This is to certify that the

thesis entitled

Photochemistry of
beta-Cyclopropylmethoxypropiophenone
and O-Benzyl Benzophenone

presented by

Varsha S. Govardhan

has been accepted towards fulfillment
of the requirements for

M.S. degree in Chemistry

Major professor

Date Aug. 23, 2001

O-7639

MSU is an Affirmative Action/Equal Opportunity Institution

PHOTOCHEMISTRY OF β-CYCLOPROPYLMETHOXY PROPIOPHENONE AND O-BENZYL BENZOPHENONE

By

Varsha S. Govardhan

A THESIS

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

MASTER OF SCIENCE

Department of Chemistry

2001

ABSTRACT

PHOTOCHEMISTRY OF β-CYCLOPROPYLMETHOXY PROPIOPHENONE AND O-BENZYL BENZOPHENONE

By

Varsha S. Govardhan

Intramolecular hydrogen abstraction is one of the major outcomes of irradiating carbonyl compounds which have a molecular structure that allows a close approach between the excited carbonyl compound and a sp^3 carbon within the same molecule. This process is favored from the γ carbon due to geometric and thermodynamic considerations. However abstraction from the δ carbon is a competing reaction that can occur with highly activated δ C-H bonds or in the absence of γ hydrogens.

β-Cyclopropylmethoxy propiophenone proved to be an interesting example of the latter. In this case 1,5 biradical formation was followed by subsequent radical ring opening of the cyclopropyl moiety as opposed to cyclopentanol formation seen with other compounds such as β-ethoxypropiophenone.

Photoenolization followed by electrocyclic ring closure to stereoselectively form the cyclobutenol was the result of irradiating o-benzyl benzophenone, which was a classic example of photoenolization. To reinforce our understanding of the ketone→enol→benzocyclobutenols chronology, this process was also studied in the solid state. The difference in the diastereoselectivity of cyclobutenol formation between the solid and liquid state confirms the fact that it is governed by the geometry of the biradical initially formed by hydrogen abstraction.

AKNOWLEDGEMENTS

I wish to thank Dr. Peter J. Wagner, for his help, guidance along with moral and financial support. His help through rough times led to the completion of this thesis.

I am also greatly indebted to members of the Wagner group, Dr. Yoon, Mr. Jong Il Lee, Mr. Yijun Tang, Dr. Ali Zand and Prof. Bong-Ser Park for their help and discussions throughout my graduate career and making it fun to work in the laboratory. I owe special thanks to Dr. Azadnia who worked with my schedule during my pregnancy.

Finally I would like to thank my husband Dr. Subodh Govardhan whose love and patience has always been a source of inspiration, my parents, Mr. Manohar and Mrs. Manisha Bhide, my parents-in-law, Dr. Manohar and Mrs. Lata Goverdhan, my brother Mr. Vivek Bhide and last but by all means one of the most important, my daughter Ms. Isheeta Govardhan.

TABLE OF CONTENT

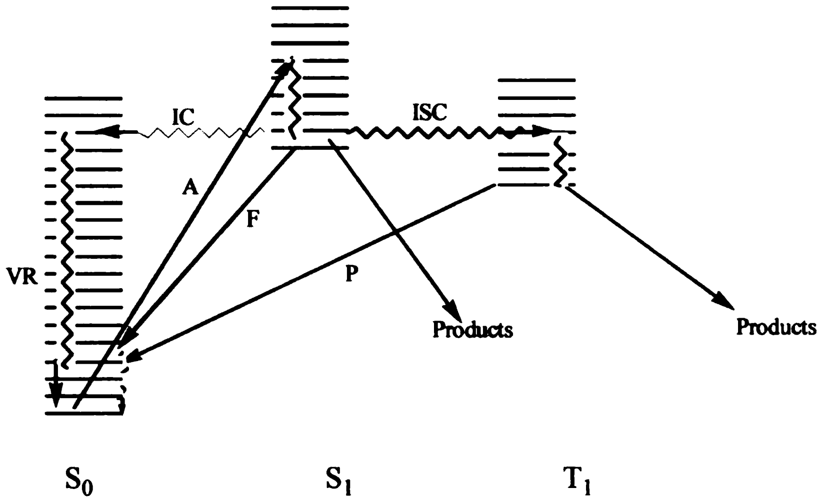
LIST OF SCHEMES

LIST OF FIGURES

INTRODUCTION

Chemical reactions can broadly be classified into two categories – thermal and photochemical.

When the source of energy in a reaction is light, it is termed as a photoreaction. For a photoreaction to occur, a molecule in its ground state, S_0, absorbs light and is excited to S_n, the singlet excited state. From here the excited molecule can intersystem cross, i.e. go to the triplet excited state T_n with a rate constant of $10^7 - 10^{11}$ s^{-1}.[1]



A = absorption
F = fluorescence
P = phosphorescence

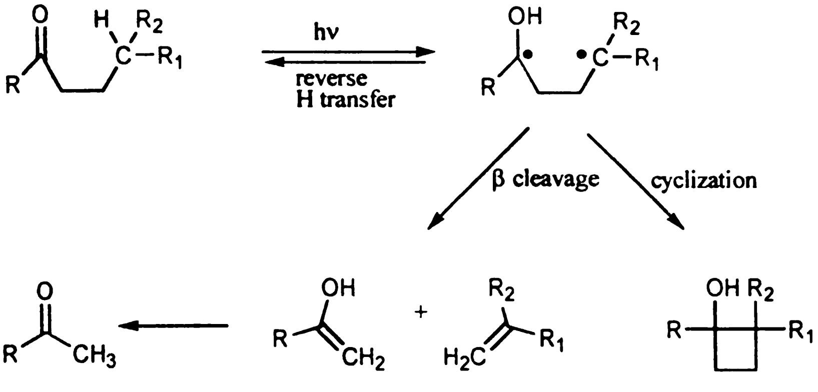
IC = internal conversion
ISC = intersystem conversion
VR = vibrational relaxation

Figure 1. Jablonski diagram

Photophysical processes like radiative decay (phosphorescence), radiationless decay, or photochemical transformations like hydrogen abstraction, α-cleavage etc. can occur from T_1. The molecule from S_n can also undergo internal conversion to the lowest excited singlet state, S_1 with a rate of the order of 10^{11}-10^{12} s^{-1}. This singlet state can decay to the ground state by emitting light, giving rise to fluorescence. Chemical reactions are possible from this state also.

Hydrogen Abstraction

Hydrogen abstraction can occur both inter- and intramolecularly. Intramolecular hydrogen abstraction and the fate of the resulting biradical is the focus of this study. The (n,π*) excited state of carbonyl compounds undergoes a 1,5 or 1,6-hydrogen shift, which is generally followed by cyclization, cleavage, or reversal to the starting ketone.[2] As in most chemical reactions various steric, electronic and physical factors affect the feasibility and rate of hydrogen abstraction and fate of the resulting biradical.



Scheme 1. Norrish type II reactions

Ketones, aldehydes, esters and cyclic imides, in which the molecular structure allows a close approach between the excited carbonyl group and hydrogen attached to a

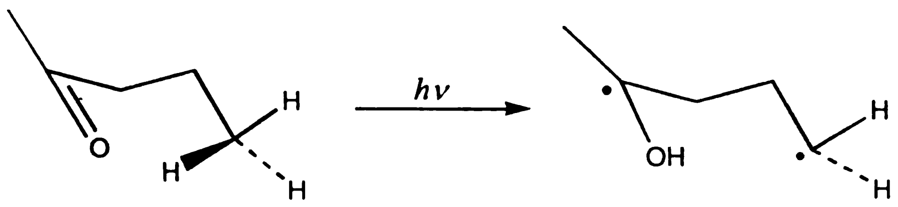
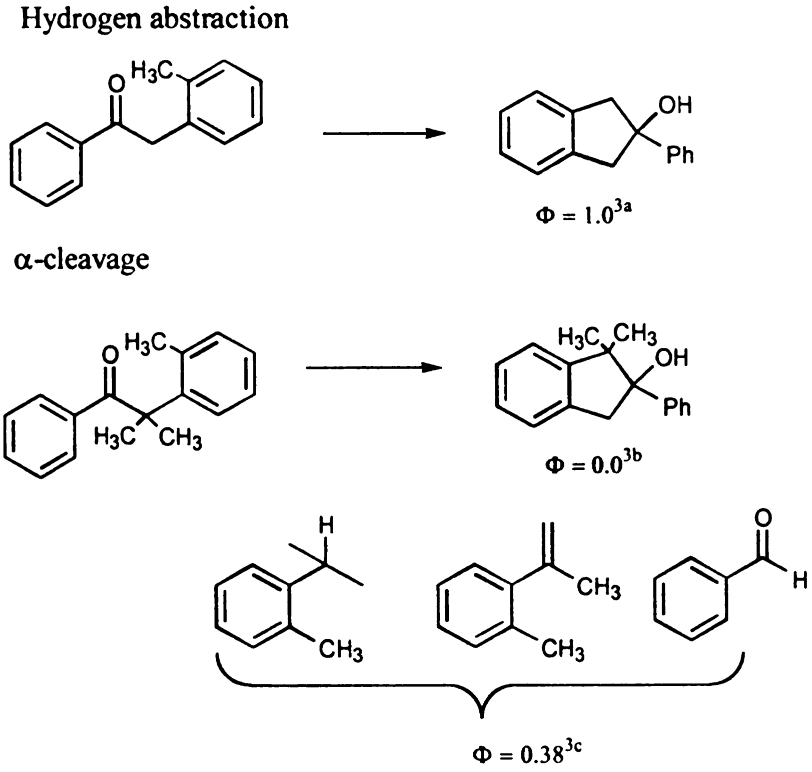


Figure 2. Chair like transition state for hydrogen abstraction

sp^3 hybridized carbon within the same molecule, undergo intramolecular abstraction. This process is favored at the γ carbon due to geometrical and thermodynamic considerations.



Scheme 2. Competition between α-cleavage and hydrogen abstraction

In the absence of γ hydrogen or when the molecular conformation allows other sites to come in close proximity to the excited carbonyl group the hydrogen shift can occur from other positions as well. Hydrogen abstraction can occur from both the singlet and triplet states, though in aromatic ketones it typically occurs from the triplet state, giving rise to a triplet biradical. If hydrogen abstraction is slowed down, α-cleavage reactions can compete.[3b, 3c] These are also called as *Norrish Type I* reactions and can occur due to a high degree of steric crowding in the reacting ketone.

Singlet vs triplet excited state

MINDO calculations performed by Dewar [4a] on butyraldehyde supported the idea that triplet reactions occur extensively via biradicals and singlet reactions promote direct radiationless decay and may form products in a concerted fashion.

