ISC can have barrier or that ISC and product forming occur simultaneously at late stage as the biradicals move along reaction coordinate.



Scheme 60

The most interesting observation in photochemistry of α-(2,4,6-triethylphenyl)propiophenone was that only one product out of eight possible stereo isomers was formed predominantly after irradiation in methanol. This is an opposite solvent effect to what has been observed in most other 1,4 and 1,5 biradical coupling reactions. Usually, the solvation of OH group by hydrogen bonding makes the size of two substituents comparable and therefore reduce the selectivity. Obviously, some other factors are operating here to cause the opposite selectivity. The reason is not clear at the moment, but conformational change due to increased size of solvated OH group has to be responsible for it. For example, minimum energy conformer cannot have the α-methyl group eclipsed with carbonyl group any longer. Further rotational restriction, which is caused by addition of the extra sizable substituent, reduces the number of conformers available More detailed analysis requires the better understanding of this system.

For α-(o-alkylphenyl)acetophenones, additional substitution at α-position reduced the quantum efficiency of indanol formation significantly and α-cleavage became the major decay pathway of their triplets. This was attributed to the fact that an additional α-substituent made the tolyl or mesityl group twist away from the carbonyl while unsubstituted ones have minimum energy geometry with an eclipsed α-aryl group with carbonyl group (Scheme 61)[55b].



Scheme 61

Thus, it occurred to us that if the geometry is fixed such that α-aryl group is always eclipsed with carbonyl group, the reactivity should be restored even with α-substituents.

One of such candidates would be α-(o-tolyl)indanone, whose aryl group cannot twist away. However, irradiation of α-(2,5-dimethylphenyl)indanone resulted in α-cleavage reaction exclusively and no cyclization products could be observed. This result indicated that the rate of α-cleavage in the α-aryl-substituted indanone system is much faster than the rate of hydrogen abstraction, which is $1.6 \times 10^8 \ s^{-1}$ for α-(o-tolyl)acetophenone.[2]

B. Photoenolization of o-alkylphenyl ketones

As mentioned in introduction, it has been commonly assumed that o-alkylphenyl ketones form enols after irradiation and the primary decay pathway for the enol in the absence of trapping reagents is regeneration of the starting ketones. Formation of cyclobutenols from the enols has not been discussed for simple o-alkylphenyl ketones because they were rarely isolated or observed by any spectroscopic methods. Recently, Wilson suggested that this may be due to thermal instability of these products because all the data were analyzed by GC injection at that time[84]. Result of our studies on this system support this idea. All the ketones we investigated form cyclobutenols in moderate to excellent chemical yield even though some acetophenones took long time to react and gave complicated mixture of products. These cyclobutenols are revert to starting ketones as they are heated to ~ 80 °C. The cyclobutenols also revert to ketones during purification by column chromatography and HPLC injection. This instability of photoproducts made kinetic studies difficult because product analysis could not be performed accurately using GC or HPLC. Parallel irradiation of o-ethylbenzophenone with valerophenone or α-(o-ethylphenyl)acetophenone in NMR tubes gave a quantum yield estimated as 0.1.

Among all the ketones investigated, o-ethylbenzophenone provided the most information on the mechanism of this reaction. o-Ethylbenzophenone forms the E-cyclobutenol quantitatively with no trace of the Z isomer. This is exactly opposite selectivity to what we have seen from other 1,4 or 1,5 biradicals, implying that this reaction follows different pathways from simple biradical coupling.

If dienols are precursors of cyclobutenols, irradiation of ketones in the presence of additives that react with the dienols would quench cyclobutenol formation. The fact that addition of p-toluenesulfonic acid or HCl quenches the reaction supports this idea. Added acid does not seem to destroy ketones' intrnsic photoreactivity, since it did not affect the reactivity of valerophenone. When o-ethylbenzophenone is irradiated in deuterated methanol, no photoproduct was observed by NMR during same time scale as in benzene, but efficient benzylic H-D exchange took place. We believe that trace of acid present in methanol[85] is quenching the enols and that H-D exchange is faster than cyclobutenol formation under this condition.

2,4,6-Triethylbenzophenone also formed only the E isomer in benzene or methanol. Matsuura reported[36] that the same ketone gave different amounts of E and Z products depending on solvent, contrary to our findings. Later, Ito repeated the same reaction and observed formation of only one isomer.[86] Ito could not explain the reason for the discrepency. Since Matsuura analyzed the cyclobutenols after workup, we strongly suspect that some acid catalyzed E→Z isomerization took place.

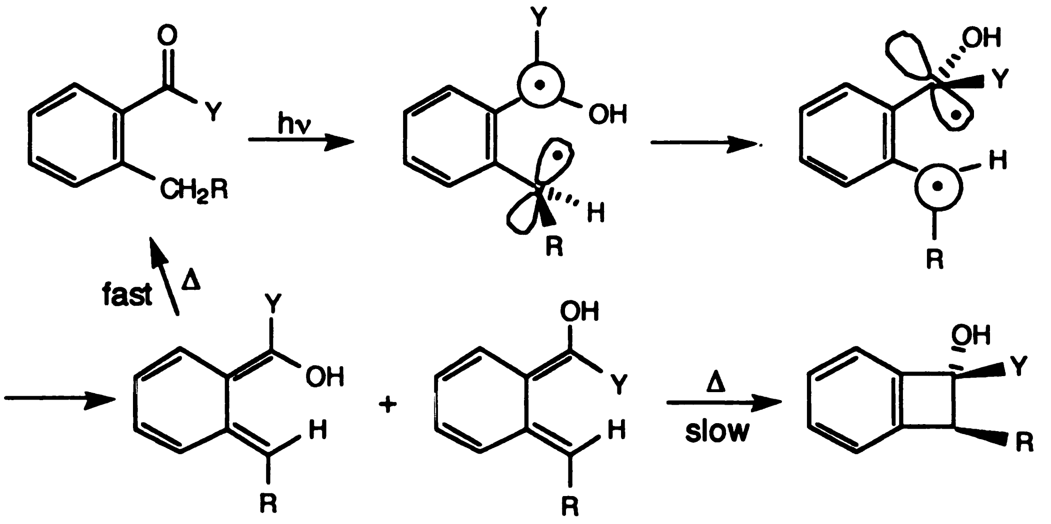
Matsuura suggested[36] that cyclobutenols are formed by stereospecific conrotatory cyclization of the dienols, with product distribution reflecting the distribution of the possible enols. Our results appear to corroborate this mechanistic picture for both o-alkyl and 2,6-dialkyl ketones.

When a single crystal of p-toluenesulfonic acid was added to the E-isomer, it was slowly isomerized to Z-isomer and reached an equilibrated ratio of 7 to 3 favoring Z-isomer, indicating that the Z-isomer is more stable thermodynamically than the E-isomer. This observation helped us to make structural assignment of each isomer.

If the observed E isomer was formed by thermal conrotatory cyclization of the dienols, what caused such a high diastereoselectivity? It is well known that both E and Z enols are formed from triplet ketones.[31a,33c] The latter undergo a very rapid 1,5-

sigmatropic H shift to regenerate ketone, while the former live for as long as a few seconds unless trapped with dienophiles or acid.

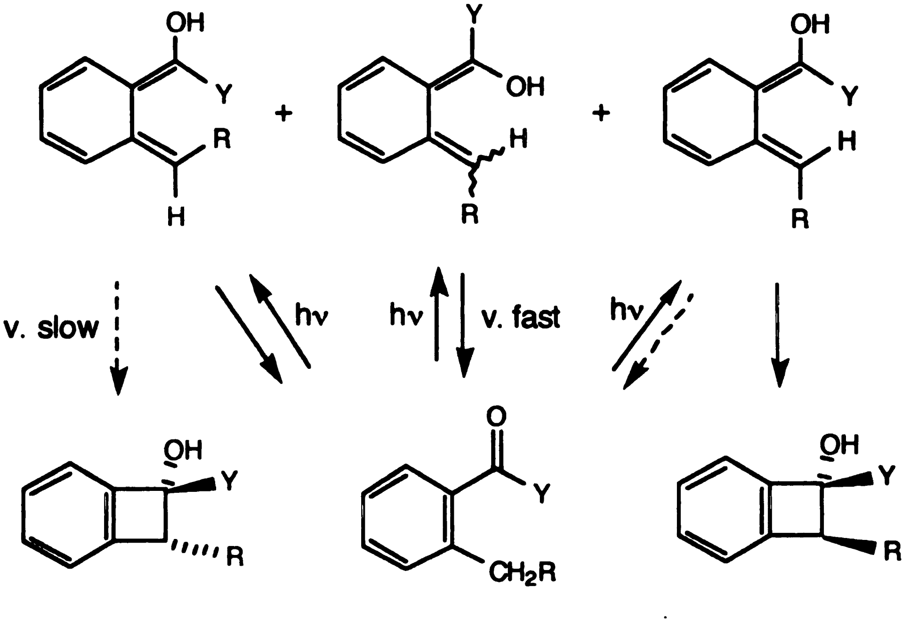
Why is only one E-enol apparently formed? The overall reaction is known to occur by triplet state γ-hydrogen abstraction[32] that yields a triplet 1,4-biradical, which coincidentally happens to be the triplet of the enol product[87]. We invoke the common assumption that the biradical triplet enol resembles a triplet diene[88] in having one conjugated benzylic radical site and one twisted 90° out of conjugation. The biradicals are quite long-lived[31a,87] and apparently can undergo facile coupled rotation about both ring-benzylic carbon bonds, otherwise Z and E enols could not both be formed.



Scheme 62

The E-enol that thermally produces the observed cyclobutenols clearly is the less congested E-enol. We conclude that the biradical assumes a conformation with the α-methyl site conjugated and the hydroxy site twisted before intersystem crossing to ground state enol occurs. In the benzophenone-derived systems, the second benzene ring can stabilize the hydroxyradical site, as has been observed in other biradicals.[89] In the acetophenone-derived systems, conjugation of the hydroxyradical with the oxygen lone-pair may be sufficient to fix the twisting preference. Whatever the exact cause, the observed stereoselectivity of cyclization indicates that the methyl radical site has time to assume its more stable geometry before biradical decay.

An alternative possibility is that the other E-enol also is formed but closes to cyclobutenol much more slowly, so that it is completely trapped by trace acid. It is well known that there is a much larger barrier to the interconversion of cyclobutenes and dienes which have terminal alkyl or alkoxy groups pointed in.[90] Therefore the possibility that the observed diastereoselectivity of cyclobutenol formation represents vastly different rates of closure of isomeric E-enols cannot be dismissed.

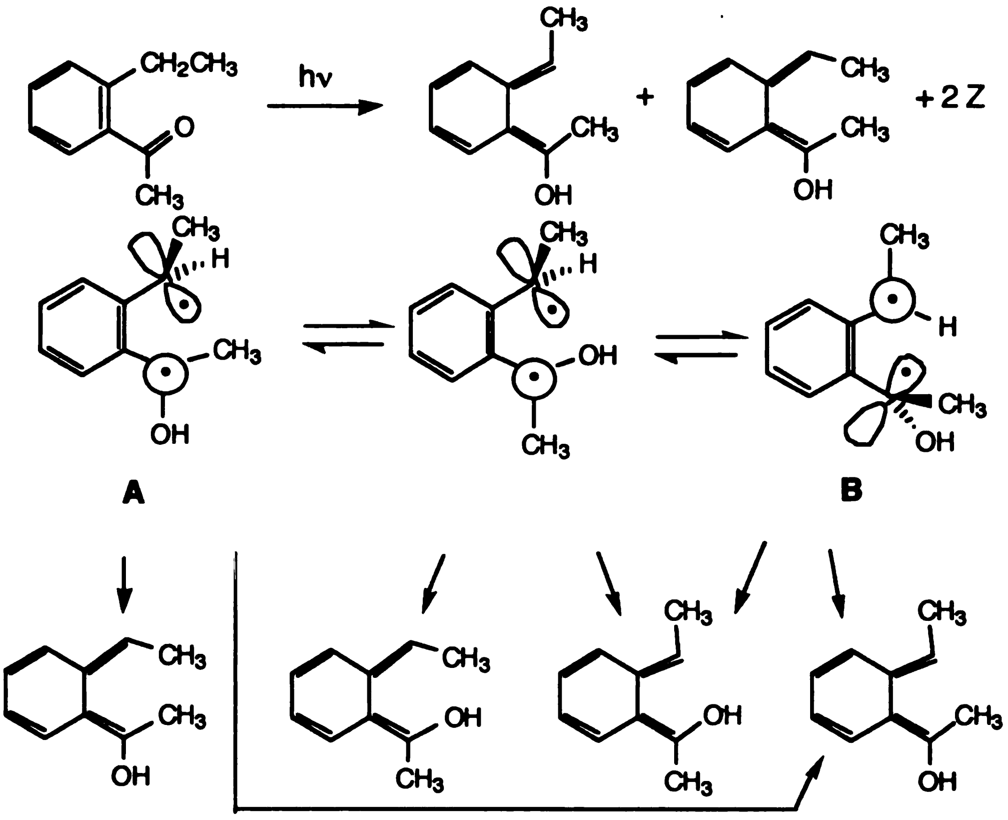


Scheme 63

This picture of dienol behavior is in accord with the general belief that steric congestion favors cyclobutenol formation.[31b,36] The rate at which the first-formed dienol closes to cyclobutenol presumably is greatly increased by additional buttressing ortho-alkyl groups, since the two benzylic centers cannot both lie coplanar with the benzene ring. The fact that such cyclobutenols are much more stable thermally than those from mono-alkyl ketones also demonstrates the effect of steric congestion on dienol energy. The difficulty in detecting transient intermediates in these congested systems also may be due to unusually short-lived enols. This short lifetime of the enol intermediate from 2,4,6-trialkylbenzophenones can also explain the less efficient quenching of cyclobutenol formation from 2,4,6-trialkyl ketones by added acids than that of cyclobutenol formation from mono-alkyl ketones.

There have been some questions about whether the product could arise directly from the biradical.[91] We observed that the reactions of ortho-ethylbenzophenone and 2,4,6-trimethylbenzophenone were efficiently quenched by a small amount of weak acid, p-toluenesulfonic acid, but 2,4,6-triethylbenzophenone was not quenched by the same acid. We also observed that 2,4,6-triethylbenzophenone was quenched partially by strong acid, HCl. This may be due to the combination of the shorter lifetime of enols from the more sterically hindered ketones and the faster quenching rates of stronger acids. If the cyclobutenol was generated from the coupling of the biradical. the additives such as p-toluenesulfonic acid or HCl should not change the efficiency of product formation. In fact, Scaiano has recently measured the quenching rate of several ketones by several different acids and bases and obtained similar results.[92]

For o-ethylacetophenone, quantum efficiency of product formation was much less than o-ethylbenzophenone, and much less diastereoselectivity, 2 to 1 favoring E-isomer, was observed. Initially formed biradical would have a geometry such that hydroxy radical maintain a benzylic conjugation and methyl radical twists 90 degree away from conjugation. The rotation around bond connecting phenyl ring and hydroxy radical site would be slower than the corresponding rotation in benzophenone derivatives due to benzyllic conjugation. This would result in formation of more Z-enols than from the corresponding biradicals of benzophenone. Their Z-enols then rapidly revert to starting ketones, which may explain the reduced quantum efficiency of this system. Since there are no extra phenyl groups to stabilize the biradical sites, either biradical site would like to stay conjugated with the parent benzene ring all the time, but not both sites at the same time. Several possible conformations of this biradical are shown in Scheme. In order to have cyclobutenols as product, E-enols have to be generated as shown below. Biradicals A and B in Scheme are responsible for the formation of these E-enols. In case of benzophenones, biradical B can be more populated than A because extra phenyl ring can stabilize the twisted hydoxy radical site and the methyl radical want to stay conjugated. In case of acetophenone, however, biradical A becomes an important contributing conformer for the reason stated above. The biradical A would then form two possible E-enols in comparable amounts. This process is analogous to photoisomerization of stilbene,[93] which vertical transition from triplet excited state surface to singlet ground state lead to formation of E- and Z- isomers in comparable amounts.

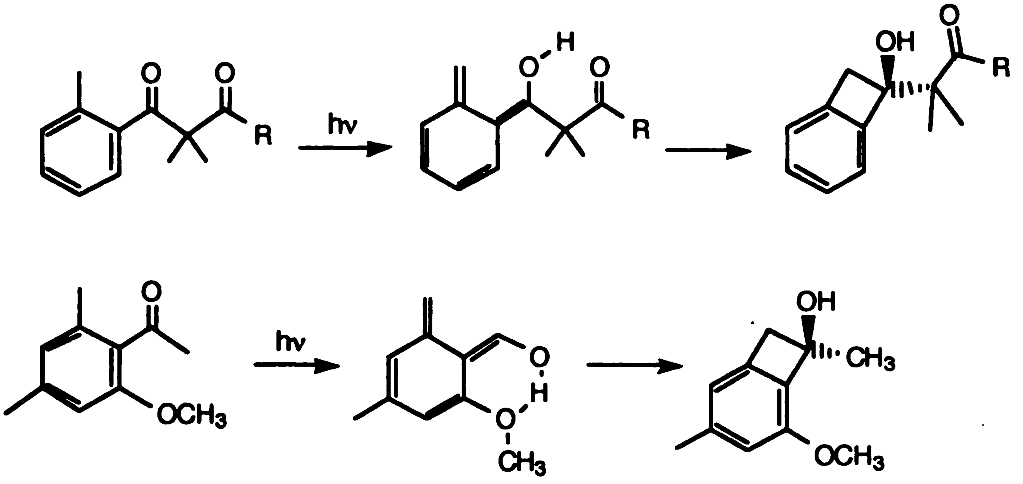


Scheme 64

The dienols could be trapped with maleic anhydride, and a mixture of two isomeric trapped products were formed in similar ratio as benzocyclobutenols, together with some other unknown products.

Benzocyclobutenol formation from dienols turned out to be quite general reaction. Investigation of more than 10 compounds of o-alkylphenyl ketones and 2,4,6-trialkylphenyl ketones led us to believe that the "stable"(in the absence of strong acid and base at room temperature) benzocyclobutenols can be useful synthetic precursors. People have used the dienol trapped products with dienophile and SO_2 as synthetic precursors for the dienols, but this reaction often led to formation of considerable amount of side products caused by releasing SO_2 or dienophile.[94]

After we discovered the generality of benzocyclobutenol formation, people started to look at this system more carefully and many new results have been reported. Hasegawa reported that irradiation of 1-(o-methylphenyl)-2,2-dimethylpropane-1,3-diones resulted in efficient formation of the corresponding cyclobutenols.[95] The author claimed that intramolecular hydrogen bonding of resulting Z-dienols suppressed the reverse transfer of hydrogen to reproduce the starting ketones as shown in Scheme 65. Similar hydrogen bonding effects may be responsible for the reactivity of 2,4-dimethyl-6-methoxyacetophenone. The intramolecular hydrogen bonding would increase the population of E-enols over Z-enols, so it leads to the efficient conversion into the cyclobutenols.

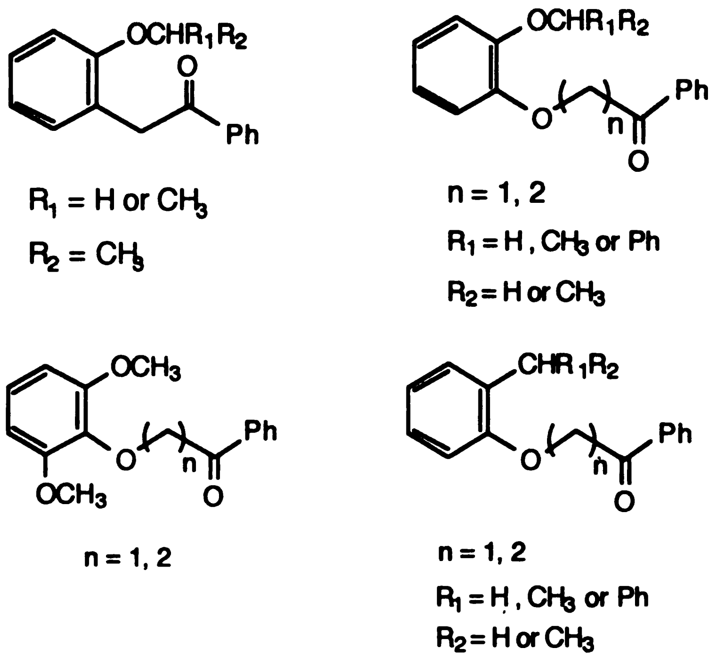


Scheme 65

The studies on o-alkylphenyl ketones can be applied to understanding a mechanistic puzzle of photochemistry in closely related system, o-substituted benzil. This will be discussed separately later in this thesis.

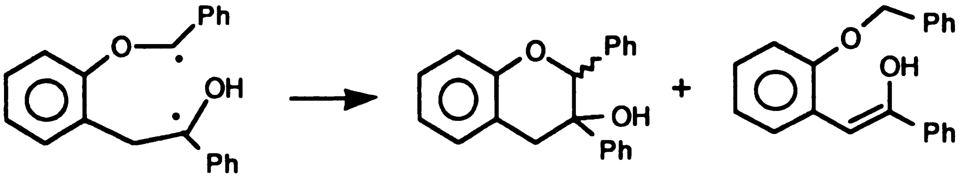
C. Remote hydrogen abstraction

We have looked at several different systems of more remote hydrogen abstraction, ranging from ε-hydrogen abstraction to η-hydrogen abstraction shown below.



Scheme 66

Wagner and Meador reported that the photocyclization of α-(o-benzyloxyphenyl)acetophenone proceeds in a quantum yield of only 0.05 pretty much independent of solvent[49](Scheme 67). The 3 x 10^7 s^{-1} triplet decay was assigned as the rate for ε-hydrogen abstraction because at the time there was no known physical decay that rapid. It is likely that CT quenching by the α-alkoxyphenyl group has a much lower rate constant, ~2 x 10^6 s^{-1}. Thus it was concluded that the low product quantum yields are primarily due to very efficient disproportionation of the 1,6-biradical intermediates to enol of starting ketone.

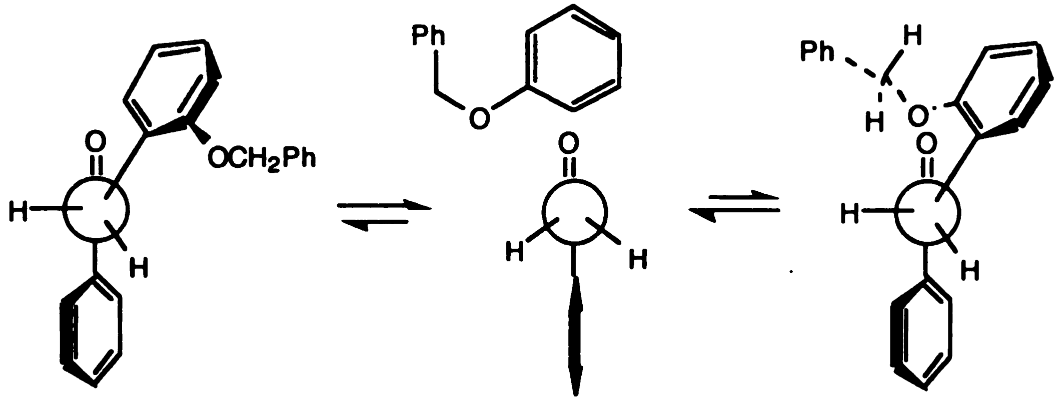


Scheme 67

A quantum yield of 0.015 was obtained for the photocyclization of α-(o-isopropoxyphenyl)acetophenone in benzene. This quantum yield is even lower than the value for α-(o-benzyloxyphenyl)acetophenone. Unlike α-(o-benzyloxyphenyl)-acetophenone, Norrish type I cleavage started to compete with Type II reaction, so this side pathway reduced the quantum efficiency of photocyclization further. The reaction is readily quenched with conjugated dienes, $k_q\tau = 69\ M^{-1}$ in benzene. With $k_q = 6 \times 10^9\ M^{-1}s^{-1}$, the rate of triplet decay is $8.7 \times 10^7\ s^{-1}$. If the hydrogen abstraction reaction is solely responsible for the triplet decay, k_H becomes $1.3 \times 10^6\ s^{-1}$.

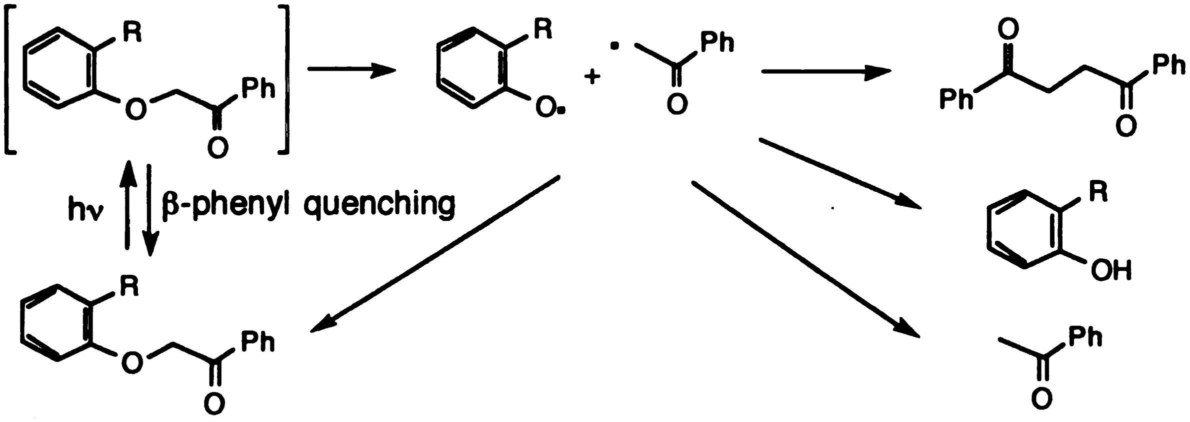
α-(o-Ethoxyphenyl)acetophenone formed two isomers with Z/E ratio of 2.5 to 1 in benzene. This ratio was not changed much in methanol,(2.3 to 1). This ratio is slightly larger than that from α-(o-benzyloxyphenyl)acetophenone. This may be caused by slightly higher rotation barrier of bond between ethyl radical and oxygen than that of bond between benzyl radical and oxygen.

The rate constant for hydrogen abstraction, $1.3 \times 10^6\ s^{-1}$, is lower than that for o-benzyloxybenzophenone ($1.9 \times 10^7\ s^{-1}$) and that for α-(o-ethylphenyl)acetophenone ($8.4 \times 10^8\ s^{-1}$). Given the known conformational preference for the α-aryl group to eclipse the carbonyl, that order of magnitude decrease in rate must reflect a *syn-anti* rotational preference as in the α-(o-tolyl) ketones as well as lost entropy.



Scheme 68

Several α-(o-alkylphenoxy)acetophenones and α-(o-alkoxyphenoxy)acetophenones were prepared in order to examine the possible ε and ξ hydrogen abstraction. Photolysis of these ketones resulted in mainly β-scission as shown below, with no trace of cyclization products.



Scheme 69

This result confirms the previous findings for unsubstituted α-phenoxyacetophenones by Scaiano and other workers.[96] This cleavage reaction turned out to be responsible for yellowing of papers on exposure to light.[97] Their rate constants for this cleavage are reported to be in the range of $5 \times 10^6 - 2.7 \times 10^9\ s^{-1}$, where the higher values are for ketones with electron-donating substituents on the α-phenoxy rings. Another major pathway for triplet deactivation in these compounds is β-phenyl quenching.

Apparently, remote hydrogen abstraction via medium sized ring is too slow to compete with these two fast decay pathways.

If solvent cage escaped radicals were responsible for the observed photoreactions, increasing cage effect would retard the reaction. However, when the ketones were irradiated in micelle, cleavage reaction was again predominant.

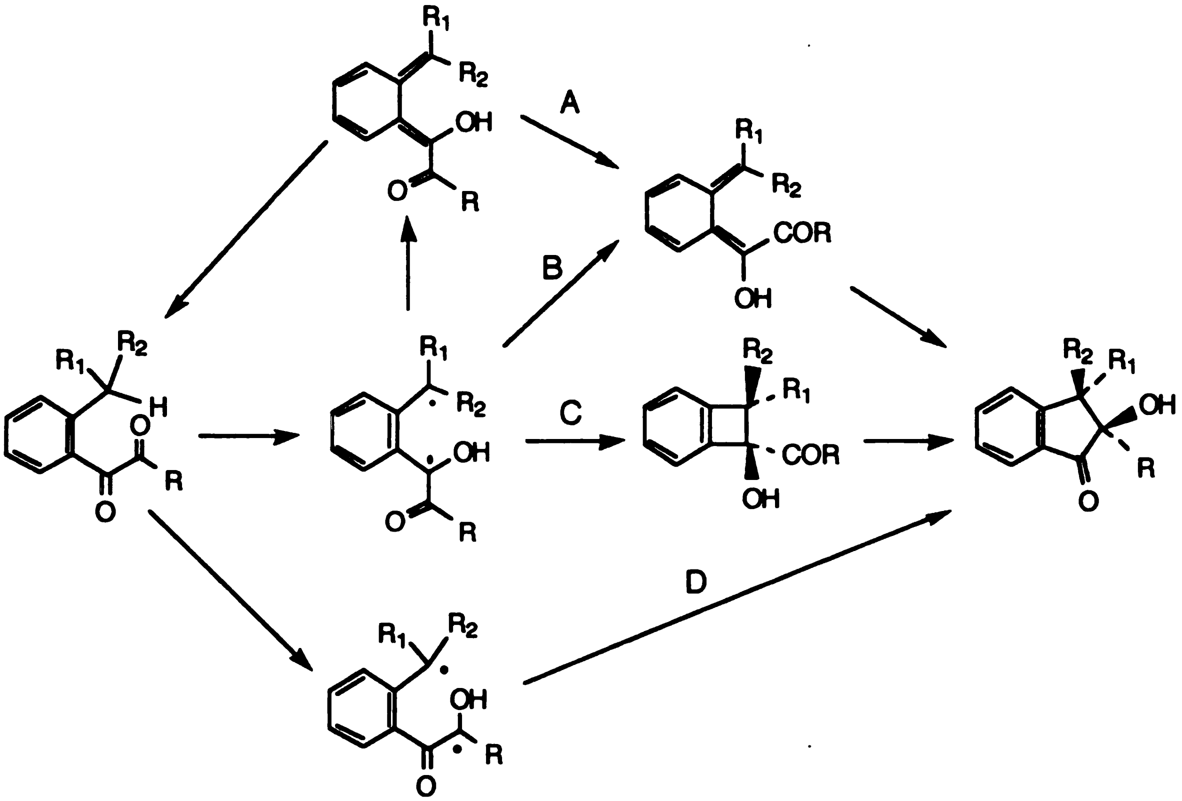
β-(o-Alkylphenoxy)propiophenones form cyclization products in very low quantum efficiency as expected. Chemical yield seemed to be quite high as long as concentration was kept low, otherwise intermolecular reaction takes over to result in polymerization. For β-(o-benzylphenoxy)propiophenone, quantum yield of tetrahydrobenzoxepinol formation in benzene was 0.0038 and $k_q\tau$ of 152 M^{-1} was obtained. This low quantum yield may be caused by entropic loss. The disproportionation of 1,7 biradical to enol of starting ketone may also be partially responsible for the low value.

The ratios of Z and E isomer in benzene were 1 to 1 for β-(o-benzylphenoxy)propiophenone and 2.4 to 1 for β-(o-ethylphenoxy)propiophenone. Carless reported ratio of Z and E isomer for β-(o-benzylphenoxy)propiophenone being 16 to 36, which is different from our value.[51] Since Carless' data was obtained after column chromatography, we suspect there was some amount of loss in one isomer or certain extent of isomerization during the separation of two isomer.

Several β-(o-alkoxyphenoxy)propiophenones were tested for possible η-hydrogen abstraction. All of these compounds turned out to be photoinert at prolonged irradiation. This reaction would require a ten membered ring transition state. Our result indicates that the ten membered ring is the limiting size of the cyclic transition state for the remote hydrogen abstraction in long chain ketones having ortho substituted benzene in the middle.

D. Sterically hindered benzil derivatives

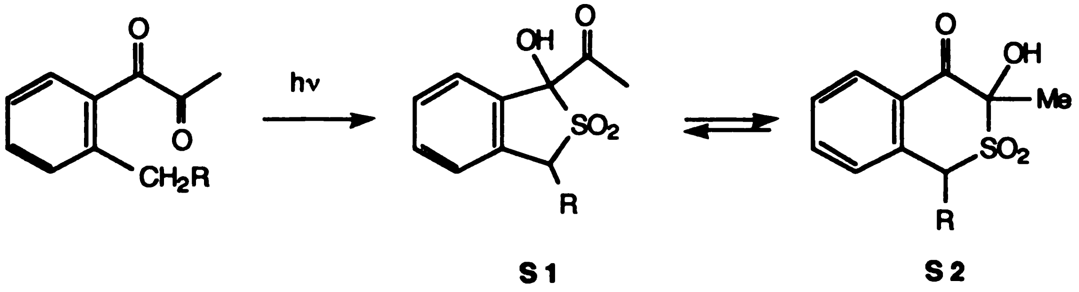
As mentioned earlier, mechanism of photoreaction of α-diketone system has been discussed for last 20 years. Several possible mechanisms of this reaction are shown below.



Scheme 70

Reaction pathways A and B were proposed by Ogata and coworkers and pathway C was proposed by Hamer. Hamer has ruled out the possibility of the intervention of enol intermediate at any stage of the reaction since no deuterium incorporation into the product or starting material occurs in photolysis in methanol-O-d.

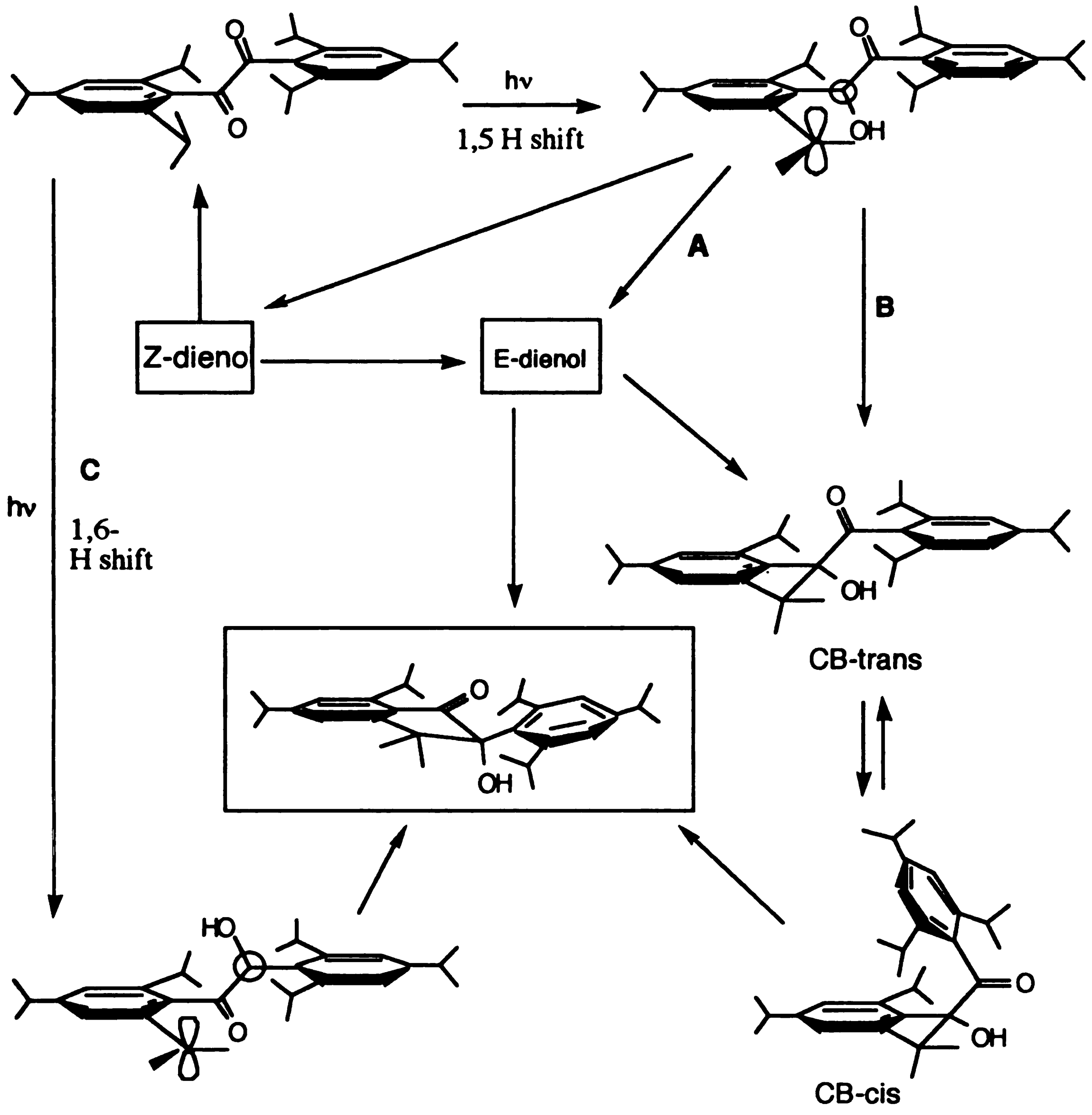
On the other hand, Ogata showed the intermediacy of the enols by trapping them with a dienophile, dimethyl acetylenedicarboxylate[71a]. When this trapped adduct was heated at 180 °C, the starting diketone and a hydroxy indanone were isolated. And Ogata suggested that no deuterium incorporation into product in photolysis in methanol-O-d was due to the stabilization of enol via intramolecular hydrogen bonding. While Ogata could trap the enol with dimethyl acetylenedicarboxylate,[71a] Hamer reported that no trapping products were isolated when the same diketone was irradiated in the presence of maleic anhydride[72]. They could, however, trap an intermediate with sulfur dioxide and isolate the product S2, which they proposed was formed by rearrangement of an initial product, S1.(Scheme 71)



Scheme 71

Direct hydrogen abstraction from the other carbonyl oxygen followed by coupling of the resulting biradical(pathway D) has been ruled out by both workers because of lack of previous examples of this kind of reaction at that time.

Due to the unsymmetrical nature of this system, it is most likely that one carbonyl oxygen is more activated toward hydrogen abstraction than the other. Accumulated evidence by these workers indicate that the carbonyl group which is attached to the benzene ring is the more reactive one. Here an interesting question can be raised: Is this mechanism also operating in photochemistry of a symmetric analogue, ortho substituted benzil system, which gives the same type of photocyclization product? This will be discussed below using the result of our mechanistic studies on this system.

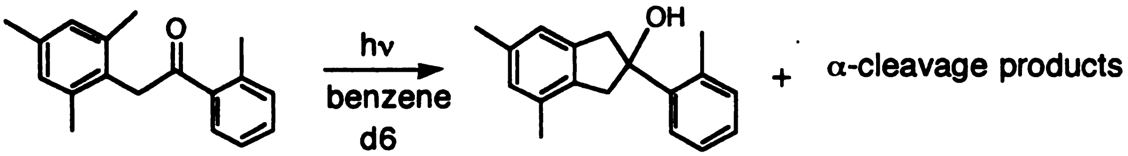


Scheme 72

A possible mechanistic Scheme for photocyclization of hexa-isopropylbenzil is shown above(Scheme 72). Now, let us evaluate the feasibility of each pathway. Reaction pathways A and B are unlikely in the solid state because rearrangement of cyclobutenol to hydroxy indanone would require a great deal of molecular motion. From studies on photochemistry of o-alkylphenyl ketones, we know that Z enols undergo a very rapid 1,5-sigmatropic H shift to regenerate ketone and only E enols live long enough to do any chemistry in following step. The Z/E isomerization requires 180 degree rotation, which seems impossible in such a restricted environment.