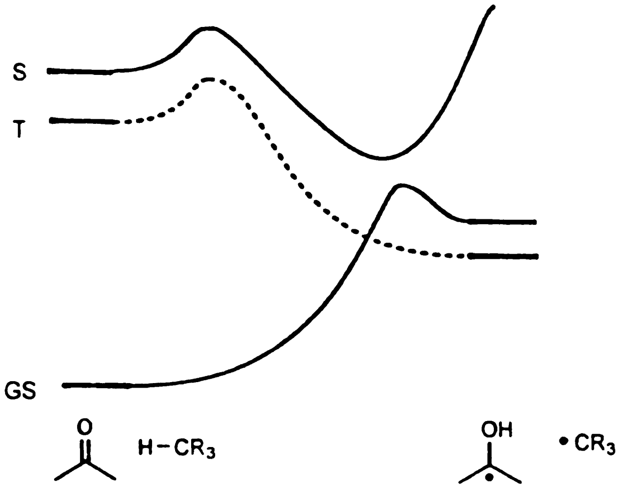
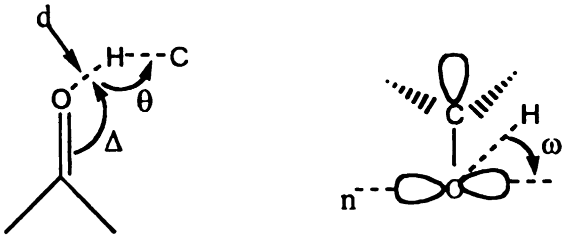


Figure 3. Reaction of singlet and triplet n,π* states with C-H bonds

It is now very easy to determine whether the reaction is singlet or triplet derived, using flash kinetics[9] or trapping studies.[4b] Photoreactions from aliphatic ketones involve both singlets and triplets,[3a] but in most phenyl ketones the rapid rate of intersystem crossing promotes exclusive triplet reactivity in bimolecular reactions.[3d]

Orientational requirements for intramolecular hydrogen transfer

In 1968 Turro suggested that the hydrogen atom to be abstracted should lie along the long axis of the carbonyl n orbital.[5] However later examples showed that hydrogen transfer took place with the H-O bond making a fairly large angle with respect to the nodal plane of the carbonyl π system.[7]



$d < 2.7$A° $\omega = 0°$ $\Delta = 90\text{-}120°$ $\theta = 180°$

Figure 4. Orientational parameters for hydrogen abstraction

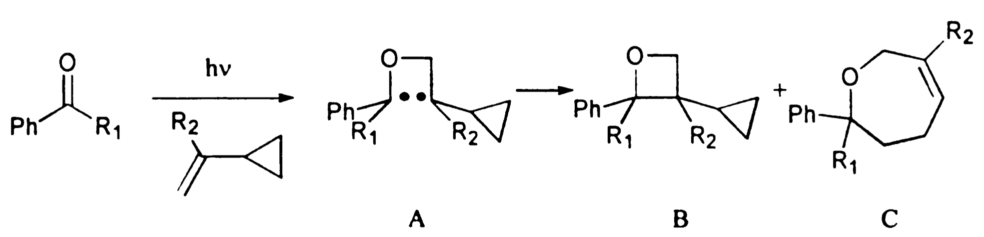
Scheffer studied various Type II reactions in crystalline state wherein the geometry was measured by x-ray diffraction.[6] He concluded that the parameters that affect abstraction are d – the distance between H and O, θ the O-H-C angle, Δ the C=O-H angle and ω, the dihedral angle that the O-H vector makes with respect to the nodal plane of the carbonyl π system. For the several ketones he studied, the values of d ranged from 2.3 – 3.1 A°, θ from 85 - 120°, Δ from 74 - 103° and ω from 0 - 62°. In the present research one of the compounds, β-cyclopropylmethoxypropiophenone has no orientational constraints, but the population of the molecules in the right geometry for abstraction could be very low due to other lower energy conformations. Secondly it was also proposed that the torsional strain present in the cycloheptane like transition state for 1,6-hydrogen transfers may be responsible for the slower rate of δ-hydrogen abstraction in straight chain systems.[8]

Biradical Lifetimes

It is now a well established fact that most of the Type II reactions are biradical in nature. Quantum yields for phenyl ketones reach unity in 2-3 M tert-butyl alcohol, but even in alcohols, aliphatic triplets do not attain 100% efficiency, leading to the inference that phenyl biradicals are longer lived than the aliphatic biradicals.[3a]

In 1977, Sciano and Small reported the first flash spectroscopic detection of the 1,4-biradical intermediate from γ-methylvalerophenone which has a 30 ns lifetime in benzene.[9] Solvents have a pronounced effect on the lifetime of hydroxy biradicals, which is considerably increased, presumably due to hydrogen bonding.[15] There is a similar parallel between solvent effects on lifetimes of some 1,5 biradicals.[15]

Nishida and co-workers[10] studied the photoreaction of arylketones with vinylcyclopropane and have estimated the lifetimes of the 1,4 biradical intermediates from the product ratios and the cyclopropylethyl rearrangement rate of $2 \times 10^7\ s^{-1}$. This reinforces the fact that oxygen-containing Norrish type II 1,4 biradicals have a short lifetime.[11] Similarly the 1,5 biradicals formed by intramolecular δ-hydrogen abstraction in o-alkoxy ketones also have a very short lifetime.[17]



	Product Ratio (B/C)	Lifetime of A
R_1=H, R_2=H	14.6	4 ns at 50°C
R_1=H, R_2=CH_3	21.0	2.3 ns at 75°C
R_1=Ph, R_2=CH_3	4.3	11 ns at 75°C

Figure 5. Life time of 1,4 biradical containing oxygen

δ - Hydrogen abstraction and fate of the consequent biradical

As noted earlier, intramolecular hydrogen abstraction can occur from sites other than the γ position, either when there is no γ hydrogen or when the molecule provides effective competition in the formation of a 7-atom cyclic transition state.

An ideal example of the latter is δ-methoxyvalerophenone,[13] in which the activation of the δ site is so great that abstraction from this position has the same rate coefficient (2.5 x 10^7 s-1) as that from the γ position. At the same time it is also true, that for equivalent C-H bonds, the δ-H abstraction rate is usually only about 5% of that from the γ position.[8] The species produced from the δ-hydrogen abstraction is a 1,5 diradical, which cannot undergo simple cleavage like the corresponding 1,4 diradical,[14] but the cyclization reaction may occur. A hydrogen-deuterium exchange that occurs between the α and δ positions shows that the efficiency of cyclization may be low due to the disproportionation (hydrogen transfer) to yield the enol of the starting ketone.[15] The Wagner group has studied δ-H abstraction for some acyclic compounds as well as some ortho-substituted phenyl ketones that impose a form of endocyclic restriction on the photochemistry. Most of the work in this area has been done on aromatic ketones and as with all such systems the hydrogen abstraction results from the triplet (n, π*) state.

The system that is very well studied by the Wagner group, is the ortho-substituted phenyl ketones.

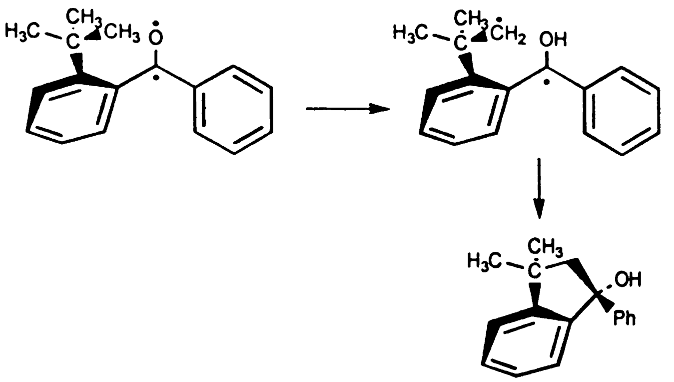


Figure 6. Conformational effect in photochemistry of o-tert-butylbenzophenone

Among the most cited examples is the ortho-tert-butylbenzophenone, which undergoes a very clean photoreaction not only in solution but also in the crystalline state.[16] Hydrogen abstraction occurs with a rate constant >10^9 s^{-1}. X-ray analysis indicates that the o-t-butylphenyl ring is twisted 69° with respect to the nearly planar benzoyl group. Two hydrogens on the t-butyl group lie within 2.7 A° of the carbonyl oxygen, one with an angle ω of 40°, the other with nearly 90°. The former makes a perfect conformation for hydrogen abstraction, and the rapid kinetics is proof of this. Various other systems have been studied, with substitutions on the benzene ring or ortho alkoxy substitution instead of the tert-butyl.

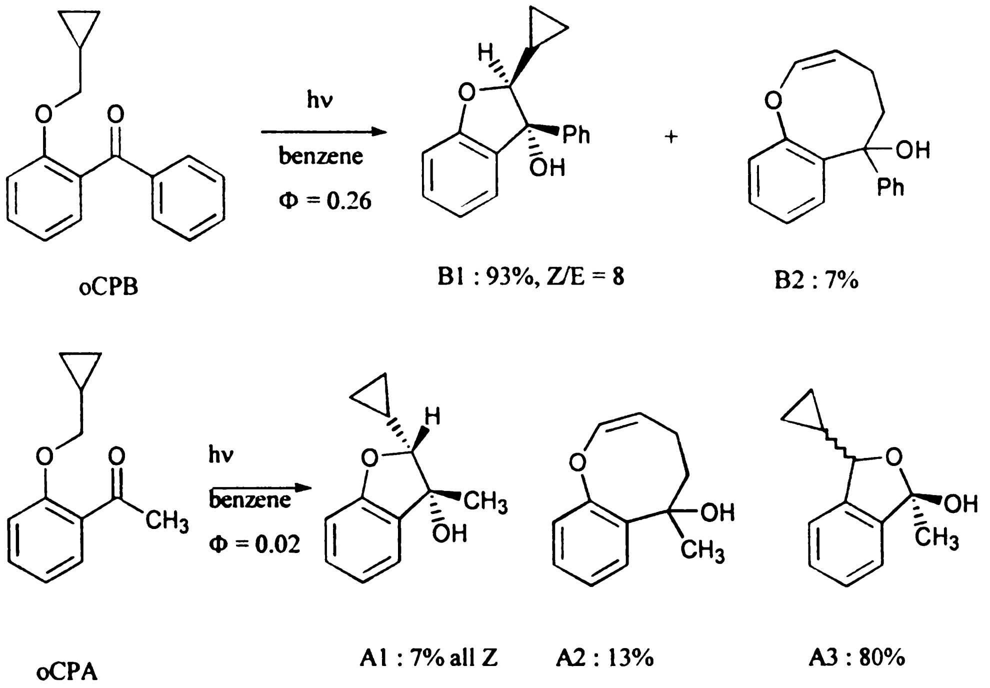


Figure 7. Different behavior of oCPB and oCPA biradicals

One of the more interesting examples in context with the present research is the photochemistry of o-(cyclopropylmethoxy) benzophenone (oCPB) and o-(cyclopropylmethoxy) acetophenone (oCPA),[17] which form different products, the oCPB cyclizing mainly to the epimeric benzfuranols and the oCPA also forming some benzfuranol but the major product being the hemiketal of an o-acetylbenzyl alcohol. In spite of this difference, both have similar short biradical lifetimes.

Acyclic β-alkoxy ketones

Two types of compounds that were extensively studied were, one in which there was no γ-hydrogen and the other where the δ C-H bond was activated by an alkoxy group.

In 1979 Wagner and Chiu thoroughly investigated the photochemistry of β-ethoxypropiophenone in order to characterize the formation and behavior of its 1,5 biradical.[18a] The triplet lifetime of the compound, which presumably is the rate of δ - hydrogen abstraction by its lowest n,π* state, is 2 x 10^7 s^{-1} which is large enough that no physical decay competes.

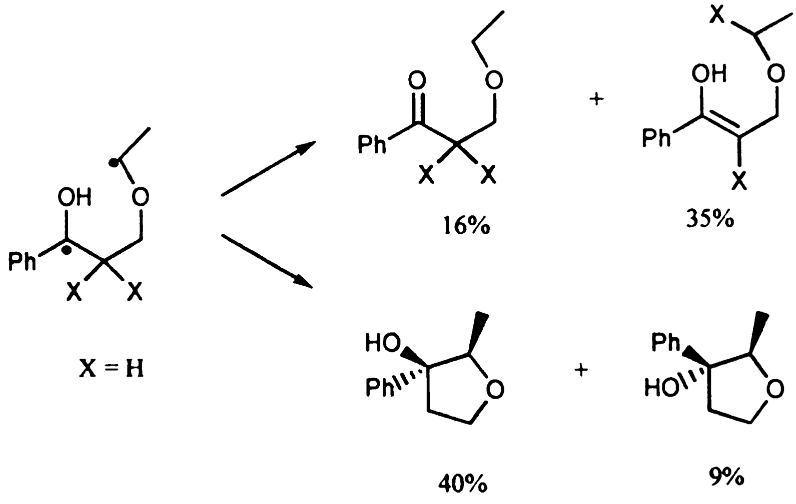
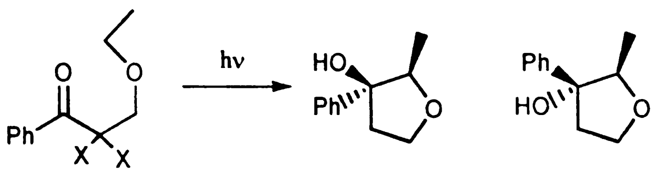


Figure 8. Products from photochemistry of β-ethoxy propiophenone

Its only photoproducts are the two diastereomeric oxacyclopentanols and the enol of the starting ketone.

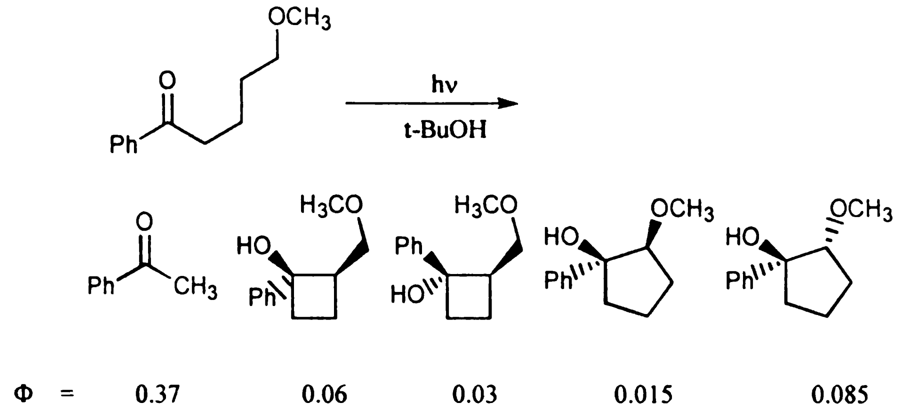


X = H	benzene	0.40	0.09
	t-BuOH	0.13	0.16
X = D	benzene	0.52	0.12
	t-BuOH	0.23	0.31

Table 1. Quantum Yields for product formation from β-ethoxypropiophenone

The Z/E product ratio depends on solvent polarity. There is little selectivity in Lewis base solvents, but solvents like benzene strongly favor the isomer with the methyl trans to the phenyl. Alcohols do not raise the cyclization quantum efficiency, as they do in the 1,4 biradicals, in which hydrogen bonding to the hydroxy group increases the effective bulk and supresses the disproportionation back to the starting ketone. In 1,5 biradicals also there is hydrogen bonding, which increases the bulk thus lowering the distereoselectivity.

In δ-methoxyvalerophenone the rate of δ hydrogen abstraction is nearly equal to that from the γ position.[13] However, it is worth noting that the quantum efficiency of cyclopentanol formation is only 10%. It can thus be concluded that there are other reactions that compete very well with cyclization of 1,5 biradicals.



Scheme 3. Photoproducts from the irradiation of δ-methoxy valerophenone

More remote hydrogen abstraction

There have been several examples of more remote hydrogen abstraction, ranging from ε hydrogen for ketones that have no γ or δ hydrogens[19a] to cyclization of benzophenones with long alkyl chains attached at the para position.[19b] This would make a very interesting but a whole different field of research.

Photoenolization

The photoreduction of benzophenone to benzopinacol is an extensively examined reaction, which led to the discovery of photoenols in ortho-alkyl phenyl ketones. The reduction process was shown to proceed by abstraction of hydrogen by the triplet (n,π*) state of the carbonyl group. In propan-2-ol the quantum yield for pinacol formation ϕ_{red} is 2.0.[20] Introduction of an ortho alkyl substituent having a benzylic hydrogen largely suppressed the pinacol formation. O-Methylbenzophenone has a quantum yield for reduction ϕ_{red} = 5% in propan-2-ol.[21] On the other hand, 4-methyl benzophenone gave high quantum yields of ϕ_{red} = *ca.*50%.[21] These experiments suggested that the reduction was not being suppressed by electronic factors and thus a photoenol intermediate was proposed.[22]

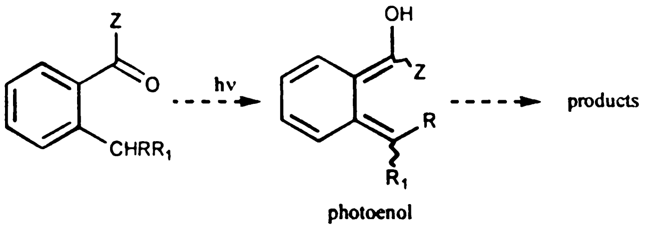
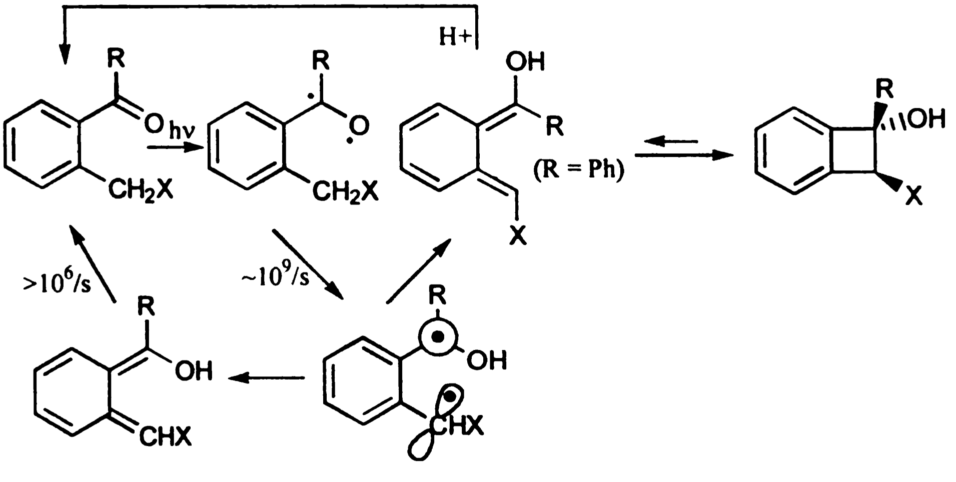


Figure 9. Photoenolization of 2-alkyl phenyl ketones

In 1961 Yang and Rivas demonstrated that dienol intermediates obtained by irradiation of 2-methyl and 2-benzylbenzophenones were sufficiently long lived to allow chemical trapping, by cycloaddition with a dienophile or quenching with oxygen. These trapping experiments facilitated a better understanding of the mechanism for photoenolization.[23] The stereoselective nature of cycloaddition products obtained from the irradiation of 2-methyl-benzophenone in the presence of maleic or fumaric acid also indicates the formation of ground state enols. The term photoenol is no longer unique due to various other forms of photoenolization and thus the term *o-xylylenols* has been suggested by the Wagner group.[26a] While chemical trapping was indirect evidence of the o-xylylenols, transient absorption spectroscopy provided direct evidence of the enol intermediates. It was not until a decade later that Matsurra reported the subsequent electrocyclic ring closure of photochemically generated dienols to benzocyclobutenols in 2,4,6-trialkyl phenyl ketones.[24] Earlier it was assumed that cyclization occurred only in sterically congested dienols. However this was not consistent with some of the other compounds that cyclized. 2-Methylbenzaldehyde on irradiation gives the benzocylobutenol.[25] Upon heating the benzocyclobutenols open to the E-enol with subsequent reversion to the parent ketone.



Scheme 4. Photochemistry of o-alkyl phenyl ketones[26a]

Scheme 4 depicts the current consensus as to the structure and chronology of the transient intermediates formed from the triplet o-alkylphenyl ketones.[26a] Hydrogen abstraction is followed by a biradical triplet o-xylylenol which decays to the ground state with both the E and Z configuration of the OH group. The Z configuration is very short lived and reverts to the starting ketone rapidly, thus all the product formation occurs from the E isomer. It undergoes acid-base catalyzed reketonization with benzylic H/D exchange, but is invariably long lived enough to undergo benzocyclobutenol formation, Diels Alder cycloadditons, dihydroanthrol formation and dimerization. From extensive research it was concluded that the product geometries and isomer distribution are set when the biradical triplet xylylenol decays to ground state.[26b]

Quantum yields and Quenching studies

Quantum Yield of a reaction is the number of molecules of product formed per photon of light absorbed. The number of photons of light absorbed are usually obtained with the help of actinometers, which are compounds with known quantum efficiencies.

The Stern-Volmer equation is a mathematical relationship between quantum yields in the absence (ϕ°) and presence (ϕ) of quencher and is written as

$$\phi^\circ/\phi = 1 + k_q \tau [Q]$$

Equation I

A plot of ϕ°/ϕ versus [Q] should give a straight line with an intercept of 1 and a slope of $k_q\tau$. For most cases the quenching is diffusion controlled and thus if k_q is known (e.g. it is $6 \times 10^9\ M^{-1}\ s^{-1}$ in benzene at room temperature), the triplet lifetime can be calculated from the slope of the Stern-Volmer plot.