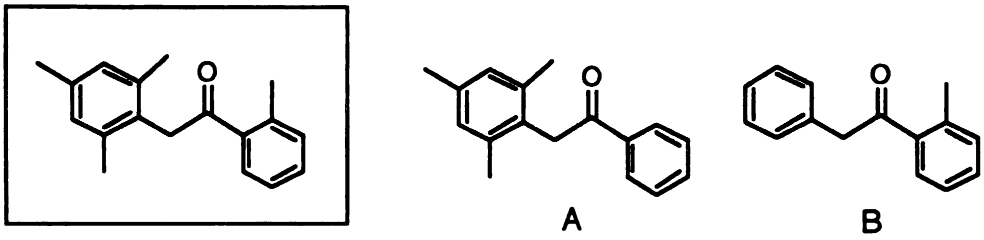
As we discussed earlier, sterically congested 2,6-dialkylphenyl ketones form cyclobutenols more efficiently than monosubstituted phenyl ketones, and the cyclobutenols are stable enough to isolate. In fact, both 2,4,6-triisopropylbenzophenone and 2,4,6-triisopropylacetophenone form corresponding cyclobutenols quantitatively. The similar cyclobutenol was not observed from irradiation of hexaisopropylbenzil even when the reaction was monitored in NMR tube scale experiment. Even though all the spectroscopic data fit our original structural assignment for the photoproduct, we sought firmer differentiation between benzocyclobutenol and hydroxyindanone. If the product was benzocyclobutenol, it would open up to regenerate the starting diketone as it heated. However, no change in NMR spectrum was made at 90 ^{o}C, confirming the original assignment. Furthermore, in order to have rearrangement of the cyclobutenol into the hydroxyindanone, the carbonyl and hydroxy group should be in cisoid conformation. This requires almost 180 degree rotation of triisopropylbenzoyl moiety, which is very unlikely to happen in solid state . Even in solution phase, this cisoid conformation may not be formed easily because of high strain energy caused by steric congestion.

We reinvestigated photochemistry of α-mesityl-2'-methylacetophenone and obtained an interesting result. This compound shares an interesting common feature with ortho substituted benzils; There are hydrogens available for abstraction not only at γ-position but also at δ-position. When the compound was irradiated in benzene-d_6, only reactions that occurred were δ-hydrogen abstraction and type I cleavage products, as previously reported by Zhou. No trace of γ-hydrogen abstraction product could be found.



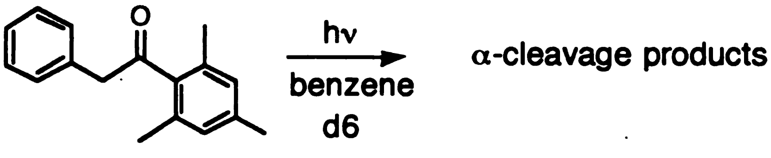
Scheme 73

From this result, it appears that δ-hydrogen abstraction and type I cleavage are much more preferred decay pathways for triplet excited state of this compound than γ-hydrogen abstraction.



Scheme 74

The reactivity of this compound can be compared to those of compound A and compound B. Compound A has been studied by Wagner and Meador and it is known to give indanol with quantum yield of 0.44 and k_H of 5.5 x 10^8 s-1. Photochemistry of compound B has not been studied carefully and we decided to examine photochemistry of α-phenyl-2'.4'.6'-trimethylacetophenone, which would form benzocyclobutenol more efficiently than the compound B would. However, α-phenyl-2'.4'.6'-trimethylacetophenone did not form benzocyclobutenol, but formed α-cleavage products in low efficiency.



Scheme 75

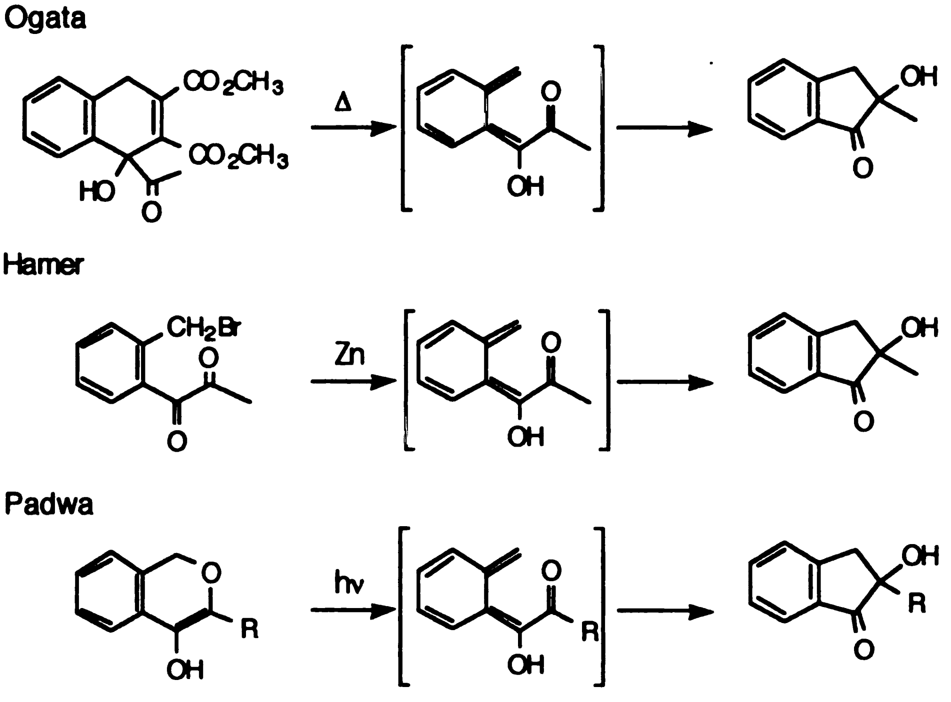
From the above results on α-mesityl-2'-methylacetophenone and α-phenyl-2'.4'.6'-trimethylacetophenone, can we rule out pathway A and B from reaction mechanism of hexaisopropylbenzil? Maybe, we can rule out the intermediacy of benzocyclobutenol, but possibility of direct rearrangement from E-dienol to the observed indanol still remains.

For unsymmetrical diketones such as 1-(o-alkylphenyl)-1,2-diones, electron density distribution at excited states would be different for two carbonyl oxygens, so either 1.5- or 1.6-H shift may be preferred over one another. However, symmetric diketones such as 2,4,6,2',4',6'-hexaalkylbenzils will have equal electron density around two carbonyl oxygens, so other things such as geometric and stereoelectronic factors will determine the reactivity.

If the other carbonyl oxygen is within the 'right reaction parameter'[39], the direct abstraction via 1,6 H shift would be a perfectly reasonable pathway. This direct 1,6-H shift is analogue of photochemistry of α-(o-alkylphenyl)acetophenones, which have been discussed in this thesis. In order to test this possibility, X ray crystallography of compound 1 was undertaken. The result of this structure determination was more intriguing. The phenyl rings and carbonyl groups are orthogonal to each other and two carbonyl groups have anti orientation. This structure is very close to that of α-(2,4,6-trimethylphenyl)-2',4',6'-trimethylacetophenone. Interestingly, the only reaction that observed for this compound was α-cleavage[14], the ease of the reaction being attributed to alignment of breaking bond orbitals with those in the phenyl ring π system. This cleavage reaction was not observed for hexaisopropylbenzil. This may be due to much faster rate of the observed reaction than the cleavage reaction, since the low triplet energy of the diketones is not high enough to break the carbon carbon bond.

MMX calculation was performed on hexaisopropylbenzil and essentially same geometry as x ray structure was obtained. According to this calculation, O-H distance of 1,5 H shift pathway is 2.7 A while that of 1,6 H shift is 3.7 A. If excited state geometry is similar to this, the reaction would occur preferentially via 1,5-H shift over 1,6-H shift. However, the close examination of molecular model of hexaisopropylbenzil reveals that a liittle rotation around the bond connecting two carbonyls brings the farther oxygen to within bonding distance quickly. If this little motion is tolerable in the solid state, 1,6-H shift could still compete with 1,5-H shift.

Considering large molecular motion necessary for pathways A and B, it would be reasonable to say that pathway C is operating in solid state photoreaction. From the fact that photoproducts were also solid and no change of appearance except color change was observed during photolysis, it is safe to say that the rigid solid framework was maintained during the reaction. However, we cannot completely rule out the possibilities of these other pathways in solution phase photochemistry, even though we presented several experimental results against those pathways. In fact, all the pathways presented above may be competing in solution phase. The fact that dienols can be precursor of the observed product, hydroxyindanone, have been demonstrated by Hamer[72], Ogata[71a] and Padwa[98] independently. These are summarized below.(Scheme 76)

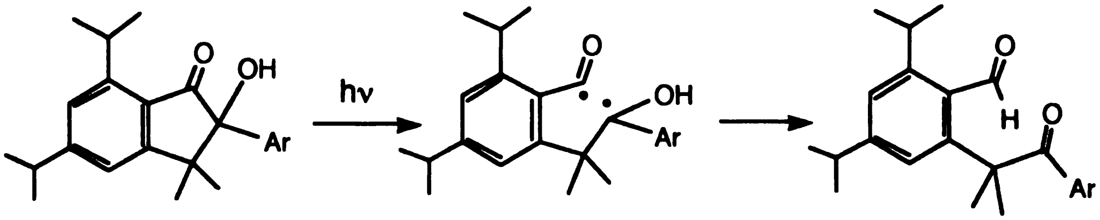


Scheme 76

From these workers's observations, we know, at least for the unsymmetrical diketones, the dienols can be precursors of the hydroxyindanone. But, whether or not same is true for symmetrical, sterically congested benzils is still an open question.

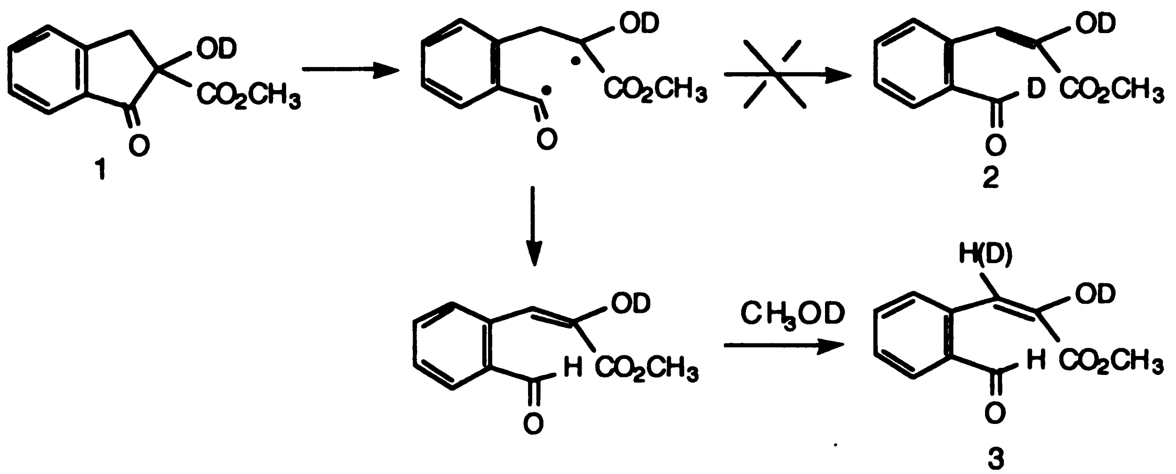
And examples of direct 1,6 H shift by excited carbonyl groups are abundant in the literature[26]. The remaining question is that if two different processes are competing in solution, which one is faster, 1,5- or 1,6-H shift? At this moment, it is hard to separate how much products are coming from 1,5- and 1,6-H shift because no rate constants are known for these systems. Therefore, more experiments remain to be done in this area.

Secondary photoreaction of initially formed photoproducts, the hydroxyindanone, can be great interest in its own right.[99] This reaction presumably occurred via Norrish type I cleavage followed by disproportionation as shown in Scheme 77.



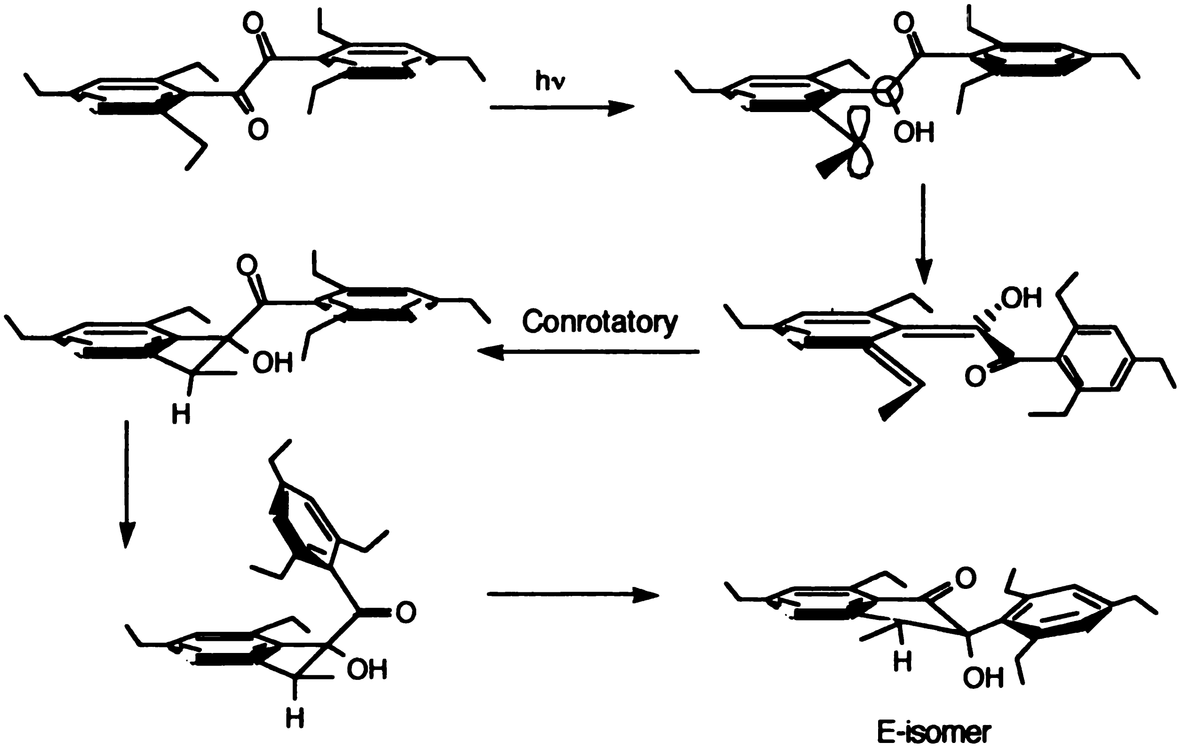
Scheme 77

Padwa reported[98] that photolysis of compound 1 in deuterio-methanol produced product 3 not product 2. He concluded that among two possible disproportionation routes, only 1,4-H transfer was operating in this reaction. However, compound 1 does not have benzylic hydrogens available for 1,4-H transfer, showing that 1,6-H can be operating in this system.



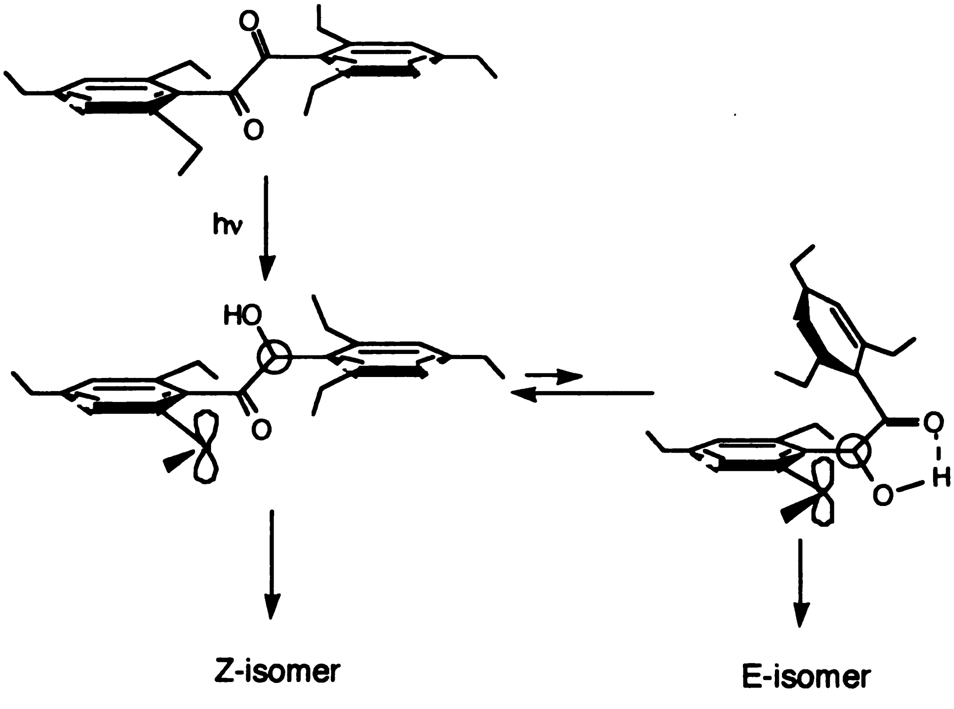
Scheme 78

2,4,6,2',4',6'-Hexaethylbenzil also formed hydroxyindanone very efficiently after irradiation in benzene at 436 nm. In this case, two diastereomers were formed in 2.5 to 1 favoring Z isomer. If this reaction occurred via 1,5-H shift, it would have given an E-isomer as a sole or major product as shown in Scheme 79.[37]



Scheme 79

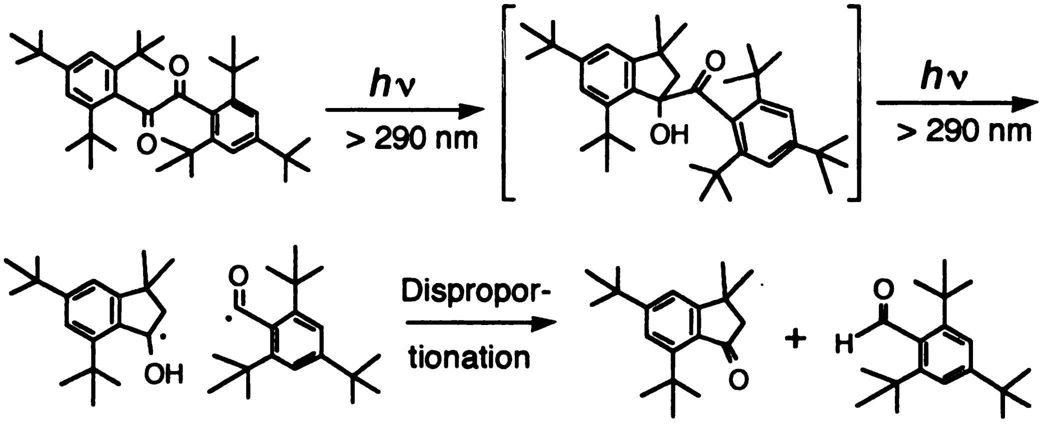
On the other hand, 1,6-H shift pathway would give a mixture of E- and Z-isomer.[79] If the biradical lifetime is long enough to set an equilibrium shown in Scheme 80, the ratio of two isomeric products will be determined by the relative stability of two biradicals. In case of monoketone analog, α-(2,4,6-triethylphenyl)acetophenone, Z-isomer was favored by 30 to 1.[79] Much lower selectivity for the diketone may be caused by the increased population of the other biradical via intramolecular hydrogen bonding. If this is true, the higher selectivity would be expected in solid state irradiation because of restrained mobility. In fact, at low conversion, Z-isomer was formed predominantly with trace of E-isomer. At higher conversion, the solid turned into liquid and the relative amount of E-isomer started to grow. At 100 % conversion, the ratio reached at 6 to 1, where all the solid turned into liquid.



Scheme 80

When 2,4,6,2',4',6'-Hexaethylbenzil was irradiated at 313 or 365 nm, the secondary photoproduct, an enal, was formed together with two isomeric hydroxy indanones. The ratio of the products was dependent on irradiation time. The ratio of Z- to E-isomer increased at longer irradiation and this may be caused by epimerization upon photolysis of initial product. This result support our assignment of two isomers, which means that less stable E-isomer is converted into more stable Z-isomer upon photolysis.

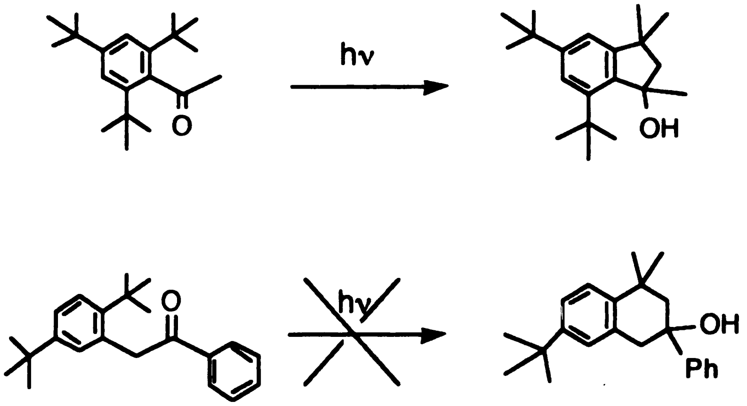
2,4,6,2',4',6'-Hexaemthylbenzil formed a hydroxyindanol much more slowly than ethyl- and isopropyl- derivatives. This different reactivity may be due to different geometry of these compounds. The reaction of benzil derivatives were known to be sensitive to number and position of substituents. Maruyama reported[70] that both 2,4,6-trimethylbenzil and 2,3,5,6-tetramethylbenzil were extremely photostable whereas 2,5,2'5'-tetramethylbenzil formed the hydroxyindanone very efficiently. Maruyama also reported that irradiation of 2,4,6,2',4',6'-hexamethylbenzil gave 2,4,6-trimethylbenzoic acid as only product. This product was presumably formed by the autoxidation of the initial product, 2,4,6-trimethylbenzaldehyde. This is contrary to our observation, which a hydroxyindanone was the major product. This reaction occurred even more cleanly in the solid state.



Scheme 81

When 2,4,6,2',4',6'-hexa-tert-butylbenzil[100] was irradiated at >290 nm, two major products were isolated.(Scheme 81) The observed indanone and 2,4,6-tert-butylbenzaldehyde were presumably formed via 1,6-H shift followed by cleavage and disproportionation. The fact that the initial product could not be detected indicate the instability of this product probably due to steric crowdness of this molecule.

The result from 2,4,6,2',4',6'-hexa-tert-butylbenzil is consistent with previous observations by us and other workers. Neckers and coworkers studied photochemistry of 2,4,6-tri-tert-butylacetophenone and found that this molecule underwent an efficient δ-hydrogen abstraction reaction from its triplet n,π* state[101]. We have looked at the photochemistry of α-(2,5-di-tert-butylphenyl)acetophenone[102] and found no evidence of ε-hydrogen abstraction reaction. When this compound was irradiated for extended period, α-cleavage products started to show up.

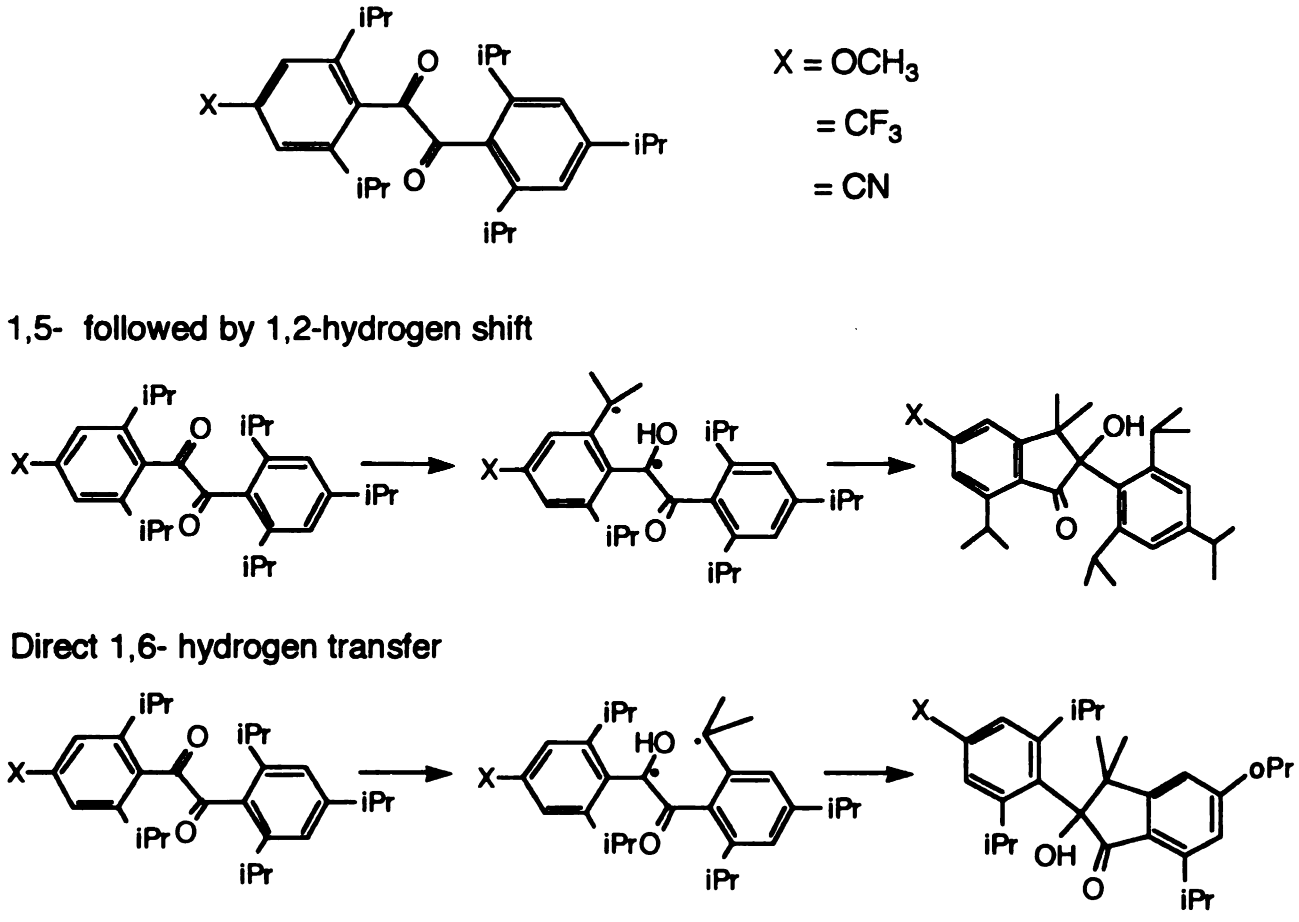


Scheme 82

In summary, photolysis of several sterically hindered benzils resulted in efficient formation of hydroxyindanone in solution and solid state. In the solid state, we believe that direct δ-hydrogen abstraction by excited state carbonyl group is responsible for the observed reaction. In solution, however, several pathways may be competing, where the extent of each pathway cannot be estimated at this moment.

Future Project. One of the two carbonyls in unsymmetrical α-dicarbonyl compounds is known to be selectively photoreduced. Ogata reported that unsymmetrical benzils were photoreduced at a carbonyl with a stronger electron-withdrawing group.[103] Application of this concept to intramolecular H abstraction may help to understand the mechanism of this reaction.

Compounds shown below would fulfil the idea because two different pathways would lead to two different products. If two mechanisms are operating at the same time in solution, the product ratio will give an insight on the relative reaction rates of these processes.



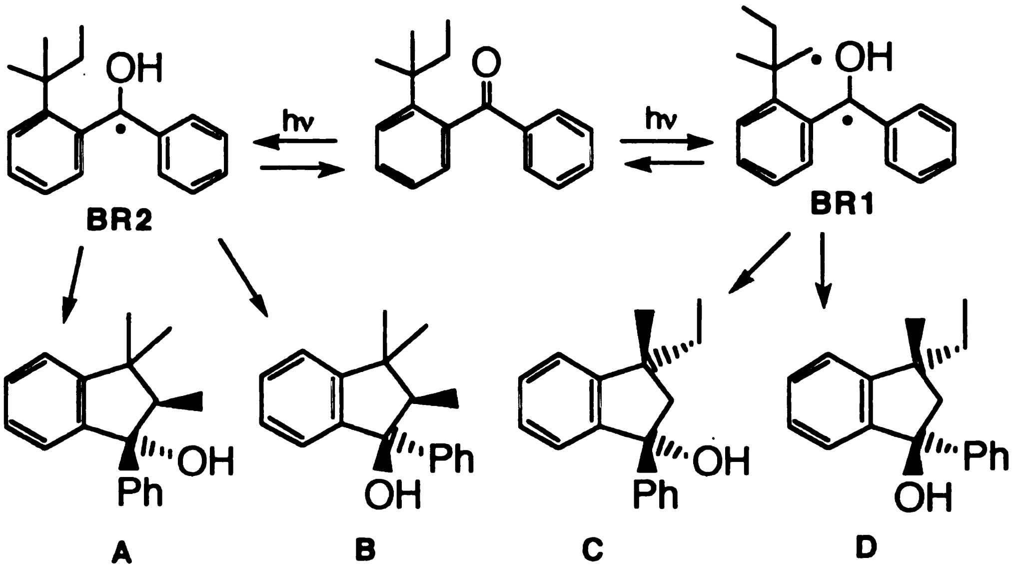
Scheme 83

E. Photochemistry of o-tert-amyl benzophenone.

(a) Structural feature of o-tert-amylbenzophenone

The x-ray structure of OTABP represents a ground state minimum, as computed by MMX calculations. This structure has two hydrogens within reaction distance and both clearly react in the solid, even though the primary hydrogen is situated at an angle ω near 90°.

In contrast to our expectation, the barrier for rotation of the *tert*-amyl group around the benzene ring turned out to be very low, only some 3 kcal/mole as computed by MMX. This estimate is borne out by the NMR studies that show freezing out of rotations around the carbonyl-benzene bonds but no independent freezing out of *tert*-amyl resonances. Thus geometries other than the x-ray one are readily accessible in solution.



Scheme 84

There are two solution minimum geometries(R90 and R270) in which the ethyl group is perpendicular to the benzene ring, one of which represents a 180° twist of the *t*-amyl group relative to the x-ray structure. There appears to be a low energy conformer near $\alpha = 100°$ in which a methyl hydrogen is only 2.80 Å from the oxygen at $\omega = 65°$. All other low energy geometries with a methyl hydrogen within bonding distance have ω values near 90°., which are expected to be very unreactive according to $\cos^2\omega$ dependence of the reaction rate.

If we just look at x-ray geometry of this molecule, hydrogens of ethyl group appear to be more reactive than methyl hydrogens due to smaller ω angle. On the other hand, biradical 2 assumes a good geometry for cyclization and it can cyclize with little motion before it can disproportionate. Thus, both factors must be taken into consideration when we analyze product ratios.

(b) Analysis of product ratios.

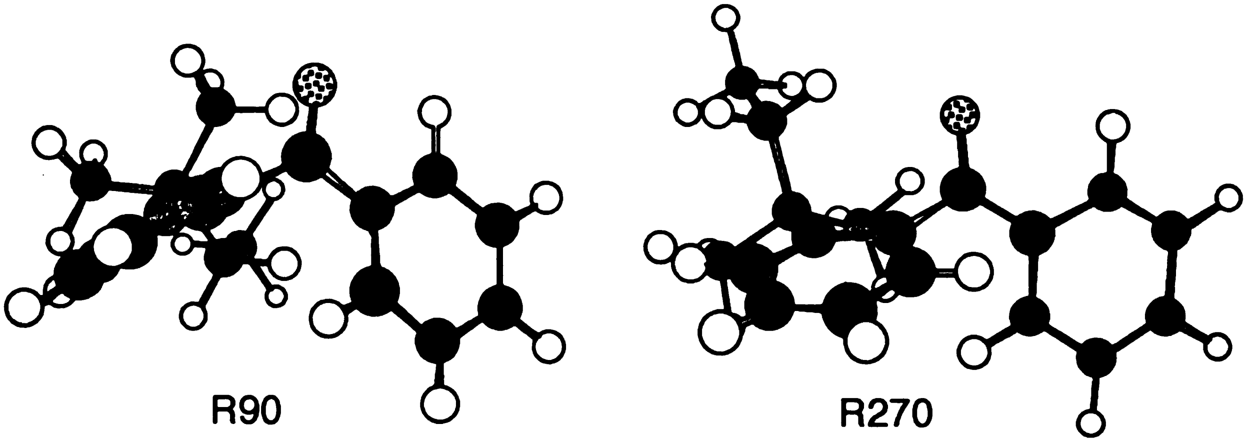
From previous studies on o-tert-butylbenzophenone(OTBBP) and solid state photoreaction of many other systems, the followings can be safely assumed:; First, with an activation energy of only 2.5 kcal/mole (OTBBP), when attack on an unactivated primary hydrogen should have an E_a of ~6 kcal/mole,[104] it is highly unlikely that reaction takes place from anything but the lowest energy conformers. Second, the excited state geometry is very similar to that of the ground state, with only the C=O bond slightly elongated. Therefore measurements and calculations on ground state geometries adequately represent excited state geometries. Third, in the solid state at low conversion, reaction takes place solely from the x-ray crystal structure geometry.

The fact that products are formed by abstraction of both hydrogens in all environments requires careful analysis, since product ratios reflect not simply the ratio of rate constants for abstraction of two different hydrogens but also the partitioning of the two different biradicals between coupling and reversion to ketone.

$$\frac{A+B}{C+D} = \frac{k_{2H}}{k_{1H}} \bullet \frac{P_{BR2}}{P_{BR1}}$$

P_{BR} is the fraction of a given biradical that cyclizes to indanol.

The two biradicals differ in two ways: structurally and conformationally. The former difference is reflected by products C+D being slightly favored over A+B in benzene, with the ratio reversed in methanol. This solvent effect on product ratios indicates that the two biradicals cyclize with different efficiencies. In benzene, all the biradicals from both ketones disproportionate to starting ketone with ≥96% efficiency. In methanol, all of the biradicals from OTBBP cyclize but not quite half of those from OTABP cyclize. **BR2** clearly cyclizes less efficiently than **BR1** and it appears that this difference is only partially corrected by hydrogen bonding to solvent. The P_{BR1}/P_{BR2} ratio is at least 2 and may be as high as 4 in benzene if **BR1** cyclizes 100% in methanol as does the OTBBP biradical . Thus k_{2H}/k_{1H} equals 1.5 to 3 in solution. This conclusion assumes no solvent effect on k_H values but only on P_{BR} values. Thus reaction at a methyl group comprises at least 25% and possibly as much as 40% of the total reaction. The temperature independence of the product ratio in solution suggests that the intrinsic k_H values are nearly identical for both methyl and ethyl hydrogens, as befits a very low activation energy reaction that is driven by relief of steric strain.[105]



Scheme 85

The significant increase in formation of C+D at -78° in toluene is in line with the calculated lower energy of R90 relative to R270.(Scheme 85) Since R90 has a methyl group swung towards the carbonyl, it may well be destabilized by solvation of the carbonyl such as occurs in methanol. That would explain why no temperature effect is observed in methanol. If this analysis is correct, then only geometry R270 reacts in methanol, with no or compensating temperature effects on both the k_H and the P_{BR} ratios.

The conformational difference is best illustrated by comparing the biradical geometries formed by abstraction of the two different hydrogens in R270, from which all reaction presumably arises in the solid state. **BR1** is formed ideally aligned to cyclize, whereas **BR2** must first rotate around the *t*-amyl group. Therefore, the observed product ratio in benzene, 40/60 in favor of C and D, may have resulted from slower intrinsic reactivity of H_A but faster cyclization of biradical 2.

In methanol, this disproportionation has been known to slow down due to hydrogen bonding to the solvent. Therefore, the observed ratio, A+B/C+D, may reflect intrinsic triplet reactivity between H_A and H_B because bond rotation to form the right geometry for cyclization cannot be product determining factor any longer. Conformational change by solvation seems very unlikely because same product ratio was observed over wide temperature range studied.(-78 - 70 ^{o}C)

Analysis of the whole study indicates large values of ω for all d values < 3 Å when the total energy is within 1 kcal of the minimum. The value of ω drops below 90° only in a narrow range around a = 95°, where only attack on a methyl can occur.

We assume that reaction occurs only from the minimum energy geometry both in the crystal and at 77° K but that rapid rotation of the *t*-amyl group around the benzene ring may allow reaction from different geometries in solution. With the low calculated barrier between the two geometries, one can assume a 2:3 equilibrium ratio of the two forms at room temperature.

Bond rotation of t-amyl group around benzene ring seems to be free as evidenced by several experiments. MMX calculations indicate low barrier for rotation of t-amyl group around the benzene ring. Low temperature NMR spectra also give no evidence for this rotation freezing out, although rotation around both benzene-carbonyl bonds freezes out at -

90 ^{O}C. And, almost nonexisting diastereoselectivity can be also attributed to the mobility of this molecule.

(c) Solid state reactivity

Like o-tert-butylbenzophenone, o-tert-amylbenzophenone reacts very efficiently in the solid state and in methanol/ethanol glass at 77 K. Studies on solid state reactivity would be good candidate to determine orientational requirement for the given reaction due to immobility of the molecule in the media. In the previous studies on o-tert-butylbenzophenone, it was ambiguous to assign which hydrogen was responsible for observed reactivity in solid state because one of those had "right" geometry for hydrogen abstraction but poor geometry for cyclization while another had "poor" geometry for H abstraction but good geometry for cyclization. With a hope to clarify this, regioselectivity of o-tert-amylbenzophenone was investigated. The result shows 30 % of products still come from biradical 2, which is formed by abstraction of H_B having "poor" geometry for H-abstraction.

The lack of regiospecificity indicates one of two kinetic extremes in which either the molecule is frozen on the nsec reaction timescale and H-abstraction occurs equally from both geometries; or sufficient rotation occurs even in the crystal and at 77 K to make a methyl reactive. Given the rapidity of hydrogen transfer($\geq$109) and the 2.5 kcal/mole activation energy, it appears very unlikely that reaction can occur from geometries much different from the conformational minimum. It is interesting in this respect that far greater diastereoselectivity is observed in the solid state reactions than in solution. Similar selectivity was also observed in methanol/ethanol glass at 77 K. The immobility imposed on each biradical by the crystal lattice or methanol/ethanol glass matrix severely restricts its ability to form both diastereomers.

There is interest to know where the reaction occurs in solid state irradiation. Large single crystal was irradiated in a test tube and the resulting crystal was quickly washed with several different solvents(benzene, hexane, methanol or methylene chloride) The product ratio was obtained by HPLC analysis. All the solvents except hexane seemed to give similar solubility toward all the products(in hexane, product ratio was slightly different; 17%:44%:13%:26%). The second and the third wash of the resulting crystal gave much less amount of products, indicating that most reactions were occurring from surface of the crystal. And also, the second wash gave slightly higher diastereoselectivity than the first wash did. If all the photoreaction take place at the surface, it is possible that molecular motion is more facile than inside the bulk crystal. Therefore, the observed product ratio may be caused by the two biradicals having very different probabilities of cyclizing in the crystal. It is not very clear that crystal packing forces control the decay pathway of two biradicals in different rate, because accurate measurement of quantum efficiency in solid state is not trivial.

In summary, studies on o-tert-amylbenzophenone added another example of hydrogen abstraction appearing relatively insensitive to atomic orientation. How far is the limiting angle of ω is still an open question. More sterically demanding o-alkylbenzophenones, such as 3-methyl-3-pentyl, 2,3-dimethyl-2-butyl would give more informations on this matter. The added steric bulk should produce larger barriers for rotation out of the molecules' favored conformations and reduce the possibility for reaction involving two rotamers rather than attack at two different sites of one rotamer.