Goals of research

Hydrogen abstraction reactions from the δ carbon have been studied for many classes of carbonyl compounds. The photochemistry of γ-cyclopropylbutyrophenone has revealed that the 1,4 biradical generated by γ-hydrogen abstraction undergoes radical rearrangements in competition with more normal type II reactions,[18b] in proportions that indicate that the lifetime of the biradical is between 35-50 ns in benzene. Besides acetophenone, 1-phenyl-4-cycloheptenol and 1-phenyl-4-hepten-1-one were identified as the other major photoproducts. The latter was obtained in a quantum yield of 0.26 in benzene as solvent, (cis/trans ratio not determined). Thus the question was asked: how will the addition of an oxygen in the tether effect the biradical lifetime and the outcome in terms of the products formed? Firstly by putting an oxygen in the chain, we will be forming a 1,5 biradical (by δ-hydrogen abstraction) and it would be interesting to know how it would differ in lifetime from the preceding 1,4 biradical. Secondly as mentioned earlier, oxygen is said to have an effect on the 1,4 biradical, wherein the eclipsing effect is reduced when the carbon atom is replaced with oxygen, which facilitates bringing the two ends of the biradical together. Another explanation offered for this effect is the spin-orbit coupling which induces intersystem crossing, probably by through-space interaction of the unpaired electrons of oxygen.[18c] This phenomenon has also been used to explain the high cyclization efficiency of the α-alkoxyacetophenones.[18d] Wagner and Jang[17] have also used the radical clock method for determining the biradical lifetimes of o-(cyclopropylmethoxy)benzophenone and o-(cyclopropylmethoxy)acetophenone, which are between 2 and 5 ns. The short lifetimes can be attributed to the ease of cyclization due to two factors, presence of oxygen and rigidity of the molecule. We designed a new molecule, β-(cyclopropylmethoxy)propiophenone keeping in mind the above two as models. It would be interesting to study how oxygen affects the biradical lifetime for this molecule. Identification of the photoproducts and their yields reveal the lifetime of the 1,5 biradical formed from δ-hydrogen abstraction. In this case the competing cyclization and cyclopropylcarbinyl-to-allylcarbinyl rearrangement of the 1,5 biradical will be studied.

Solution photoenolization of o-benzyl benzophenone and cyclization of the o-xylylenols have been studied.[26a] The outcome in the solid state would help answer some of the conformational effects on the lifetime on the resulting biradical. Thus these became the two target molecules of the present research.

RESULTS AND DISCUSSION

Irradiation of β-cyclopropylmethoxypropiophenone (CMP)

The ultraviolet absorption spectrum of β-cyclopropylmethoxypropiophenone was first taken and 313 nm was the wavelength chosen for irradiation. 0.05 M solutions of the compound in both benzene-d_6 and acetonitrile-d_3 were then irradiated at 313 nm at room temperature.

The reaction was first followed by ^{1}H-NMR, at time intervals of 10 minutes for the first 30 minutes followed by 30 minute intervals. The time intervals were subsequently increased and the reaction monitored for 24 hours. ^{1}H-NMR spectra indicated the formation of more than one compound, but did not show any one in a substantially higher yield than other. The reaction was then followed by HPLC, using a silica column and 97 : 3 mixture of hexane and ethyl acetate. HPLC showed formation of two distinct compounds with similar absorption patterns, whose peak intensities increased for the first 24 hours. After 24 hours there was an appearance of the third peak, with a subsequent increase in its formation while the peak size of the first two compounds diminished. The reaction was allowed to run for seven days. The two compounds that were initially formed, at low conversion were isolated by semi-preparative HPLC and characterized.

Through various spectroscopic evidence, the structure of the first peak isolated on HPLC was confirmed as being A. The ^{1}H-NMR spectrum shows two distinct olefinic protons with chemical shifts characteristic of enol ethers, and carbonyl proton. The presence of a carbonyl carbon is confirmed by IR which shows a carbonyl stretch at 1684 cm $^{-1}$.

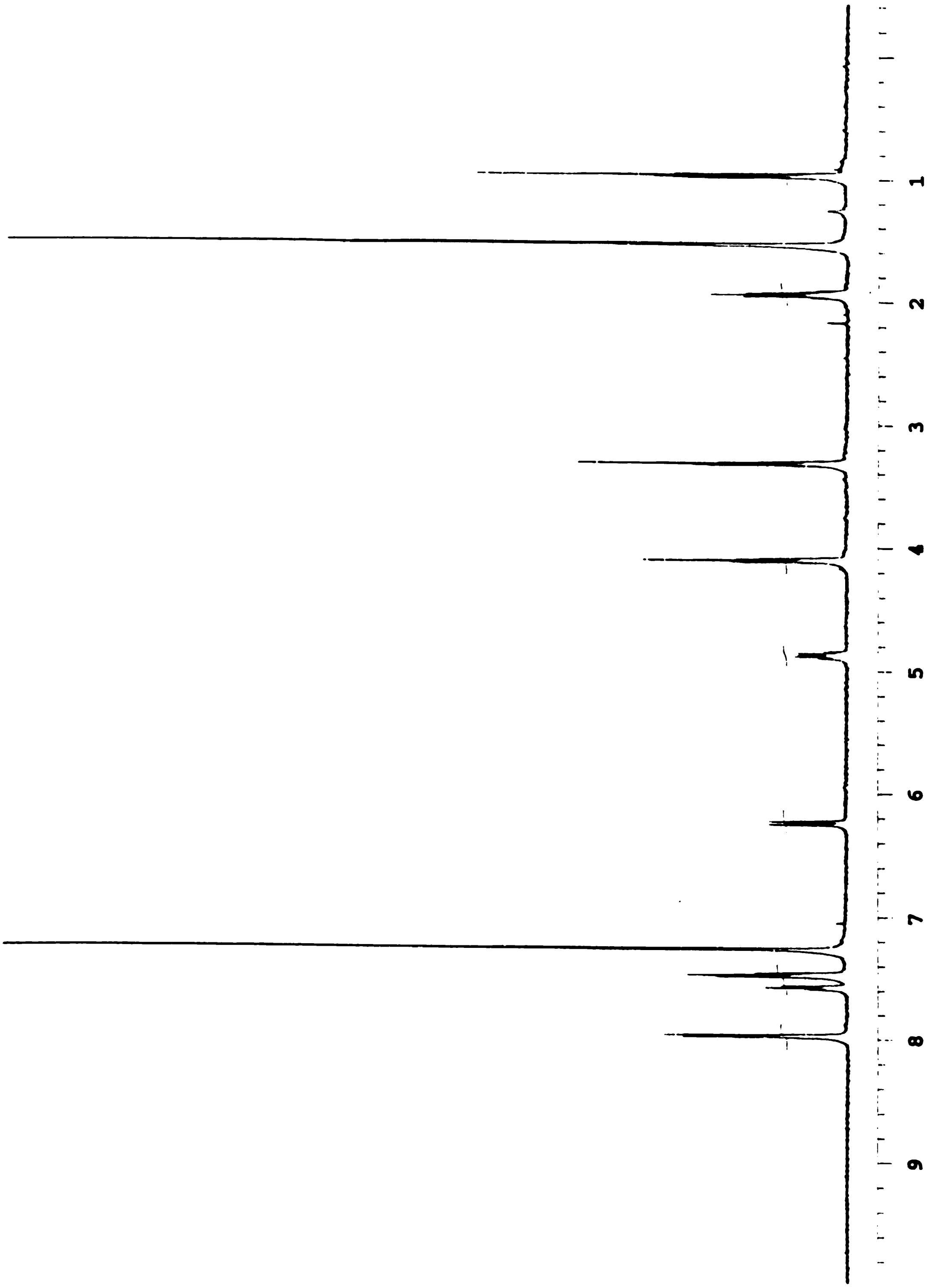


Figure 10. ^{1}H-NMR of compound A

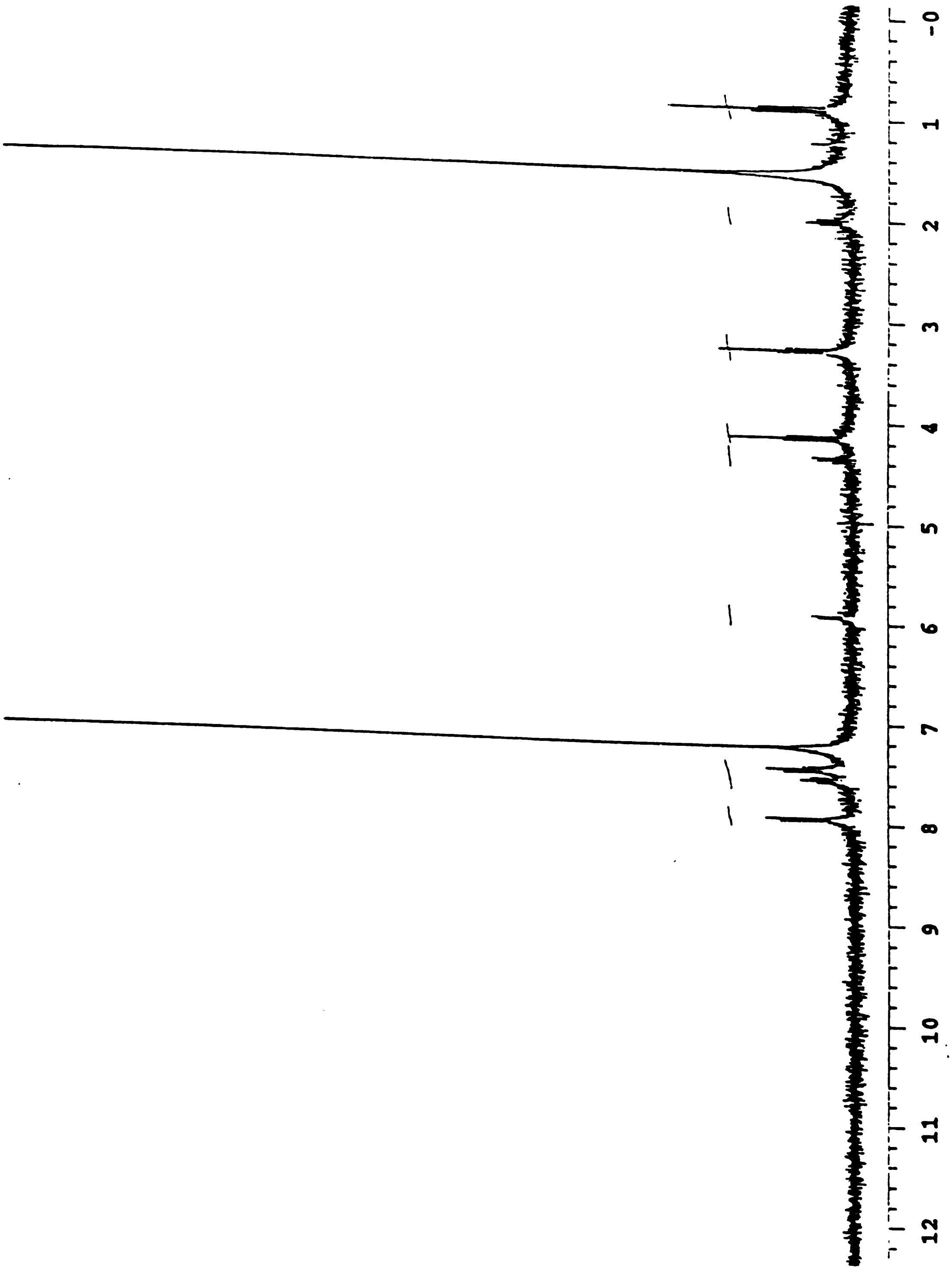


Figure 11. ^{1}H-NMR of compound B

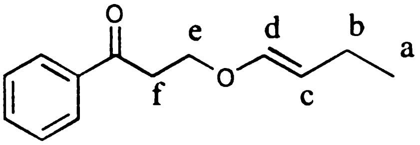


Figure 12. Structure of compound A

Proton decoupling NMR experiment shows Hb coupling with Ha and Hc, Hc coupling with Hb and Hd. Coupling can also be seen between He and Hf.