Experimental

I. General procedure

All ^{1}H NMR and ^{13}C NMR spectra were obtained using a 250 MHz Bruker WM250 FT spectrometer, a 300 MHz Varian Gemini, a 300 MHz Varian VXR-300 or a 500 MHz Varian VXR-500 instrument. All the IR spectra were recorded using solution in CCl4 on a Perkin-Elmer 599 IR spectrometer. UV spectra were recorded on a Shimadzu UV-160 spectrometer. Mass spectra were recorded on a Finigan 4000 GC/MS. Phosphorescence spectra were recorded on a Perkin-Elmer MPF-44A Fluorescence Spectrometer.

Gas chromatographic anayses were performed on Varian 1400 or 3400 machines with flame ionization detectors. The GC was connected to either a Hewlett-Packard 3393A, or 3392A Integrating recorder. Three types of columns have been used for GC analysis; Magabore DB1, Megabore DB210 and Megabore DBWAX. HPLC analyses were performed on a Beckman 332 gradient system equipped with a Perkin Elmer LC-75 UV detector, on a silica column. The HPLC system was connected to a Hewlett-Packard 6080 Integrating Recorder. Preparative collections were done on Rainin Dynamax HPLC system equipped with a dual wavelength programmable detector and fraction collector. For the preparative TLC, Analtech Uniplate silica gel plates of 20 x 20 cm, 1000 micron were used.

II. Purification of Chemicals

A. Solvents

Benzene[106]- 3.5 L of reagent grade benzene was mixed with 0.5 L conc. sulfuric acid and the mixture was stirred for 2-3 days. The benzene layer was separated and was extracted with 200 ml portions of comc. sulfuric acid several times until the sulfuric acid layer does not turn yellow. The benzene was washed with distilled water and then saturated aqueous sodium bicarbonate solution. The benzene was separated , dried over magnesium sulfate and filtered into a 5 L round bottomed flask. Phosphorous pentoxide (about 100 g) was added and the solution was refluxed overnight. After refluxing, the benzene was distilled through a one meter column packed with stainless steel helices. The first and last 10 % were discarded.(b. p.: 78 ^{o}C)

Hexane- Reagent grade hexane was purified the same way as benzene.

Methanol[107]-Reagent grade absolute methanol was refluxed over magnesium turnings for 2 hrs and distilled through a half meter column packed with glass helices. The first and last 10 % were discarded.

B. Internal standards

pentadecane(C15) - Pentadecane (Columbia Organics) was washed with sulfuric acid and distilled by Dr. Peter J. Wagner.

Hexadecane(C16) -Hexadecane (Aldrich) was washed with sulfuric acid and distilled by Dr. Peter J. Wagner.

Heptadecane(C17)-Heptadecane (Aldrich) was washed with sulfuric acid and distilled by Dr. Peter J. Wagner.

Nonadecane(C19) - Nonadecane(Chemical Samples Company) was recrystallized from ethanol.

Eicosane(C20) - Eicosane(Aldrich) was purified by recrystallization from ethanol.

Heneicosane(c21) - Heneicosane(Chemical Samples Company) was recrystallized from ethanol.

Tetracosane(C24) - Tetracosane(Aldrich) was purified by recrystallization from ethanol

Methyl benzoate - Methyl benzoate was purified by fractional distillation, by Dr. Quenjian Cao.

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n-Octylbenzoate - n-Octylbenzoate was purified by fractional distillation, by Dr. Quenjian Cao.

o-methyl(phenoxy)acetate - o-methyl(phenoxy)acetate was purified by fractional distillation.

C. Quenchers

2,5-Dimethyl-2,4-hexadiene - 2,5-Dimethyl-2,4-hexadiene (Aldrich) was allowed to sublime in the refrigerator.

Naphthalene - Naphthalene was recrystallized from methanol.

Ethylsorbate - Ethyl sorbate was used as received.

Pyrene - Pyrene that was found in the lab was used as it was.

pipyrelene - Pipyrelene(Aldrich, 90 %) was distilled through a half meter column packed with glass helices. The first and last 10 % were discarded.

III Equipment and Procedures.

A. Photochemical glassware

All the photolysis glassware(pippettes, volumetric flasks, syringes and the pyrex test tubes for irradiations) were rinsed with acetone, then with distilled water, and boiled in a solution of Alconox laboratory detergent in distilled water for 24 hrs. The glassware was carefully rinsed with distilled water, abd boiled in distilled water for 2 or 3 days, with the water being changed every 24 hrs. After final rinse with distilled water, the glassware was dried in an oven at 140 °C.

Ampoules used for irradiation were made by heating 13 x 100 mm pyrex culture tubes (previously cleaned by the procedure described above) approximately 2 cm from the top with an oxygen-natural gas torch and drawing them out to an uniform 15 cm length.

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B. Sample preparations.

All solutions were prepared either by directly weighing the desired material into volumetric flasks or by dilution of a stock solution. Equal volumes (2.8 ml) of sample were placed via syringes into each ampoule.

C. Degassing procedure.

Filled irradiation tubes were attached to a vacuum line. 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 to liquid nitrogen temperature and evacuated with a diffusion pump for 5- 10 min. The stopcocks were closed and the tubes were allowed to thaw at room temperature. This freeze -pump-thaw cycle was repeated three times. The tubes were then sealed with an oxygen-natural gas torch while still under vacuum.

D. Calculation of Quantum Yields

Quantum yields were calculated with the following equation,

$$\Phi = [P]/I$$

where [P] is the concentration of photoproducts and I is the intensity of light absorbed by samples.

The intensity of light. I, was determined by either valerophenone or o-methylvalerophenone actinometer depending on the efficiency of the photoreaction. Thus, a degassed 0.10 M valerophenone or o-methylvalerophenone solution in benzene was irradiated in parallel with the samples to be analysed. After irradiation was stopped after less than 10 % conversion, the valerophenone or o-methylvalerophenone sample was analysed for acetophenone or o-methylacetophene using the following equation.

$$[AP] = R_f \times [Std] \times A_{AP}/A_{Std}$$
$$\text{or}\quad [MAP] = R_f' \times [Std] \times A_{MAP}/A_{Std}$$

where [AP] is the concentration of acetophenone, R_f is the instrument response factor for acetophenone, A_{AP} is the integrated area for acetophenone, [MAP] is the concentration of o-methylacetophenone, R_f' is the instrument response factor for o-methylacetophenone, A_{MAP} is the integrated area for o-methylacetophenone, [Std] is the concentration of the added internal standard, and A_{Std} is the integrated area for the internal standard. The intensity of light can be calculated using the acetophenone or o-methylacetophenone concentration based on $\Phi_{AP} = 0.33$[108] for acetophenone, and $\Phi_{AP} = 0.016$[109] for o-methylacetophenone.

$$I = [AP]/0.33 \quad \text{or} \quad I = [MAP]/0.016$$

The concentration of the photoproduct, [P], can be calculated using the following equation.

$$[P] = R_{f(P)} \times [Std] \times A_P/A_{Std}$$

where $R_{f(P)}$ is the response factor of photoproduct and A_P is the integrated area for the photoproduct.

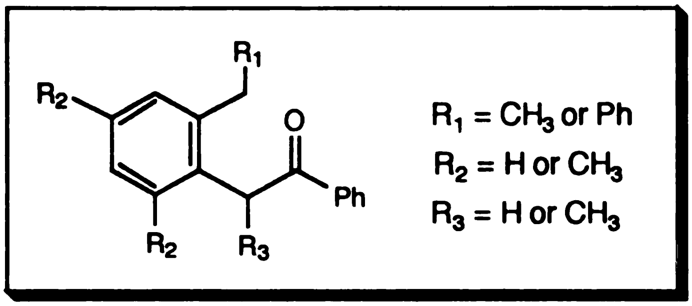
The instrumental response factors for photoproducts were obtained using the following relationship.

$$R_{f(p)} = ([P]/[Std]) \text{ X } (A_{Std}/A_P)$$

If photoproducts are difficult to be isolated or too unstable to analyze accurately, the following equations have been used to calculate the response factors.. This method is known to give pretty reasonable value for G. C. response factor.

$$\text{R. F.} = \frac{\{\ \#\text{ of Carbons} + 1/2\ (\ \#\text{ of C-O bonds}\ )\ \}_{\text{Std}}}{\{\ \#\text{ of Carbons} + 1/2\ (\ \#\text{ of C-O bonds}\ )\ \}_{\text{Photo}}}$$

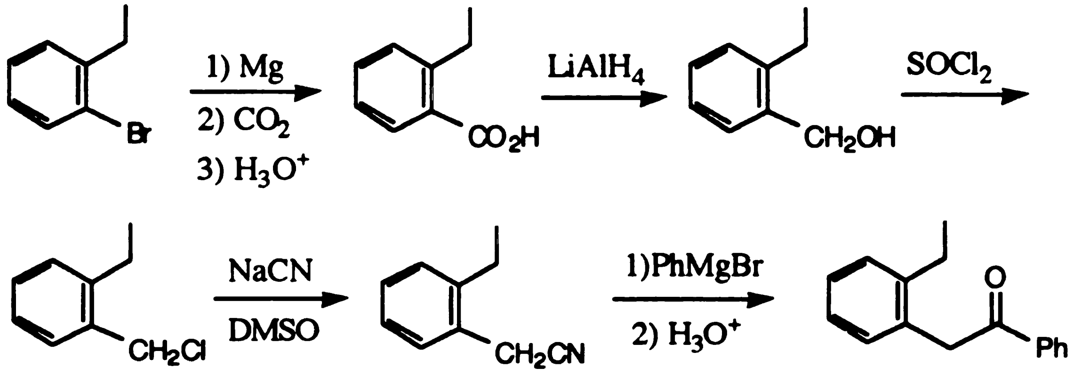
IV. Preparation of Starting Ketones.



R_1 = CH_3 or Ph
R_2 = H or CH_3
R_3 = H or CH_3

α-(2-Ethylphenyl)acetophenone

α-(2-Ethylphenyl)acetophenone was prepared by the reaction of phenyl Grignard reagent with o-ethylphenylacetonitrile following the route given below.[110]



(a) 2-Ethylbenzoic acid

All the glassware was dried oven-dried overnight and magnesium was dried in the oven (at 120 °C) for 10 - 15 min. just before reaction. A 250 ml 3-necked r.b. flask was equipped with an addition funnel, and flushed with either nitrogen or argon. The bromide (12 g, 0.0648 mol) was added dropwise to the freshly dried magnesium(1.73 g, 0.071 mol) in 15-20 ml of freshly distilled ether. The reaction was initiated either by heat gun or by addition of small amount of 1,2-dibromoethane. When the reaction was initiated, 20-30 ml of ether was added. The bromide was added dropwise for ca. 30 min. After the addition was completed, the mixture was refluxed for 1-2 hrs to ensure the formation of Grignard reagent. The solution was cooled to room temperature. A large excess of dry ice (typically 150-200 g) was grinded completely by pestle. The Grignard reagent was poured into the freshly prepared dry ice powder in beaker. The resulting slush was stirred vigorously and was allowed to warm to room temperature. Ca. 30 ml of 10 % HCl was added to the mixture. The mixture was extracted with ether and the combined ether layer was extracted with 10 % NaOH. The aqueous layer was acidified again with dilute HCl. After ether layer was washed with distilled water several times, it was dried over $MgSO_4$. The solvent was evaporated to give 6.8 g of creamy powder.(72 % yield) This crude product was used for next step without further purification.

^1H NMR($CDCl_3$): δ 1.15(3H, t), 2.96(2H, quartet), 7.1-7.4(3H, m), 7.91(2H, d)

(b) 2-Ethylbenzyl alcohol

A solution of 2-ethylbenzoic acid (6.8 g, 0.045 mol) in 10 ml anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride(3.4 g, 0.090 mol) in 100 ml anhydrous ether at room temperature under argon atmosphere. The resulting mixture was refluxed for 4 to 5 hours and was cooled to room temperature, and the excess lithium aluminum hydride decomposed by careful addition of ice. Acidic workup afforded 6.3 g of pale yellowish oil.(100 %) This was used for next step without further purification.

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^{1}H NMR($CDCl_3$): δ 1.25(3H,t), 2.72(2H, quartet), 2.12(1H, broad s), 4.73(2H, s), 7.2-7.4(4H, m)

(c) 2-Ethylbenzyl chloride

A solution of 2-ethylbenzyl alcohol(6.3 g, 0.046 mol) in benzene was added to a stirred solution of thionyl cloride (9.7 g, 0.081 mol) in benzene. The solution was refluxed under argon for 4 hours, cooled to room temperature, and poured into ice cold water. The layers were separated and the aqueous phase was extracted with ether. The organic layers were combined, washed with saturated sodium bicarbonate solution and dried by magnesium sulfate. The solvent was removed on a rotary evaporator to afford 7.2 g of product as a brownish oil.(100 %) This was used for next step without further purification.

^{1}H NMR($CDCl_3$): δ 1.12(3H, t), 2.63(2H, quartet), 4.48(2H, s), 7.0-7.3(4H, m)

(d) α-(2-Ethylphenyl)acetonitrile

A mixture of sodium cyanide(3.4 g, 0.069 mol) in 120 ml dimethylsulfoxide was heated at 80 °C until all the sodium cyanide had dissolved. 2-ethylbenzyl chloride(7.2 g, 0.0466 mol) was added to this solution and the mixture was stirred at this temperature for 4 hrs. The mixture was cooled to room temperature and poured into 200 ml distilled water. The resulting solution was extracted with ether and the ether layer was washed with distilled water several times, and dried($MgSO_4$). The solvent was removed on a rotary evaporator to afford 5.5 g of product as a brownish solid. (81 % yield)

^{1}H NMR($CDCl_3$): δ 1.23(3H, t), 2.68(2H, quartet), 3.71(2H, s), 7.2-7.4(4H, m)

(e) α-(2-Ethylphenyl)acetophenone

A solution of α-(2-ethylphenyl)acetonitrile(5.4 g, 0.037 mol) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 1.04 g of magnesium turnings and 6.4 g of bromobenzene in 100 ml anhydrous ether) under an argon atmoshere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The mixture was cooled to room temperature and was poured to ice cold water. The aqueous layer was separated and acidified with 10 % HCl. The solution was heated overnight at 80-90 °C. The solution was allowed to cool to room temperature and 200 ml of ether was added. Two layers were separated and the aqueous layer was extracted with ether three times. The combined organic layer was washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. After it was dried over $MgSO4$, solvent was evaporated to give a yellowish oil This oil was mixed with hot ethanol and was recrystallized using seed which was obtained from mother liquid.(m. p. = 35 °C, colorless cubic crystals)

^1H NMR($CDCl_3$) : δ 1.22(3H, t, J = 7.5 Hz), 2.62(2H, quartet. J = 7.5 Hz), 4.36(2H, s), 7.14-7.23(2H, m), 7.27(2H, dd, J = 4.8, 1.5 Hz), 7.50(2H, tt, J = 7.3, 1.4 Hz), 7.60(1H, tt, J = 7.3, 1.4 Hz), 8.04(2H, dd, J = 7.1, 1.4 Hz)

^{13}C NMR($CDCl_3$) : δ 14.5, 25.8, 42.7, 126.2, 127.9, 128.5, 128.6, 128.8, 130.7, 132.9, 133.3, 137.1, 142.8, 198.2

IR(CCl_4): 2971, 1698, 1449, 1208 cm^{-1}

Mass: 225.1279(MH^+); Calc. 225.1280(MH^+); Molecular Formular($C_{16}H_{16}O$)

α-(2-benzylphenyl)acetophenone

α-(2-benzylphenyl)acetophenone was prepared by the reaction of phenyl magnesium bromide and α-(2-benzylphenyl)acetonitrile following the route given below.

(a) (2-benzyl)benzylalcohol

A solution of 2-benzylbenzoic acid (10 g, 0.047 mole) in 150 ml anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride(3 g) in 50 ml anhydrous ether at room temperature under argon atmosphere. The resulting mixture was refluxed for 4 to 5 hours and was cooled to room temperature, and the excess lithium aluminum hydride decomposed by careful addition of ice. Acidic workup afforded 9 g(97 %) of yellowish oil. This was used for next step without further purification.

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^{1}H NMR($CDCl_3$) : δ 4.10(2H, s), 4.68(2H, s), 7.15- 7.45(9H, m)

(b) (2-benzyl)benzyl chloride

A solution of 2-benzylbenzyl alcohol(9 g, 0.045 mole) in benzene was added to a stirred solution of thionyl cloride (8 g, 0.068 mole) in benzene. The solution was refluxed under argon for 4 hours, cooled to room temperature, and poured into ice cold water. The layers were separated and the aqueous phase was extracted with ether. The organic layers were combined, washed with saturated sodium bicarbonate solution and dried by magnesium sulfate. The solvent was removed on a rotary evaporator to afford 9.7 g of product as a brownish oil. This was used for next step without further purification.

^{1}H NMR($CDCl_3$) : δ 4.19(2H,s), 4.58(2H,s), 7.10 - 7.4(9H,m)

(c) α-(2-benzylphenyl)acetonitrile

A mixture of sodium cyanide(1.7 g, 0.035 mole) in 120 ml dimethylsulfoxide was heated at 80 °C until all the sodium cyanide had dissolved. 2-benzylbenzylchloride(5 g, 0.023 mole) was added to this solution and the mixture was stirred at this temperature for 4 hrs. The mixture was cooled to room temperature and poured into 200 ml distilled water. The resulting solution was extracted with ether and the ether layer was washed with distilled water several times, and dried($MgSO_4$). The solvent was removed on a rotary evaporator to afford 4.3 g of product as a brownish oil.

H1NMR($CDCl_3$) : δ 3.35 (2H, s), 4.01(2H, s), 7.06 - 7.40(9H, m)

(d) α-(2-benzyl)phenylacetophenone

A solution of α-(2-benzylphenyl)acetonitrile(4.3 g, 0.021 mole) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 1.0 g of magnesium turnings and 3.6 g of bromobenzene in 100 ml anhydrous ether) under an argon atmosphere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The mixture was cooled to room temperature and was poured to ice cold water. As 10 % HCl solution was added to the mixture, white solids were precipitated out. These solids were collected by suction filtration and were transferred to a 500 ml round bottomed flask. About 200 ml of 10 % HCl was added to the solid and this mixture was refluxed for 4 to 5 hours. The solution was allowed to cool to room temperature and 200 ml of ether was added. Two layers were separated and the aqueous layer was extracted with ether three times. The combined organic layer was washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. After it was dried over $MgSO4$, solvent was evaporated to give a brownish oil, which was solidified by standing at room temperature. This crude porduct was connected to short column chromatography to filter out polymeric material and the resulting yellowish solid was recrystallized over ether and pet. ether mixture.(2.8 g, 47 %)

m. p. ; 54.0 - 54.5 ^{o}C(colorless powder)

^{1}H NMR($CDCl_3$) : δ 3.9(2H,s), 4.26(2H, s), 7.1 - 7.3(4H, m), 7.42(2H, distorted triplet), 7.55(1H, tt, J = 7.3, 1.3 Hz), 7.89(2H, distorted d)

^{13}C NMR($CDCl_3$) : δ 39.5, 43.0, 126.1, 126.8, 127.3, 128.3, 128.5, 128.57, 128.76, 130.77, 130. 82, 133.11, 133.60, 136.7, 139.2, 140.1, 197.6

IR(CCl_4): 3065, 3029, 2913, 1694, 1495, 1449 cm^{-1}

Mass: 286.13576(M^{+}); Calc. 286.1358(M^{+}); Molecular Formular($C_{21}H_{18}O$)

α-(2-Ethylphenyl)propiophenone

α-(2-Ethylphenyl)propiophenone was prepared by the reaction of phenyl magnesium bromide and α-(2-Ethylphenyl)propionitrile following the route given below.

(a) α-(2-Ethylphenyl)propionitrile

The similar procedure to that used to synthesize α-mesitylpropionitrile[80] was used.. Diisopropylamine(3,24 g, 0.032 mole) in 20 ml of dry THF was added to 23 ml of n-BuLi(1.6 M in hexane) at 0 ^{o}C. The mixture was stirred for 30 min., and then cooled to -78 ^{o}C with a dry ice/acetone bath. α-(2-Ethylphenyl)acetonitrile(5 g, 0.032 mole) in 15 ml of dry THF was added. The content was warmed to room temperature and stirred for 2 hours. Methyl iodide(6 g, 0.042 mole) was added. The mixture was stirred at room temperature for another 2 hrs and was refluxed overnight. After cooled to r.t., the solvent was removed by rotary evaporator. The residue was mixed with ether/water and the mixture was separated. The aqueous layer was extracted with ether several times and was combined with other ether layer. The combined ether layer was washed with water several times and dried over MgSO4. The solvent was removed at low pressure to give brown liquid. (4.4 g, 82 %)

^{1}H NMR($CDCl_3$):: δ 1.28(3H, t), 1.65(3H, d), 2.69(2H, quartet), 4.11(1H, quartet), 7.2-7.5(4H, m)

(b) α-(2-Ethylphenyl)propiophenone

A solution of α-(2-Ethylphenyl)propionitrile(4.4 g, 0.026 mole) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 0.8 g of magnesium turnings and 5 g of bromobenzene in 100 ml anhydrous ether) under an argon atmosphere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The mixture was cooled to room temperature and was poured to ice cold water. The aqueous layer was separated and acidified with 10 % HCl. The solution was heated overnight at 80-90 ^{o}C. The solution was allowed to cool to room temperature and 200 ml of ether was added. Two layers were separated and the aqueous layer was extracted with ether three times. The combined organic layer was washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. After it was dried over MgSO4, solvent was evaporated to give a yellowish oil The crude product was chromatographed using 3 % ethylacetate in hexane and the resulting oil was recrystallized over ethanol to give colorless solid. (3.7 g, 57 %)

m. p. : 38.0 - 39.0 ^{o}C(colorless cubic crystals)

^{1}H NMR($CDCl_3$):: δ 1.33(3H, t, J = 7.5 Hz), 1.49(3H, d, J = 6.8 Hz), 2.84, 2.85(2H, AB quartet, J = 7.5 Hz), 4.81, (1H, quartet, J = 6.8 Hz), 7.03(1H, dd, J = 6.5, 1.0 Hz), 7.07(1H, td, 7.6, 1.5 Hz), 7.15(1H, td, J = 1.5, 6.5 Hz), 7.24(1H, dd, 7.6, 1.0 Hz), 7.33(2H, distorted t), 7.44(1H, tt, J = 7.5, 1.2 Hz), 7.83(2H, distorted d)

^{13}C NMR($CDCl_3$):: δ 15.1, 19.0, 25.5, 43.9, 126.5, 127.0, 127.2, 128.4, 128.5, 129.0, 132.6, 136.7, 139.3, 140.4, 201.2

IR(CCl_4): 3067, 3027, 2973, 2934, 2876, 1688, 1449, 1219 cm^{-1}

Mass: 238.1358(M^+); Molecular Formular($C_{17}H_{18}O$)

<u>α-(2-benzylphenyl)propiophenone</u>

(a) α-(2-benzylphenyl)propionitrile

Diisopropylamine(4.50 g, 0.044 mole) in 25 ml of dry THF was added to 32 ml of n-BuLi(1.6 M in hexane) at 0 °C. The mixture was stirred for 30 min., and then cooled to -78 °C with a dry ice/acetone bath. α-(2-benzylphenyl)acetonitrile(9.11 g, 0.044 mole) in 25 ml of dry THF was added. The content was warmed to room temperature and stirred for 2 hours. Methyl iodide(7.1 g, 0.050 mole) was added. The mixture was stirred at room temperature for another 2 hrs and was refluxed overnight. After cooled to r.t., the solvent was removed by rotary evaporator. The residue was mixed with ether/water and the mixture was separated. The aqueous layer was extracted with ether several times and was combined with other ether layer. The combined ether layer was washed with water several times and dried over MgSO4. The solvent was removed at low pressure to give brown liquid. (6 g, 62 %) This crude product was used for next step without further purification.

^{1}H NMR($CDCl_3$):: δ 1.40(3H, d), 3.98(1H, quartet), 4.02(2H, s, 7.05-7.50(9H, m)

(b) α-(2-benzyl)phenylpropiophenone

A solution of α-(2-benzylphenyl)propionitrile(6 g, 0.027 mole) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 0.8 g of magnesium turnings and 5.2 g of bromobenzene in 100 ml anhydrous ether) under an argon atmosphere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The mixture was cooled to room temperature and was poured to ice cold water. The aqueous layer was separated and acidified with 10 % HCl. The solution was heated overnight at 80-90 ^{o}C. The solution was allowed to cool to room temperature and 200 ml of ether was added. Two layers were separated and the aqueous layer was extracted with ether three times. The combined organic layer was washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. After it was dried over MgSO4, solvent was evaporated to give a yelloish oil The crude product was chromatographed using 3 % ethylacetate in hexane and 3.6 g of very viscous, colorless liquid was obtanied.(Yield: 44 %) Several attempts to crystallize this liquid failed.

^{1}H NMR(CDCl$_3$): δ 1.39(3H, d, J = 6.8 Hz), 4.19(2H, s), 4.75(1H, quartet, J = 6.8 Hz), 7.04(1H, dd, J = 6.8, 1.0 Hz), 7.10-7.40(1^{1}H, m), 7.48(2H, distorted d)

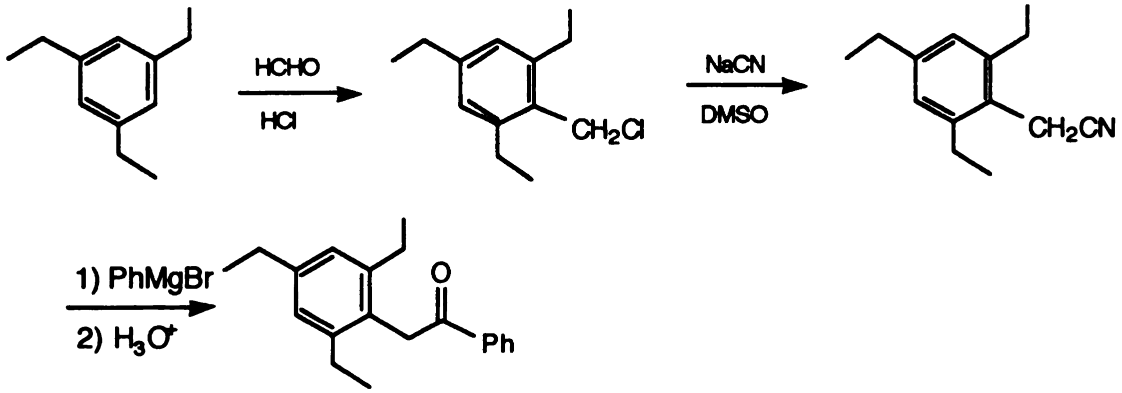
^{13}C NMR(CDCl$_3$): δ 18.6, 39.5, 44.0, 126.4, 126.9, 127.4, 127.6, 128.3, 128.4, 128.6, 128.9, 131.6, 132.4, 136.3, 137.1, 140.0, 140.2, 201.0

IR(CCl$_4$): 3065, 3029, 2980, 2932, 1688 cm^{-1}

Mass: 300.1515(M$^+$); Molecular Formular($C_{22}H_{20}O$)

α-(2,4,6-triethylphenyl)acetophenone

α-(2,4,6-triethylphenyl)acetophenone was prepared by the reaction of phenyl magnesium bromide with α-(2,4,6-triethylphenyl)acetonitrile following the route shown below.



(a) 2,4,6-triethylbenzyl chloride

The same method as that was used to synthesize 2,4,6-trimethylbenzyl chloride.[111] 10 g of 1,3,5-triethylbenzene was placed in a 250 ml round bottomed flask with 100 ml of conc. HCl and 2.6 g of 37 % formaldehyde solution. The solution was stirred vigorously and the temperature was maintained at 60 - 70 °C throughout the reaction. Concentrated HCl was introduced by bubbling through a drying tube. At the halfway point, an additional 2.6 g of formaldehyde was added. The mixture was stirred for total 8 hrs. After the mixture had been cooled to room temperature, it was extracted with three 50 ml portion of benzene. The combined benzene extracts were washed successively with water, 10 % NaOH and water, dried over MgSO4 and filtered. After evaporation of solvent, 7.3 g of milky colored gel (half solid half liquid) was obtained. This was used for next step without purification.

^{1}H NMR (250 MHz Bruker, $CDCl_3$) : δ 3.14 (2H, quartet), 3.02(4H, quartet) 1.59(6H, t), 1.63(3H, t), 5.10(2H, s), 7.25 (1H, s)

(b) 2,4,6-triethylphenylacetonitrile

A mixture of sodium cyanide(2.55 g) in 120 ml dimethylsulfoxide was heated at 80 °C until all the sodium cyanide had dissolved. 2,4,6-triethylbenzyl chloride(7.3 g) was added to this solution and the mixture was stirred at this temperature for 4 hrs. The mixture was cooled to room temperature and poured into 200 ml distilled water. The resulting solution was extracted with ether and the ether layer was washed with distilled water several times, and dried($MgSO_4$). The solvent was removed on a rotary evaporator to afford 5.42 g of product as a brownish oil. The crude product was used without further purification for next step.

(c) α-(2,4,6-triethylphenyl)acetophenone

A solution of 2,4,6-triethylphenylacetonitrile(5.4 g, 0.037 mol) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 1.04 g of magnesium turnings and 6.4 g of bromobenzene in 100 ml anhydrous ether) under an argon atmoshere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The mixture was cooled to room temperature and was poured to ice cold water. The aqueous layer was separated and acidified with 10 % HCl. The solution was heated overnight at 80-90 ^{o}C. The solution was allowed to cool to room temperature and 200 ml of ether was added. Two layers were separated and the aqueous layer was extracted with ether three times. The combined organic layer was washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. After it was dried over MgSO4, solvent was evaporated to give a yellowish oil This oil was mixed with hot ethanol and was recrystallized using seed which was obtained from mother liquid.(3.6 g, 35 %)

m. p. : 70.0 - 70.5 ^{o}C(colorless powder)

^{1}H NMR($CDCl_3$): δ 1.19(6H, t, J = 7.5 Hz), 1.25(3H, t, J = 7.5 Hz), 2.51(4H, q, 7.5 Hz), 2.63(2H, q, J = 7.5 Hz), 4.40(2H, s), 6.97(2H, s), 7.52(2H, distorted t), 7.60(1H, tt, J = 7.5, 1.2 Hz), 8.09(2H, distorted d)

^{13}C NMR($CDCl_3$): δ 14.8, 15.2, 26.5, 28.5, 38.0, 125.9, 128.1, 128.3, 128.9, 133.3, 137.4, 143.0, 143.2, 198.1

IR(CCl_4): 2967, 2934, 2874, 1696, 1549, 1213 cm^{-1}

Mass: 280.18312(M$^+$); Calc. 280.1828M$^+$); Molecular Formular($C_{20}H_{24}O$)

α-(2,4,6-triethylphenyl)propiophenone

α-(2,4,6-triethylphenyl)propiophenone was prepared by the reaction of phenyl magnesium bromide with α-(2,4,6-triethylphenyl)propionitrile following the route given below.

(a) α-(2,4,6-triethylphenyl)propionitrile

Diisopropylamine(3.5 g, 0.035 mole) in 15 ml of dry THF was added to 21.5 ml of nBuLi(1.6 M in hexane) at 0 °C. The mixture was stirred for 30 min., and then cooled to -78 °C with a dry ice/acetone bath. α-(2,4,6-triethylphenyl)acetonitrile(5.4 g, 0.027 mole) in dry THF was added. The content was warmed to room temperature and stirred for 2 hours. Methyl iodide(7.5 ml) was added . The mixture was stirred at room temperature for another 2 hrs and was refluxed overnight. After cooled to r.t., the solvent was removed by rotary evaporator. The residue was mixed with ether/water and the mixture was separated. The aqueous layer was extracted with ether several times and was combined with other ether layer. The combined ether layer was washed with water several times and dried over MgSO4. The solvent was removed at low pressure to give brown liquid. The crude product was used for next step without further purification.

^{1}H NMR($CDCl_3$): δ 1.20-1.35(9H, m), 1.62(3H, d), 2.55-2.85(4H, m), 2.92(2H, quartet), 6.93(2H, broad d)

(b) α-(2,4,6-triethylphenyl)propiophenone

A solution of α-(2,4,6-triethylphenyl)propionitrile(5.8 g, 0.027 mole) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 0.8 g of magnesium turnings and 5 g of bromobenzene in 100 ml anhydrous ether) under an argon atmoshere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The mixture was cooled to room temperature and was poured to ice cold water. The aqueous layer was separated and acidified with 10 % HCl. The solution was heated overnight at 80-90 °C. The solution was allowed to cool to room temperature and 200 ml of ether was added. Two layers were separated and the aqueous layer was extracted with ether three times. The combined organic layer was washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. After it was dried over MgSO4, solvent was evaporated to give a yellowish oil The crude product was chromatographed using 3 % ethylacetate in hexane and the resulting oil was recrystallized over ethanol to give colorless solid.(2.9 g, 36.5 %)

m. p. : 75.5 - 76.5 ^{o}C(fluffy, cotton-like solid)

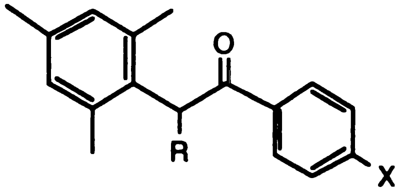
^{1}H NMR(CDCl$_3$): δ 1.18(6H, broad), 1.21(3H, t, J = 7.5 Hz), 1.57(3H, d, J = 6.8 Hz), 2.59(2H, q, J = 7.5 Hz), 2.61(4H, broad), 4.51(1H, q, J = 6.8 Hz), 6.89(2H, broad s), 7.26(2H, t, J = 7.5 Hz), 7.39(1H, distorted t), 7.70(2H, distorted d)

^{13}C NMR(CDCl$_3$): δ 15.2, 17.4, 25.9(broad), 28.4, 45.6, 126.7, 128.1, 128.6, 132.2, 135.8, 137.1, 141.4(broad), 142.6, 202.9

IR(CCl$_4$): 2969, 2936, 2878, 1682, 1449, 1221 cm^{-1}

Mass: 294.1986(M$^+$); Calc. 294.1985(M$^+$); Molecular Formular($C_2{}^1H_{26}O$)

Varable temperature ^{1}H NMR experiment of α-(2,4,6-triethylphenyl)propiophenone in toluene-d$_8$ was performed using a Varian 300 MHz NMR instrument at the temperature range of -60 - 80 ^{o}C. The results are shown in Figure 5.6 and 7.



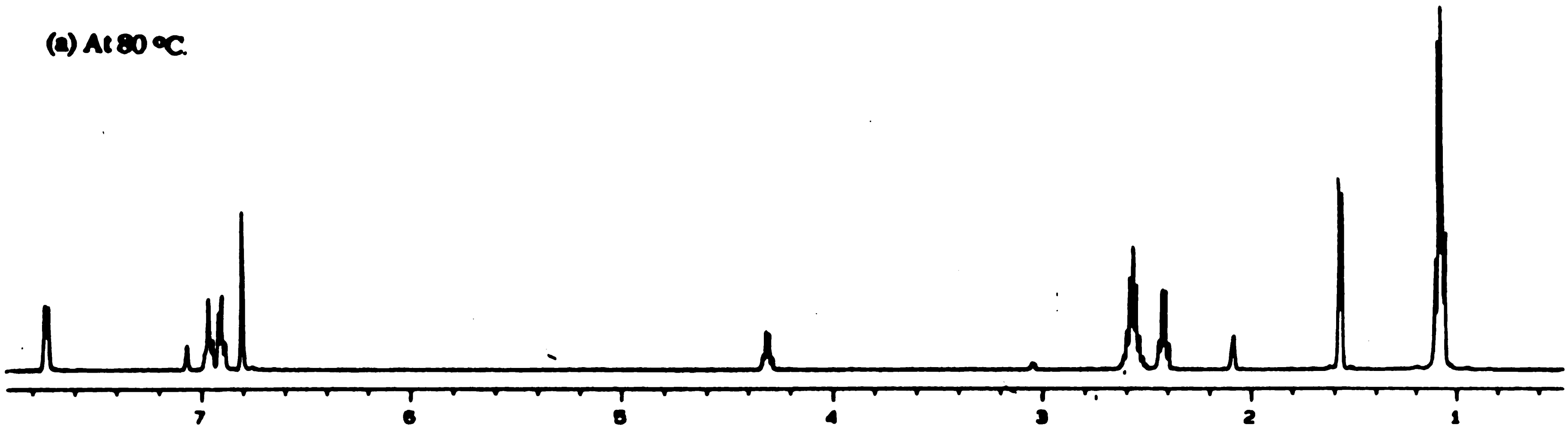
R = H or CH_3

X = OCH_3 or CF_3

α-(2,4,6-trimethylphenyl)-4'-trifluoromethylacetophenone

A solution of 1-trifluoromethyl-4-cyanobenzene(5.1 g) in 25 ml ether was added dropwise to stirred solution of 2,4,6-trimethylbenzylmagnesium-chloride (prepared from

(a) At 80 °C.