Compound B

The second compound was isolated and characterized in the similar fashion by NMR, IR and proton decoupling.

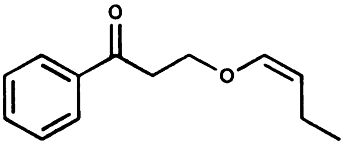


Figure 13. Structure of compound B

From absorption pattern and NMR data it can be concluded that the two compounds are isomers. J value from the NMR data also suggests that A is the trans isomer with respect to the olefinic double bond (J=14.0Hz) and B is the cis isomer (J=9.3Hz). The third product that appears after higher conversion was not identified.

Based on our knowledge of kinetics of hydrogen abstraction and cyclopropyl ring opening, we can propose the following mechanism for the reaction. Since the products are derived from a biradical species, we can safely assume the reaction to be occuring from the triplet (n, π*) state, the product formation would be different if the reaction were to go through the singlet state.

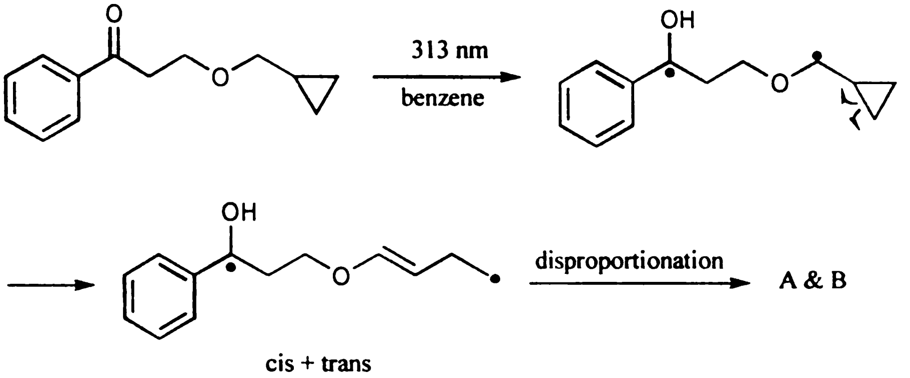


Figure 14. Proposed mechanism for product formation

Quantum Yield

Quantum yields for formation of both the compounds A and B were measured at room temperature. A 0.05 M solution of β-cyclopropylmethoxypropiophenone was irradiated in benzene at 313 nm, with 0.1 M valerophenone solution as actinometer. The yield was measured on HPLC. The observed quantum yield was 0.09 for the cis isomer and 0.14 for the trans isomer as compared to 0.49 (cis and trans oxacyclopentanols) formed from β-ethoxypropiophenone.

The quantum yield of product formation appears to be low because 1,5 biradicals often disproportionate to the enol of the starting ketone and then reketonize rapidly. Previous studies have indicated that the 1,5 biradical generated photochemically from β-ethoxypropiophenone,[18] undergoes internal disproportionation by two pathways, 1,6–H transfer which generates the starting ketone and 1,4–H transfer, the major pathway, generating the enol of the starting compound. The γ oxygen in the molecule imparts a unique characteristic wherein the five-atom transition state leading to the enol is free of any significant eclipsing interaction. Only two products were obtained from the reaction, the (Z) and (E)-oxacyclopentanols. Photochemistry of o-(cyclopropylmethoxy) benzophenone also shows formation of the cyclopentanol ring with a quantum yield of 0.26; some formation (7% chemical yield) of the cyclooctenol was also observed.[18] But no product derived from the biradical with trans double bond was obtained, as opposed to CMP, where we obtained both the cis and trans double bond. In our present system, there was no cyclopentanol formation. This is because of the competition between cyclization of the biradical and high rate of radical opening of the cyclopropyl ring. The rate of cyclopropyl ring opening is generally on the order of 10^8 s^{-1}.[27]

Quenching Study

A quenching study was carried out on a 0.028 M solution in benzene d_6 with 2, 5-dimethylhexa-2,4-diene as the quencher. A 0.01 M solution of valerophenone was used as the actinometer. The ampoules holding the sample were placed in a merry-go-round setup, at room temperature and irradiated at 313 nm for five hours. Analysis was carried out using HPLC. Values of 360 and 215 for $k_q\tau$ were obtained from the Stern-Volmer plots. As discussed in the introduction, the reciprocal of τ is equal to the rate constant of hydrogen abstraction. Based on k_q=6x10^9 $M^{-1}s^{-1}$ quenching study shows the rate of triplet ketone decay to be about 2x10^7 s^{-1} as compared to that measured for β-ethoxypropiohenone and 2x10^9 s^{-1} measured for α-ethoxyacetophenone

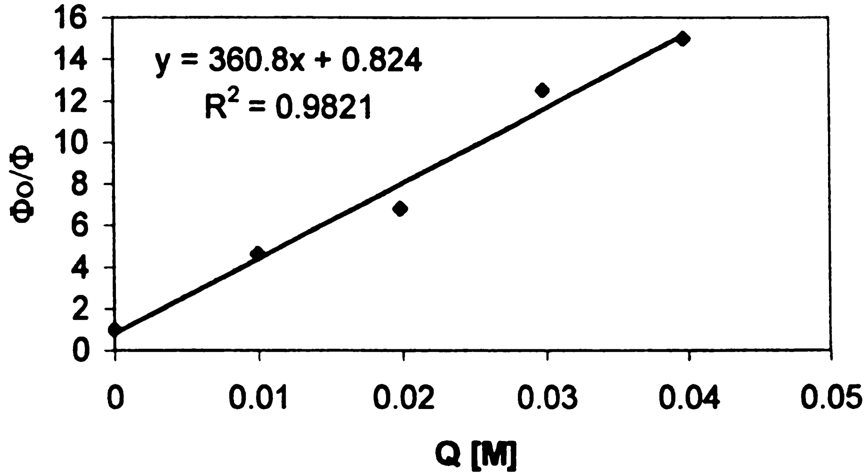


Figure 15. Stern Volmer quenching results for compound A

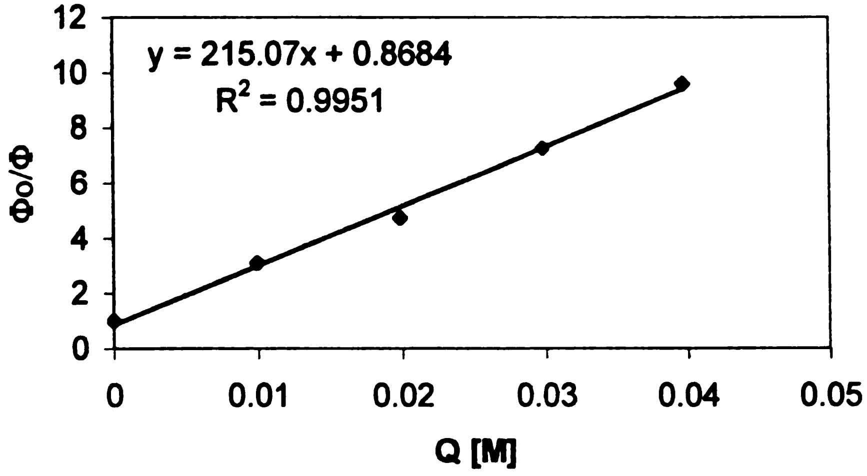


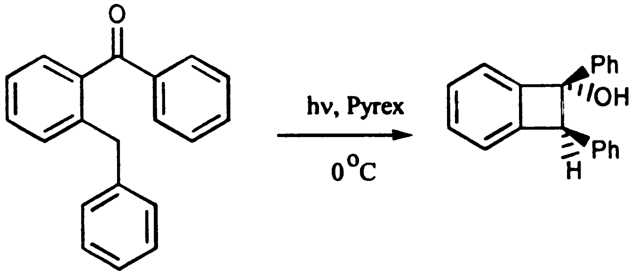
Figure 16. Stern Volmer quenching results for compound B

In the present system only products from ring opening are observed and thus it can be assumed that the lifetime of the biradical in this case is considerably long. We cannot predict the exact lifetime of the biradical, but based on the radical clock technique, which takes into account all the products formed from the biradical and uses the rate of formation of the products to calculate the lifetime of the biradical, we can propose that the lifetime of our biradical is closer to 50 ns, assuming minimal formation of the cyclization product. It is perplexing however, that no cyclization is observed inspite of the presence of the oxygen atom. Moreover a total quantum yield of 0.26, and no other product formed, means that 74% of reversal to the starting ketone is observed. To revert to the starting ketone, the biradical has to go through a cyclic transition state, so it is surprising that no cyclization products are formed.

In conclusion radical rearrangement is the only observed process, followed by disproportionation to yield the two products, through a considerably long lived biradical. Oxygen does not seem to play a role deciding the fate of the biradical, contrary to expectations. The trans isomer would be expected to cyclize into an eight membered ring, but probably does not due to the competing disproportionation.

Photochemistry of o-benzyl benzophenone

A 0.01 M sample of o-BzBP was irradiated in acetonitrile-d_4, toluene-d_8 and methanol-d_4, at 0°C and temperature of dry ice. Irradiation was done in a medium pressure mercury lamp (Pyrex filtered). The samples turned greenish-yellow on irradiation. It took 1hr and 40 minutes for the reaction to go to completion with the formation of o-BzBP-ECB at 0°C in toluene-d_8. It took approximately similar time frame in the other solvents. Sobzack has previously characterized the structure and thus the ^{1}H-NMR and ^{13}C-NMR structures were compared to his results. In toluene-d_8 the benzylic methylene at 4.03 ppm disappeared and a new singlet appeared at 4.71 ppm. There is also appearance of another singlet at 2.21 ppm, which is the hydroxy group. The ^{13}C-NMR shows two distinct aliphatic resonances, which are consistent with the o-BzBP-ECB structure. The sample was stable at dry ice temperature but reverted back to the starting ketone at room temperature. A significant yellow-green fluorescence was retained even on reversal to the ketone.