(b) At Room Temperature (21 °C)

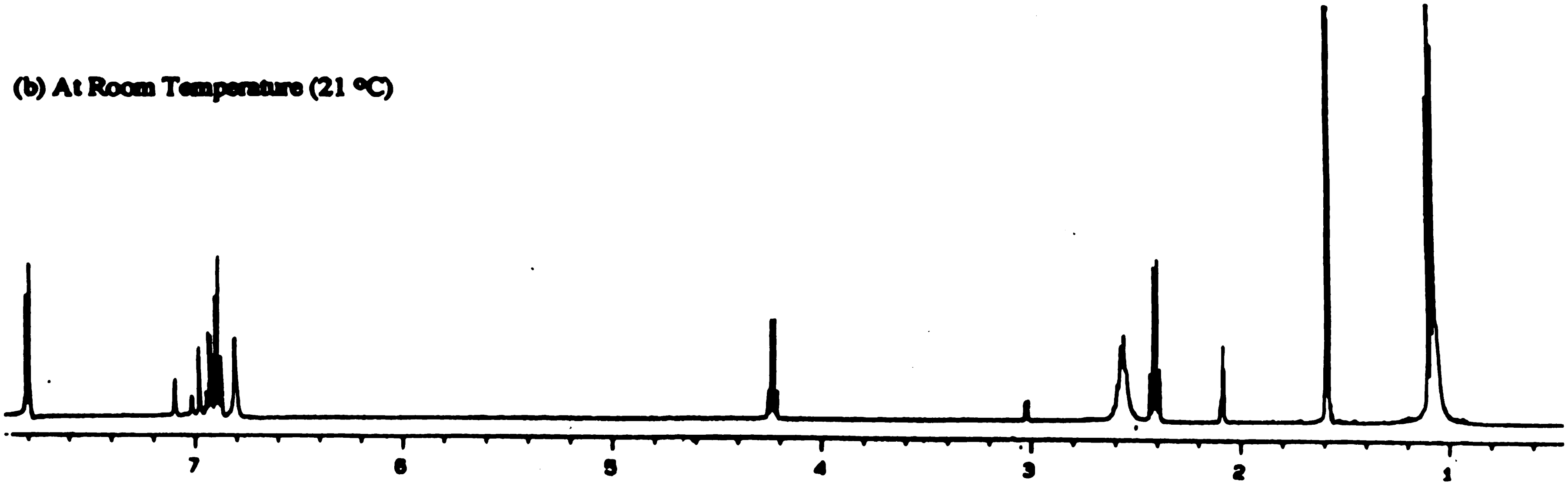


Figure 5. Variable Temperature ^{1}H NMR Spectra of α-(2,4,6-triethylphenyl)propiophenone: (a) At 80 °C, (b) At 21 °C

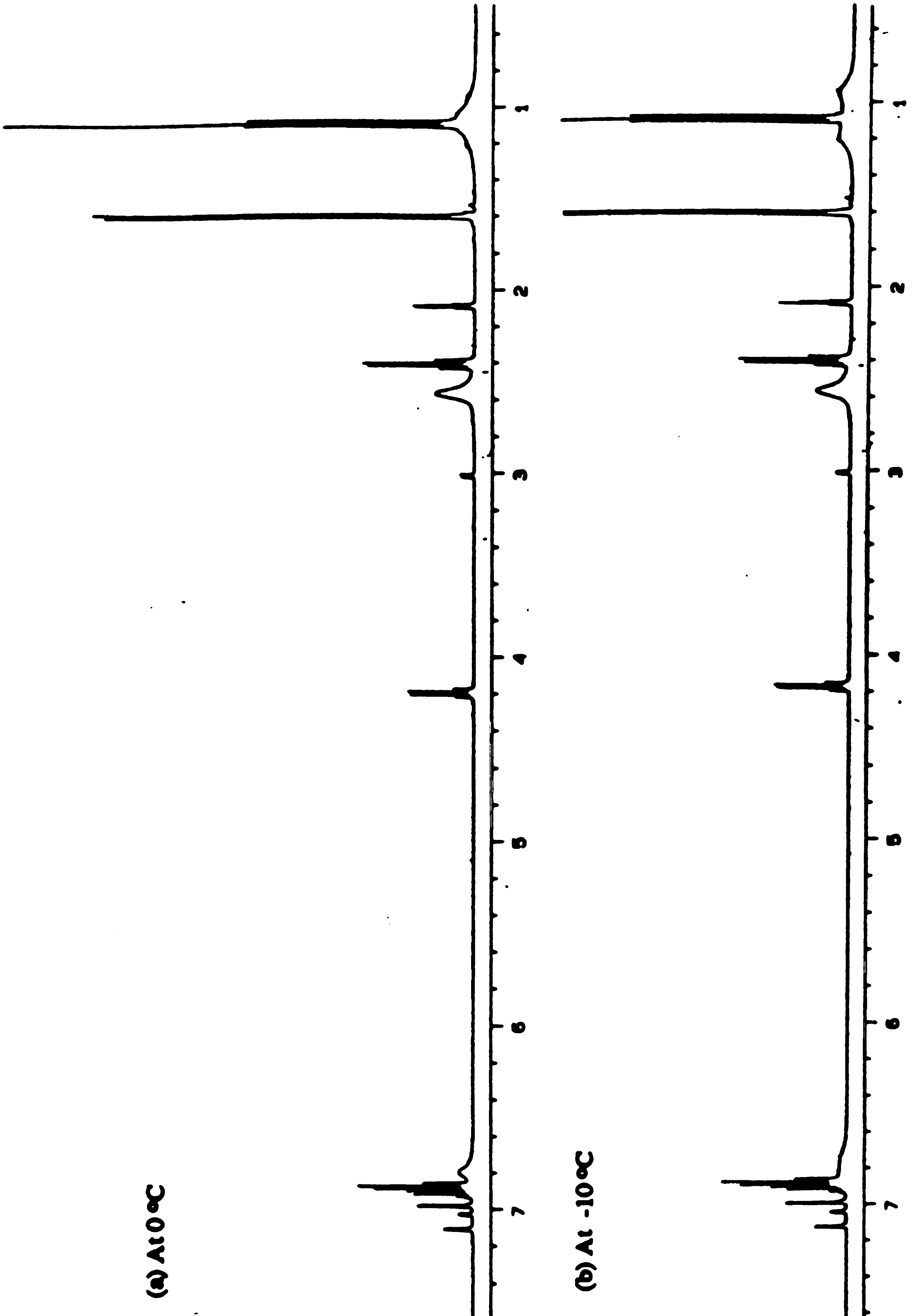
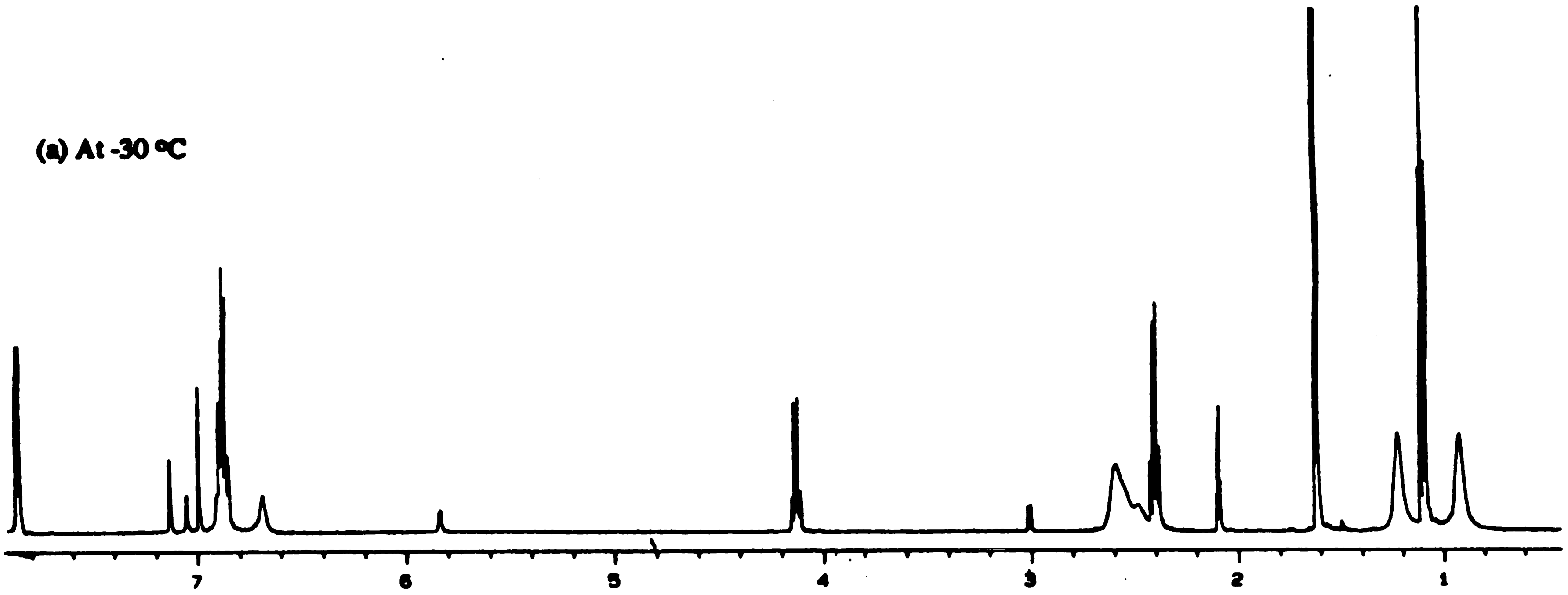


Figure 6. Variable Temperature ^{1}H NMR Spectra of α-(2,4,6-triethylphenyl)propiophenone: (a) At 0 °C, (b) At -10 °C

(a) At -30 °C



(b) At -60 °C

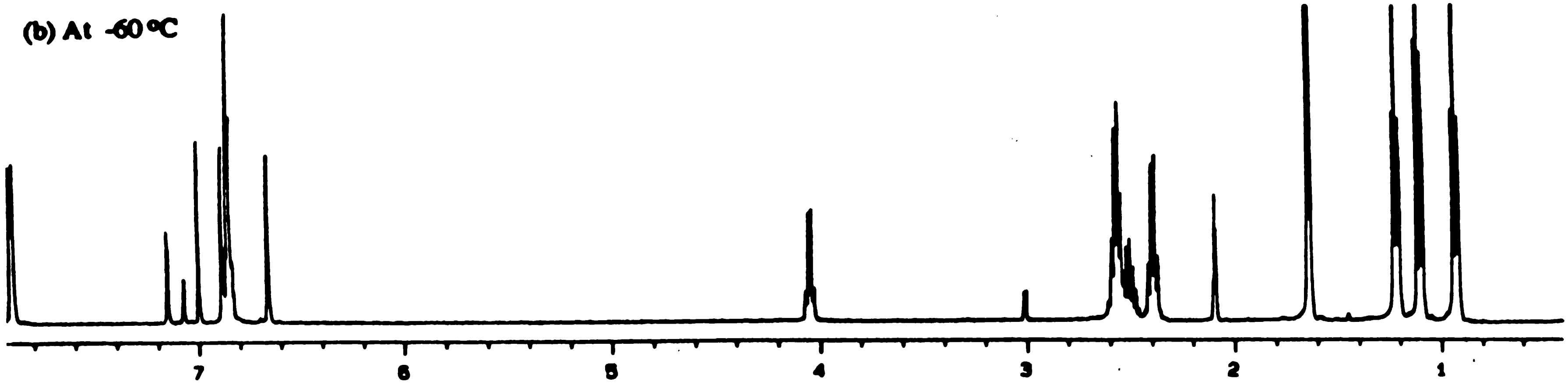


Figure 7. Variable Temperature ^{1}H NMR Spectra of α-(2,4,6-triethylphenyl)propiophenone: (a) At -30 °C, (b) At -60 °C

0.75 g of magnesium turnings and 5 g of 2,4,6-trimethylbenzyl chloride in 100 ml anhydrous ether) under an argon atmosphere at room temperature. The solution turned dark red as soon as one drop was added. The resulting mixture was refluxed under argon for 4-5 hrs and was cooled to room temperature. After being acidified with ice cold water, the aqueous layer was separated. The aqueous layer was heated at 80 °C for 3-4 hrs. and cooled to room temperature. After regular workup(extraction with ether, benzene, washing with $NaHCO_3$, H_2O and NaCl, drying over $MgSO_4$), yellow oil was obtained. The crude product was purified by recrystallization over 95 % ethanol to give 4 g of colorless solid. (44 %)

m. p. : 106 - 108 °C(colorless needles)

^{1}H NMR($CDCl_3$): δ 2.16(6H, s), 2.27(3H, s), 4.32(2H, s), 6.89(2H, s), 7.75(2H, d), 8.15(2H, d)

^{13}C NMR($CDCl_3$): δ 20.3, 20.9, 39.7, 125.4, 125.7(quartet, J= 4 Hz), 128.4, 128.6, 128.9, 134.5(quartet, J= 33 Hz), 136.66, 136.72, 139.72, 196.3

IR(CCl_4): 2976, 2921, 2867, 1701, 1319 cm^{-1}

Mass: 306.12351(M^+); Calc. 306.1232(M^+); Molecular Formular($C_{18}H_{17}OF_3$)

α-(2,4,6-trimethylphenyl)-4'-methoxyacetophenone

α-mesitylacetic acid(5 g, 0.028 mole) in phosphorous trichloride (4.24 g, 0.031 mole) was heated at 70-80 °C for 2 hrs. The mixture was cooled and mixed with anisole(40 ml). The resulting solution was added into aluminum chloride(4.5 g, 0.034 mole) in anisole(20 ml) at 0 °C. The mixture was stirred at room temperature for 30 min and then heated at 75 °C for 3 hrs. After cooling, it was poured into iced aqueous HCl. The aqueous layer was separated and extracted with a mixture of benzene and ether. The combined organic layers were washed with saturated sodium bicarbonate solution and distilled water, and were dried over magnisium sulfate. The solvent was evaporated to give yelloish solid. The crude product was recrystallized from ethanol to give the pure product as colorless solid.(5.2 g, 69 %)

m.p. : 88.0 - 89.0 °C(colorless powder)

^{1}H NMR($CDCl_3$): δ 2.15(6H, s), 2.25(3H, s), 3.86(3H, s), 4.26(2H, s), 6.86(2H, s), 6.95(2H, d), 8.04(2H, d)

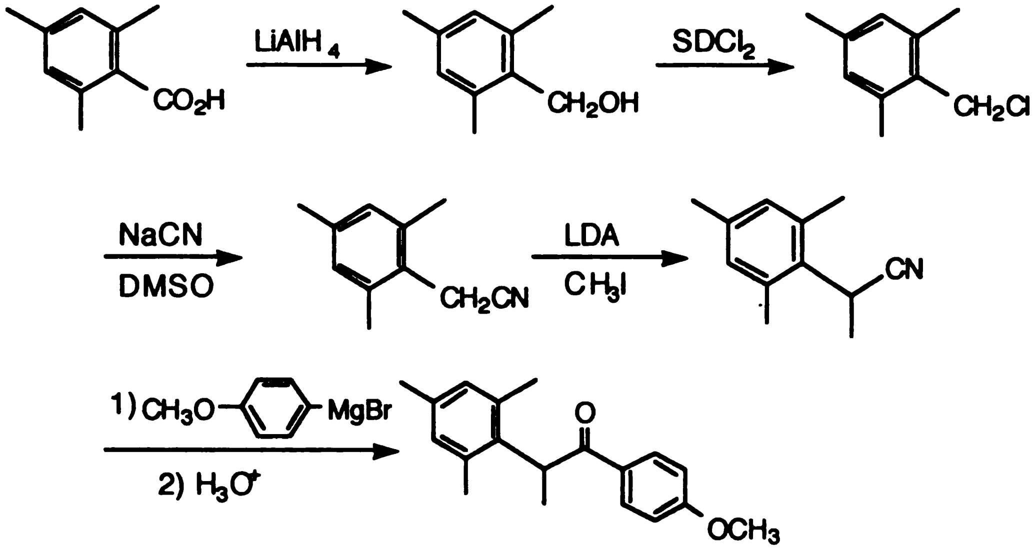
^{13}C NMR($CDCl_3$): δ 20.2, 20.9, 38.8, 55.4, 113.7, 128.7, 129.5, 130.1, 130.3, 136.1, 136.7, 163.4, 195.6

IR(CCl_4): 3007, 2963, 2917, 2840, 1688, 1601, 1510, 1323, 1261, 1169 cm^{-1}

Mass: 268.1456(M$^+$); Calc. 268.1464(M$^+$); Molecular Formular($C_{18}H_{20}O_2$)

α-(2,4,6-trimethylphenyl)-4'-methoxypropiophenone

α-(2,4,6-trimethylphenyl)-4'-methoxypropiophenone was prepared by the reaction of p-methoxyphenyl magnesium bromide with α-(2,4,6-trimethylphenyl)propionitrile following the route shown below.



(a) 2,4,6-trimethylbenzyl alcohol

A solution of 2,4,6-trimethylbenzoic acid(15 g, 0.09 mole) in 150 ml anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride(3.5 g, 0.09 mole) in 50 ml anhydrous ether at room temperature under argon atmosphere. The resulting mixture was refluxed for 4 to 5 hours and was cooled to room temperature, and the excess lithium aluminum hydride wsa decomposed by careful addition of methanol followed by ice. Acidic workup afforded 13 g of yellowish oil. This was used for next step without further purification.

^{1}H NMR($CDCl_3$): δ 2.27(3H, s), 2.40(6H, s), 4.70(2H, s), 6.89(2H, s)

(b) 2,4,6-trimethylbenzyl chloride

A solution of 2,4,6-trimethylbenzyl alcohol(13 g, 0.087 mole) in benzene was added to a stirred solution of thionyl cloride (20 g) in benzene. The solution was refluxed under argon for 4 hours, cooled to room temperature, and poured to ice cold water. The layers were separated and the aqueous phase was extracted with ether. The organic layers were combined, washed with saturated sodium bicarbonate solution and dried by magnesium sulfate. The solvent was removed on a rotary evaporator to afford 14 g of product as a brownish oil. This was used for next step without further purification.

^{1}H NMR($CDCl_3$): δ 2.28(3H, s), 2.41(6H, s), 4.68(2H, s), 6.89(2H, s)

(c) (2,4,6-trimethylphenyl)acetonitrile

A 250 ml 3-necked round bottomed flask was charged with sodium cyanide(3 g, 0.06 mole) and 100 ml of DMSO. The mixture was warmed to 80 ^oC and was stirred for about an hour. 2,4,6-trimethylbenzyl chloride(6.5 g, 0.039 mole) in DMSO was added into the solution dropwise at the same temperature. The mixture was stirred at this temperature for 4 hours and was cooled to room temperature. The solution was poured into ice cold water and this was extracted with ether several times. The combined organic layer was washed with distilled water and saturated sodium chloride solution and was dried over $MgSO_4$. After solvent was evaporated, dark brownish oil was obtained. This crude oil was used for next step without further purification.

^1H NMR($CDCl_3$): δ 2.27(3H, s), 2.36(6H, s), 3.60(2H, s), 6.89(2H, s)

(d) α-(2,4,6-trimethylphenyl)propionitrile

Diisopropylamine(2.6 g, 0.026 mole) in dry THF was added to 16 ml of n-BuLi(1.6 M in hexane) at 0 °C. The mixture was stirred for 30 min., and then cooled to -78 °C with a dry ice/acetone bath. The nitrile(4 g, 0.025 mole) in dry THF was added. The content was warmed to room temperature and stirred for 2 hours. At this stage, the solution turned dark brown. As methyl iodide(5.3 g, 0.038 mole) was added into the solution, the color became lighter. The mixture was stirred at room temperature for another 2 hrs and was refluxed overnight. After cooled to r.t., the solvent was removed by rotary evaporator. The residue was mixed with ether/water and the mixture was separated. The aqueous layer was extracted with ether several times and was combined with other ether layer. The combined ether layer was washed with water several times and dried over $MgSO_4$. The solvent was removed at low pressure to give brown liquid. The crude mixture, which contained ca. 10 % of dimethylated adducts, was connected to vacuum distillation at 10 Torr. The fraction, which boiled at 139-140 °C, was used for the next step.

^1H NMR($CDCl_3$): δ 1.59(3H, d), 2.27(3H, s), 2.41(6H, s), 4.28(1H, quartet), 6.89(2H, s)

(e) α-(2,4,6-trimethylphenyl)-4'-methoxypropiophenone

A solution of α-(2,4,6-trimethylphenyl)propionitrile(3.2 g, 0.019 mole) in 25 ml anhydrous ether was added dropwise to stirred solution(This solution contained lots of white precipitates, which disappeared as the nitrile was added.) of 4-methoxyphenyl magnesium bromide(prepared from 0.5 g of magnesium turnings and 3.5 g of 1-bromo-4-methoxybenzene in 100 ml anhydrous ether) under an argon atmosphere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. After the reflux, the slightly brownish solution turned into milky white solution, which seemed to be white precipitate. The mixture was cooled to room temperature and was poured into ice cold water containing about 20 ml of conc. HCl. The aqueous layer was separated and more conc. HCl was added. The solution was heated overnight at 80-90 °C. The solution was allowed to cool to room temperature and 200 ml of ether was added. Two layers were separated and the aqueous layer was extracted with ether three times. The combined organic layer was washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. After it was dried over MgSO4, solvent was evaporated to give a yellowish oil This oil was mixed with hot ethanol and was recrystallized to give colorless solid.(2.8 g, 52 %)

m. p. : 117.5 - 118.0 °C, cubic shaped crystals

^{1}H NMR(CDCl$_3$): δ 1.90(3H, broad d), 2.17(3H, s), 2.28(6H, broad s), 3.79(3H, s), 4.75(1H, broad q), 6.75(2H, broad s), 6.86(2H, d), 8.02(2H, d)

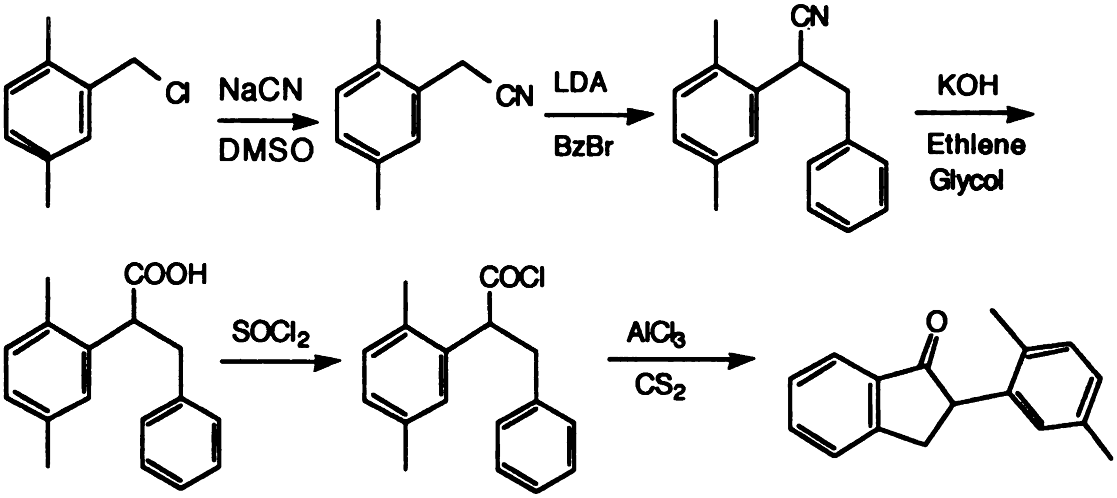
^{13}C NMR(CDCl$_3$): δ 15.1, 20.4, 20.7, 45.5, 55.3, 113.4, 129.9, 130.2, 130.4, 135.4, 136.0, 137.3, 162.8, 200.9

IR(CCl$_4$): 1695 (C=O)

Mass: 282.16109(M+); Calc. 282.1621(M$^+$); Molecular Formular($C_{19}H_{22}O_2$)

α-(2,5-dimethylphenyl)indanone

α-(2,5-dimethylphenyl)indanone was prepared following the route shown below.



(a) α-(2,5-dimethylphenyl)acetonitrile

A 250 ml 3-necked round bottomed flask was charged with sodium cyanide(3 g, 0.06 mole) and 100 ml of DMSO. The mixture was warmed to 80 °C and was stirred for about an hour. 2,4-Dimethylbenzyl chloride (Aldrich, 8 g, 0.056 mole) in DMSO was added into the solution dropwise at the same temperature. The mixture was stirred at this temperature for 4 hours and was cooled to room temperature. The solution was poured into ice cold water and this was extracted with ether several times. The combined organic layer was washed with distilled water and saturated sodium chloride solution and was dried over MgSO4. After solvent was evaporated, dark brownish oil was obtained. This crude oil was used for next step without further purification.(7 g, 93 %)

H1NMR($CDCl_3$): δ 2.27(3H,s), 2.32(3H,s), 3.61(2H,s), 7.04(1H, broad d), 7.08(1H, d), 7.15(1H, broad s)

(b) α,α-(2,5-dimethylphenyl)benzylacetonitrile

Diisopropylamine(5.3 g, 0.053 mole) in dry THF was added to n-BuLi(33 ml, 0.053 mole) at 0 °C. The mixture was stirred for 30 min., and then cooled to -78 °C with a dry ice/acetone bath. The nitrile(7 g, 0.053 mole) in dry THF was added. The content was warmed to room temperature and stirred for 2 hours. Bromomethylbenzene(9 g, 0.053 mole) was added . The mixture was stirred at room temperature for another 2 hrs and was refluxed overnight. After being cooled to r.t., the solvent was removed by rotary evaporator. The residue was mixed with ether/water and the mixture was separated. The aqueous layer was extracted with ether several times and was combined with other ether layer. The combined ether layer was washed with water several times and dried over MgSO4. The solvent was removed at low pressure to give brown liquid. The crude product was distilled with long vigreux column at low pressure(-0.3 Torr) to give 3.9 g(31 %) of colorless solid.(B.P. 128-130 °C)

H1NMR($CDCl_3$): δ 2.14(3H,s), 2.19(3H,s), 3.06(2H, doublets of AB quartet), 4.08(1H,dd), 6.98-7.30(8H, m)

(c) α,α-(2,5-dimethylphenyl)benzylacetic acid

A 250 ml one necked fround bottomed flask was charged with the nitrile(3.9 g, 0.017 mole), KOH (2.8 g, 0.05 mole) and 80 ml of ethylene glycol. This mixture was stirred at ca. 150 °C for 5 - 6 hrs. After the solution was cooled to r.t., it was acidified with 20 % ice cold HCl. The solution was extracted with ether and benzene. The organic layer was dried over $MgSO_4$ and the solvent was removed to give dark brown solid. NMR of the crude product showed that the major product was the acid, but it contained about 20 % of unknown side product, which has very similar NMR pattern to the acid. Several purification methods were tried, but unsuccessful. Column chromatography was discouraged by the insolubility of this material in most common solvents around. Therfore, this was used without further purification for next step.

H1NMR($CDCl_3$): δ 2.20(3H,s), 2.42(3H, d), 2.94(1H, dd), 3.41(1H, dd), 4.10(1H, dd), 6.98 - 7.25(8H, m)

(d) α-(2,5-dimethylphenyl)indanone

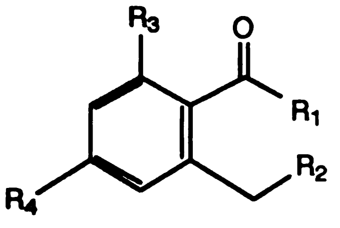
The same method as that was used to synthesize α-phenylindanone was used.[112] A 100 ml r.b. flask was charged with the acid(4.3 g, 0.017 mole) and 40 ml of thionyl chloride, and the mixture was refluxed for about an hour. The extra thionyl chloride was distilled off at atmospheric pressure. 50 ml of CS_2 was added to the residue and aluminum chloride(3.16 g, 0.024 mole) was added to the solution slowly. The mixture was refluxed for 2 hours and it was allowed to cool to r.t.. The solution was diluted with 10 % HCl aq. solution. (note: Be careful not to cause violent reaction) The solution was extracted with ethyl acetate and ether, and the organic layer was washed with distilled water several times. After drying over $MgSO_4$ and evaporation of solvent, dark brownish oil was obtained. This crude oil was connected to column chromatography using 5 % ethyl acetate in hexane. All the collected fractions containing desirable product were concentrated to give a yellow oil. The oil was further purified by recrystallization over 95 % ethanol to give 2.3 g of colorless solid.(87.0 - 87.5 °C, powder)

^{1}H NMR(CDCl$_3$) ; δ 2.21(3H,s), 2.28(3H,s), 3.15(1H,dd, J = 17.5, 4.5 Hz), 3.68(1H, dd, J =17.5, 8.5 Hz), 4.05(1H, dd, J = 4.5, 8.5 Hz), 6.77(1H,s), 6.96(1H,d, J = 7.4 Hz), 7.07(1H,d, J = 7.7 Hz), 7.41(1H,t, J = 7.4 Hz), 7.50(1H,d, J = 7.7 Hz), 7.63(1H, t, J = 7.4 Hz), 7.82(1H, d, J = 7.4 Hz)

^{13}C NMR(CDCl$_3$) : δ 19.6, 20.9, 35.6, 50.9, 124.3, 126.5, 127.7, 127.8, 128.2, 130.6, 133.4, 134.9, 135.8, 136.7, 138.3, 153.4, 207.0

IR(CCl$_4$): 3029, 1721, 1688 cm^{-1}

Mass: 236.12103(M$^+$); Calc. 236.1202(M$^+$); Molecular Formular($C_{17}H_{16}O$)



$R_1 = CH_3$ or Ph
$R_2 = CH_3$, CN, Ph
$R_3 = CH_3$, CH_2CH_3, OCH_3
$R_4 = CH_3$, CH_2CH_3, OCH_3

2-ethylbenzophenone

A solution of benzonitrile(4.4 g, 0.043 mole) in 25 ml anhydrous ether was added dropwise to stirred solution of 2-ethylphenyl magnesium bromide(prepared from 1.1 g of magnesium turnings and 8 g of 2-ethyl-1-bromobenzene in 100 ml anhydrous ether) under an argon atmosphere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The resulting milky heterogeneous solution was cooled to room temperature and extracted with hydrochloric acid(HCl/water was approximately 1:1 by volume). Ether layer(A) and aqueous layer(B) were separated and extra amount (50 ml) of conc. HCl was added to each layer. Each layer was refluxed separately overnight. After regular workup(ether extraction, NaHCO3 wash and drying with MgSO4), the solution B gave quite a pure compound according to NMR, which was further purified by column chromatography using 3 % ethyl acetate in hexane. Same workup of solution A resulted in dark brown oil, which contained several compounds including small amount of the desirable product. The product was isolated by column chromatography using 3 % ethyl acetate in hexane. The combined yield was 5.6 g.(62.4 %, colorless oil)

^{1}H NMR($CDCl_3$) 300 MHz(Gemini): δ 1.16(3H, t, J= 7.4 Hz), 2.67(2H, quartet, J=7.4 Hz), 6.84(1 H, d, J= 8.25 Hz), 6.89(1H, td, J= 7.4 Hz , J= 1.1 Hz), 7.17-7.23(2H, m), 7.41-7.47(2H, distorted t), 7.56(1H,tt, J=7.4 Hz, J= 2.6 Hz), 7.80-7.84(2H, dstortted d, J=7 Hz),

^{13}C NMR($CDCl_3$) 300 MHz(Gemini): δ 199.2, 143.2, 138.6, 138.0, 133.4, 130.4, 130.35, 129.6, 128.5, 128.4,125.3, 26.2, 15.7

IR(CCl_4):3067, 3027, 2971, 2936, 2876, 1671, 1269

Mass: 210.10424; Calc. 210.1045(M^+); Molecular Formular($C_{15}H_{14}O$)

2-methylbenzophenone

This compound was purchased from Aldrich(98 %) and was further purified by fractional distillation. B. P. : 126-128 °C/ 0.5 Torr

2,4,6-trimethylbenzophenone

A 250 ml 3-necked rb flask was charged with benzoyl chloride(10 g, 0.07 mole) and mesitylene(50 ml). Aluminum chloride(11-12 g) was slowly added into the solution. After the addition was over, the mixture was stirred vigorously for 2 hrs at 30 - 40 °C. The mixture was poured into about 100 g of ice containing 50 ml of conc. HCl. 100 ml of ether was added into the mixture and the organic layer was separated. Aquous layer was extracted with ether several times and the combined organic layer was washed with distilled water, sat. $NaHCO_3$ and sat. NaCl solution. After dried over $MgSO_4$, the solvent was removed to give yellowish oil. This oil was further purified by fractional distillation. The fraction, which was collected at 180-182 ^{o}C at 15 torr, turned out to be the desirable product.(13.6 g, 87 %, colorless liquid)

^{1}H NMR(CDCl$_3$) 300 MHz(Gemini); δ 2.07(6H,s), 2.32(3H,s), 6.88(2H, s), 7.42(2H, distorted t), 7.56(1H, tt), 7.79(2H, distorted d)

^{13}C NMR(CDCl$_3$) 300 MHz(Gemini); δ 200.75, 138.5, 137.3, 136.8, 134.2, 133.5, 129.4, 128.8, 128.3, 21.1, 19.3

IR(CCl$_4$): 2923, 1674, 1449, 1267, 1171 cm^{-1}

Mass: 224.12109(M$^+$); Calc. 224.1202(M$^+$); Molecular Formular($C_{16}H_{16}O$)

<u>2,4,6-triethylbenzophenone</u>

A 250 ml 3-necked rb flask was charged with benzoyl chloride(8 g, 0.057 mole) and 2,4,6-triethylbenzene(15 ml). Aluminum chloride(10 g) was slowly added into the solution. After the addition was over, the mixture was stirred vigorously for 2 hrs at 30 - 40 ^{o}C. The mixture was poured into about 100 g of ice containing 50 ml of conc. HCl. 100 ml of ether was added into the mixture and the organic layer was separated. Aquous layer was extracted with ether several times and the combined organic layer was washed with distilled water, sat. NaHCO$_3$ and sat. NaCl solution. After dried over MgSO4, the solvent was removed to give yellowish oil. This oil was further purified by fractional distillation. The fraction, which was collected at 185 -188 ^{o}C at 15 torr, turned out to be the desirable product.(9.2 g, 60.7 %, colorless liquid)

^{1}H NMR(CDCl$_3$) 300 MHz(Gemini); δ 1.06(6H, t), 1.26(3H, t), 2.37(4H, quartet), 2.65(2H, quartet), 6.95(2H, s), 7.41(2H, distorted t), 7.55(1H, tt), 7.79(2H, distorted d)

^{13}C NMR(CDCl$_3$) δ 15.47, 15.52, 26.3, 28.8, 125.5, 128.6, 129.5, 133.5, 136.0, 137.9, 140.5, 145.1, 200.8

IR(CCl$_4$): 2969, 2936, 2876, 1671, 1449, 1277, 1244 cm^{-1}

Mass: 266.16617(M$^+$); Calc. 266.1672(M$^+$); Molecular Formular($C_{19}H_{22}O$)

2-ethylacetophenone

A solution of 2-ethyl magnesium bromide in THF was added to a solution of acetic anhydride(1.5 to 2 equivalents) in freshly distilled THF at - 78 °C either by cannular technique(transfer of solution through a double-headed syringe by pressure) or syringe. The mixture was stirred for 3-4 hrs at this temperature. The mixture was quenched by saturated ammonium chloride solution at this temperature. White precipitates were immediately formed which could be dissolved by extra amount of water. The solution was extracted by ether and the organic layer was washed with 10 % NaOH solution several times in order to wash extra acetic anhydride. The ether layer was dried with magnesium sulfate. After evaporation of solvent, slightly yellow oil was obtained. This oil was connected to column chromatography using 5 % ethyl acetate in hexane. The resulting oil was further purified by fractional distillation B.P. 94-98 °C/10 torr (colorless liquid)

^{1}H NMR($CDCl_3$): δ 1.16(3H, t, 7.5 Hz), 2.53(3H, s), 2.82(2H, quar, 7.5 Hz), 7.18-7.23(2H, m), 7.35(1H, dt, 7.5 Hz, 1.4 Hz), 7.57(1H, dd, 7.5 Hz, 1.4 Hz)

^{13}C NMR($CDCl_3$) δ 15.9, 27.0, 29.9, 125.6, 128.9, 130.4, 131.4, 125.9, 144.2, 202.3

IR(CCl_4): 3071, 2973, 2934, 2874, 1690, 1354, 1256 cm^{-1}

Mass:148.0875(M^+); Calc. 148.0888(M^+); Molecular Formular($C_{10}H_{12}O$)

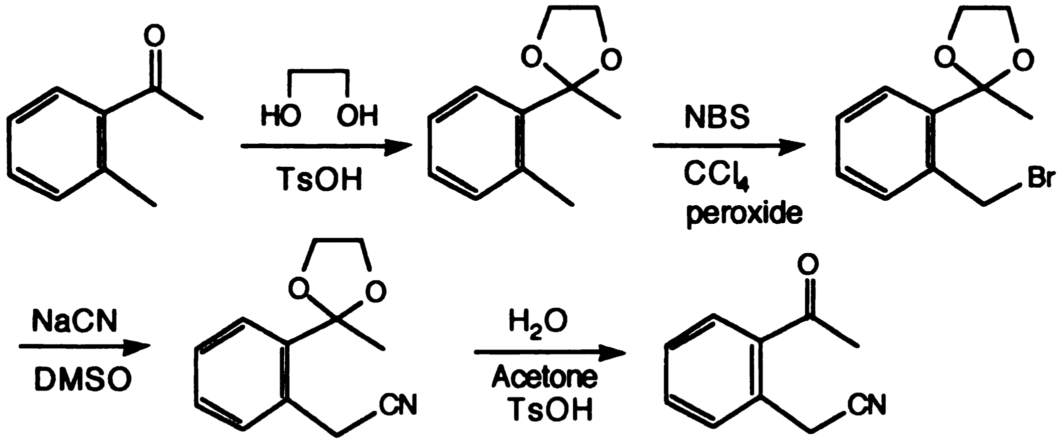
2-methylacetophenone

This compound was purchased from Aldrich(98 %) and was further purified by fractional distillation. B.P.: 83-85 °C/ 10 Torr

2,4,6-trimethylacetophenone

This compound was purchased from Aldrich(98 %) and was used without further purification.

2-cyanomethylacetophenone



(a) 2-methylacetophenone ketal

2-methylacetophenone(6 g, 0.045 mole), ethylene glycol(16.8 g, 0.27 mole) and p-toluenesulfonic acid(a few crystals) in benzene were added into 250 ml round bottomed flask which was equiped with Dean Stark trap. This mixture was refluxed for 2-3 days until theoretical amount of water was collected in the trap. The solution was cooled to room temperature and washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. The combined organic layer was dried over magnisium sulfate and the solvent was evaporated to give yellowish oil.(8 g, 100 %)

^{1}H NMR($CDCl_3$): δ 1.7(3H, s), 2.5(3 H, s), 3.74(2H, m), 4.04(2H, m), 7.14 - 7.22(3H, m), 7.56(1H, d)

(b) 2-bromomethylacetophenone ketal

A 500 ml r. b. flask was charged with the ketal(8 g, 0.045 mole), N-bromosuccinimide(8 g, 0.045 mole) and benzoyl peroxide.(0.25 g) About 100 ml of CCl_4 was added into the mixture. The solution was allowed to reflux and at certain point the reflux caused sudden vigorous condensation and the color of the solution started to turn reddish. When red color turned white all of a sudden, the heating mantle was taken away. The mixture was stirred for another hour and solid precipitate was filtered out while it was hot. Solvent was evaporated to give yellowish powder. The NMR and TLC analysis of this crude product showed that this contained a lot of side products. However, the major product seemed to be the desired bromide. After 24 hrs at room temperature, the compound started decomposed. (NMR showed that new peaks were growing) Thus, this crude mixture was immediately connected to next step.

^{1}H NMR($CDCl_3$): δ 1.72(3H, s), 3.77(2H, m), 4.04(2H, m), 4.88(2H, s), 7.2 - 7.3(2H, m), 7.42(1H, d), 7.53(1H,d)

(c) 2-cyanomethylacetophenone ketal

A 250 ml 3-necked round bottomed flask was charged with sodium cyanide(1.4 g, 0.029 mole) and 100 ml of DMSO. The mixture was warmed to 80 °C and was stirred for about an hour. 2-bromomethylacetophenone ketal(6.2 g, 0.024 mole) in DMSO was added into the solution dropwise at the same temperature. The mixture was stirred at this temperature for 4 hours and was cooled to room temperature. The solution was poured into ice cold water and this was extracted with ether several times. The combined organic layer was washed with distilled water and saturated sodium chloride solution and was dried over MgSO4. After solvent was evaporated, dark brownish oil was obtained. This crude oil was chromatographed using hexane and ethyl acetate and light yellowish soild was obtained.(2 g)

^{1}H NMR($CDCl_3$): δ 1.68(3H, s), 3.78(2H, m), 4.01(2H, s), 4.06(2H, m), 7.3 - 7.45(3H, m), 7.6(1H, d)

(d) 2-cyanomethylacetophenone

The ketal(2 g, 0.01 mole) was added into 25 ml acetone in 50 ml round bottomed flask and a few crystals of p-toluenesulfonic acid were added. The mixture was refluxed for 4 hours. Solvent was evaporated by rotary evaporator. The residue was mixed with ether and the ether solution was washed with water, $NaHCO_3$ and distilled water. The solution was dried over $MgSO_4$ and the solvent was evaporated to give a yellowish oil. This oil was subjected to column chromatograpghy with 10 % ethyl acetate in hexane. The zone with desirable compound was noticeable from the column because it gave milky color on the column. The resulting solid was recrystallized over 95 % ethanol to give 1.2 g of colorless solid.

^{1}H NMR($CDCl_3$) : δ 2.63(3H,s), 4.14(2H,s), 7.4 - 7.6(3H, m), 7.89(1H,d)

^{13}C NMR($CDCl_3$): δ 23.2, 28.8, 118.0, 128.4, 130.6, 130.7, 130.9, 132.9, 135.2, 200.3

IR(CCl4): 3075, 3007, 2973, 2249, 1688, 1489, 1358, 1252 cm^{-1}

Mass: 159.0679(M^+); Calc. 159.0684(M^+); Molecular Formular($C_{10}H_9NO$)

2-benzylacetophenone

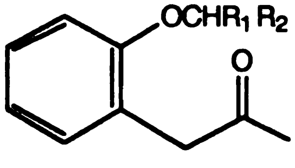
2-Benzylacetophenone was prepared by the same method that was used by Bradsher and Webster.[113] Methyl lithium was generated by the procedure described by Tegner.[114] Lithium wire was weighed in a beaker containing mineral oil after it was washed with hexane briefly. The lithium(3 g, 0.43 mole) was washed with hexane twice before it was added into freshly purified ether in 250 ml 3 necked round bottomed flask. Methyl iodide(13 ml, 0.2 mole) in ether (1:1 v/v) was added slowly to the ether containing lithium at room temperature under argon atmosphere. The addition took 2 ours. (It turned greyish opaque solution containing precipitate.) α-Phenyl-o-toluic acid(4 g, 0.02 mole) in ether(1:1v/v) was added dropwise to the methyl lithium solution at room temperature. The solution turned dark brown. The color became darker and darker as addition continues. After completing the addition, the solution was quenched by ice.(Note: The reaction is quite vigorous. It is recommended that ice is added piece by piece slowly.) The color turned white and a lot of white precipitate was formed. As more ice and water was added, the white precipitate started disappearing and went into solution. At this point, remaining lithium metal should be destroyed carefully with ice water. The solution was extracted with ether and organic layer was washed with water several times. The ether layer was dried over $MgSO_4$ and solvent was evaporated to give yellowish oil.. NMR showed that it is a mixture of several compounds including desirable ketone. The crude mixture was distilled by Kugelrohr aparatus. The distillate was chromatographed through silica gel(95:5 Hex:EtOAC) The resulting oil was mixed with petroleum ether and cooled in a dry ice bath. Soon precipitate appeared. The solid recrystallized in pet. ether again to give nice crystalline(cubic) solid. (mp= 47-48 °C)

^{1}H NMR($CDCl_3$): δ 2.44(3H, s), 4.26(2H, s), 7.10-7.30(7H, m), 7.38(1H, td), 7.63(1H, dd)

^{13}C NMR($CDCl_3$): δ 29.8, 39.2, 125.9, 126.2, 128.3, 128.9, 129.1, 131.3, 131.8, 138.3, 140.5, 140.9, 202.3

IR(CCl4): 3067, 3031, 2923, 1767, 1692 cm^{-1}

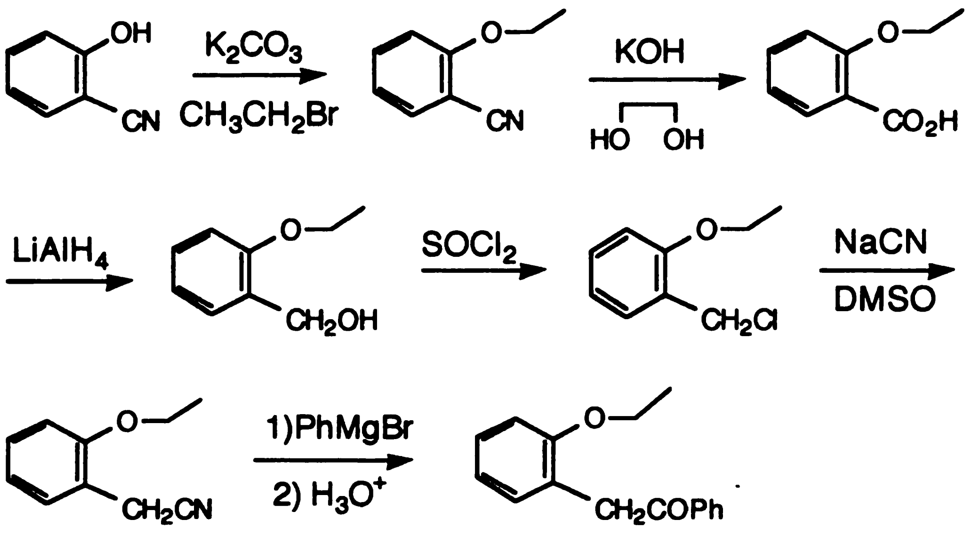
Mass: 210.1044(M$^+$); Calc.210.1045(M$^+$); Molecular Formular($C_{15}H_{14}O$)



1. $R_1 = H$, $R_2 = CH_3$
2. $R_1 = CH_3$, $R_2 = CH_3$

<u>α-(2-ethoxyphenyl)acetophenone</u>

α-(2-ethoxyphenyl)acetophenone was prepared by the reaction of phenyl magnesium bromide with α-(2-ethoxyphenyl)acetonitrile following the route shown below.



(a) 2-ethoxybenzonitrile

A 250 ml round bottomed flask was charged with 30 g of K_2CO_3(0.22 mole), 36 g of ethylbromide(0.33 mole) and 20 g of 2-hydroxybenznitrile(0.17 mole) in DMF. The mixture was stirred for three days at 60-70 °C. The resulting solution was extracted with ether and the ether layer was washed with saturated sodium bicarbonate solution several times. The normal drying procedure(saturated NaCl solution, MgSO4) followed by evaporation of solvent gave 20 g (95 % yield) of dark yellowish liquid. This was used for next step without further purification.

^1H NMR($CDCl_3$): δ 1.46(3H, t), 4.14(2H, quartet), 6.94(1H, d), 6.96(1H, t), 7.49(1H, d), 7.52(1H, t)

(b) 2-ethoxybenzoic acid[115]

A solution of 30 g of potassium hydroxide(0.54 mole) in 150 ml of ethylene glycol was mixed with 20 g of 2-ethoxybenznitrile(0.14 mole) in a 250 ml round bottomed flask. The solution was heated at 150-150 °C for six hours. The reaction mixture was cooled, diluted with 150 ml of water, and extracted with ether. The ether layer was washed with water several times. The combined aqueous phases were acidified with concentrated hygrochloric acid and extracted with benzene several times. The benzene extracts were washed successively with water and saturated sodium chloride solution, then dried over

$MgSO_4$. Evaporation of solvent gave 25 g of yellowish liquid. This was used for next step without further purification.

^{1}H NMR($CDCl_3$): δ 1.55(3H, t), 4.30(2H, quartet), 7.01(1H, d), 7.10(1H, t), 7.55(1H, t), 8.18(1H, d)

(c) 2-ethoxybenzyl alcohol

A solution of 2-ethoxybenzoic acid (25 g, 0.15 mole) in 150 ml anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride(10 g, 0.26 mole) in 50 ml anhydrous ether at room temperature under argon atmosphere. The resulting mixture was refluxed overnight, cooled to room temperature, and the excess lithium aluminum hydride decomposed by careful addition of methanol. Acidic workup afforded 20 g of yelloswish oil. This was used for next step without further purification.

^{1}H NMR($CDCl_3$): δ 1.45(3H, t), 2.48(1H, broad s -OH), 4.10(2H, quartet), 4.70(2H, s), 6.89(1H, d), 6.93(1H, t), 7.22-7.30(2H, m)

(d) 2-ethoxybenzyl chloride

A solution of 2-ethoxybenzyl alcohol(20 g, 0.13 mole) in benzene was added to a stirred solution of thionyl cloride (30 g, 0.25 mole) in benzene. The solution was refluxed under argon for 4 hours, cooled to room temperature, and poured into distilled water. The layers were separated and the aqueous phase extracted with ether. The organic layers were combined, washed with saturated sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed on a rotary evaporator to afford 20 g of product as a brownish oil. This was used for next step without further purification.

^{1}H NMR($CDCl_3$): δ 1.45(3H, t), 4.09(2H, quartet), 4.68(2H, s), 6.88(1H, d), 6.92(1H, t), 7.26(1H, t), 7.36(1H, d)

(e) α-(2-ethoxyphenyl)acetonitrile

A mixture of sodium cyanide(8.6 g, 0.18 mole) in 120 ml dimethylsulfoxide was heated at 80 °C until all the sodium cyanide had dissolved. 2-ethoxybenzylchloride(20 g, 0.12 mole) was added to this solution and the mixture was stirred at this temperature for 6 hrs. The mixture was cooled to room temperature and poured into 200 ml distilled water. The resulting solution was extracted with ether and the ether layer was washed with distilled water several times, and dried(MgSO4). The solvent was removed on a rotary evaporator to afford 17 g of product as a brownish oil.

^{1}H NMR($CDCl_3$): δ 1.45(3H, t), 3.69(2H, s), 4.07(2H, quartet), 6.87(1H, d), 6.93(1H, t), 7.27(1H,t), 7.33(1H,d)

(f) α-(2-ethoxy)phenylacetophenone

A solution of α-(2-ethoxyphenyl)acetonitrile(8 g, 0.05 mole) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 1.4 g of magnesium turnings and 9 g of bromobenzene in 100 ml anhydrous ether) under an argon atmoshere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The resulting milky heyerogeneous solution was cooled to room temperature and extracted with hydrochloric acid(conc. HCl/water was approximately 1 in volume). Ether layer(A) and aqueous layer(B) were separated and extra amount (50 ml) of conc. HCl was added to each layer. Each layer was refluxed separately overnight. After regular workup(ether extraction, NaHCO3 wash and drying with MgSO4), the solution B gave quite a pure compound according to NMR, which was further purified by recrystallization(EtOH/water) to give 2 g of white powder. Same workup of solution A resulted in dark brown oil, which had to be further purified by column chromatography and recrystallization.(m.p.; 45- 46 ^oC)

^{1}H NMR($CDCl_3$) 300 MHz(Gemini); δ 8.06-8.02(2H, dstorted d J=7 Hz), 7.53(1H,tt, J=7.4 Hz, J= 2.6 Hz), 7.47-7.41(2H, distorted t), 7.23-7.17(2H, m), 6.89(1H, td, J= 7.4 Hz , J= 1.1 Hz), 6.84(1H, d, J= 8.25 Hz), 4.24(2H,s), 3.99(2H, q, J=6.9 Hz), 1.27(3H, t, J= 6.9 Hz)

^{13}C NMR($CDCl_3$) 300 MHz(Gemini); δ 198.8, 156.7, 137.3, 133.0, 131.2, 128.6(two carbons), 128.4, 124.1, 120.6, 111.5, 63.5, 39.8, 14.4

IR(CCl_4): 3069, 3031, 2984, 2930, 2901, 2880, 1698, 1684, 1246, 1049 cm^{-1}

Mass: 240.11516(M$^+$); Calc. 240.1151(M$^+$); Molecular Formular($C_{16}H_{16}O_2$)

α-(2-isopropoxy)phenylacetophenone

(a) 2-isopropoxybenzonitrile

A 250 ml round bottomed flask was charged with 20 g of K_2CO_3(0.14 mole), 25 g of isopropylbromide(0.20 mole) and 15 g of 2-hydroxybenzonitrile(0.13 mole) in DMF. The mixture was stirred for three days at 60-70 °C. The resulting solution was extracted with ether and the ether layer was washed with saturated sodium bicarbonate solution several times. The normal drying procedure(saturated NaCl solution, MgSO4) followed by evaporation of solvent gave 19.5 g (93 % yield) of dark yellowish liquid. This was used for next step without further purification.

^{1}H NMR($CDCl_3$); δ 1.40(6H, d), 4.65(1H, septet), 6.94-7.00(2H, m), 7.50(1H, t), 7.55(1H, d)

(b) 2-isopropoxybenzoic acid

A solution of 17 g of potassium hydroxide(0.30 mole) in 150 ml of ethylene glycol was mixed with 19.5 g of 2-isopropoxybenzonitrile(0.12 mole) in a 250 ml round bottomed flask. The solution was heated at 150-150 °C for six hours. The reaction mixture was cooled, diluted with 150 ml of water, and extracted with ether. The ether layer was washed with water several times. The combined aqueous phases were acidified with concentrated hygrochloric acid and extracted with benzene several times. The benzene extracts were washed successively with water and saturated sodium chloride solution, then dried over $MgSO_4$. Evaporation of solvent gave 20 g of yellowish liquid.(93 %) This was used for next step without further purification.

^{1}H NMR($CDCl_3$); δ 1.49(6H, d), 4.88(1H, septet), 7.05(1H,d), 7.11(1H, t), 7.55(1H, t), 8.19(1H, d)

(c) 2-isopropoxybenzy lalcohol

A solution of 2-isopropoxybenzoic acid (20 g, 0.11 mole) in 150 ml anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride(5.3 g, 0.14 mole) in 50 ml anhydrous ether at room temperature under argon atmosphere. The resulting mixture was refluxed overnight, cooled to room temperature, and the excess lithium aluminum hydride decomposed by careful addition of methanol. Acidic workup afforded 16.5 g of yelloswish oil.(90 %) This was used for next step without further purification.

^{1}H NMR($CDCl_3$); δ 1.38(6H, d), 4.64(1H, septet), 4.67(2H, s), 6.88-6.95(2H,m), 7.21-7.28(2H, m)

(d) 2-isopropoxybenzyl chloride

A solution of 2-isopropoxybenzyl alcohol(16.5 g, 0.10 mole) in benzene was added to a stirred solution of thionyl cloride (18 g, 0.15 mole) in benzene. The solution was refluxed under argon for 4 hours, cooled to room temperature, and poured into distilled water. The layers were separated and the aqueous phase extracted with ether. The organic layers were combined, washed with saturated sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed on a rotary evaporator to afford 17.5 g of product as a brownish oil.(95 %) This was used for next step without further purification.

^{1}H NMR($CDCl_3$); δ 1.39(6H, d), 4.62(1H, septet), 4.67(2H, s), 6.88-6.95(2H,m), 7.25-7.40(2H, m)

(e) α-(2-isopropoxyphenyl)acetonitrile

A mixture of sodium cyanide(6.4 g, 0.13 mole) in 120 ml dimethylsulfoxide was heated at 80 ^{o}C until all the sodium cyanide had dissolved. 2-isopropoxybenzyl chloride(17.5 g, 0.095 mole) was added to this solution and the mixture was stirred at this temperature for 6 hrs. The mixture was cooled to room temperature and poured into 200 ml distilled water. The resulting solution was extracted with ether and the ether layer was washed with distilled water several times, and dried($MgSO_4$). The solvent was removed on a rotary evaporator to afford 13.7 g of product as a brownish oil. (83 %)

^1H NMR($CDCl_3$); δ 1.38(6H, d), 3.68(2H, s), 4.61(1H, septet), 6.89(1H, d), 6.92(1H,t), 7.24-7.38(2H, m)

(f) α-(2-isopropoxy)phenylacetophenone

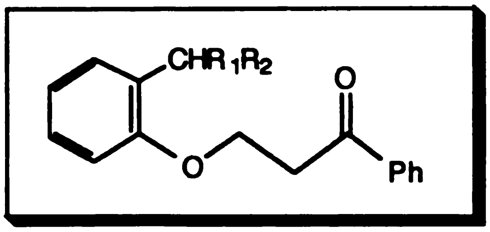
A solution of α-(2-isopropoxyphenyl)acetonitrile(7 g, 0.04 mole) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 1.2 g of magnesium turnings and 7 g of bromobenzene in 100 ml anhydrous ether) under an argon atmoshere at room temperature. The resulting mixture was refluxed under argon for 7 hrs. The resulting milky heyerogeneous solution was cooled to room temperature and extracted with hydrochloric acid(conc. HCl/water was approximately 1 in volume). Ether layer(A) and aqueous layer(B) were separated and extra amount (50 ml) of conc. HCl was added to each layer. Each layer was refluxed separately overnight. After regular workup(ether extraction, $NaHCO_3$ wash and drying with $MgSO_4$), the solution B gave quite a pure compound according to NMR, which was further purified by column chromatography using 3 % ethyl acetate in hexane. Same workup of solution A resulted in dark brown oil, which contained a lot of compounds including the desired product. The product was isolated by column chromatography using 3 % ethyl acetate in hexane. After the solvent was evaporated, colorless liquid was obtained. The combined yield was 5.2 g.(51 %)

^1H NMR($CDCl_3$); δ 1.21(6H, d, J = 6 Hz), 4.21(2H, s), 4.53(1H, septet, J = 6 Hz), 6.84(1H, d, J = 8.5 Hz), 6.87(1H, dt, J = 7.5, 1.1 Hz), 7.15-7.22(2H, m), 7.42(2H, distorted t), 7.52(1H, tt, J = 7.2, 1.4 Hz), 8.02(2H, distorted d)

^{13}C NMR($CDCl_3$); δ 21.8, 40.0, 69.8, 112.7, 120.4, 125.0, 128.3, 128.6, 128.7, 131.4, 133.0, 137.4, 155.5, 198.9

IR(CCl_4): 3069, 3031, 2980, 2934, 1700, 1684, 1491, 1244, 1121 cm^{-1}

Mass: 254.1310; Calc. 254.1307(M^+); Molecular Formular($C_{17}H_{18}O_2$)



β-(2-isopropylphenoxy)propiophenone

A 100 ml round bottomed flask was charged with β-chloropropiophenone(2 g, 0.012 mole), K_2CO_3(3.32 g, 0.024 mole) and 2-isopropylphenol(1.62 g, 0.012 mole) in benzene. This mixture was stirred for 2-3 days at room temperature. The resulting solution was extracted with ether and the ether layer was washed with saturated aq.NaCl solution. The solution was further dried by MgSO4 and the solvent was evaporated to give yellowish oil. The regular crystallization procedure using 95 % ethanol gave yellowish powder. This powder was further purified by recryatallization with i-propanol/water mixture to give 2.1 g of white powder.(66 % yield)

m.p. (49.5-51 ^{o}C)

^{1}H NMR($CDCl_3$): δ 1.12(6H, d, J = 6.9 Hz), 3.19(1H, septet, J = 6.9 Hz), 3.47(2H, t, J = 6.5 Hz), 4.42(2H, t, J = 6.5 Hz), 6.90(1H, d, J = 7.7 Hz), 6.92(1H, t, J = 7.4 Hz), 7.15(1H, t, J = 7.7 Hz), 7.18(1H, d, J = 7.4 Hz), 7.48(2H, distorted t), 7.58(1H, tt), 8.01(2H, distorted d)

^{13}C NMR($CDCl_3$): δ 22.6, 26.7, 38.2, 63.7, 111.3, 120.8, 126.0, 126.5, 128.2, 128.6, 133.3, 136.95, 137.04, 155.7, 198.1

IR(CCl_4): 3067, 3036, 2963, 2870, 1688, 1493, 1449, 1240, 1211 cm^{-1}

Mass: 268.14629(M$^+$); Calc. 268.1464(M$^+$); Molecular Formular($C_{18}H_{20}O_2$)

β-(2-benzylphenoxy)propiophenone

This compound was prepared following the same procedure used to prepare β-(2-isopropylphenoxy)propiophenone. After recrystallization with ethanol twice, white powder was obtained with typical yield 30 - 40 %. (m. p. = 62-63 °C)

^{1}H NMR(CDCl$_3$): δ 3.35(2H, t, 6.3 Hz), 3.87(2H, s), 4.40(2H, t, 6.3 Hz), 6.85(1H, dt, 1.2 Hz, 7.5 Hz), 6.92(1H, d, 8.4 Hz), 7.02-7.10 (7H, m), 7.45(2H, distorted triplet), 7.57(1H, tt), 7.95(2H, distorted d)

^{13}C NMR(CDCl$_3$): δ 36.1, 38.1, 63.6, 111.5, 120.7, 125.7, 127.5, 128.1(2 carbons), 128.6, 128.9, 129.8, 130.4, 133.3, 136.8, 141.0, 156.4, 197.9

IR(CCl$_4$): 3065, 3031, 2913, 1688, 1493, 1453, 1244, 1211 cm^{-1}

Mass: 316.14568(M$^+$); Calc. 316.1464(M$^+$); Molecular Formular($C_{22}H_{20}O_2$)

β-(2-ethylphenoxy)propiophenone

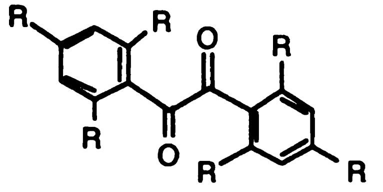
A 100 ml round bottomed flask was charged with β-chloropropiophenone(8.3 g, 0.05 mole), K_2CO_3(14 g, 0.1 mole) and 2-ethylphenol(6 g, 0.05 mole) in benzene. This mixture was stirred for 3 days at room temperature. The resulting solution was extracted with ether and the ether layer was washed with saturated aq.NaCl solution. The solution was further dried by MgSO4 and the solvent was evaporated to give yellowish oil. The regular crystallization procedure using 95 % ethanol gave white powder.(m. p. = 54 - 55 °C)

^{1}H NMR(CDCl$_3$) 300 MHz(Gemini); δ 8.03-7.99(2H, dstorted d, J = 7 Hz), 7.58(1H,tt, J=7.1 Hz, J= 1.4 Hz), 7.50-7.45(2H, distorted t), 7.18-7.10(2H, m), 6.91-6.86(2H,m), 4.42(2H, t, J= 6.6 Hz), 3.46(2H, t, J= 6.6 Hz), 2.53(2H, q, J=7.5 Hz), 1.09(3H, t, J= 7.5Hz)

^{13}C NMR(CDCl$_3$) 300 MHz(Gemini); δ 198.5, 137.2, 133.5, 133.0, 129.2, 128.8, 128.4, 126.9, 120.9, 111.3,63.5, 38.1, 23.1, 13.9

IR(CCl_4): 3065, 3040, 2967, 2934, 2876, 1688, 1495, 1453, 1242, 1211 cm^{-1}

Mass: 254.13051(M^+); Calc. 254.1307(M^+); Molecular Formular($C_{17}H_{18}O_2$)



R = Me, Et, i-Pr

or t-bu

2,4,6,2',4',6'-hexaisopropylbenzil, 2,4,6,2',4',6'-hexamethylbenzil, 2,4,6,2',4',6'-hexaethylbenzil, 2,4,6,2',4',6'-hexa-tert-butylbenzil were gifts from Prof. Zvi Rappoport of Hebrew University in Jerusalem.

2,4,6,2',4',6'-hexaisopropylbenzil

m. p.: 152 - 153 °C, orange colored powder.

^{1}H NMR($CDCl_3$): δ 1.13(24H, d, J = 6.8 Hz), 1.23(12H, d, J = 6.9 Hz), 2.88(2H, septet, J = 6.9 Hz), 2.59(4H, septet, J = 6.8 Hz), 7.01(4H, s)

^{13}C NMR($CDCl_3$): δ 23.9, 24.0, 32.0, 34.4, 121.2, 132.2, 145.8, 150.9, 200.8

2,4,6,2',4',6'-hexamethylbenzil

m. p. : 118 - 119 °C, orange colored powder.

^{1}H NMR(C_6D_6): δ 2.04(6H, s), 2.16(12H, s), 6.61(4H, s)

^{13}C NMR($CDCl_3$): δ 20.1, 21.2, 128.8, 133.6, 135.4, 140.1, 197.4

2,4,6,2',4',6'-hexaethylbenzil

m. p. : 75 - 76 °C, orange colored powder.

^{1}H NMR(C_6D_6): δ 1.12(6H, t, J = 7.5 Hz), 1.14(12H, t, J = 7.5 Hz), 2.46(4H, quartet, J = 7.5 Hz), 2.57(8H, quartet, J = 7.5 Hz), 6.83(4H, s)

^{1}H NMR(CD_3OD): δ 1.11(6H, t, J = 7.5 Hz), 1.25(12H, t, J = 7.5 Hz), 2.43(4H, quartet, J = 7.5 Hz), 2.65(8H, quartet, J = 7.5 Hz), 7.0(4H, s)

2,4,6,2',4',6'-hexa-tert-butylbenzil

m. p. : 204 - 205 °C, light ivory colored powder.

^{1}H NMR(C_6D_6): δ 1.03(18H, broad s), 1.28(18H, s), 1.65(18H, broad s), 7.33(2H, broad s), 7.60(2H, broad s)

^{1}H NMR($CDCl_3$): δ 0.87(18H, broad s), 1.30(18H, s), 1.48(18H, broad s), 7.20(2H, broad s), 7.45(2H, broad s)

o-tert-amylbenzophenone

o-tert-amylbenzophenone was prepared by Dr. R. Pabon.

o-ethoxybenzophenone

(1) o-ethoxybenzonitrile

A 250 ml round bottomed flask was charged with K_2CO_3(11.6 g, 0.084 mol), ethyl bromide(90 g, 0.83 mol) and o-hydroxybenzonitrile(10 g, 0.084 mol) in DMF. The mixture was stirred vigorously at 30-40 °C for 3-4 days. After cooled to room temperature, the mixture was poured into ice cold water in a separatory funnel. The organic layer was washed with distilled water and saturated sodium bicarbonate solution several times. After the organic layer was washed with saturated NaCl solution, the solution was dried over $MgSO_4$ and was concentrated to give yellowish oil(12 g, 97.6 % yield).

(2) o-ethoxybenzophenone

A solution of o-ethoxybenzonitrile(12 g, 0.082 mol) in 25 ml anhydrous ether was added dropwise to stirred solution of phenyl magnesium bromide(prepared from 2.4 g of magnesium turnings and 15.4 g of bromobenzene in 100 ml anhydrous ether) under an argon atmoshere at room temperature. The resulting mixture was refluxed under argon for 5 hrs. The mixture was cooled to room temperature and was poured into ice cold water. The aqueous layer was separated and acidified with 10 % HCl. The solution was heated overnight at 80-90 ^{o}C. The solution was allowed to cool to room temperature and 200 ml of ether was added. Two layers were separated and the aqueous layer was extracted with ether three times. The combined organic layer was washed with distilled water, saturated sodium bicarbonate solution and NaCl solution. After it was dried over $MgSO_4$, solvent was evaporated to give a yellowish oil The crude product was distilled at reduced pressure (B.P.= 128-130 ^{o}C) and the resulting oil was recrystallized over ethanol to give colorless solid. (M.P.; 38.5-39.0 ^{o}C)

IR(CCl_4): 3065, 3034, 2986, 1669(C=O) cm^{-1}

^{1}H NMR($CDCl_3$): δ 1.04(3H, t, J = 7 Hz), 3.92(2H, q, J = 7 Hz), 6.94(1H, d, J = 8.4 Hz), 7.01(1H, td, J = 0.9, 7.4 Hz), 7.36-7.46(4H, m), 7.51(1H, tt, J = 2.2, 7.1 Hz), 7.77(2H, distorted d)

^{13}C NMR($CDCl_3$): δ 13.0, 63.9, 112.6, 120.6, 128.2, 129.3, 129.7, 129.9, 132.2, 132.8, 138.5, 157.1, 197.2

Mass: MH$^+$ = 227.10715; Calc. 227.1072(MH$^+$);Molecular Formular($C_{15}H_{15}O_2$)

V. Identification of photoproducts.

All samples for kinetic measurements were irradiated in parallel with actinometer solutions in a merry-go-round apparatus immersed in a water bath at approximately 25 ^{o}C. A water cooled Hanovia medium pressure mercury lamp was used as the irradiation source. An alkaline potassium chromate solution (0.002 M K_2CrO_4 in 1 % aqueous potassium carbonate, 1 cm path length) was used to isolate the 313 nm emmission band. A Corning CS 7-37 Filter was used for 365 nm emission band. 436 nm emission was obtained by a uranium glass filter sleeve and a 1 cm thickness of the following solution: 20 g of $CuSO_4$, 25 g of $NaNO_2$ and 34 ml of concentrated ammonium hydroxide diluted into 500 ml.

For quantum yield measurement using NMR, the NMR tubes containing samples were fixed into13 x 100 mm Pyrex culture tubes using corks and were irradiated in merry-go-round apparatus. If a wavelength other than 313 nm was required, the corresponding filter solution was added to the culture tubes.

NMR tube scale irradiation was done as follows; A NMR tube containing sample solution (0.01 - 0.02 M in 0.75 ml of deuterated solvents) was degassed by bubbling argon through for 10 minutes. The NMR tube was attached to an immersion well by wire and was irradiated.

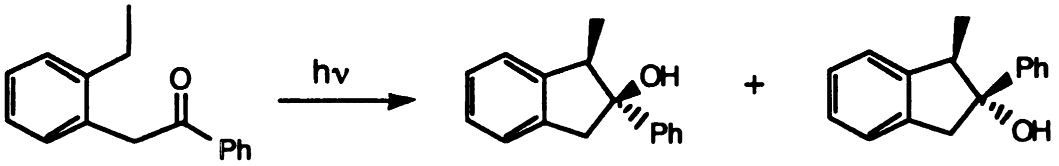
Preparative scale irradiation was done in two different ways. A large test tube containing sample solution(0.01 -0.02 M in 70 - 100 ml) was fitted with a 24/40 rubber septum and the sample was degassed by bubbling argon through for 10 min. or throughout the irradiation. The test tube was attached to an immersion well by wire and was irradiated. For the larger scale reaction(0.01 - 0.02 M in 250 ml), photolysis was done in an immersion well equipped with a quartz cooling jacket, a water cooling condenser. Hanovia 450 W medium pressure lamp with a Pyrex filter tube was used as a light source and argon was bubbled throughout the irradiation.

Irradiation in solid state was performed in two different ways; If a sample can be obtained as a large single crystal, the sample was irradiated in a test tube or a sample vial by attaching it to an immersion well. After irradiation, the sample was quickly extracted with a few drops of any given solvent. If a sample is in powder form or small crystals, the sample was packed into a melting point capillary tube and the tube was inserted into a test tube. This sample was irradiated by attaching it to an immersion well. The irradiated capillary tube containing a sample was broken into pieces and it was extracted with a deuterated solvent.

Products from α-(o-ethylphenyl)acetophenone

α-(o-ethylphenyl)acetophenone((0.0028 g) in 0.75 ml of benzene-d6 was irradiated for 20 minutes. Two isomeric photoproducts were formed in ca. 20 to 1 in favor of an isomer with a methyl doublet at 1.18 ppm over the other one with a methyl doublet at 0.84 ppm. A similar solution in dioxane-d_8 was irradiated to 90 % conversion. The Z and E methyl groups appeared at 1.16 and 0.75 ppm, respectively, in a 4.6 to 1 ratio.

α-(o-ethylphenyl)acetophenone(0.1 g) in methanol(70 ml) was irradated in a test tube until 100 % ketone conversion by GC. The solvent was removed and the resulting oil was chromatographed by preparative TLC using 3 % ethyl acetate in hexane. Two major components(>95 %) were isolated as colorless oil and these were identified as two isomeric 1-methyl-2-phenyl-2-indanols by their spectroscopic data.



Z-1-methyl-2-phenyl-2-indanol

^{1}H NMR(C_6D_6): δ 1.18(3H, d, J= 6.9 Hz), 2.97, 3.34((2H, AB quartet, J = 16.3 Hz), 3.39(1H, quartet, J = 6.9 Hz), 7.07-7.30(7H, m), 7.48(2H, d, J = 7 Hz)

^{1}H NMR(CDCl$_3$): δ 1.16(3H, d, J= 6.9 Hz), 3.05, 3.39((2H, AB quartet, J = 16.3 Hz), 3.47(1H, quartet, J = 6.9 Hz), 7.18-7.30(5H, m), 7.37(2H, t, J = 7 Hz), 7.60(2H, d, J = 7 Hz)

^{13}C NMR(CDCl$_3$): δ 10.31, 49.31, 50.39, 85.44, 121.69, 124.87, 125.36, 126.95, 127.01, 127.06, 128.17, 140.09, 144.14, 145.0

IR(CCl$_4$): 3596, 1170 cm^{-1}

E-1-methyl-2-phenyl-2-indanol

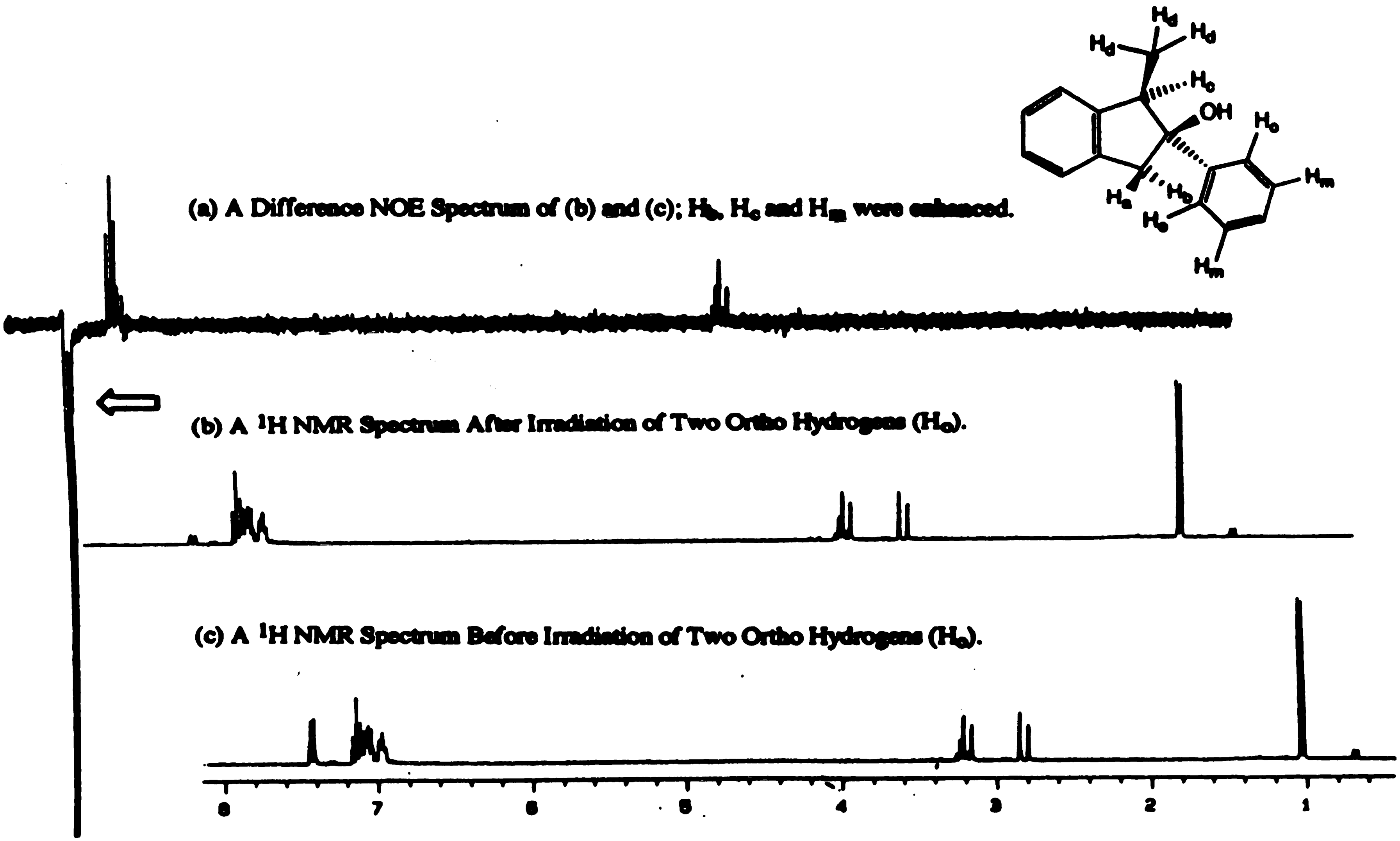
^{1}H NMR(CDCl$_3$): δ 0.72(3H, d, J= 6.8 Hz), 3.10, 3.68((2H, AB quartet, J = 15.9 Hz), 3.22(1H, quartet, J = 6.8 Hz), 7.21(4H, m), 7.29(1H, m), 7.34(2H, t, J = 6.5 Hz), 7.45(2H, d, J = 6.3 Hz)

^{13}C NMR(CDCl$_3$): δ 17.63, 44.58, 52.39, 86.10, 124.34, 124.88, 126.16, 126.92, 126.97, 127.36, 128.16, 140.1, 141.2, 146.7

IR(CCl$_4$): 3603, 3450(br.), 1050 cm^{-1}

NOE experiment was done using Varian 500 MHz NMR with samples in CDCl$_3$. Doublets at 7.4(E isomer) and 7.6 ppm(Z isomer) that corespond to the two ortho hydrogens on the 2-phenyl group were irradiated. The result of this experiment is shown in Figure 8 and 9.

An NMR experiment with a shift reagent was performed on Varian 300 MHz Gemini instrument. A shift reagent, Eu(dpm)3, was added to E- and Z- 1-methyl-2-phenyl-2-indanol in 0.75 ml of CDCl$_3$ up to 0.0040 g. The maximum downfield shifts recorded for the 2-phenyl ortho protons, the methyl, the methine, the upfield CH2, and the downfield CH2 were as follows; for Z, 0.30, 0.36, 0.25, 0.40, 0.25 ppm; for E, 0.85, 0.56, 1.40, 1.25, 0.78 ppm. The E isomer complexed with this shift reagent about ten times more strongly than did the Z.

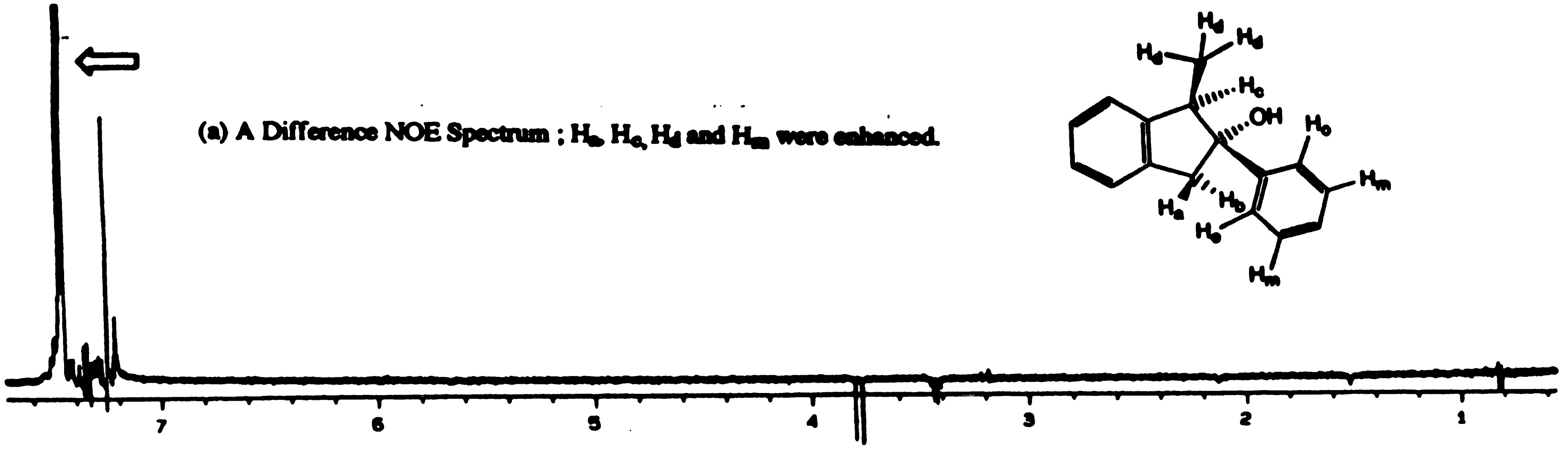


(a) A Difference NOE Spectrum of (b) and (c); H_b, H_c and H_m were enhanced.

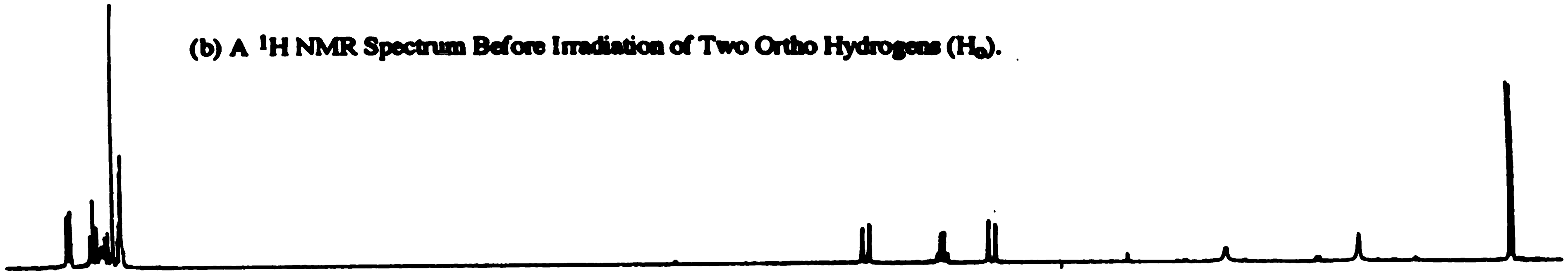
(b) A ^1H NMR Spectrum After Irradiation of Two Ortho Hydrogens (H_o).