o-BZBP

o-BZBP-*ECB*

Figure 17. Photochemistry of BZBP

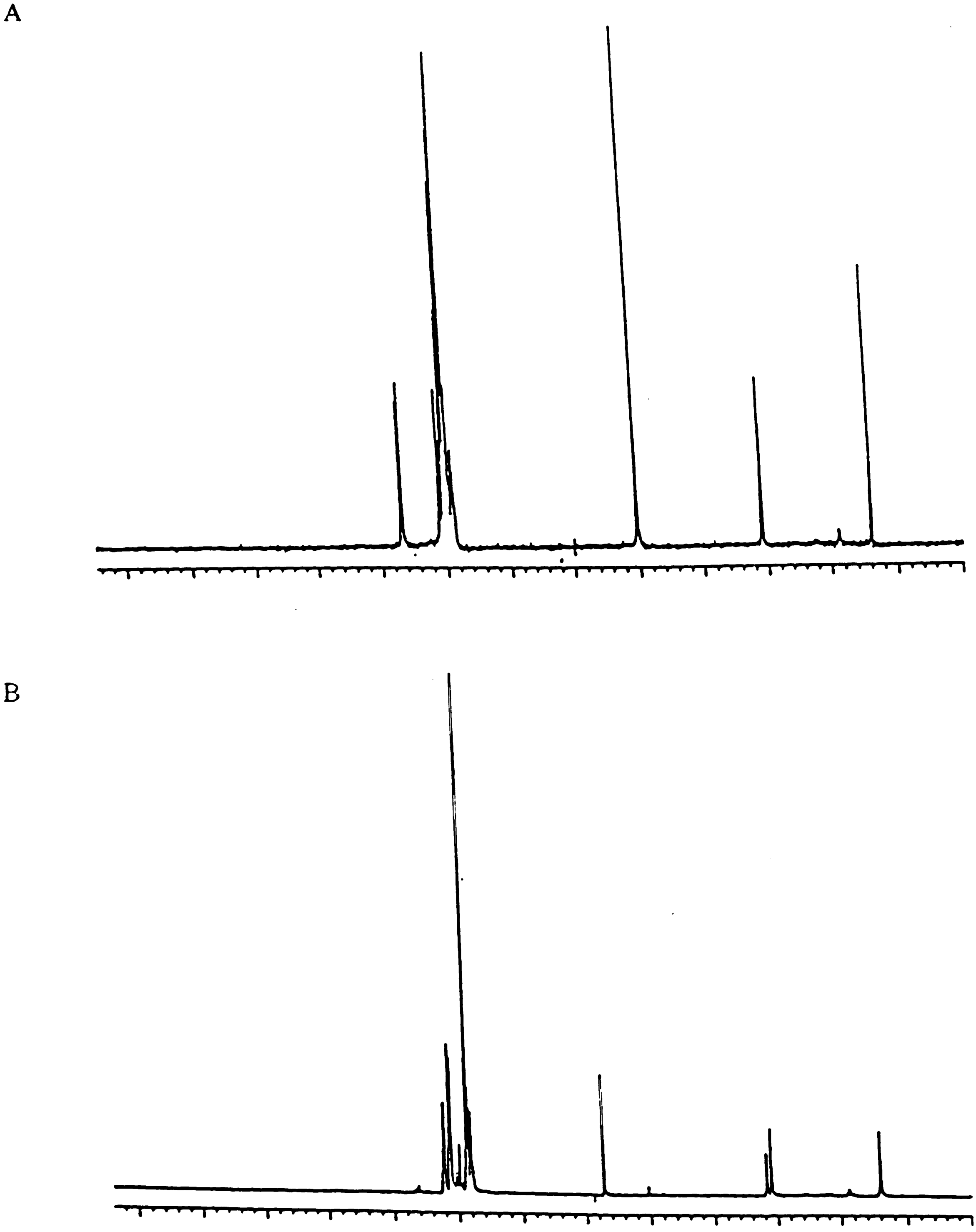


Figure 18. ^{1}H-NMR for BzBP in toluene-*d6* Before (A) and After (B) irradiation

Degassed solid o-BzBP was irradiated under medium pressure mercury lamp. ^{1}H-NMR was taken of its $CDCl_3$ solution. No significant change was observed in the spectrum after four hours, but the color of the solid turned a light shade of yellow. After longer irradiation period, i.e. 20 hours, two singlets appear at 4.96 and 4.99 ppm. The color of the solid becomes more intense. The conversion is very low. The two peaks can be assigned to the two benzylic methylene protons in – o-BzBP-ECB and o-BzBP-ZCB, respectively, based on the characterization by Sobzack.[29] The o-BzBP-ECB hydroxy group appears at 2.25 ppm and for the Z-isomer appears at 2.9 ppm. The Z isomer is short lived, because ^{1}H-NMR of the same sample, stored at 0°C, for 4 hrs. shows considerable decrease and near disappearance of the peaks at 4.99 and 2.9 ppm.

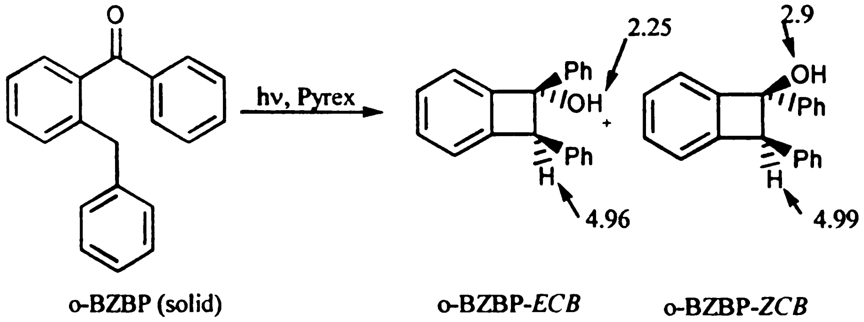


Figure 19. Irradiation of solid BzBP

Though the ^{1}H-NMR shows formation of only two products, when the sample is injected into HPLC, there is another product observed, whose intensity is more than that for the o-BzBP-ECB and o-BzBP-ZCB. This peak was isolated on HPLC and characterized by ^{1}H-NMR and mass spectroscopy.

From the absence of the methylene proton and presence of aromatic protons only, in ^{1}H-NMR and the distinct m/z peak at 286.0 and other mass peaks, this compound was identified as o-dibenzoyl benzene. In spite of rigorous degassing, there was some oxygen, which probably gave this result. O-BzBP is a low melting solid, which is clumpy in nature and must have trapped the oxygen.

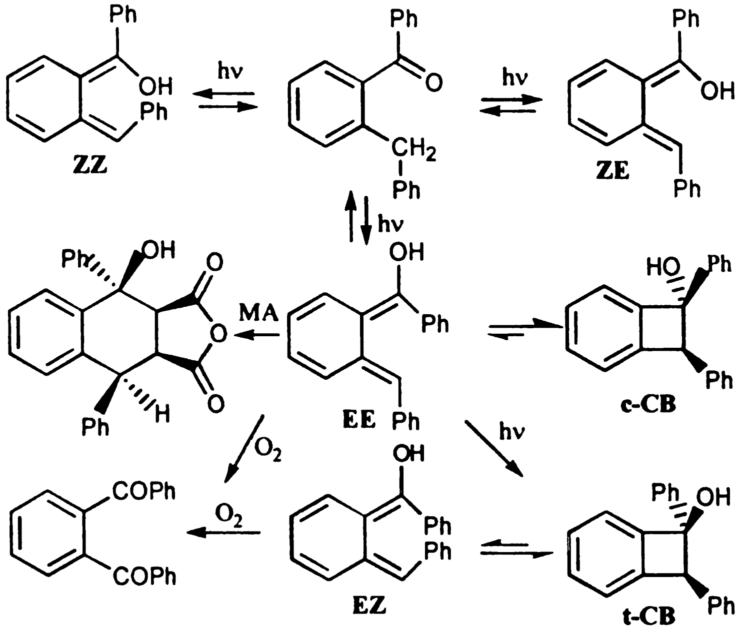


Figure 20. Formation of the four o-xylylenols and benzocyclobutenols

Photoenolization and the chronology of benzocyclobutenol formation has been studied by the Wagner group for some time, especially with respect to substituent effects. Factors that affect this chronology are 1) initial geometry for hydrogen abstraction; 2) nature of excited state; 3) lifetime of the biradical; 4) fate of the o-xylylenols; 5) stability of benzocyclobutenols.

Various studies, like trapping experiments with maleic anhydride and oxygen, kinetic data and computational studies provided more insight into the formation of the ortho-xylylenols. The results seem to support the mechanism which shows formation of four different geometries of the triplet biradical, yielding four different ortho-xylylenols.

In solution the photoreaction is very stereoselective which is confirmed by the Diels-Alder reaction when o-BzBP is irradiated in presence of MA. Brief irradiation converts the o-BzBP quantitatively into c-CB.

From our results, it is observed that in the solid state, the stereoselectivity of cyclobutenol formation is lost. When the ^{1}H-NMR is taken as soon as irradiation is complete and the tube stored at 0°C, formation of both the isomers is seen. When left in solution for several hours the NMR peak for the t-CB disappears, which probably goes to the EZ xylylenol and forms the o-dibenzoyl benzene or the starting ketone.

EXPERIMENTAL

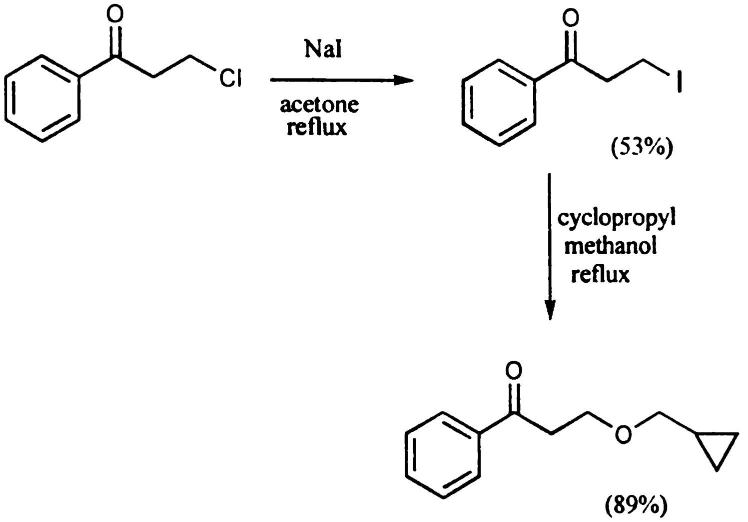
General Procedures

^{1}H-NMR, ^{13}C-NMR, proton decoupling, DEPT and hetero-COSY spectra were obtained using Varian Gemini 300 MHz and VXR 500 MHz spectrophotometers, with VXNMR software. Deuterated solvents used were obtained from Aldrich Chemical. Chemical shifts were measured relative to chloroform-d_1 (7.24 ppm for ^{1}H and 77.0 ppm for ^{13}C), benzene-d_6 (7.10 ppm for ^{1}H-NMR) and toluene-d_8 (2.09 ppm for ^{1}H). Fourier Transform Infrared spectra were obtained using a Nicolet IR/42. Samples were prepared in a 0.025mm solution cell with carbon tetrachloride as solvent or on NaCl plates using chloroform as the solvent. UV-VIS absorption spectra were obtained on a Shimadzu UV-160 spectrophotometer with matched 1.0 cm quartz cells. Low resolution mass spectra were recorded using a Hewlett Packard 5890 GC/MS. Gas Chromatograpic analyses were performed on a Varian 3400 chromatograph equipped with flame ionization detector. HPLC analyses were conducted on a Rainin system equipped with a two solvent delivery pumps, a UV detector, a 20 µL loop and a normal phase Microsorb Si80-125-CS column. The data were acquired using a Dell PC. Melting point was determined using a capillary Uni-Melt melting point apparatus.

Synthesis

A. β-Cyclopropylmethoxypropiophenone

CMP was made in a simple two step manner according to the following scheme.