(c) A ^1H NMR Spectrum Before Irradiation of Two Ortho Hydrogens (H_o).

Figure 8. NOE Experiment of Z-1-methyl-2-phenyl-2-indanol in $CDCl_3$



(a) A Difference NOE Spectrum ; H_b, H_c, H_d and H_m were enhanced.

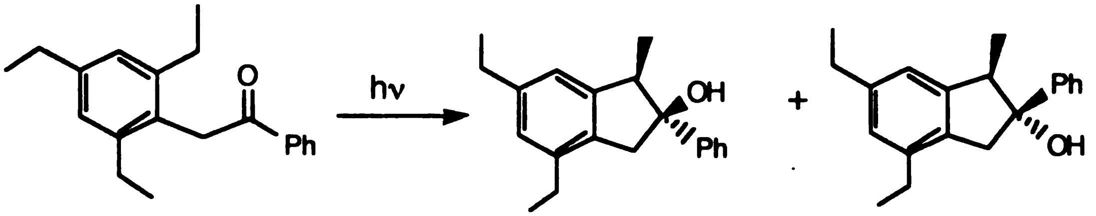


(b) A ^1H NMR Spectrum Before Irradiation of Two Ortho Hydrogens (H_o).

Figure 9. NOE Experiment of E-1-methyl-2-phenyl-2-indanol.in CDCl3

Products from α-(2,4,6-triethylphenyl)acetophenone

α-(2,4,6-triethylphenyl)acetophenone(0.02 g) in benzene (10 ml) was irradated until 100 % ketone conversion by GC. After the solvent was evaporated, the resulting oil was mixed into 0.75 ml of $CDCl_3$. Two isomeric products were identified by the NMR spectra of the crude product. The product ratio was taken from integration of methyl doublet of each isomer in NMR. NMR data of E isomer had to be collected from photolysis in deuterated methanol because Z to E ratio was much smaller in methanol than in benzene.



Z-1-methyl-4,6-diethyl-2-phenyl-2-indanol

^1H NMR($CDCl_3$): δ 1.25(3H, d, J= 7.2 Hz), 1.22(3H, t, J = 7.5 Hz), 1.28(3H, t, J = 7.5 Hz), 1.85(1H, broad s), 2.60(2H, quartet, J=7.5 Hz), 2.67(2H, quartet, J = 7.5 Hz), 3.15, 3.36((2H, AB quartet, J = 18.0 Hz), 4.00(1H, quartet, J = 7.2 Hz), 6.92(1H, s), 6.95(1H, s)

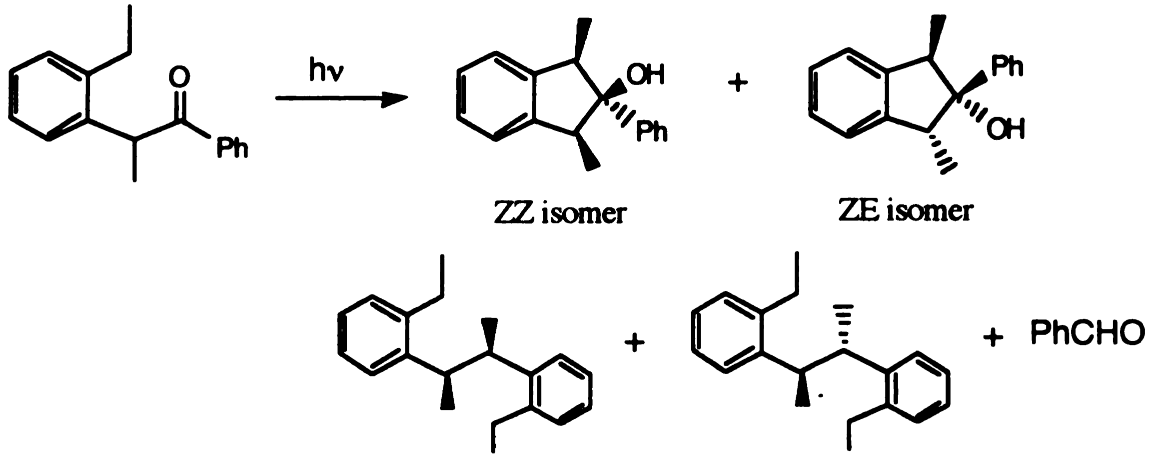
E-1-methyl-4,6-diethyl-2-phenyl-2-indanol

^1H NMR(CD_3OD): δ 0.75(3H, d, J= 7.2 Hz), 1.20(3H, t, J = 7.5 Hz), 1.22(3H, t, J = 7.5 Hz), 2.55-2.65(4H, m, This region could not be resolved due to overlap with major isomer.), 3.14, 3.58((2H, AB quartet, J = 18.0 Hz), 3.34(1H, quartet, J = 7.2 Hz), 6.82(1H, s), 6.85(1H, s)

Products from α-(o-ethylphenyl)propiophenone

α-(o-ethylphenyl)propiophenone(0.0020 g) in benzene-d_6(0.75 ml) was irradated for 15 min. The NMR showed the appearance of mixture of several products including benzaldehyde. The ratio of two isomeric products was about 5 to 1 in favor of the isomer with a methyl doublet at 1.19 ppm. The ratio was determined based on the integration of methyl doublets. Since it was hard to identify each product in the mixture, preparative scale photolysis was performed to isolate each product.

α-(o-ethylphenyl)propiophenone(0.1 g) in benzene(70 ml) was irradated until 100 % ketone conversion by GC. The solvent was removed and the resulting oil was subjected to column chromatography using 3 % ethyl acetate in hexane. Four major products were isolated and identified based on ^{1}H NMR data of each product.



Z,Z-1,3-dimethyl-2-phenyl-2-indanol

^{1}H NMR(CDCl$_3$):δ 1.19(6H, d, J = 7.1 Hz), 1.52(1H, broad s, -OH), 3.53(2H, quartet, J = 7.1 Hz), 7.17-7.20(2H, m), 7.25-7.32(3H, m), 7.38(2H, distorted t), 7.61(2H, distorted d)

Z,E-1,3-dimethyl-2-phenyl-2-indanol

^{1}H NMR($CDCl_3$):δ 0.75(3H, d, J = 7.1 Hz), 1.34(3H, J = 7.1 Hz), 3.27(1H, quartet, J = 7.1 Hz), 3.92(1H, quartet, J = 7.1 Hz), 7.10-7.30(5H, m), 7.36(2H, distorted t), 7.52(2H, distorted d); When the peak at 0.75 ppm was irradiated, the quartet at 3.27 ppm was decoupled.

E-1,2-di(2-ethylphenyl)-1,2-dimethylethane

^{1}H NMR($CDCl_3$):δ 1.07(6H, t, J = 7.4 Hz), 1.32(6H, distorted d, J = 6.5 Hz), 2.35, 2.58(4H, quartet of AB quartet, J = 14.4 Hz, 7.4 Hz), 3.29(2H, complicated but symmetrical 8 or 10 lines), 6.90-7.06(5H, m), 7.21(3H, m)

Z-1,2-di(2-ethylphenyl)-1,2-dimethylethane

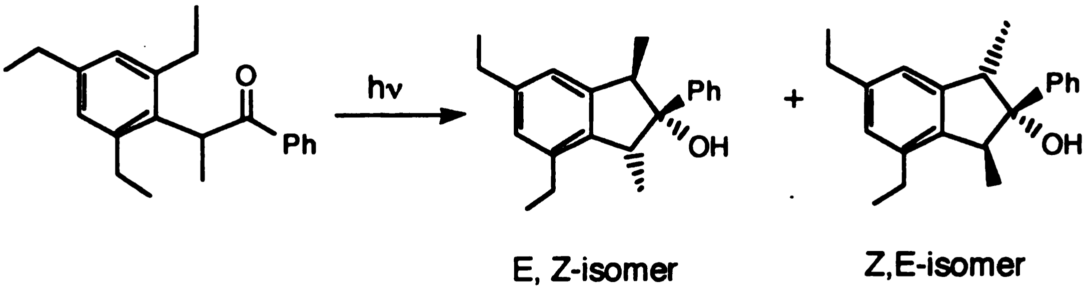
^{1}H NMR($CDCl_3$):δ 0.96(6H, t, J = 6.5Hz), 1.26(6H, distorted d, J = 7.5 Hz), 2.69, 2.83(4H, quartet of AB quartet, J = 14.3 Hz, 7.5 Hz), 3.26(2H, broad singlet with fine couplings), 7.14 - 7.50(5H, m), 7.59(3H, m)

Products from α-(2,4,6-triethylphenyl)propiophenone

α-(2,4,6-triethylphenyl)propiophenone(0.0022 g) in 0.75 ml of benzene-d_6 was irradiated for 10 min. Two major products were shown in ^{1}H NMR spectra and they were identified as two isomeric 1,3-dimethyl-4,6-diethyl-2-phenyl-2-indanols. No other products were present in the ^{1}H NMR. The ratio of these two isomeric products was 55 to 45 in favor of the isomer with methyl doublets at 0.85 and 1.33 ppm in $CDCl_3$, judging from the integration of methyl doublets.

α-(o-2,4,6-triethylphenyl)propiophenone(0.0022 g) was also irradiated in 0.75 ml of CD_3OD. After 10 minutes' irradiation, all the starting material turned into one major product (94.4 %) with small amount of other isomeric product(5.6 %). This isomer is the one with a methyl doublets at 0.85 and 1.33 ppm in $CDCl_3$. Using NMR data of this predomint photoproduct, NMR peaks for the other isomer could be differentiated from ^{1}H NMR of two photoproducts in benzene.

In order to compare photoproducts in two different solvents, benzene-d_6 and methanol-d_4 were evaporated and $CDCl_3$ was added into each tubes. ^{1}H NMR spectra of two samples were taken and they turned out to be the same products.



Z,E-1,3-dimethyl-4,6-diethyl-2-phenyl-2-indanol

^{1}H NMR(C_6D_6): δ 0.90(3H, d, J= 7.2 Hz), 1.06-1.21(The peaks in this region could not be assigned because of overlapping peaks from both isomers), 2.30-2.60(The peaks in this region could not be assigned because of overlapping peaks from both isomers), 3.20(1H, quartet, J=7.2 Hz), 3.35(1H, quartet, J = 7.2 Hz), 6.70(1H, s), 6.89(1H, s), 6.95-7.50(5H, m)

^{1}H NMR($CDCl_3$): δ 0.85(3H, d, J= 7.2 Hz), 1.22(3H, t, J = 7.6 Hz), 1.27(3H, t, J = 7.6 Hz), 1.33(3H, d, J = 7.2 Hz), 2.60(2H, quartet, 7.6 Hz), 2.69(2H, m), 3.46(1H, quartet, J=7.2 Hz), 3.56(1H, quartet, J = 7.2 Hz), 6.73(1H, s), 6.90(1H, s), 7.16-7.26(5H, m)

^{1}H NMR(CD_3OD, 500 MHz): δ 0.81(3H, d, J= 7.2 Hz), 1.20(3H, t, J = 7.6 Hz), 1.25(3H, t, J = 7.6 Hz), 1.30(3H, d, J = 7.2 Hz), 2.59(2H, quartet, 7.6 Hz), 2.68(2H, quartet of AB quartet, 7.6, 14.5 Hz), 3.42(1H, quartet, J=7.2 Hz), 3.50(1H, quartet, J = 7.2 Hz), 6.67(1H, s), 6.91(1H, s), 7.10-7.20(5H, m)

E,Z-1,3-dimethyl-4,6-diethyl-2-phenyl-2-indanol

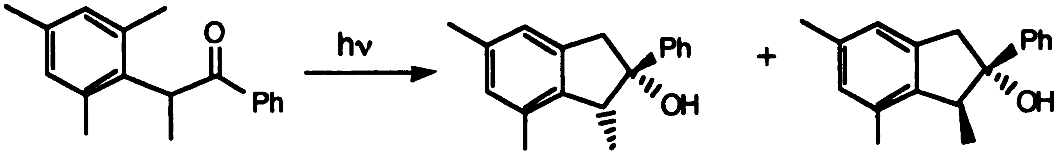
^{1}H NMR(C_6D_6): δ 0.65(3H, d, J= 7.2 Hz), 1.06-1.21(The peaks in this region could not be assigned because of overlapping peaks from both isomers), 2.30-2.60(The peaks in this region could not be assigned because of overlapping peaks from both isomers), 3.35(1H, quartet, J = 7.2 Hz), 3.72(1H, quartet, J = 7.2 Hz), 6.87(2H, broad s), 6.9-7.5(5H, m)

^{1}H NMR($CDCl_3$): δ 0.70(3H, d, J= 7.2 Hz), 1.250(3H, t, J = 7.5 Hz), 1.251(3H, t, J = 7.5 Hz), 1.33(3H, d, J =7.2 Hz), 2.65(2H, quartet, J = 7.5 Hz), 2.52-2.63(2H, m), 3.28(1H, quartet, J=7.2 Hz), 3.95(1H, quartet, J = 7.2 Hz), 6.92(2H, broad s), 7.2-7.4(3H, m), 7.57(2H, distorted d)

Products from α-mesitylpropiophenone

α-Mesitylpropiophenone(0.0028 g) in 0.75 ml of benzene-d_6 was irradiated for 10 min. Two major products were shown in 10 to 1 ratio in favor of the isomer with a methyl doublet at 1.25 ppm in $CDCl_3$ in ^{1}H NMR spectra and they were identified as two isomeric 1,5,7-trimethyl-2-phenyl-2-indanols by comparing them with ^{1}H NMR spectra of these compounds which were reported by Zhou[80]. The compound with a methyl doublet at 1.25 ppm in $CDCl_3$ was assigned as Z isomer. No other products were present in the ^{1}H NMR. α-Mesitylpropiophenone(0.0028 g) was also irradiated in 0.75 ml of CD_3OD. After 10 minutes' irradiation, all the starting material turned into one major product(>99.5 %) with trace amount of other isomeric product. This isomer is the one with a methyl group at 1.25 ppm in $CDCl_3$.

In order to compare photoproducts in two different solvents, benzene-d_6 and methanol-d_4 were evaporated and $CDCl_3$ was added into each tubes. After comparing the ^{1}H NMR of photoproducts in same solvent, the major product in methanol turned out to be same as the major one in benzene.



Z-isomer E-isomer

Z-1,5,7-trimethyl-2-phenyl-2-indanol

^{1}H NMR(C_6D_6): δ 1.20(3H, d, J = 8.5 Hz), 2.08(3H, s), 2.18(3H, s), 3.13, 3.21(2H, AB quartet, J = 18.6 Hz), 3.32(1H, quartet, J = 8.5 Hz), 6.70(1H, s), 6.72(1H, s), 7.0-7.2(3H, m), 7.48(2H, distorted d)

^{1}H NMR($CDCl_3$): δ 1.25(3H, d, J = 8.5 Hz), 2.30(3H, s), 2.32(3H, s), 3.28, 3.36(2H, AB quartet, J = 18.6 Hz), 3.51(1H, quartet, J = 8.5 Hz), 6.86(1H, s), 6.90(1H, s), 7.20-7.45(3H, m), 7.49(2H, distorted d)

E-1,5,7-trimethyl-2-phenyl-2-indanol

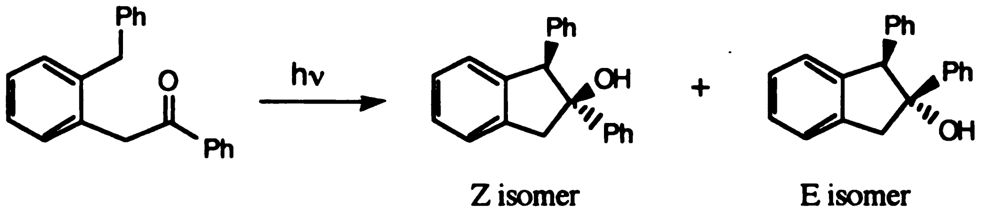
^{1}H NMR(C_6D_6): δ 0.68(3H, d, J = 8.1 Hz), 2.11(3H, s), 2.25(3H, s), 2.72, 3.65(2H, AB quartet, J = 18.6 Hz), A quartet around 3.3 ppm could not be found due to overlapping with peaks for major product, 6.75(1H, s), 6.87(1H, s), 7.0-7.25(3H, m), 7.46(2H, distorted d)

^{1}H NMR($CDCl_3$): δ 0.74(3H, d, J = 8.1 Hz), 2.32(3H, s), 2.35(3H, s), 3.03, 3.88(2H, AB quartet, J = 18.6 Hz), 3.95(1H, quartet, J = 8.1 Hz), 7.03(1H, s), 7.20-7.50(3H, m), 7.60(2H, distorted d); The other singlet at aromatic region could not be found due to overlapping with peaks of other isomer.

Products from α-(o-benzylphenyl)acetophenone

α-(o-benzylphenyl)acetophenone(0.0020 g) in 0.75 ml of benzene-d_6 was irradiated for 10 min. Two major products were shown in ^{1}H NMR spectra and they were identified as two isomeric 1,2-diphenyl-2-indanols. No other products were present in the ^{1}H NMR.

α-(o-benzylphenyl)acetophenone(0.0020 g) was also irradiated in 0.75 ml of methanol-d_4. After 15 minuites' irradiation, almost equal amount of two isomeric products were formed. Again, no other products were present in the ^{1}H NMR. It was hard to assign each peak to the corresponding product because they were formed in almost equal amount in both solvents. Thus, the ketone(0.1 g) in 70 ml benzene was irradiated and two isomeric products were isolated by preparative TLC using 3 % ethyl acetate in hexane.



E-1,2-diphenyl-2-indanol

^{1}H NMR($CDCl_3$): δ 1.75(1H, broad), 3.29, 3.87(2H, AB quartet, J= 16.0Hz), 4.63(1H, s), 6.60(2H, broad d), 6.95-7.10(8H, m), 7.13(1H, d), 7.25(1H, t), 7.33(1H, t), 7.43(1H, d)

^{1}H NMR(CD_3OD):δ 3.27, 3.84(2H, AB quartet, J= 16.0Hz), 4.56(1H, s), 6.59(2H, broad d), 6.90-7.55(The peaks in this region could not be assigned because of overlapping peaks from both isomers)

^{1}H NMR(C_6D_6): δ 1.62(1H, broad), 2.97, 3.58(2H, AB quartet, J= 16.0Hz), 4.50(1H, s), 6.65(2H, broad d), 6.85-7.25(The peaks in this region could not be assigned because of overlapping peaks from both isomers)

Z-1,2-diphenyl-2-indanol

^{1}H NMR($CDCl_3$): δ 1.81(1H, broad), 3.41, 3.68(2H, AB quartet, J= 16.5 Hz), 4.97(1H, s), 7.04-7.07(2H, m), 7.13(1H, d), 7.28-7.42(9H, m), 7.52(2H, d)

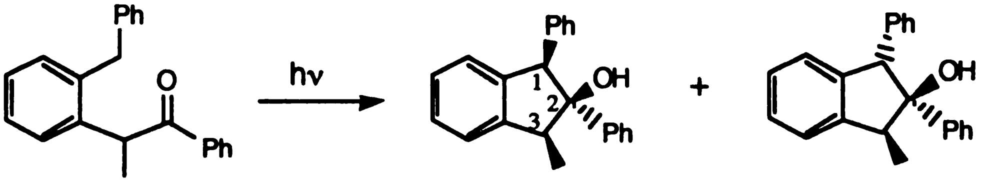
^1H NMR(CD_3OD): δ 3.28, 3.65(2H, AB quartet, J= 16.0Hz), 4.77(1H, s), 6.90-7.55(The peaks in this region could not be assigned because of overlapping peaks from both isomers)

^1H NMR(C_6D_6): δ 3.29, 3.37(2H, AB quartet, J= 16.0Hz), 4.70(1H, s), 6.85-7.25(The peaks in this region could not be assigned because of overlapping peaks from both isomers)

Products from α-(o-benzylphenyl)propiophenone

α-(o-benzylphenyl)propiophenone(0.08 g) in benzene-d_6(0.75 ml) was irradated for 15 min. The NMR showed the appearance of mixture of several products including benzaldehyde. Since it was hard to identify each product in the mixture, preparative scale photolysis was performed to isolate each product.

α-(o-benzylphenyl)propiophenone(0.1 g) in benzene(70 ml) was irradated until 100 % ketone conversion by GC. The solvent was removed and the resulting oil was subjected to preparative TLC using 3 % ethyl acetate in hexane. Four major products were isolated and identified based on ^1H NMR data of each product.



Z,Z isomer

E,Z isomer

Z,Z-1,2-diphenyl-3-methyl-2-indanol

^1H NMR($CDCl_3$): δ 1.30(3H, d), 1.60(1H, s, -OH), 3.69(1H, quartet), 4.98(1H, s), 7.02-7.06(2H, m), 7.13(1H, d), 7.25-7.40(9H, m), 7.52(2H, distorted d)

E,Z-1,2-diphenyl-3-methyl-2-indanol

^{1}H NMR($CDCl_3$): δ 1.35(3H, d), 2.21(1H, broad s, -OH), 3.97(1H, quartet), 4.50(1H, s), 6.52(2H, distorted d), 6.94-7.05(3H, m), 7.11-7.33(7H, m), 7.40(2H, distorted d)

Z-1,2-di(2-benzylphenyl)-1,2-dimethylethane
^{1}H NMR($CDCl_3$): δ 1.17(6H, broad d), 3.22(2H, broad s with fine couplings), 3.67, 3.84(4H, AB quartet), 6.87(2H, d), 6.97-7.08(8H, m), 7.15-7.30(8H, m)

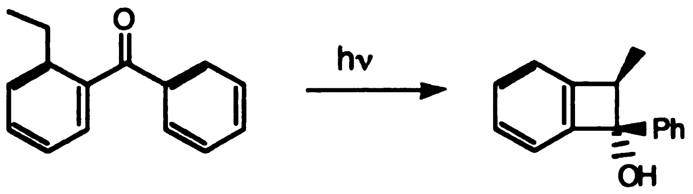
E-1,2-di(2-benzylphenyl)-1,2-dimethylethane
^{1}H NMR($CDCl_3$): δ 0.62(6H, broad d), 3.16(2H, broad s with fine couplings), 4.00, 4.11(4H, AB quartet), 7.00-7.30(18H, m)

Products from α-(2,5-dimethylphenyl)indanone

α-(2,5-dimethylphenyl)indanone (0.0025 g) in benzene-d_6(0.75 ml) was irradiated until completion. Two peaks at 10.02 and 10.11 ppm indicated that there are two compounds with aldehyde functionality. The ratio of the two peaks were 3 to 1 in favor of the peak at 10.11ppm. If cyclization product was formed, it would have shown AB quartets at ca. 3 ppm. But, no AB quartets were shown in the ^{1}H NMR spectra. No attempts were made to isolate the photoproducts.

Product from 2-ethylbenzophenone

2-Ethylbenzophenone(0.0018 g) in 0.75 ml of benzene-d_6 was irradiated for 10 min. All the starting materials disappeared and only one product was formed. This product was identified as E-1-phenyl-2-methylbenzocyclobutenol. After evaporating the benzene-d_6, ^{1}H NMR of the photoproduct was taken in $CDCl_3$.



E-1-phenyl-2-methylbenzocyclobutenol

^{1}H NMR($CDCl_3$): δ 0.90(3H, d, J=7 Hz), 1.60(1H, broad s, -OH), 3.77(1H, q, J=7 Hz), 7.20-7.40(9H, m)

^{1}H NMR(C_6D_6):δ 0.80(3H, d, J=7 Hz), 1.96(1H, broad s, -OH), 3.49(1H, q, J=7 Hz), 6.95-7.18(7H, m), 7.33(2H, d)

A single crystal of p-toluenesulfonic acid was added into E-1-phenyl-2-methylbenzocyclobutenol in benzene-d_6. After 3 days at room temperature, Z to E ratio was 2 to 1.

^{1}H NMR data of the Z isomer was obtained from isomerization by p-toluenesulfonic acid.

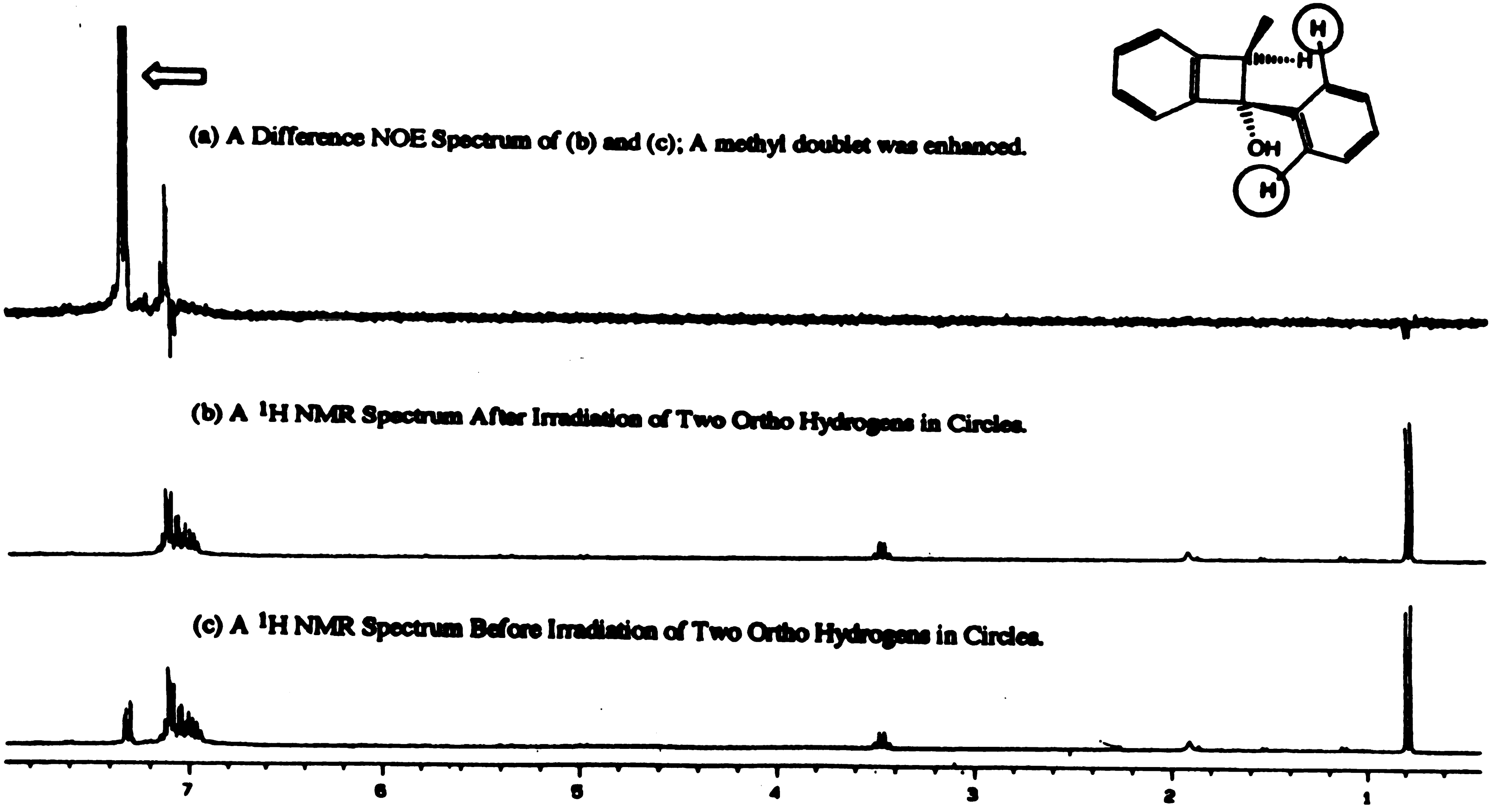
Z-1-phenyl-2-methylbenzocyclobutenol

^{1}H NMR(C_6D_6): δ 1.20(3H, d, J =7 Hz), 3.55(1H, q, J =7 Hz), 6.90-7.18(7H, m), 7.43(2H, d)

2-Ethylbenzophenone(0.0029 g) and maleic anhydride(0.0017 g) in 0.75 ml of benzene-d_6 was irradiated for 20 minutes. One major product was observed in ^{1}H NMR and this product was identified as Diels-Alder adduct between maleic anhydride and dienol from o-ethylbenzophenone. This product was identified by comparing it with a reported spectroscopic data by Pfau.[78]

Trapped product with maleic anhydride

^{1}H NMR($CDCl_3$): δ 1.46(3H, d, J = 7.3 Hz), 2.72(1H, dq, J = 7.3, 8.3 Hz), 3.41(1H, dd, J = 9.6, 8.3 Hz), 4.33(1H, d, J = 9.6 Hz), 7.15-7.55(8H, m), 7.90(1H, d, J = 7.2 Hz)



(a) A Difference NOE Spectrum of (b) and (c); A methyl doublet was enhanced.

(b) A ^{1}H NMR Spectrum After Irradiation of Two Ortho Hydrogens in Circles.

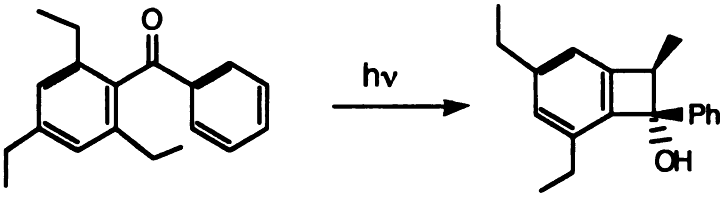
(c) A ^{1}H NMR Spectrum Before Irradiation of Two Ortho Hydrogens in Circles.

Figure 10. NOE Experiment of Z-2-methyl-1-phenyl-benzocyclobutenol in benzene-d_6

NOE experiment was done on 300 MHz Varian NMR. o-Ethylbenzophenone(0.0029 g) in 0.75 ml benzene-d$_6$ was irradiated for 10 min. This sample was used for NOE experiment. Two ortho hydrogens of 1-phenyl group were irradiated and the result is shown in Figure 10.

Products from 2,4,6-triethylbenzophenone

2,4,6-triethylbenzophenone(0.0020 g) in 0.75 ml of benzene-d$_6$ was irradiated for 15 min. Only one product was shown in ^{1}H NMR spectrum and this product was identified as E-1-phenyl-2-methyl-4,6-diethylbenzocyclobutenol. ^{1}H NMR of this product was also taken in CDCl$_3$ after the benzene-d$_6$ was replaced by CDCl$_3$.



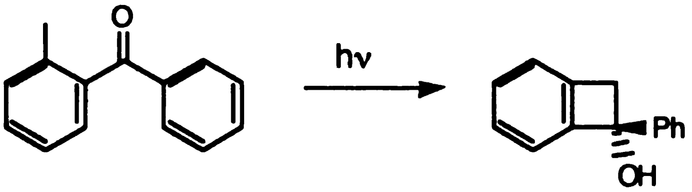
E-1-phenyl-2-methyl-4,6-diethylbenzocyclobutenol

^{1}H NMR(C$_6$D$_6$): δ 0.90(3H, d, J = 7 Hz), 1.10(3H, t, J = 7.4 Hz), 1.21(3H, t, J = 7.4 Hz), 1.95(1H, broad s, -OH), 2.42, 2.50(2H, quartet of AB quartet, J = 7.4, 14.5 Hz), 2.57(2H, quartet, J = 7.4 Hz), 3.43(1H, quartet, J = 7 Hz), 6.80(1H, s), 6.94(1H, s), 7.05-7.20(3H, m), 7.41(2H, distorted d)

^{1}H NMR(CDCl$_3$): δ 0.80(3H, d, J = 7 Hz), 1.15(3H, t, J = 7.4 Hz), 1.25(3H, t, J = 7.4 Hz), 1.52(1H, broad s, -OH), 2.45-2.59(2H, m), 2.65(2H, quartet, J = 7.4 Hz), 3.61(1H, quartet, J = 7 Hz), 6.89(1H, s), 6.99(1H, s), 7.22-7.32(5H, m)

Products from 2-methylbenzophenone

2-Methylbenzophenone(0.0018 g) in 0.75 ml of benzene-d_6 was irradiated for 30 min. One major product was shown in ^{1}H NMR and this product was identified as 1-phenylbenzocyclobutenol.



1-phenylbenzocyclobutenol

^{1}H NMR(C_6D_6): δ 3.23, 3,40(2H, AB quartet, J= 14 Hz), 6.9-7.15(7H, m), 7.50(2H, d)

Products from 2,4,6-trimethylbenzophenone

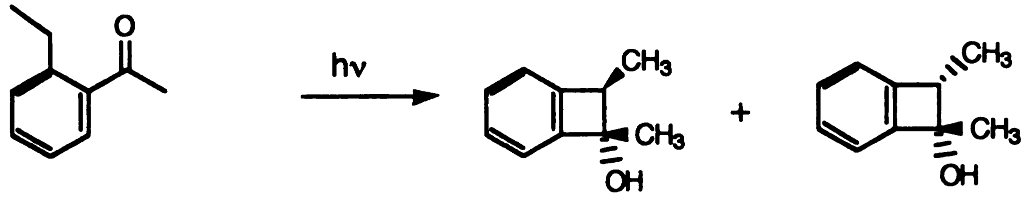
2,4,6-trimethylbenzophenone(0.0022 g) in 0.75 ml of benzene-d_6 was irradiated After 25 minuites' irradiation, ca. 75 % of starting material turned into one major product, which was identified as 1-phenyl-4,6-dimethylbenzocyclobutenol.

1-phenyl-4,6-dimethylbenzocyclobutenol.

^{1}H NMR(C_6D_6): δ 1.98(3H, s), 2.20(3H, s), 3.18, 3,37(2H, AB quartet, J= 14 Hz), 6.72(2H, broad s), 7.0-7.2(3H, m), 7.51(2H, d)

Products from 2-ethylacetophenone

2-Ethylacetophenone(0.0020 g) in 0.75 ml of benzene-d_6 was irradiated. After 15 hrs' irradiation, a complicated ^{1}H NMR spectrum was obtained. Since this spectrum could not be interpreted, isolation of photoproducts was necessary. 0.1 g of 2-ethylacetophenone in 100 ml of benzene was irradiated for one week. After evaporation of the solvent, yellow oil was obtained. The crude reaction mixture was chromatographed through silica gel column using 3 % ethyl acetate in hexane. Two isomeric compounds were isolated and identified as Z and E-1,2-dimethylbenzocyclobutenols. The product ratio was determined from ^{1}H NMR spectrum of crude reaction mixture by integration of two methyl doublets.



E-1,2-dimethylbenzocyclobutenol

^{1}H NMR($CDCl_3$): δ 1.32(3H, d, J=7.4 Hz), 1.50(3H, s), 2.45(1H, broad s, -OH), 3.44(1H, q, J=7.4 Hz), 7.13-7.31(4H, m)

^{13}C NMR($CDCl_3$): δ 14.2, 21.2, 53.4, 79.9, 120.5, 122.6, 127.5, 129.2, 146.5, 149.7

Z-1,2-dimethylbenzocyclobutenol

^{1}H NMR($CDCl_3$): δ 1.30(3H, d, J=7.4 Hz), 1.61(3H, s), 3.48(1H, q, J=7.4 Hz), 7.10-7.30(4H, m)

An NMR sample containing Z- and E--1,2-dimethylbenzocyclobutenol in 3 to 1 ratio in $CDCl_3$ was prepared and 0.0015 g of Eu(dpm)$_3$ was added into the solution. The NMR spectrum of the sample was essentially same as that without shift reagent, except some peaks from the shift reagent. When 0.0070 g of Eu(dpm)$_3$ was added into the sample, two methyl doublets, whose chemical shifts were same for both isomers, were separated by ca. 0.1 ppm. The doublet from Z isomer was shifted more downfield than that from E isomer. Based on this result, the compound, whose methyl doublet shifted more, was assigned as Z isomer.

2-Ethylacetophenone(0.0020 g) and maleic anhydride(0.0017 g) in 0.75 ml of benzene-d_6 was irradiated for 3 hrs. Two major isomeric products(ca. 80 %) were formed with 20 %

of other products. These two products were temporarily assigned as trapped products of dienol intermediates with maleic anhydride based on their ^{1}H NMR spectra. The product ratio was 5 to 4, judging from integration of two methyl doublets. Stereochemical assignment of these two products could not be made.

Trapped product with maleic anhydride(the major product of two in 5 to 4 ratio)

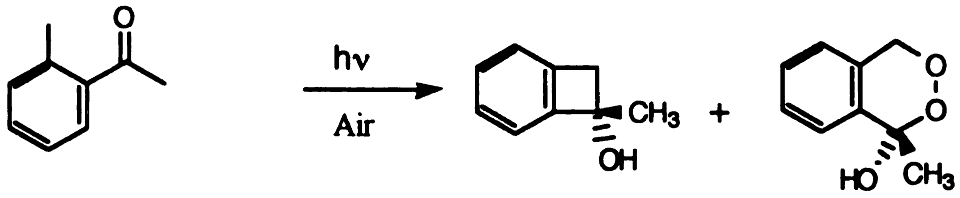
^{1}H NMR(C_6D_6): δ 1.21(3H, d, J = 7 Hz), 1.55(3H, s), 5.21(1H, quartet, J = 7 Hz), 6.68(1H, m), 6.85-7.22(4H, m)

Trapped product with maleic anhydride(the minor product of two in 5 to 4 ratio)

^{1}H NMR(C_6D_6): δ 1.44(3H, d, J = 7 Hz), 1.54(3H, s), 4.64(1H, quartet, J = 7 Hz), 6.54(1H, m), 6.85-7.22(4H, m)

Products from 2-methylacetophenone

2-Methylacetophenone(0.0018 g) in 0.75 ml of benzene-d_6 was irradiated for 3 hours. Two major products were formed in 3 to 1 ratio and these were identified as 1-methylbenzocyclobutenol and oxygen trapped product of dienol intermediate. This type of oxygen trapped product has been observed by Matsuura[36b]. When 0.1 g of 2-methylacetophenone in 80 ml benzene was irradiated with argon purged throughout the reaction, only one product was formed, which was identified as 1-methylbenzocyclobutenol. The solvent was removed and yellow oil was obtained. The crude product was purified by preparative TLC using 3 % ethyl acetate in hexane. The resulting colorless oil soildified upon standing at room temperature.



1-methylbenzocyclobutenol

^{1}H NMR(C_6D_6): δ 1.49(3H, s), 2.91, 3.07(2H, AB quartet, J=14 Hz), 6.85-7.20(4H, m)

^{1}H NMR($CDCl_3$): δ 1.69(3H, s), 1.98(1H, broad s, -OH), 3.24, 3.38(2H, AB quartet, J=14 Hz), 7.15-7.30(4H, m)

^{13}C NMR($CDCl_3$): δ 25.6, 48.3, 78.3, 120.4, 124.0, 127.2, 129.3, 141.1, 151.0

Oxygen trapped product

^{1}H NMR(C_6D_6): δ 1.52(3H, s), 4.32, 5.07(2H, AB quartet, J=14 Hz), 6.85-7.20(4H, m)

<u>Product from 2,4,6-trimethylacetophenone</u>

2,4,6-Trimethylacetophenone(0.0018 g) in 0.75 ml of benzene-d_6 was irradiated for 1 hour. Two major products were formed in 3 to 1 ratio and these were identified as 1,4,6-trimethylbenzocyclobutenol and oxygen trapped product of dienol intermediate. When the irradiation was continued for 3 hours, the ratio of two products were reduced to 1:1, which showed that more oxygen trapped product were formed. In addition to these two products, 15 to 20 % of other product was also shown in ^{1}H NMR, which could not be identified.

1,4,6-trimethylbenzocyclobutenol

^{1}H NMR(C_6D_6): δ 1.55(3H, s), 2.14(3H, s), 2.18(3H, s), 2.90, 3.08(2H, AB quartet, J=14 Hz), 6.69(1H, broad s), 6.70(1H, broad s)

Oxygen trapped product.