Scheme 5. Synthesis of CMP

β-iodopropiophenone (IP)

Standard literature method was used to carry out the first step.[27] To a solution of 16.17 g (0.1078 moles) of sodium iodide in 25 mL of anhydrous acetone was added a solution of 2.175 g (0.013 moles) of previously recrystallized β-chloropropiophenone (from petroleum ether) in 75 mL of anhydrous acetone. The solution was refluxed for 5 hours and then concentrated under reduced pressure to afford a solid residue. This residue was triturated with ether. The ether was then filtered to remove any traces of sodium chloride. Upon distilling off the ether, a solid residue was obtained which was recrystallized from petroleum ether to yield 1.94 g of pure β-iodopropiophenone (53%) as a slightly yellow colored solid which melted at 61-63°C (lit.[28a] mp 61-62°C).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm: 3.46 (t, 2H), 3.62 (t, 2H), 7.42-7.62 (m, 3H), 7.92 (d, 2H).

β-(cyclopropylmethoxy)propiophenone (CMP)

0.5 g (1.92 mmoles) of IP was then refluxed with 16 mL (0.2 mole) of cyclopropylmethanol for 16 hours. The excess cyclopropylmethanol was distilled off leaving behind the crude product. The material was purified by column chromatography using a 77 : 13 mixture of hexane and ethyl acetate. Chromatography for the second time with the same eluant yielded 0.35 g (1.72 mmoles) of pure CMP (89% yield). Characterization was done using NMR, ^{13}C-NMR, Hetero-COSY, proton decoupling experiments, DEPT and mass spectroscopy

^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm: 0.16 (dd, 2H, J = 5.4 Hz, 8.01Hz), 0.49 (dd, 2H, J = 5.4 Hz, 8.01Hz), 1.02 (ttt, 1H, J = 6.6 Hz), 3.25 (t, 2H, J = 7.3 Hz), 3.28 (d, 2H, J = 6.6 Hz), 3.84 (t, 2H, J = 7.3 Hz), 7.4-7.6 (m, 3H), 7.93 (d, 2H)

^{13}C-NMR ($CDCl_3$, 75MHz) δ ppm: 2.98, 10.5, 38.8, 65.7, 75.9, 128, 128.5, 133.1, 170.0, 198.0.

GC-MS (m/z): 204 (100%), 203 ($M^{+\cdot}$), 133, 105, 77.

DEPT spectra accounts for four secondary carbons (two equivalent) and four tertiary carbons (four equivalent).

FTIR ($CHCl_3$, cm^{-1}) 3020 (s), 1684 (m-s), 1215 (s)

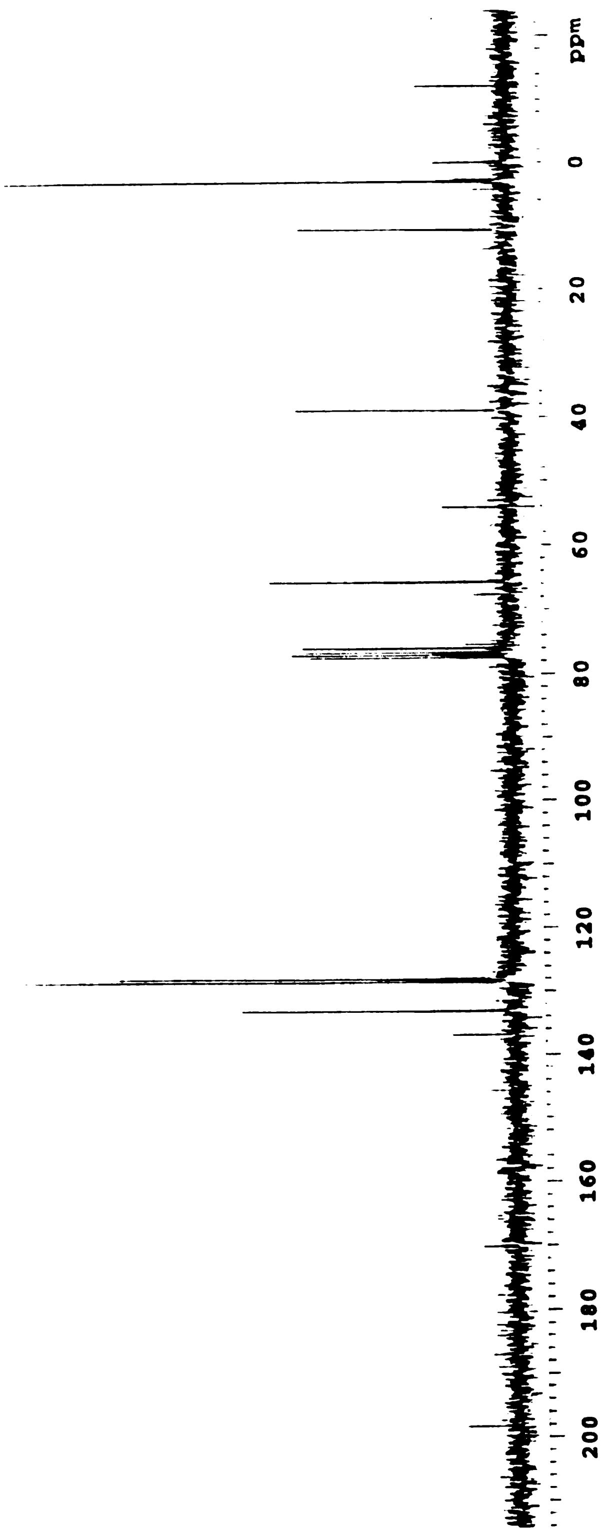


Figure 21. ^{13}C-NMR of β-cyclopropylmethoxypropiophenone

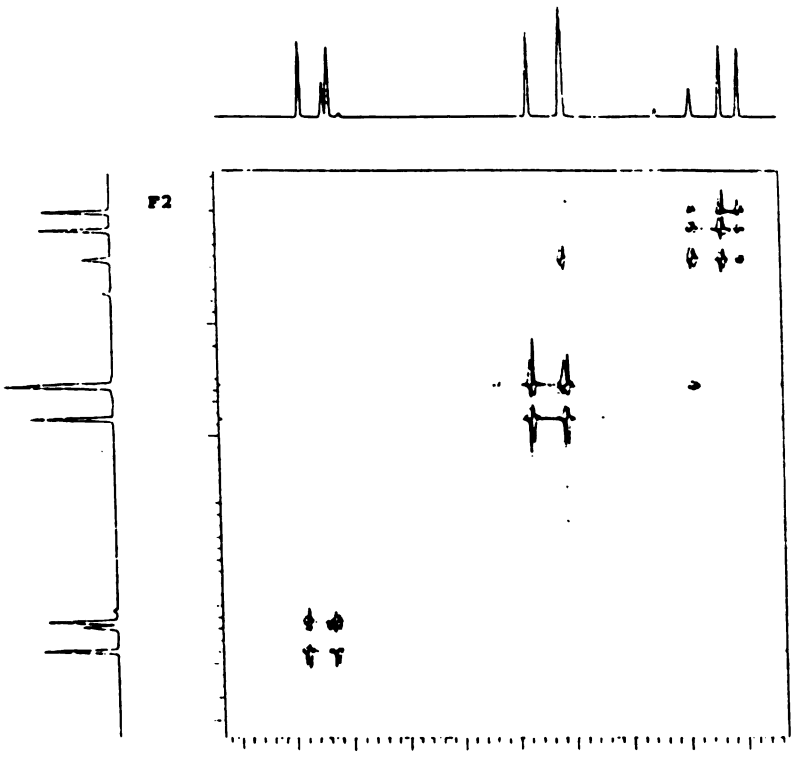
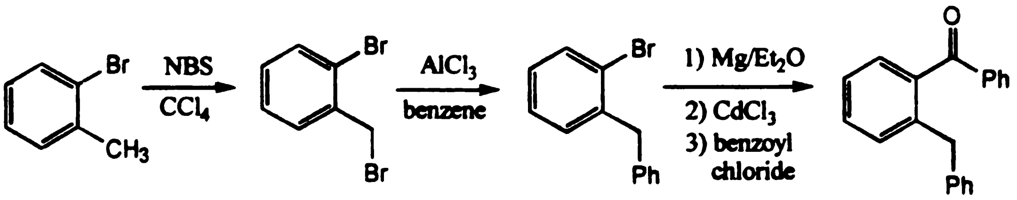


Figure 22. Hetero-COSY spectrum of CMP

B. O-Benzyl benzophenone

BZBP was made according to the following scheme.



Scheme 6. Synthesis of BZBP

2-bromobenzylbromide

To a 500 mL flask was added 45.5 g (0.25 mole) of 2-bromotoluene (Aldrich), 42 g (0.24 mole) of N-bromosuccinimide and 200 mL of carbon tetrachloride. 0.25 g of benzoyl peroxide was added to the flask, with a very strong (400 watts) light shining on the reaction vessel during addition. The reaction was allowed to reflux overnight, with the light still on. The succinimide was filtered off and carbon tetrachloride was removed by rotory evaporation. The crude product was allowed to stand undisturbed in the refrigerator for several hours to obtain crystals of 2-bromobenzyl bromide. 2-Bromotoluene was poured off from the top and the remaining crystals were rinsed and filtered several times with hexanes to yield 49.1g (80%) of 2-bromobenzyl bromide as white crystals.[28b]

^{1}H-NMR (CDCl3, 300 MHz) δ ppm: 4.6(s, 2H), 7.15 (ddd, J=7.7, 7.6, 1.8 Hz 1H), 7.44 (dd, 7.6, 1.7Hz, 1H), 7.56 (d, 7.7 Hz, 1H).

2-bromodiphenylmethane

The reaction flask, under argon, was charged with 12.5 g (0.08 mole) of aluminum trichloride and 100 ml of 1,2 dichloroethane and cooled to 0°C with stirring. 24.5 g (0.1 mole) of 2 bromobenzyl bromide was then added and the reaction flask cooled to -40°C. To this a mixture of 23.4 gms (0.3 mole) of dry benzene and 25 mL of 1,2 dichloroethane was added over a period of 15 minute via a syringe. The reaction was allowed to stir for four hours at 0°C. It was then quenched by pouring the contents of the flask into a mixture of 100 g of crushed ice and 100 mL of aq. HCl. This mixture was extracted with three 50 mL aliquots of ether. The ether layer was washed with saturated sodium bicarbonate solution until neutral and then dried over anhydrous sodium sulfate. The crude product was purified by column chromatography, by first eluting with hexanes to remove diphenyl methane, followed by 90:10 mixture of hexane and ethyl acetate. 6.2 g (25.3%) of pure 2-bromodiphenyl methane was obtained as white crystalline powder.[28b] **^{1}H-NMR** (CDCl3, 300 MHz) δ ppm: 4.10 (s, 2H), 7.06(m, 8H), 7.6 (dd, 1H).