^{1}H NMR(C_6D_6): δ 1.60(3H, s), 2.03(3H, s), 2.30(3H, s), 4.45, 5.10(2H, AB quartet, J=14 Hz), 6.20(1H, broad s), 6.68(1H, broad s)

Product from 2,4-dimethyl-6-methoxyacetophenone

2,4-dimethyl-6-methoxyacetophenone (0.0020 g) in 0.75 ml of benzene-d_6 was irradiated for 2 hours. ^{1}H NMR showed that 50 % of the starting material was converted into one product, which was identified as 2'-methoxy-4'-methyl-1-methylbenzocyclobutenol. No other products were apparent in NMR.

2'-methoxy-4'-methyl-1-methylbenzocyclobutenol

^{1}H NMR(C_6D_6): δ 1.49(3H, s), 2.10(3H, s), 2.80, 2.99(2H, AB quartet, J=14 Hz), 3.61(3H, s), 6.46(1H, s), 6.60(1H, s)

Product from 2-methyl-4-methoxyacetophenone

2-methyl-4-methoxyacetophenone (0.0020 g) in 0.75 ml of benzene-d_6 was irradiated. After 3 hours' irradiation, the conversion was ca. 70 % and one major product was formed with less than 5 % of other unidentified product. The major product was identified as 3'-methoxy-1-methylbenzocyclobutenol.

3'-methoxy-1-methylbenzocyclobutenol

^{1}H NMR(C_6D_6): δ 1.52(3H, s), 2.90, 3.05(2H, AB quartet, J =14 Hz), 3.32(3H, s), 6.71(1H, dd), 6.91(1H, d), 7.35(1H, d)

Product from 2,6-dimethyl-4-methoxyacetophenone

2,6-dimethyl-4-methoxyacetophenone (0.0022 g) in 0.75 ml of benzene-d_6 was irradiated. After 3 hours' irradiation, all the starting material disappeared and one major product was formed. ^{1}H NMR showed that less than 10 % of other product was also formed, but this product could not be identified. The major product was identified as 2'-methyl-4'-methoxy-1-methylbenzocyclobutenol

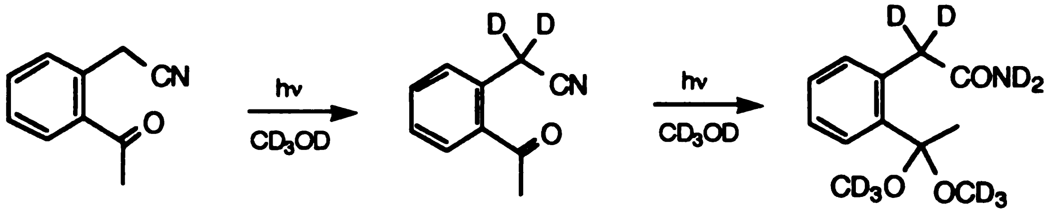
2'-methyl-4'-methoxy-1-methylbenzocyclobutenol

^{1}H NMR(C_6D_6): δ 1.57(3H, s), 2.11(3H, s), 2.88, 3.03(2H, AB quartet, J=14 Hz), 3.37(3H, s), 6.48(1H, s), 6.60(1H, s)

Products from 2-(cyanomethyl)acetophenone

2-(Cyanomethyl)acetophenone(0.0023 g) in methanol-d_4(0.75 ml) was irradiated through pyrex filter and the reaction was monitored by NMR. After 20 minutes, a peak at 4.13 ppm, which corresponded to methylene hydrogens, almost disappeared. Three new singlets at 1.52, 1.67 and 1.70 ppm showed up after 20 minutes' irradiation. As the irradiation continued, the singlet at 1.52 ppm became bigger and bigger. After 3 hours' irradiation, all the peaks at nonaromatic region were eventually replaced by the singlet at 1.52 ppm. At this stage, the product could not be identified, so large scale photolysis was performed. The same ketone(0.1 g) in methanol(70 ml) was irradiated under the same condition. The solvent was evaporated and yellow oil was obtained. The crude product contained only one compound(>95 %). This product was assigned to be o-amidomethylacetophenone methylketal The presence of amido functionality was supported by ^{1}H and ^{13}C NMR spectra of this compound. ^{1}H NMR showed two broad singlets around 6 ppm, which was indicative of NH2 of amide group. Also, ^{13}C NMR showed a peak at 176 ppm, which is the characteristic resonance of carbonyl carbon of amide group[116].

If this compound was connected to column chromatography, deketallization occurred and a new set of peaks appeared in NMR spectrum.



o-amidomethylacetophenone methylketal d10

^{1}H NMR(CD3OD): δ 1.52(3H, s), 7.20-7.28(3H, m), 7.50-7.55(1H, m)

o-amidomethylacetophenone methylketal

^{1}H NMR(CDCl$_3$): δ 1.51(3H, s), 3.20(6H, s), 3.75(2H, s), 5.84, 6.26(2H, broad singlet each), 7.23-7.27(3H, m), 7.50-7.55(1H, m)

^{13}C NMR(CDCl$_3$): δ 25.0, 42.0, 48.5, 103.0, 127.0, 128.0, 128.2, 132.7, 133.0, 140.2, 175.8

Products from α-(2,4,6-trimethylphenyl)-4'-trifluoromethylacetophenone

α-(2,4,6-trimethylphenyl)-4'-trifluoromethylacetophenone(0.0028 g) in 0.75 ml of benzene-d$_6$ was irradiated for 10 minutes. All the starting materials were gone and only one product was formed. This product was identified as 4,6-dimethyl-2-(4'-trifluoromethylphenyl)-2-indanol. After the benzene-d$_6$ was replaced by CDCl$_3$, ^{1}H NMR spectrum of the product was taken.

4,6-dimethyl-2-(4'-trifluoromethylphenyl)-2-indanol

^{1}H NMR(CDCl$_3$): δ 2.22(3H, s), 2.31(3H, s), 3.20, 3.36(2H, AB quartet, J = 16.8 Hz), 3.23, 3.49(2H, AB quartet, J = 16.4 Hz), 6.88(1H, s), 6.93(1H, s), 7.60(2H, d, J = 8.3 Hz), 7.68(2H, d, J = 8.3 Hz)

^{1}H NMR(C$_6$D$_6$): δ 2.02(3H, s), 2.21(3H, s), 2.80, 2.91(2H, AB quartet, J = 16.8 Hz), 2.90, 3.11(2H, AB quartet, J = 16.4 Hz), 6.72(1H, s), 6.77(1H, s), 7.27(2H, d, J = 8.3 Hz), 7.38(2H, d, J = 8.3 Hz)

Products from α-(2,4,6-trimethylphenyl)-4'-methoxyacetophenone

α-(2,4,6-trimethylphenyl)-4'-methoxyacetophenone(0.0030 g) in 0.75 ml of benzene-d_6 was irradiated for 30 minutes. One major product was formed and this product was identified as 4,6-dimethyl-2-(4'-methoxyphenyl)-2-indanol.

4,6-dimethyl-2-(4'-methoxyphenyl)-2-indanol

^{1}H NMR(C_6D_6): 2.06(3H, s), 2.22(3H, s), 2.97, 3.12(2H, AB quartet, J = 17 Hz), 3.06, 3.31(2H, AB quartet, J = 17 Hz), 3.33(3H, s), 6.78(2H, broad s), 6.81(2H, d, J = 8.5 Hz), 7.41(2H, d, J = 8.5 Hz)

Products from α-(2,4,6-trimethylphenyl)-4'-methoxypropiophenone

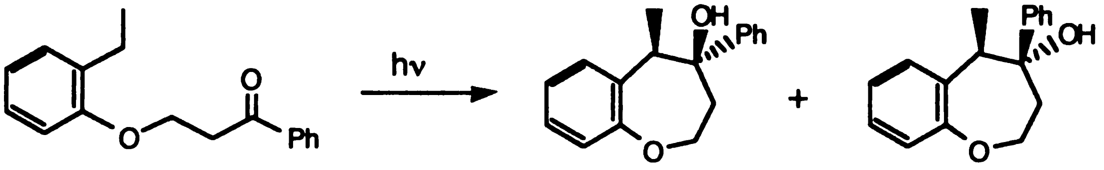
α-(2,4,6-trimethylphenyl)-4'-methoxypropiophenone(0.0028 g) in 0.75 ml of benzene-d_6 was irradiated for 30 minutes. One major product(>90 %) was formed and this product was identified as Z-3,4,6-trimethyl-2-(4'-methoxyphenyl)-2-indanol. Small amount of other isomer was also shown in ^{1}H NMR.(The ratio of two isomer was 10 to 1.) The product ratio was determined based on integration of two methyl doublets. The methyl doublet of the minor isomer appeared at 0.72 ppm in benzene-d_6, but other peaks could not be assigned due to overlapping.

Z-3,4,6-trimethyl-2-(4'-methoxyphenyl)-2-indanol

^{1}H NMR(C_6D_6): δ 1.22(3H, d, J = 7 Hz), 2.10(3H, s), 2.19(3H, s), 3.04, 3.24(2H, AB quartet, J = 17 Hz), 3.28(3H, s), 3.31(1H, quartet, J = 7 Hz), 6.72(2H, broad s), 6.73(2H, d, J = 8.5 Hz), 7.40(2H, d, J = 8.5 Hz)

Products from β-(o-ethylphenoxy)propiophenone

β-(o-ethylphenoxy)propiophenone(0.0030 g) in 0.75 ml of benzene-d_6 was irraduated Even after 18 hours' irradiation, the conversion was only a few percent. Since ^{1}H NMR spectrum of reaction mixture was hard to interpret, isolation of the photoproducts was necessary. 0.1 g of the ketone in 100 ml of benzene was irradiated for a week. The solvent was evaporated and the crude reaction mixture was separated by preparative TLC using 5 % ethyl acetate in hexane. Two isomeric products were isolated and they were identified as Z- and E-4-methyl-3-phenyltetrahydrobenzoxepinol. The product ratio was determined based on integration of two methyl doublets in ^{1}H NMR spectrum of crude product mixture.



Z-4-methyl-3-phenyltetrahydrobenzoxepinol

^{1}H NMR($CDCl_3$): δ 1.12(3H, d, J = 7.^{1}Hz), 1.59(1H, broad s), 1.83(1H, ddd or dt, 14.8 Hz, 1.3 Hz, 3.0 Hz), 3.07(1H, q, J = 7.1 Hz), 3.15(1H, ddd, 3.9 Hz, 12.4Hz, 14.8 Hz), 4.14(1H, ddd, 1.3 Hz, 12.4 Hz, 12.4 Hz), 4.39(1H, ddd, 3.9 Hz, 3.0 Hz, 12.4 Hz), 7.0-7.4(7H, m), 7.60(2H, distorted d)

^{13}C NMR($CDCl_3$): δ 16.1, 37.5, 53.5, 67.8, 75.0, 122.0, 124.1, 125.8, 127.3, 128.1, 128.4, 131.7, 134.4, 147.3, 159.2

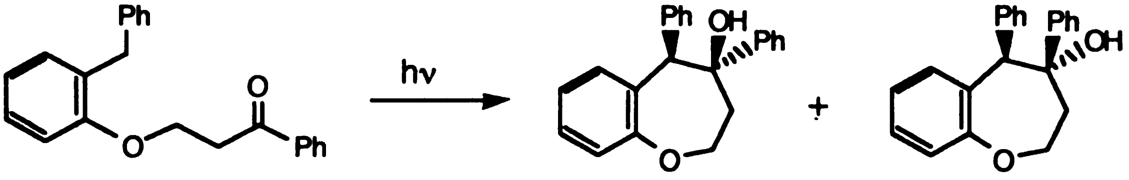
E-4-methyl-3-phenyltetrahydrobenzoxepinol

^{1}H NMR($CDCl_3$): δ 1.05(3H, d, J = 7.2Hz), 1.70(1H, broad s), 1.95(1H, ddd, 2.7 Hz, 6.2 Hz, 15.0 Hz), 2.46(1H, ddd, 3.7 Hz, 9.2 Hz, 15.0 Hz), 3.85(1H, q, J = 7.2 Hz), 3.93(1H, ddd, 2.7 Hz, 9.2 Hz, 12.2 Hz), 4.28(1H, ddd, 3.7 Hz, 6.2 Hz, 12.2 Hz), 7.0-7.4(7H, m), 7.55(2H, d)

^{13}C NMR($CDCl_3$): δ 14.5, 42.9, 44.8, 68.4, 74.1, 121.3, 124.2, 125.1, 126.7, 128.3, 128.4, 128.8, 134.1, 146.8

Products from β-(o-benzylphenoxy)propiophenone

β-(o-benzylphenoxy)propiophenone(0.0032 g) in 0.75 ml of benzene-d_6 was irraduated Reaction was very slow.. Since ^{1}H NMR spectrum of reaction mixture was hard to interpret, isolation of the photoproducts was necessary. 0.1 g of the ketone in 100 ml of benzene was irradiated for a week. The solvent was evaporated and the crude reaction mixture was separated by preparative TLC using 3 % ethyl acetate in hexane. Two isomeric products were isolated and they were identified as Z- and E-3,4-diphenyltetrahydrobenzoxepinol.



Z -3,4-diphenyltetrahydrobenzoxepinol

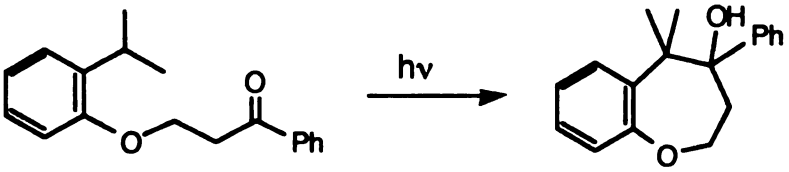
^{1}H NMR(CDCl$_3$, 500 MHz): δ 1.84(1H, ddd, J = 1.5 Hz, 3.0 Hz, 15 Hz), 3.15(1H, ddd, J = 4.0 Hz, 12.0 Hz, 15.0 Hz), 4.39(1H, ddd, J =1.5 Hz, 12.0 Hz, 12.5 Hz), 4.46(1H, ddd, J = 3.0 Hz, 4.0 Hz, 12.5 Hz), 4.21(1H,s), 6.95-7.40(14H, m)

E-3,4-diphenyltetrahydrobenzoxepinol

^{1}H NMR(CDCl$_3$, 500 MHz): δ 2.04(1H, ddd, J = 3.0 Hz, 4.0 Hz, 15 Hz), 2.70(1H, ddd, J = 4.5 Hz, 11.0 Hz, 15.0 Hz), 4.09(1H, ddd, J =3.0 Hz, 11.0 Hz, 12.5 Hz), 4.32(1H, ddd, J = 4.0 Hz, 4.5 Hz, 12.5 Hz), 5.07(1H,s), 6.81(2H, d), 6.95-7.30(10H, m), 7.40(2H, d)

Products from β-(o-isopropylphenoxy)propiophenone

β-(o-isopropylphenoxy)propiophenone(0.1 g) in 100 ml of benzene was irradiated for a week. The solvent was evaporated and the crude reaction mixture was separated by preparative TLC using 3 % ethyl acetate in hexane. One major product was isolated and it was identified as 4,4-dimethyl-3-phenyltetrahydrobenzoxepinol.

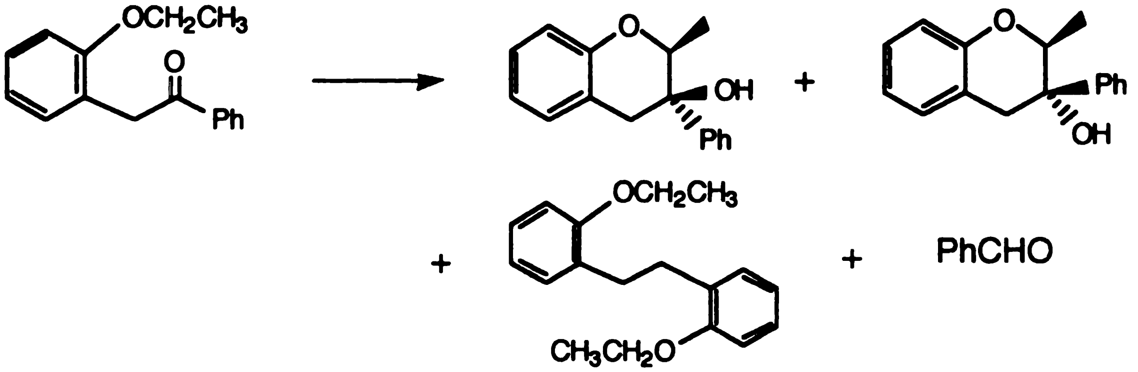


4,4-dimethyl-3-phenyltetrahydrobenzoxepinol

^{1}H NMR($CDCl_3$): δ 1.01(3H, s), 1.52(3H, s), 1.70(1H, broad, -OH), 1.72(1H, ddd, J= 1.7, 2.7, 14.9 Hz), 3.28(1H, ddd, J = 4.3, 12.6, 14.9 Hz), 3.92(1H, ddd, J = 1.7, 12.6, 12.6 Hz), 4.36(1H, ddd, J = 2.7, 4.3, 12.6 Hz), 7.04-7.13(2H, m), 7.20-7.41(5H, m), 7.59(2H, broad d)

<u>Products from α-(o-ethoxyphenyl)acetophenone</u>

α-(o-ethoxyphenyl)acetophenone(0.1 g) in 100 ml of benzene was irradiated until 100 % ketone conversion by GC. The solvent was evaporated and the resulting oil was chromatographed by preparative TLC using 5 % ethyl acetate in hexane. Three major products were isolated. The product ratio was determined from ^{1}H NMR spectrum of crude product mixture.



Z-1-methyl-2-phenyl-2-dihydrobenzopyranol

^{1}H NMR($CDCl_3$):δ 1.07(3H, d J = 6.6 Hz), 2.37(1H, broad s, -OH), 3.01, 3.58(2H, AB quartet, J = 16.5 Hz), 4.34(1H, q, J= 6.6 Hz), 6.92(1H, d), 6.95(1H, t), 7.12-7.21(2H, m), 7.30-7.41(3H, m), 7.54(2H, distorted d)

^{13}C NMR($CDCl_3$): δ 15.5, 34.7, 71.9, 78.3, 117.2, 120.1, 121.1, 126.1, 127.8(2 carbons), 128.4, 130.2, 142.1, 151.9

E-1-methyl-2-phenyl-2-dihydrobenzopyranol

^{1}H NMR($CDCl_3$): δ 1.06(3H, d J= 6.4 Hz), 2.05(1H, broad s, -OH), 2.90, 3.41(2H, AB quartet, J = 17.0 Hz), 4.31(1H, q, J= 6.4 Hz), 6.90-6.96(2H, m), 7.08(1H, d), 7.17(1H, t), 7.29(1H, distorted tt), 7.39(2H, distorted t), 7.47(2H, distorted d)

^{13}C NMR($CDCl_3$): δ 14.7, 41.6, 71.2, 77.3, 116.7, 121.3, 125.0, 127.1, 127.6, 128.4, 130.3, 132.5, 143.3, 153.7

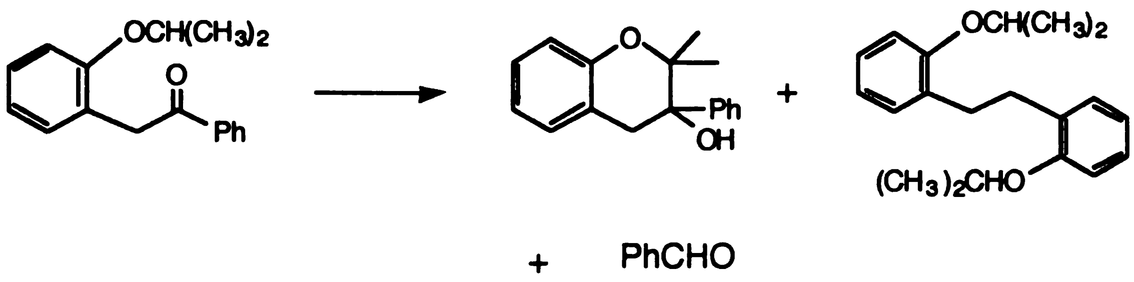
1,2-di(2-ethoxyphenyl)ethane

^{1}H NMR($CDCl_3$): δ 1.40(6H, t, J = 6.9 Hz), 2.88(4H, s), 4.01(4H, q, J = 6.9 Hz), 6.80-6.90(4H, m), 7.10-7.22(4H, m)

To a mixture of two isomers in $CDCl_3$, Eu(dpm)$_3$ was added up to 0.0032 g. However, no useful information could be obtained to assign the structure due to broadness of the spectra, which was caused by the paramagnetic shift reagent.

Products from α-(o-isopropoxyphenyl)acetophenone

α-(o-isopropoxyphenyl)acetophenone(0.1 g) in 80 ml benzene was irradiated until 100 % conversion by GC. The solvent was evaporated and the resulting crude reaction mixture was separated by preparative TLC using 3 % ethyl acetate in hexane. Two major products were isolated. The ^{1}H NMR spectrum of crude product mixture showed the presence of benzaldehyde.



1,1-dimethyl-2-phenyl-2-dihydrobenzopyranol

^{1}H NMR(CDCl$_3$): δ 1.26(6H, s), 2.67(1H, broad s, -OH), 2.84, 3.73(2H, AB quartet, J = 17.0 Hz), 6.94(1H, d, J = 7.4 Hz), 6.95(1H, t, J = 7.7 Hz), 7.13(1H, d, J = 7.4 Hz), 7.19(1H, t, J = 7.7 Hz), 7.31-7.41(3H, m), 7.65(2H, distorted d)

^{13}C NMR(CDCl$_3$): δ 22.5, 22.6, 36.6, 73.9, 80.3, 117.5, 120.5, 121.1, 126.8, 127.3, 127.7, 127.8, 130.2, 141.8, 152.2

1,2-di-(2-isopropoxyphenyl)ethane

^{1}H NMR(CDCl$_3$): δ 1.37(12H, d, J = 6.2 Hz), 2.89(4H, s), 4.58(2H, septet, J = 6.2 Hz), 6.82-6.90(4H, m), 7.11-7.20(4H, m)

Products from ortho-tert-amylbenzophenone

Ortho-tert-amylbenzophenone(0.025 g) in 50 ml benzene was irradiated until 100 % ketone conversion by HPLC. Four isomeric products were formed and these products were isolated by semi preparative HPLC using fraction collector. For analysis purpose, a silica column (4.6 x 250 mm) was used with a flow rate of 1.0 by eluting with 3 % ethyl acetate in hexane. For separation, a silica column (10 x 250 mm) was used with a flow rate of 5.0 by eluting with 3 % ethyl acetate in hexane.

For solid state irradiation, a single crystal was irradiated in a test tube or a sample vial by attaching it to an immersion well. After irradiation, the sample was quickly extracted with a few drops of any given solvents.

For irradiation in silica gel, the ketone was dissolved in methylene chloride with 200 mesh silica gel. After the solvent was evaporated under low pressure, the resulting sample doped silica gel was packed into a melting point capillary tube. This sample was irradiated by attaching it to an immersion well. The irradiated capilary tube containing a sample was broken into pieces and it was extracted with a deuterated solvent.

Z-2,3,3-trimethyl-1-phenylindan-1-ol

^{1}H NMR ($CDCl_3$): δ 0.82(3H, d, J= 7.3 Hz), 0.89(3H, s), 1.36(3H, s), 2.41(1H, quartet, J=7.3 Hz), 7.09(2H, distorted d), 7.2-7.45(7H, m)

E-2,3,3-trimethyl-1-phenylindan-1-ol

^{1}H NMR ($CDCl_3$): δ 1.01(3H, d, J= 7.3 Hz), 1.30(3H, s), 1.39(3H, s), 2.22(1H, quartet, J=7.3 Hz), 6.98(1H, d), 7.2-7.5(8H, m)

Z-3-methyl-3-ethyl-1-phenyl-indan-1-ol

^{1}H NMR ($CDCl_3$): δ 0.96(3H, t, J= 7.4 Hz), 1.27(3H, s), 1.80(1H, quartet, J=7.4 Hz), 2.29, 2.56(2H, AB quartet, J= 14.1 Hz), 7.07(1H, d), 7.2-7.5(8H, m)

E-3-methyl-3-ethyl-1-phenyl-indan-1-ol

^{1}H NMR ($CDCl_3$): δ 0.81(3H, t, J= 7.4 Hz), 1.42(3H, s), 1.92(1H, quartet, J=7.4 Hz), 2.26, 2.45(2H, AB quartet, J= 14.1 Hz), 7.01(1H, d), 7.2-7.5(8H, m)

Products from 2,4,6,2',4',6'-hexaisopropylbenzil

2,4,6,2',4',6'-hexaisopropylbenzil(0.03 g) in 80 ml of benzene was irradiated to 100 % ketone conversion by GC. The solvent was evaporated and the crude product mixture was separated by column chromatography using 4 % ethyl acetate in hexane. These were further purified by preparative TLC using 3 % ethyl acetate in hexane. Two major products were isolated as white solid.

2-hydroxy-2-(2',4',6'-triisopropylphenyl)-3.3-dimethyl-5,7-diisopropylindanone

m.p. = 150 - 151 °C; colorless powder

The ^1H NMR spectrum of this compound in $CDCl_3$ is shown in Figure 11 and an expanded spectrum at 0.8 - 1.4 ppm is shown in Figure 12.

^1H NMR($CDCl_3$): δ 0.86(3H, d, J= 6.8 Hz), 1.14(3H, d, J = 6.8 Hz), 1.15(3H, s), 1.21(3H, d, J = 6.8 Hz), 1.22(3H, d, J = 6.8 Hz), 1.223(3H, d, J = 6.8 Hz), 1.25(3H, d, J = 6.8 Hz), 1.27(3H, d, J = 6.8 Hz), 1.30(6H, d, J = 6.8 Hz), 1.33(3H, d, J = 6.8 Hz), 1.59(3H, s), 2.69(1H, s, OH), 2.19(1H, septet, J = 6.8 Hz), 2.83(1H, septet, J = 6.8 Hz), 2.99(1H, septet, J = 6.8 Hz), 4.02(1H, septet, J = 6.8 Hz), 4.21(1H, septet, J = 6.8 Hz), 6.86(1H, d, J = 2 Hz), 7.09(1H, d, J = 2 Hz), 7.14(1H, d, J = 1 Hz), 7.18(1H, d, J = 1 Hz)

Assignment of each peak was made based on the results from 2D COSY and NOE experiments. These experiments were done on Varian 500 MHz instrument. The result of 2D COSY experiment is shown in Figure 13 and 14. And also shown are the results of NOE experiment after several different peaks are irradiated.(Figure 15 through 17)

^1H NMR(C_6D_6): δ 0.78(3H, d, J= 6.8 Hz), 1.10(6H, d, J = 6.8 Hz), 1.20(3H, d, J = 6.8 Hz), 1.21(3H, d, J = 6.8 Hz), 1.29(3H, s), 1.32(3H, d, J = 6.8 Hz), 1.35(3H, d, J = 6.8 Hz), 1.36(3H, d, J = 6.8 Hz), 1.38(6H, d, J = 6.8 Hz), 1.49(3H, d, J = 6.8 Hz), 1.79(3H, s), 2.57(1H, septet, J = 6.8 Hz), 2.70(1H, septet, J = 6.8 Hz), 2.77(1H, septet, J = 6.8 Hz), 2.90(1H, s, OH), 4.30(1H, septet, J = 6.8 Hz), 4.66(1H, septet, J =

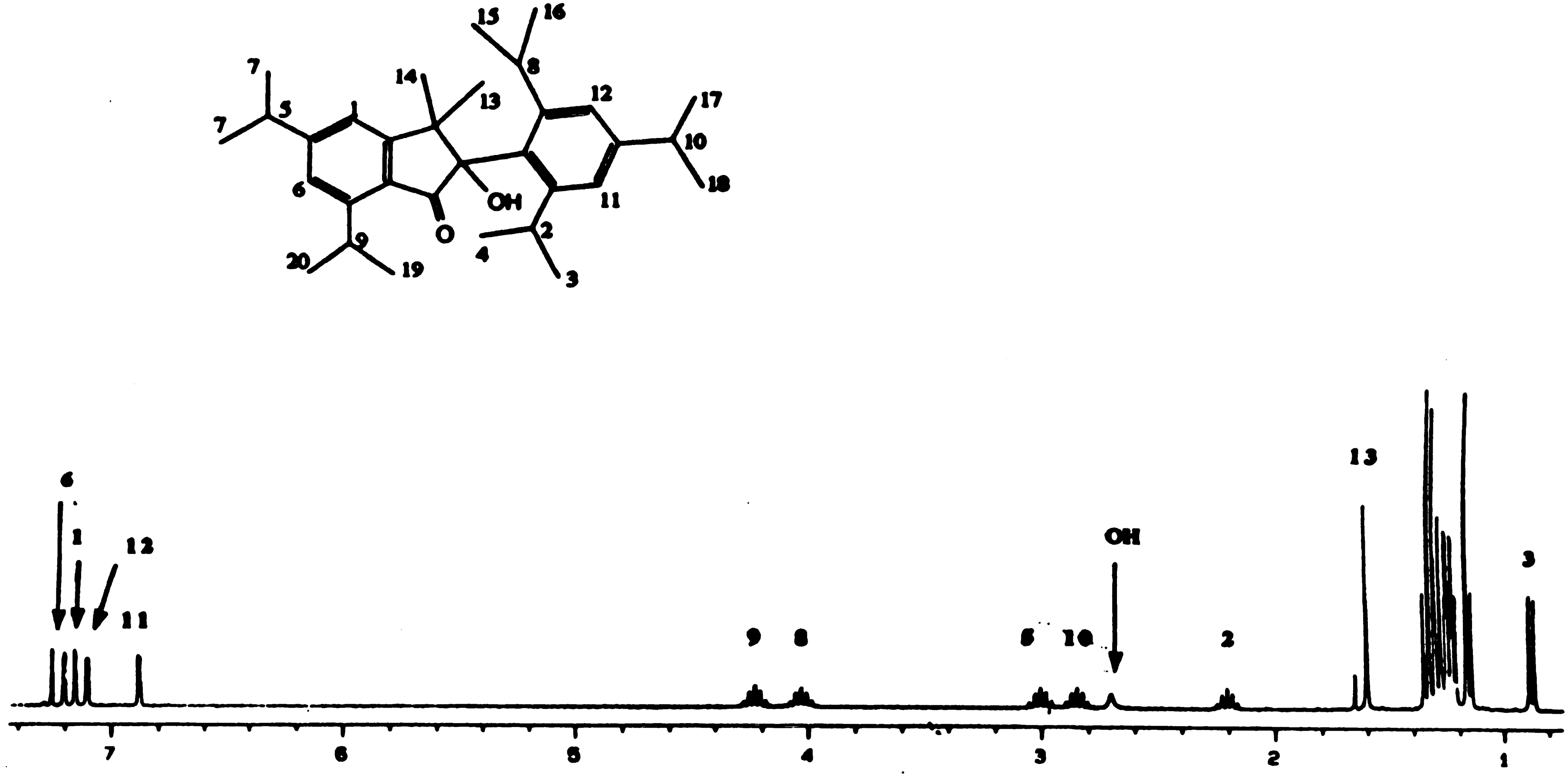


Figure 11. ^1H NMR Spectrum of a Major Product from 2,4,6,2',4',6'-hexaisopropylbenzil in $CDCl_3$.

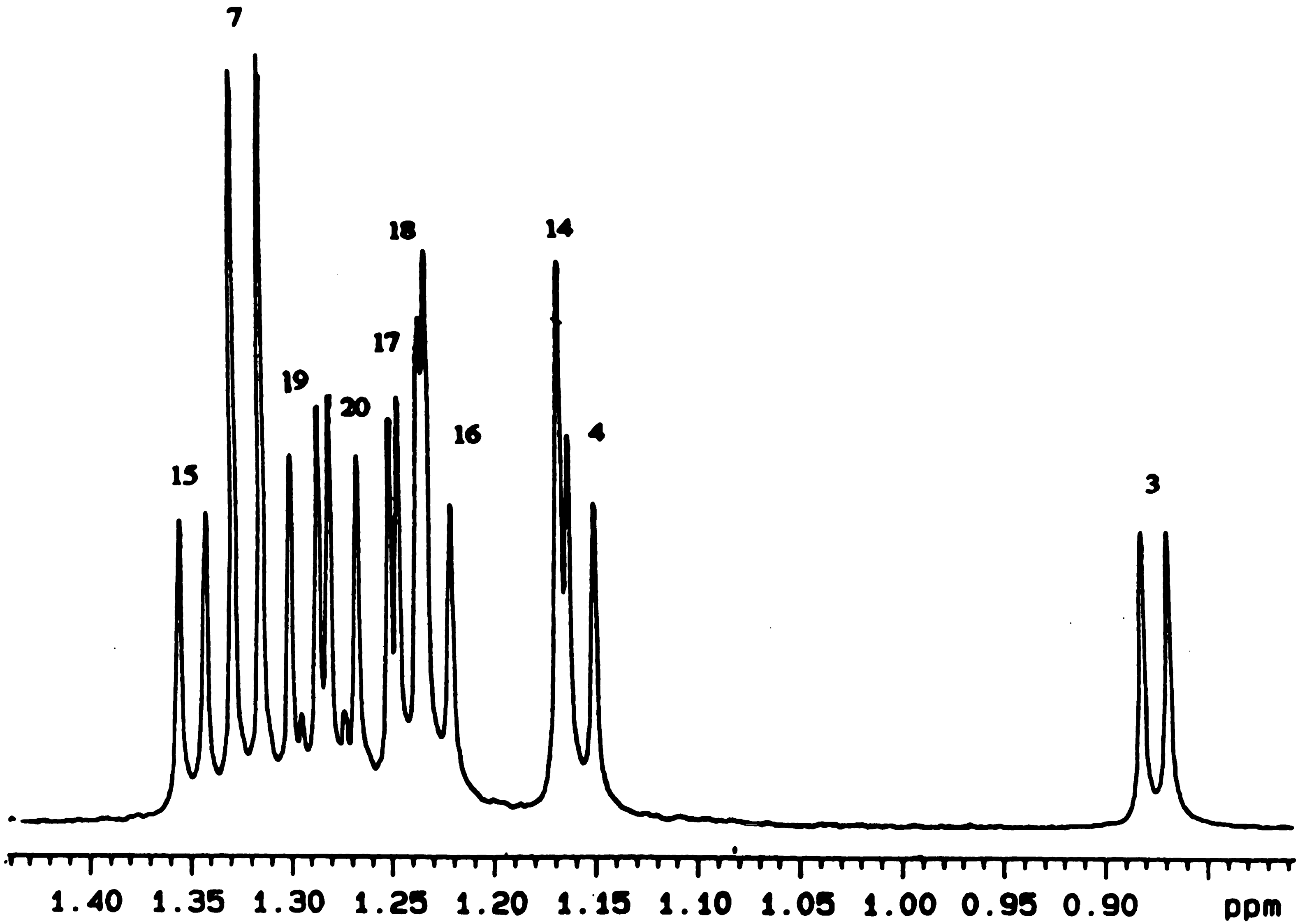


Figure 12. Expanded ^1H NMR Spectrum of a Major Product from 2,4,6,2',4',6'-hexaisopropylbenzil at 0.8-1.4 ppm in $CDCl_3$.

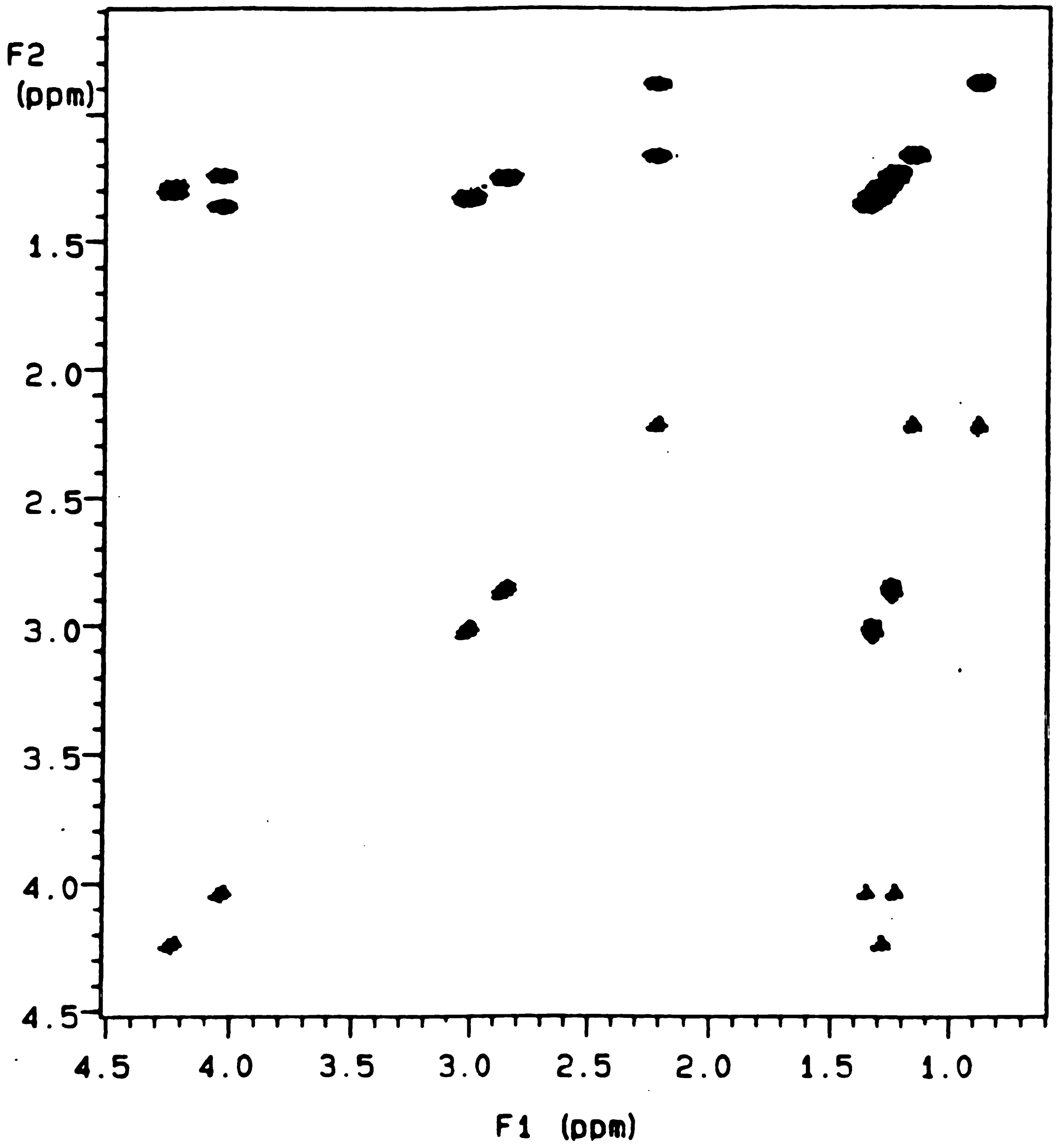


Figure 13. 2D COSY NMR Spectrum of a Major Product from 2,4,6,2',4',6'-hexaisopropylbenzil in $CDCl_3$.

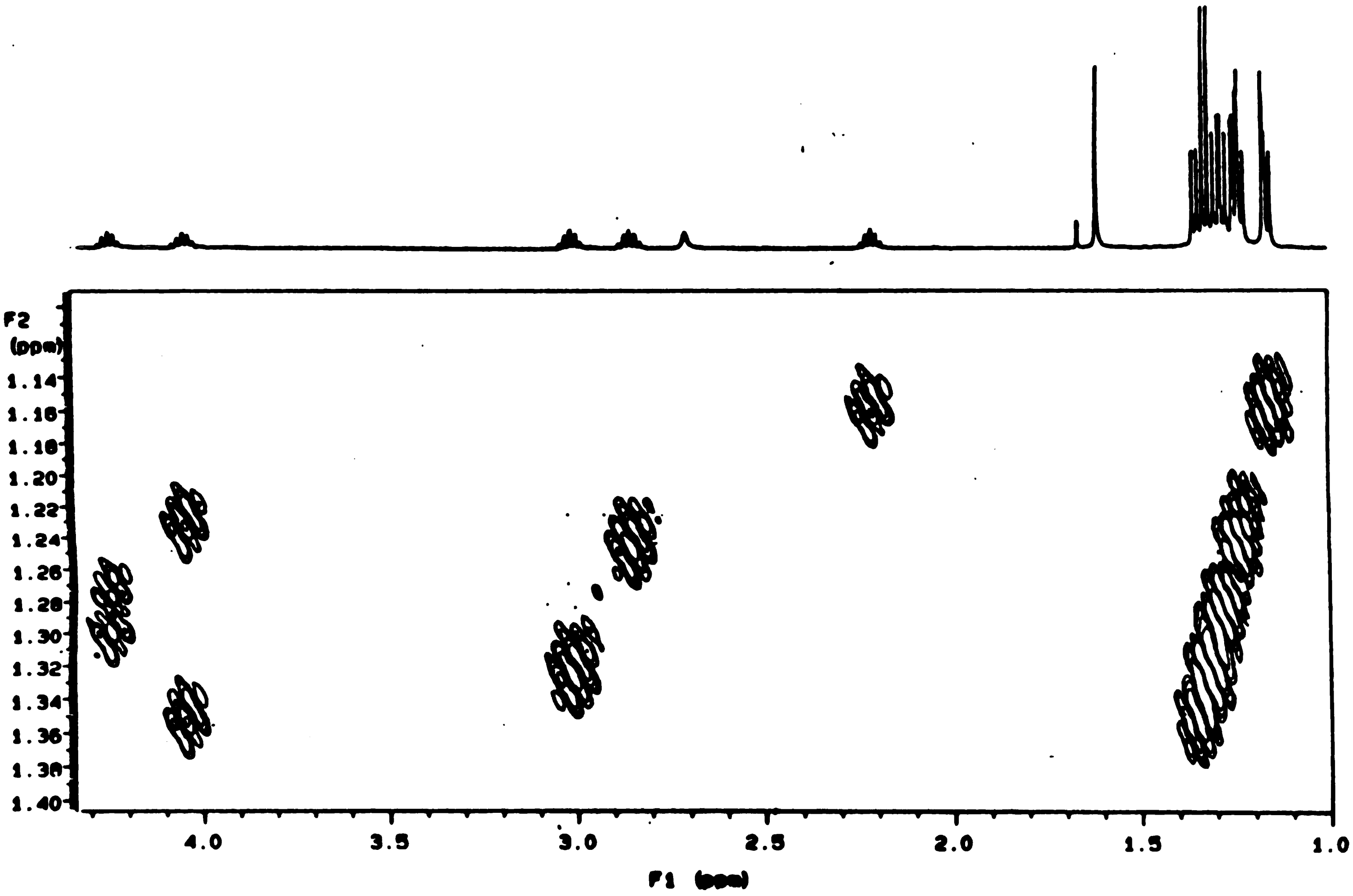
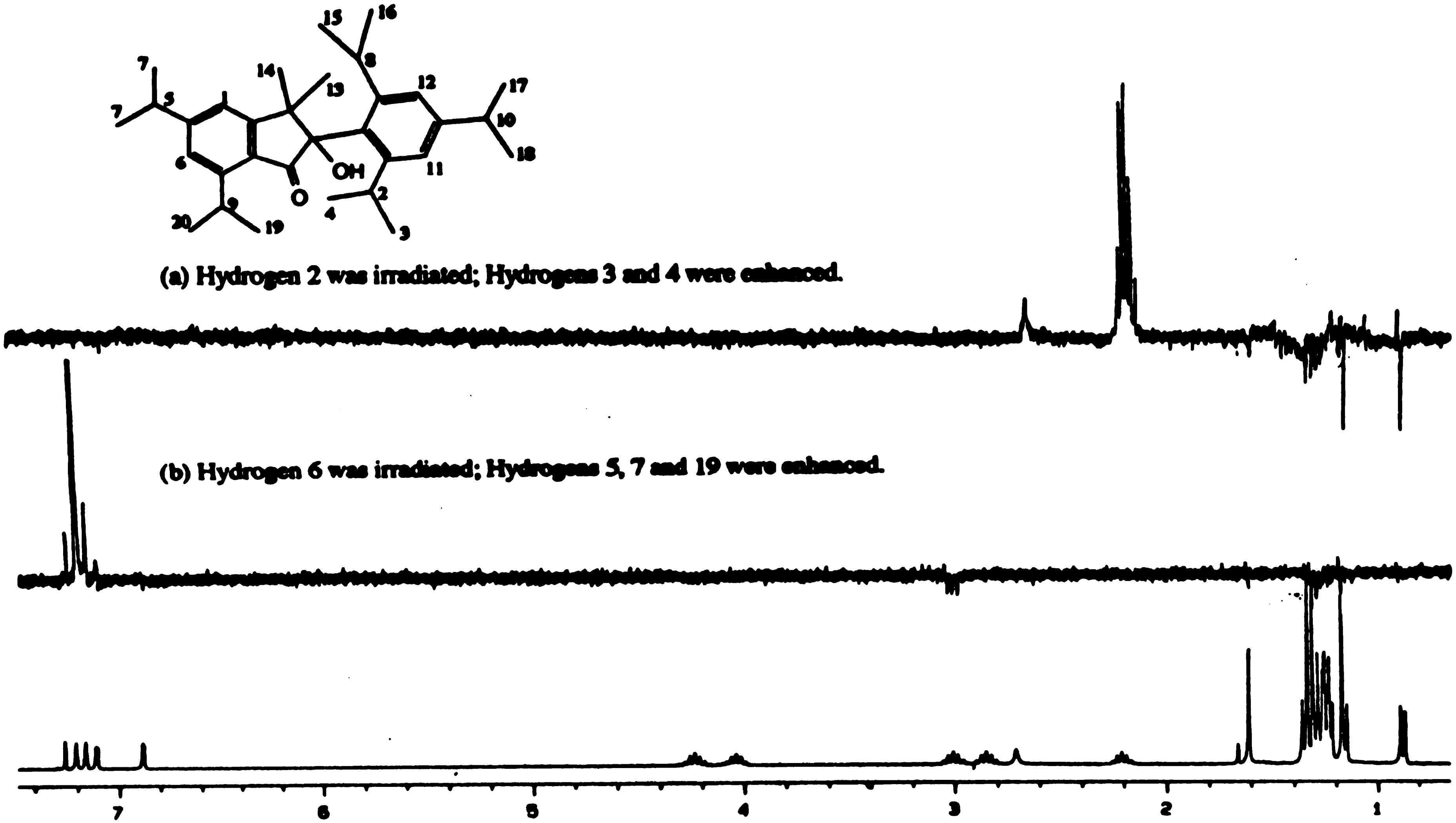


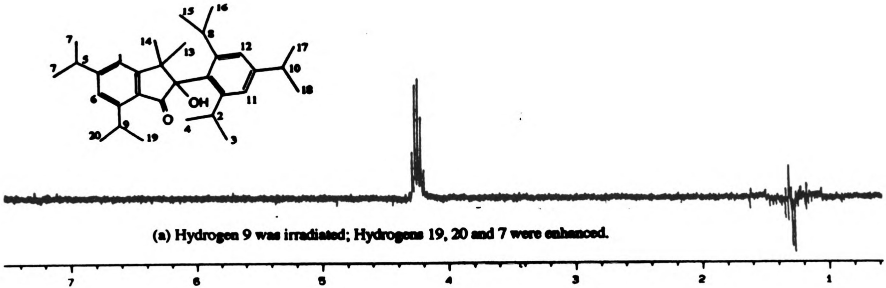
Figure 14. Expanded 2D COSY NMR Spectrum of a Major Product from 2,4,6,2',4',6'-hexaisopropylbenzil in $CDCl_3$.



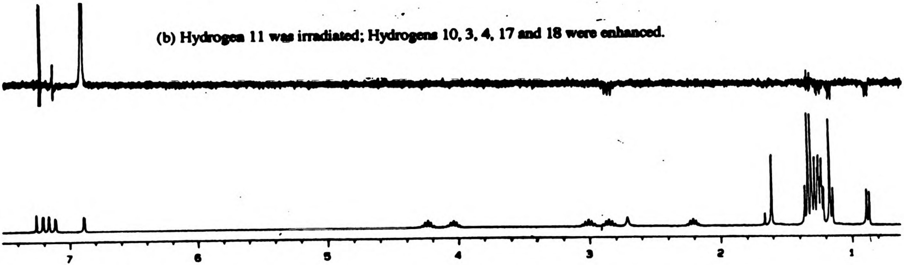
(a) Hydrogen 2 was irradiated; Hydrogens 3 and 4 were enhanced.

(b) Hydrogen 6 was irradiated; Hydrogens 5, 7 and 19 were enhanced.

Figure 15. NOE experiment of a Major Product from 2,4,6,2',4',6'-hexaisopropylbenzil in $CDCl_3$.(A)

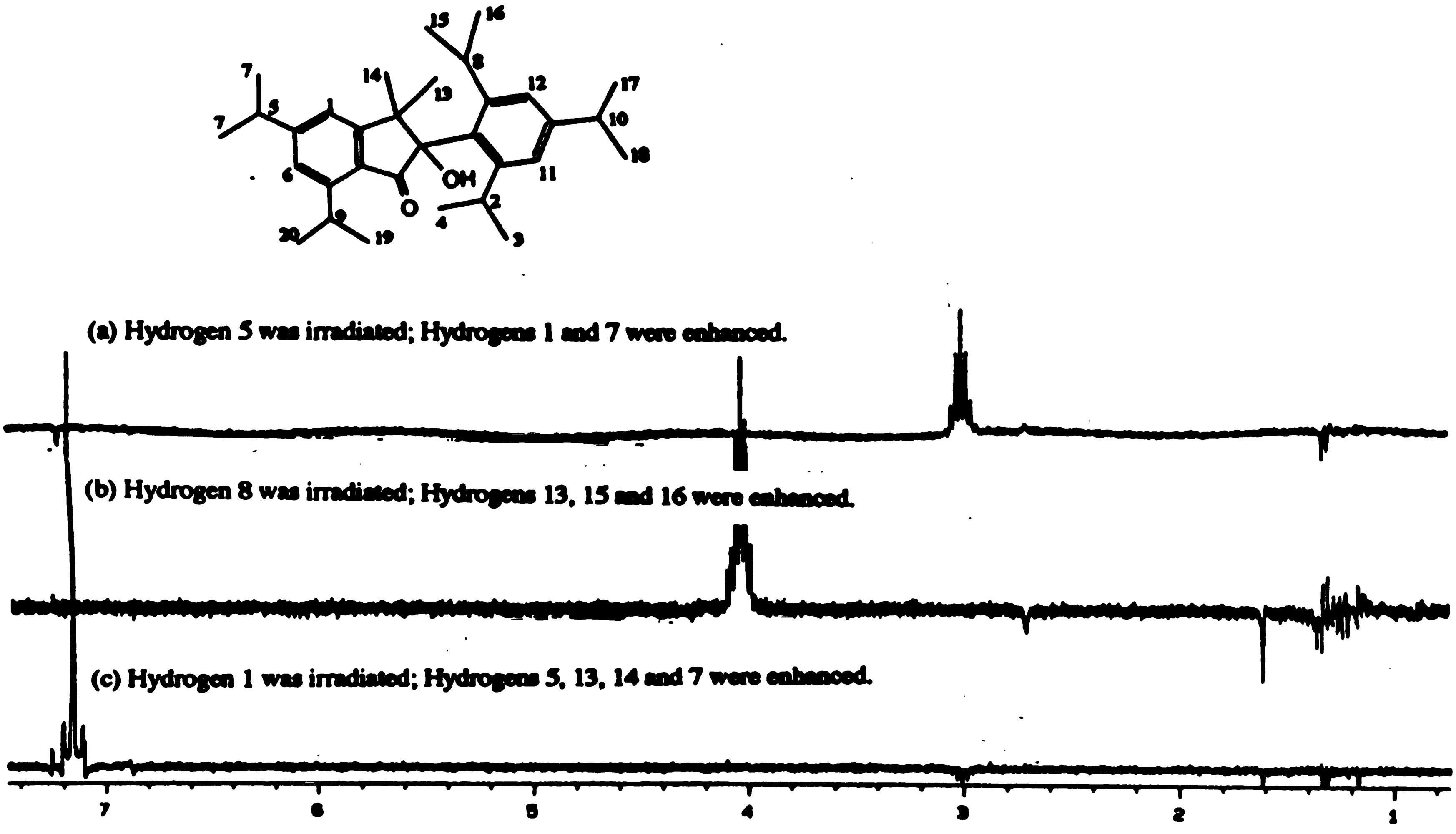


(a) Hydrogen 9 was irradiated; Hydrogens 19, 20 and 7 were enhanced.



(b) Hydrogen 11 was irradiated; Hydrogens 10, 3, 4, 17 and 18 were enhanced.

Figure 16. NOE experiment of a Major Product from 2,4,6,2',4',6'-hexaisopropylbenzil in $CDCl_3$.(B)



(a) Hydrogen 5 was irradiated; Hydrogens 1 and 7 were enhanced.

(b) Hydrogen 8 was irradiated; Hydrogens 13, 15 and 16 were enhanced.

(c) Hydrogen 1 was irradiated; Hydrogens 5, 13, 14 and 7 were enhanced.

Figure 17. NOE experiment of a Major Product from 2,4,6,2',4',6'-hexaisopropylbenzil in $CDCl_3$.(C)

6.8 Hz), 7.05(1H, d, J = 2 Hz), 7.15(1H, d, J = 1 Hz), 7.22(1H, d, J = 1 Hz), 7.29(1H, d, J = 2 Hz)

^{13}C NMR(CDCl$_3$) : δ 205.3, 162.47, 157.16, 150.80, 150.58, 146,98, 146.08, 135.76, 126.84, 124.06, 123.20, 122.20, 119.10, 86.2, 35.00, 33.60, 33.34, 30.46, 28.97, 27.18, 26.22, 25.96, 25.55, 25.42, 23.84, 23.78, 23.74, 23.43, 23.37

IR(CCl$_4$): 3551(O-H str.), 2966, 1704(C=O str.)

Mass: 462.35211; Calc. 462.3500; Molecular Formular ($C_{32}H_{46}O_2$)

α-(2-Formyl-3,5-diisopropylphenyl)-2',4',6'-triisopropylisobutyrophenone

^{1}H NMR(CDCl$_3$): δ 0.944(6H, d, J = 6.8 Hz), 1.023(6H, d, J = 6.8 Hz), 1.188(6H, d, J = 6.8 Hz), 1.198(6H, d,J = 6.8 Hz),1.200(6H, d, J = 6.8 Hz), 1.63(6H, s), 2.21(2H, septet, J = 6.8 Hz), 2.82(1H, septet, J = 6.8 Hz), 2.84(1H, septet, J = 6.8 Hz), 3.13(1H, septet, J = 6.8 Hz), 6.88(2H, s), 7.12(1H, d, J = 1 Hz), 7.13(1H, d, J = 1 Hz), 10.71(1H, s)

^{13}C NMR(CDCl$_3$): 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

Phosphorescence spectrum of 2,4,6,2',4',6'-hexaisopropylbenzil showed (0,0) band at 505.6 nm. Using the following equation, triplet energy(E_T) was estimated.

$$E_T \text{ (kcal/mol)} = h \cdot c / \lambda = 2.86 \times 10^4 / \lambda \text{ (nm)}$$

where h and c are Planck constant and velocity of light, respectively. As a result, 56.6 kcal/mol was obtained for the triplet energy of 2,4,6,2',4',6'-hexaisopropylbenzil.

Products from 2,4,6,2',4',6'-hexamethylbenzil

2,4,6,2',4',6'-hexamethylbenzil(0.0035 g) in 0.75 ml of benzene-d_6 was irradiated through 435 nm filter solution. One major product(>90%) was shown the ^1H NMR spectrum. 2,4,6,2',4',6'-hexamethylbenzil was also irradiated in solid state. The sample was packed through a melting point capillary tube up to ca. 1 cm and this sample was inserted to a test tube. After the sample was irradiated, the capillary tube was broken into pieces inside a small round bottomed flask and the residue was extracted with a deuterated solvent for NMR measurement. Again, one major product was formed and this product was identified as 2-hydroxy-2-(2',4',6'-trimethylphenyl)-5,7-dimethylindanone.

2-hydroxy-2-(2',4',6'-trimethylphenyl)-5,7-dimethylindanone
^1H NMR($CDCl_3$): δ 2.23(3H, s), 2.26(6H, broad s), 2.41(3H, s), 2.66(3H, s), 3.36, 3.57(2H, AB quartet), 6.90(2H, s), 7.0(1H, s), 7.06(1H, s)

Products from 2,4,6,2',4',6'-hexaethylbenzil

2,4,6,2',4',6'-hexaethylbenzil(0.0040 g) in 0.75 ml of benzene-d_6 was irradiated through 435 nm filter solution. Two isomeric products were formed in ca. 2.5 to 1 ratio, judging from integration of methyl doublets in ^1H NMR. When this diketone was irradiated through $CuSO_4$ solution(>320 nm), secondary photoproduct(the ketoaldehyde) was also observed. The ratio of two isomeric photoproducts and the secondary photoproduct was 26:67:7.

2,4,6,2',4',6'-hexaethylbenzil was irradiated also in the solid state. 0.004 g of the diketone in a small sample vial was allowed to photolyze under sun light beside window for 3 weeks. Deuterated solvent was added to the resulting liquid and ^1H NMR spectrum was taken. The reaction was complete and two isomeric photoproducts were formed in ca. 6 to 1 ratio.

When 2,4,6,2',4',6'-hexaethylbenzil(0.0040 g) was irradiated in 0.75 ml of methanol-d_4, the reaction slowed down dramatically. The ketone conversion in methanol was only a few percentage after 2 days' irradiation at 435 nm whereas it was more than 70 % in benzene under the same irradiation conditions. And also, the reaction mixture contained a lot of other unidentified products. The ratio of two isomeric photoproducts was ca. 3-4 to 1 at low conversion.

Z-2-hydroxy-2-(2',4',6'-triethylphenyl)-3-methyl-5,7-diethylindanone

^{1}H NMR(C_6D_6): δ 1.01(3H, t, J = 7.5 Hz), 1.14(3H, t, J = 7.5 Hz), 1.18(6H, broad t, J = 7.5 Hz), 1.34(3H, t, J = 7.5 Hz), 1.49(3H, d, J = 6.8 Hz), 6.76(1H, s), 6.86(1H, s), 6.89(2H, s)

E-2-hydroxy-2-(2',4',6'-triethylphenyl)-3-methyl-5,7-diethylindanone(Some peaks could not be assigned due to overlapping)

^{1}H NMR(C_6D_6): δ 0.96(3H, d, J = 6.8 Hz), 1.03(3H, t, J = 7.5 Hz), 1.22(6H, broad t, J = 7.5 Hz), 1.33(3H, t, J = 7.5 Hz), 1.34(3H, t, J = 7.5 Hz), 6.82(1H, s), 6.86(2H, s), 7.02(1H, s)

Products from 2,4,6,2',4',6'-hexa-tert-butylbenzil

2,4,6,2',4',6'-hexa-tert-butylbenzil(0.02 g) in 80 ml of benzene was irradiated through Pyrex filter for 3 days. The solvent was evaporated and the crude product mixture was separated by preparative TLC using hexane. Three major products were isolated. One product, which did not move on TLC plate, was identified as 2,4,6-tri-tert-butylbenzoic acid after the NMR spectrum was compared with reported one by Neckers.[99] The other two were identified as 2,4,6-tert-butylbenzaldehyde and 5,7-di-tert-butyl-3,3-dimethylindanone based on their ^{1}H NMR data.

2,4,6-tri-tert-butylbenzoic acid

^{1}H NMR($CDCl_3$): δ 1.31(9H, s), 1.49(18H, s), 7.45(2H, s), Carboxylic acid -OH peak was not found.(This peak was also missing from Neckers' paper.)

2,4,6-tri-tert-butylbenzaldehyde

^{1}H NMR($CDCl_3$): δ 1.36(9H, s), 1.40(18H, s), 7.40(2H, s), 11.15(1H, s, -CHO)

5,7-di-tert-butyl-3,3-dimethylindanone

^{1}H NMR($CDCl_3$): δ 1.38(9H, s), 1.40(6H, s), 1.48(9H, s), 2.59(2H, s), 7.32(1H, s), 7.41(1H, s)

^{13}C NMR ($CDCl_3$): δ 29.8, 30.4, 31.2, 31.4, 36.0, 37.2, 54.3, 117.7, 122.4, 150.9, 157.0, 158.0, 167.2, 205.0

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Appendix

Table 10 . Quantum Yield Measurement for α-(o-ethylphenyl)acetophenone in Benzene.

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 160 °C
Rate: 20 °C/min., Hold time: 2 min.
Final col. temp. #2: 180 °C
Rate: 20 °C/min., Hold time: 10 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.32	0.00156	0.73

Sample: [Ketone] = 0.0273 M, [Int. Std.] = [C19] = 0.00321 M
R. F. (indanol vs. C19) = 1.52
Actinometer: [VP] = 0.12 M, [C16] = 0.00246 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.13, [AP] = 0.000704 M

Table 11. Quantum Yield Measurement for α-(o-ethylphenyl)acetophenone in Methanol[a]

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 160 °C
Rate: 20 °C/min., Hold time: 2 min.
Final col. temp. #2: 180 °C
Rate: 20 °C/min., Hold time: 10 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.212	0.00105	0.49

a. Methanol with 10 % ethanol

Sample: [Ketone] = 0.0273 M, [Int. Std.] = [C19] = 0.00321 M
R. F. (indanol vs. C19) = 1.52
Actinometer: [VP] = 0.12 M, [C16] = 0.00246 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.13, [AP] = 0.000704 M

Table 12. Quantum Yield Measurement for α-(2,4,6-triethylphenyl)acetophenone in Benzene.

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 160 °C
Rate: 20 °C/min., Hold time: 2 min.
Final col. temp. #2: 180 °C
Rate: 20 °C/min., Hold time: 10 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.578	0.00186	0.52

Sample: [Ketone] = 0.0303 M, [Int. Std.] = [C21] = 0.00314 M
R. F. (indanol vs. C21) = 1.024
Actinometer: [VP] = 0.101 M, [C16] = 0.00227 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.238, [AP] = 0.00119 M

Table 13. Quantum Yield Measurement for α-(o-isopropoxyphenyl)acetophenone in Benzene

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 180 °C
Rate: 10 °C/min., Hold time: 2 min.
Final col. temp. #2: 200 °C
Rate: 10 °C/min., Hold time: 5 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
dihydrobenzo-pyranol	0.130	0.000243	0.015

Sample: [Ketone] = 0.0245 M, [Int. Std.] = [C20] = 0.00174 M
R. F. (dihydrobenzopyranol vs. C20) = 1.081
Actinometer: [VP] = 0.101 M, [C16] = 0.00227 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 1.057, [AP] = 0.00528 M

Table 14. Quantum Yield Measurement for α-(2,4,6-triethylphenyl)propiophenone in Benzene

GC analysis: 1400 Varian GC
DB-1 Megabore column
Column temp.: 180 °C

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol(Z,E-isomer)	0.971	0.00195	0.122
Indanol(E,Z-isomer)	0.913	0.00184	0.115

Sample: [Ketone] = 0.0213 M, [Int. Std.] = [C20] = 0.00216 M
R. F. (indanol vs. C20) = 0.930
Actinometer: [VP] = 0.101 M, [C16] = 0.00227 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 1.057, [AP] = 0.00528 M

Table 15. Quantum Yield Measurement for β-(o-benzylphenoxy)propiophenone in Benzene

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 180 °C .
Rate: 10 °C/min., Hold time: 2 min.
Final col. temp. #2: 200 °C
Rate: 10 °C/min., Hold time: 5 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Z-tetrahydro-benzoxepinol	0.137	0.000557	0.0018
E-tetrahydro-benzoxepinol	0.144	0.000585	0.0019

Sample: [Ketone] = 0.0399 M, [Int. Std.] = [C24] = 0.00373 M
R. F. (tetrahydrobenzoxepinol vs. C24) = 1.09
Actinometer: [o-methyl VP] = 0.101 M, [C15] = 0.00891 M
R. F. (o-methyl AP vs. C15) = 1.84
A(o-MAP)/A(std) = 0.301, [o-MAP] = 0.00493 M

Table 16. Quantum Yield Measurement for β-(o-ethylphenyl)propiophenone in Benzene

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 90 °C
Rate: 2 °C /min., Hold time: 1 min.
Final col. temp. #2: 150 °C
Rate: 9 °C /min., Hold time: 5 min.
Final col. temp. #3: 180 °C
Rate: 5 °C /min., Hold time: 5 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.142	0.000626	0.0663
2,3-di-(o-ethylphenyl)buthane	0.139	0.000537	0.0568

Sample: [Ketone] = 0.0225 M, [Int. Std.] = [C17] = 0.00454 M
R. F. (Indanol vs. C17) = 0.97
R. F. (2,3-di-(o-ethylphenyl)buthane vs. C17) = 0.85
Actinometer: [VP] = 0.101 M, [C16] = 0.00227 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.624, [AP] = 0.00312 M

Table 17. Quantum Yield Measurement for α-(o-benzylphenyl)acetophenone in Benzene

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 90 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 160 °C
Rate: 20 °C /min., Hold time: 2 min.
Final col. temp. #2: 180 °C
Rate: 20 °C /min., Hold time: 20 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol(Z-isomer)	0.265	0.00091	0.165
Indanol(E-isomer)	0.315	0.00108	0.196

Sample: [Ketone] = 0.0235 M, [Int. Std.] = [C21] = 0.00351 M
R. F. (indanol vs. C21) = 0.977
Actinometer: [VP] = 0.101 M, [C16] = 0.00227 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.364, [AP] = 0.00182 M

Table 18. Quantum Yield Measurement for α-(o-benzylphenyl)acetophenone in Methanol[a]

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 90 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 160 °C
Rate: 20 °C /min., Hold time: 2 min.
Final col. temp. #2: 180 °C
Rate: 20 °C /min., Hold time: 20 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol(Z-isomer)	0.506	0.00100	0.240
Indanol(E-isomer)	0.450	0.00089	0.214

a Methanol with 10 % ethanol

Sample: [Ketone] = 0.0244 M, [Int. Std.] = [C21] = 0.00203 M
R. F. (indanol vs. C21) = 0.977

Actinometer: [VP] = 0.101 M, [C16] = 0.00246 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.254, [AP] = 0.00138 M

Table 19. Quantum Yield Measurement for α-Mesityl-(4-trifluoromethyl)acetophenone in Benzene

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 180 °C
Rate: 10 °C/min., Hold time: 2 min.
Final col. temp. #2: 200 °C
Rate: 10 °C/min., Hold time: 5 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.49	0.00124	0.30

Sample: [Ketone] = 0.016 M, [Int. Std.] = [C20] = 0.00188 M
R. F. (indanol vs. C20) = 1.35
Actinometer: [VP] = 0.101 M, [C16] = 0.00246 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.254, [AP] = 0.00138 M

Table 20. Quantum Yield Measurement for α-Mesityl-(4-trifluoromethyl)acetophenone in Methanol[a]

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 180 °C
Rate: 10 °C/min., Hold time: 2 min.
Final col. temp. #2: 200 °C
Rate: 10 °C/min., Hold time: 5 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.86	0.00206	0.49

a Methanol with 10 % ethanol

Sample: [Ketone] = 0.017 M, [Int. Std.] = [C20] = 0.00177 M
R. F. (indanol vs. C20) = 1.35
Actinometer: [VP] = 0.101 M, [C16] = 0.00246 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.254, [AP] = 0.00138 M

Table 21. Quantum Yield Measurement for α-Mesityl-4-methoxy-acetophenone in Benzene

GC analysis: 1400 Varian GC
DB-1 Megabore column
Column temp.: 200 °C

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.836	0.00167	0.18

Sample: [Ketone] = 0.021 M, [Int. Std.] = [C24] = 0.00163 M
R. F. (indanol vs. C24) = 1.23
Actinometer: [VP] = 0.101 M, [C16] = 0.00227 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.626, [AP] = 0.00947 M

Table 22. Quantum Yield Measurement for α-Mesityl-4-methoxy-propiophenone in Benzene

GC analysis: 1400 Varian GC
DB-1 Megabore column
Column temp.: 200 °C

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.88	0.00079	0.14

Sample: [Ketone] = 0.01 M, [Int. Std.] = [C21] = 0.000878 M
R. F. (indanol vs. C21) = 1.024
Actinometer: [VP] = 0.101 M, [C16] = 0.00211 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 0.626, [AP] = 0.00947 M

Table 23. Quantum Yield Measurement for α-(o-benzylphenyl)-propiophenone in Benzene

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 90 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 160 °C
Rate: 20 °C /min., Hold time: 2 min.
Final col. temp. #2: 180 °C
Rate: 20 °C /min., Hold time: 20 min.

Photoproduct	A(product)/A(std.)	Concentration	Φ
Indanol	0.216	0.000638	0.051
2,3-di-(o-benzyl-phenyl)buthane	0.312	0.000676	0.054

Sample: [Ketone] = 0.0201 M, [Int. Std.] = [C24] = 0.00271 M
R. F. (Indanol vs. C24) = 1.09
R. F. (2,3-di-(o-benzylphenyl)buthane vs. C24) = 0.8
Actinometer: [VP] = 0.101 M, [C16] = 0.00140 M
R. F. (AP vs. C16) = 2.2
A(AP)/A(std) = 1.35, [AP] = 0.00140 M

Table 24. Quenching Indanol Formation from α-(benzylphenyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in benzene at 313 nm

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 90 ^{o}C
Initial col. hold time: 1 min.
Final col. temp. #1: 160 ^{o}C
Rate: 20 ^{o}C /min., Hold time: 2 min.
Final col. temp. #2: 180 ^{o}C
Rate: 20 ^{o}C /min., Hold time: 20 min.

[Q], M	A(photo)/A(std)	Φ^{o}/Φ
0.000	0.299	1.000
0.495	0.113	2.646
0.989	0.056	5.339

[Ketone] = 9.8 X 10^{-3} M, [Internal standard] = [C_{21}] = 2.86 X 10^{-3} M
$k_q\tau = 3.8$

Ta

Na

Table 25. Quenching Indanol Formation from α-(benzylphenyl)acetophenone with Naphthalene in benzene at 365 nm

HPLC analysis (5 % Ethylacetate in hexane)
Normal phase silica column

[Q], M	A(photo)/A(std)	Φ^o/Φ
0.00	0.480	1.000
0.10	0.385	1.247
0.20	0.308	1.558
0.40	0.234	2.051
0.60	0.181	2.652
0.80	0.136	3.529

[Ketone] = 0.0106 M, [Internal standard] = [methyl-2-phenoxyacetate] = 1.18 X 10^{-3} M
$k_q\tau = 2.8$

Table 26. Quenching of the Benzodihydropyranol Formation from α-(2-isopropoxyphenyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in benzene at 313 nm

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 180 °C
Rate: 10 °C/min., Hold time: 2 min.
Final col. temp. #2: 200 °C
Rate: 10 °C/min., Hold time: 5 min.

$[Q]\times10^3$, M	A(photo)/A(std)	Φ^o/Φ
0.00	0.791	1.000
2.58	0.769	1.029
5.16	0.593	1.334
10.3	0.462	1.712
15.5	0.374	2.115
20.6	0.330	2.397

[Ketone] = 0.012 M, [Internal standard] = $[C_{20}] = 8.156 \times 10^{-4}$ M
$k_q\tau = 69$

Table 27. Quenching of the tetrahydrobenzoxepinol Formation from β-(2-benzylphenoxy)propiophenone with 2,5-Dimethyl-2,4-Hexadiene in benzene at 313 nm

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 180 °C
Rate: 10 °C/min., Hold time: 2 min.
Final col. temp. #2: 200 °C
Rate: 10 °C/min., Hold time: 5 min.

[Q], M	A(photo)/A(std)	Φ^o/Φ
0.0000	0.2270	1.00
0.0103	0.0880	2.58
0.0206	0.0770	2.95
0.0309	0.0455	4.99
0.0412	0.0297	7.64

[Ketone] = 0.04 M, [Internal standard] = [C_{24}] = 3.57×10^{-3} M
$k_q\tau = 150$

Table 28. Quenching Indanol Formation from α-(2-ethylphenyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in benzene at 313 nm

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 160 °C
Rate: 20 °C/min., Hold time: 2 min.
Final col. temp. #2: 180 °C
Rate: 20 °C/min., Hold time: 10 min.

[Q], M	A(photo)/A(std)	Φ^o/Φ
0.0000	1.133	1.00
0.1056	0.661	1.72
0.2112	0.529	2.14
0.4224	0.359	3.16
0.6336	0.238	4.76
0.8448	0.208	5.45

[Ketone] = 0.013 M, [Internal standard] = [C_{19}] = 4.25 X 10^{-4} M
$k_q\tau = 5.5$

Table 29. Quenching Indanol Formation from α-(2-ethylphenyl)acetophenone with Naphthalene in benzene at 365 nm

HPLC analysis (5 % Ethylacetate in hexane)
Normal phase silica column

[Q] , M	A(photo)/A(std)	Φ^o/Φ
0.0000	0.9188	1.000
0.0348	0.7466	1.231
0.0696	0.7291	1.260
0.1392	0.5367	1.712
0.2088	0.4818	1.907
0.2784	0.3732	2.462

[Ketone] = 0.014 M, [Internal standard] = [methylbenzoate] = 1.632×10^{-3} M

$k_q\tau = 4.9$

Table 30. Quenching Indanol Formation from α-(o-ethylphenyl)propiophenone with piperylene in benzene at 313 nm

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 ^{o}C
Initial col. hold time: 1 min.
Final col. temp. #1: 90 ^{o}C
Rate: 2 ^{o}C /min., Hold time: 1 min.
Final col. temp. #2: 150 ^{o}C
Rate: 9 ^{o}C /min., Hold time: 5 min.
Final col. temp. #3: 180 ^{o}C
Rate: 5 ^{o}C /min., Hold time: 5 min.

[Q], M	A(photo)/A(std)	Φ^o/Φ
0.00	0.606	1.00
0.10	0.247	2.45
0.20	0.161	3.76
0.40	0.113	5.36
0.60	0.081	7.48
0.80	0.066	9.18

[Ketone] = 0.0102 M, [Internal standard] = [C17] = 1.54 X 10^{-3} M
$k_q\tau = 12$

Table 31. Quenching Indanol Formation from α-mesityl-4-methoxypropiophenone with Naphthalene in benzene at 365 nm

HPLC analysis (5 % Ethylacetate in hexane)
Normal phase silica column

[Q] X 10^3, M	A(photo)/A(std)	Φ^o/Φ
0.000	2.212	1.00
0.578	0.374	5.91
1.156	0.202	10.94

[Ketone] = 0.0106 M, [Internal standard] = [methyl-2-phenoxyacetate] = 1.012 X 10^{-3} M
$k_q\tau = 8750$

Table 32. Quenching Indanol Formation from α-mesityl-(4-trifluoromethyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in benzene at 313 nm

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 ^{o}C
Initial col. hold time: 1 min.
Final col. temp. #1: 180 ^{o}C
Rate: 10 ^{o}C/min., Hold time: 2 min.
Final col. temp. #2: 200 ^{o}C
Rate: 10 ^{o}C/min., Hold time: 5 min.

[Q], M	A(photo)/A(std)	Φ^{o}/Φ
0.0000	0.671	1.000
0.2428	0.481	1.395
0.4857	0.444	1.511
0.9714	0.314	2.137
1.4571	0.250	2.684
1.9428	0.188	3.569

[Ketone] = 0.01 M, [Internal standard] = [C_{20}] = 1.014 X 10^{-3} M
$k_q\tau$ = 1.26

*Table 33. Quenching Indanol Formation from α-mesityl-(4-trifluoromethyl)acetophenone with piperylene in benzene at 313 nm

GC analysis: 3400 Varian GC
DB-210 Megabore column
Initial column temp.: 80 °C
Initial col. hold time: 1 min.
Final col. temp. #1: 180 °C
Rate: 10 °C/min., Hold time: 2 min.
Final col. temp. #2: 200 °C
Rate: 10 °C/min., Hold time: 5 min.

[Q], M	A(photo)/A(std)	Φ^o/Φ
0.0000	0.756	1.000
0.1934	0.737	1.026
0.3868	0.591	1.279
1.1604	0.467	1.619
1.5472	0.377	2.005

[Ketone] = 0.016 M, [Internal standard] = [C_{20}] = 1.773 X 10^{-3} M
$k_q\tau$ = 0.63

Table 34. Quenching Indanol Formation from α-(2,4,6-triethylphenyl)acetophenone with Naphthalene in benzene at 365 nm

HPLC analysis (6 % Ethylacetate in hexane)
Normal phase silica column

[Q], M	A(photo)/A(std)	Φ^o/Φ
0.0000	0.345	1.000
0.1226	0.327	1.055
0.2451	0.285	1.211
0.4902	0.233	1.481
0.7353	0.204	1.691
0.9804	0.174	1.983

[Ketone] = 0.02 M, [Internal standard] = [methyl-2-phenoxyacetate]
= 3.47 X 10^{-3} M
$k_q\tau = 1.02$

Table 35. Quenching Indanol Formation from α-mesityl-4-methoxyacetophenone with Ethylsorbate in benzene at 313 nm

GC analysis with DB 1 column
!90 ^{o}C Column Temperature

$[Q] \times 10^3$, M	A(photo)/A(std)	Φ^o/Φ
0.000	1.875	1.000
0.254	1.458	1.286
0.508	1.353	1.386
1.016	1.007	1.862
3.048	0.454	4.130
4.064	0.378	4.960

[Ketone] = 0.01 M, [Internal standard] = $[C_{24}] = 6.75 \times 10^{-4}$ M
$k_q\tau = 950$

Table 36. Quenching Indanol Formation from α-(2,4,6-triethylphenyl)propiophenone with naphthalene in benzene at 365 nm

HPLC analysis (5 % Ethylacetate in hexane)
Normal phase silica column

[Q], M	A(photo)/A(std)	Φ^o/Φ
0.0000	0.510	1.000
0.0334	0.439	1.162
0.0668	0.363	1.405
0.1336	0.269	1.896
0.2004	0.223	2.287
0.2672	0.183	2.787

[Ketone] = 0.0107 M, [Internal standard] = [Methylbenzoate] = 2.25×10^{-3} M
$k_q\tau = 6.5$

Table 37. Quenching keto-Indanol Formation from 2,4,6,2',4',6'-hexaisopropylbenzil with pyrene in benzene at 365 nm

GC analysis with DB210 column

[Q] X 10^3, M	A(photo)/A(std)	Φ^o/Φ
0.00	0.247	1.000
1.07	0.173	1.428
4.78	0.059	4.186

[Ketone] = 0.01 M, [Internal standard] = [C20] = 2.27 X 10^{-3} M
$k_q\tau$ = 535

Correction using Beer-Lambert Law

Extinction coeff. of the ketone at 365 nm = 371
Extinction coeff. of pyrene at 365 nm = 213

At [Q] = 0, Φ_0 = [prod]$_0$/I,

At [Q] = 0.00107,

$A = \varepsilon_1 c_1 + \varepsilon_q c_q = 3.68 + 0.228$
% A of sample: 94 %,
Φ_1 = [prod]$_0$/I X 0.94,
Φ_0/Φ_1 = ([prod]0/[prod]1)X 0.94,
= 1.428 X 0.94 = 1.342

At [Q] = 0.00478,

$A = \varepsilon_2 c_2 + \varepsilon_q c_q = 3.68 + 1.02$
% A of sample: 78 %,
Φ_2 = [prod]$_0$/I X 0.78,
Φ_0/Φ_2 = ([prod]$_0$/[prod]$_2$)X 0.78,
= 4.186 X 0.78 = 3.265

$k_q\tau$ becomes 400 s^{-1}