2-benzyl benzophenone

Under argon, 2.3 g (9.4mmoles) of 2-bromodiphenyl methane was added to 5ml of anhydrous ether and 0.238 g (9.9 mmoles) of magnesium metal. A few crystals of iodine were added and the mixture stirred vigorously to initiate the complex formation. The reaction flask was warmed to reflux for 10 minutes followed by cooling to room temperature. 0.916 g of dry $CdCl_2$ was then added and the mixture refluxed for an additional 1 hour. The ether was then distilled off and 10 mL of anhydrous toluene added. 0.983 g (7.1 mmoles) of benzoyl chloride in 7 ml of toluene was then added to the reaction at room temperature, upon complete addition the reaction was allowed to reflux for 3 hours then worked up in water and dilute sulfuric acid. The organic phase was separated and the aqueous phase was extracted 3 times with toluene, the combined toluene layers were washed with water, 5% sodium bicarbonate solution, again with water and finally brine. It was then dried over anhydrous sodium sulfate and the toluene was removed by rotory evaporation. The crude product was purified by column chromatography two times using 85:15 mixture of hexane and ethyl acetate as eluant followed by recrystallization using petroleum ether. 1.09 gms (43%) of pure white product was obtained which melted at 48-50°C, lit.[28c] 50-52°C.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm: 4.09 (s, 2H), 7.05-7.15 (m, 4H), 7.2-7.3 (m, 4H), 7.3-7.4 (m, 3H), 7. 5-7.52 (distorted ddd, 1H), 7.68-7.71 (m, 2H).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ ppm: 38.84, 125.6, 126.02, 128.26, 128.31, 128.65, 129.19, 130.17, 130.34, 130.82, 133.14, 137.63, 138.8, 140.0, 140.5, 199.0.

LRMS, m/z: 272.2 (100%), 271 ($M^{+\cdot}$), 194, 165, 105, 77.

UV ($\lambda_{max\ nm}$ (ε_{max} M^{-1})): 248 (15,200), 211(21,700).

Photochemistry of CMP

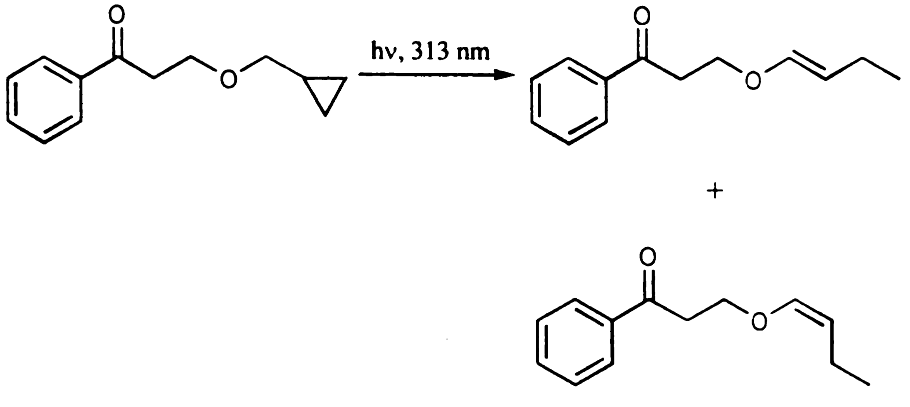


Figure 23. Photochemistry of CMP

^{1}H-NMR experiment

This experiment was repeated several times for reproducibility. The reaction was sensitive to irradiation time.

In a typical experiment a 0.05M solution (10.2 mg/mL in benzene-d_6) was first degassed by passing argon through it for one hour in an NMR tube. Irradiation was conducted at 313 nm filtered light at room temperature. The 313 nm light was isolated from a medium pressure 450 W Hanovia mercury arc lamp by using a solution of alkaline potassium chromate (0.002 M K_2CrO_4 in 1% aq. potassium carbonate) as the filter. The tube was suspended close to the light source and together with the light source was loosely wrapped in foil. The reaction was followed by ^{1}H-NMR. The reaction proceeded slowly. Appearance of peaks at 6.2 ppm and 4.97 ppm for the first 24 hours seemed to slowly diminish after that. The reaction was later carried out on a larger scale by irradiating 5mL of 0.05M solution, and the products at low conversion, i.e after five hours of irradiation, were isolated and identified as cyclopropyl ring opened products A and B in a yield of about 4% each. Isolation was carried out using HPLC (Rainin system equipped with two solvent delivery pumps, Dynamax software and a UV detector, 100 μl loop and a normal phase semi-prep Silica column), compounds A and B were eluted at about 11 and 14 minutes respectively and CMP was eluted at 24 minutes.

Compound A

^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm: 0.9 (t, 3H, J = 8.0 Hz), 1.95 (dt, 2H, J = 8.0, 14.6 Hz), 3.3 (t, 2H, J = 7.3 Hz), 4.12 (t, 2H, J = 7.3 Hz), 4.91 (m, 1H, J = 14, 14.6 Hz), 6.26 (d, 1H J = 14 Hz), 7.47-7.57 (m, 3H), 8.0 (d, 2H).

Proton decoupling experiments were carried out to correctly identify the sample.

FTIR ($CHCl_3$, cm^{-1}). 3020 (s), 1684 (m-s), 1601 (m), 1452 (s), 1437 (m), 1217 (vs).

The λ_{max} is 277 nm in UV.

Compound B

^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm: 0.85 (t, 3H J = 8.0 Hz), 2.0 (dt, 2H J = 8.0, 14.6 Hz), 3.3 (t, 2H J = 7.2 Hz), 4.15 (t, 2H J = 7.2 Hz), 4.4 (m, 1H, J = 9.3 Hz), 5.9 (d, 1H, J = 9.3, 14.6 Hz), 7.4-7.6(m, 3H), 8.0 (d, 2H).

Proton decoupling experiments were carried out to correctly identify the sample.

FTIR ($CHCl_3$, cm^{-1}). 3020 (s), 1684 (s), 1599 (m), 1450(m), 1437(m), 1219 (vs).

The λ_{max} is 278 nm in UV.

Quantum Yield

Quantum yield was studied for formation of the two isomers. Formation of acetophenone from valerophenone was used as the standard to calculate the intensity of the light absorbed. Hexadecane was used as the internal standard and the analysis was carried out by gas chromatography. The gas chromatograph used was Varian 3400, with 3392A integrator. The column used was DB-210, the temperature of which was set at 200°C. The temperature of the injector was 200°C and that of the detector was set at 220°C. The pressure of the carrier gas, helium was 80 lbs per square inch. The acetophenone peak appeared after 19.4 minutes, followed by the hexadecane at 22.7 minutes and lastly the valerophenone at 25.6 minutes.

Special precaution was taken for cleaning all the glassware used for the experiment. Ampoules used were prepared from Pyrex culture tubes. The instrument used for analysis of the photoproducts from CMP was HPLC (Varian with Dynamax software and UV detector, a normal phase Si column and a 20μl loop, with the flow rate of 0.8ml/min). The solvent used was a 98:2 mixture of hexane and ethyl acetate, with this solvent mixture and the above conditions, the retention time for compound A was about 4.2 minutes, for compound B was 6.5 minutes, the internal standard, methyl benzoate appeared at 7.1 minutes and β-cyclopropylmethoxypropiophenone appeared at 20 minutes.

The instrumental response factor was calculated using various concentrations of the analyte versus a single concentration of internal standard. Response factor was calculated according to the equation:

that was pre-evacuated for about an hour. The sample tubes were then frozen in liquid nitrogen and evacuated, the stopcocks on the vacuum lines were then closed and the tubes allowed to warm to room temperature. The freeze-pump-thaw cycle was conducted four times and the tubes were then sealed while still under vacuum.

The irradiation was done at 313 nm filtered light, in which the light source was mounted in the center of a merry-go-round setup. The ampoules were then loaded in the holes of the setup and irradiated for 5 hours.

The quantum yields were calculated using equation 4

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

Equation 4.

The intensity of light is determined from equation 5, since [AP] is known

$$I = [AP] / 0.33$$

Equation 5.

The concentration of photoproduct is calculated from equation 6

$$[PP] = R_{fPP} * [IS] * (A_{PP} / A_{IS})$$

Equation 6.

Quenching Studies

Stern-Volmer quenching studies were carried out using 2,5 dimethyl-2,4-hexadiene as the triplet quencher. Sampling was done in the similar manner to quantum yield studies. The ampoules were charged with known concentration of CMP and internal standard (methyl benzoate) and various concentrations of the quencher, the first ampoule contained no quencher. The ampoules were degassed by the freeze-pump-thaw

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

Equation 4.

The intensity of light is determined from equation 5, since [AP] is known

$$I = [AP] / 0.33$$

Equation 5.

The concentration of photoproduct is calculated from equation 6

$$[PP] = Rf_{PP} * [IS] * (A_{PP} / A_{IS})$$

Equation 6.

sample	Photoproduct(PP)	%Area (PP)	%Area (IS)	[PP]	Φ
1	Compound A inj.1	1.662	7.443	$2.13x10^{-5}$	0.09
	Compound A inj.2	1.608	7.270	$2.11x10^{-5}$	0.09
2	Compound B inj 1	2.940	7.443	$3.54x10^{-5}$	0.14
	Compound B inj 2	2.883	7.270	$3.55x10^{-5}$	0.14

ACT = VP, [VP] = 0.099 M, IS_{ACT} = HD, [IS_{ACT}] = 0.001 M, [ketone] = 0.0499 M, IS_{KET} = MB, [IS_{KET}] = 0.00069 M, I = 0.000239, Irradiation time = 5 hrs., λ = 313 nm, $Rf_{acetophenone}$= 1.89, Rf_A=0.1384

Quenching Studies

Stern-Volmer quenching studies were carried out using 2,5-dimethyl-2,4-hexadiene as the triplet quencher. Sampling was done in the similar manner to quantum yield studies. The ampoules were charged with known concentration of CMP and internal standard (methyl benzoate) and various concentrations of the quencher, the first ampoule contained no quencher. The ampoules were degassed by the freeze-pump-thaw method and then set on the merry-go-round apparatus and irradiated at 313 nm for 5 hours. Analysis was done in a manner similar to that for quantum yield studies. The Stern-Volmer expression is

$$\Phi_\circ / \Phi = 1 + k_q[Q]\,\tau_\circ$$

Equation 7.

$\Phi_\circ$ is the quantum yield without the quencher

Φ is the quantum yield in the presence of the quencher

$[Q]$ is the concentration of the quencher

kq is the bimolecular rate constant for quenching

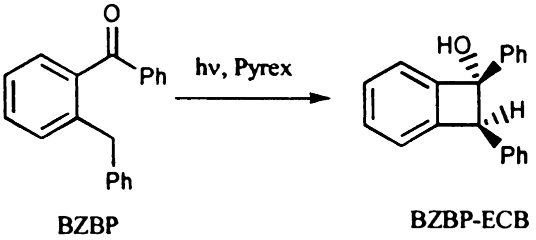
$\tau_\circ$ is the lifetime of the excited state being quenched

The quenching is assumed to be diffusion controlled with a rate constant of $6\text{x}10^9$ $M^{-1}s^{-1}$.

Photochemistry of BZBP

Experiment 1

The photoreaction was carried out in an NMR tube. The experiment was repeated several times to ensure repeatability. A 0.01M solution of BZBP in toluene-d_8 was first degassed and then irradiated with a Pyrex filtered light using a medium pressure mercury arc lamp. The reaction was sensitive to temperature and thus the temperature was maintained at 0°C. The reaction was completed in 1 hour and 40 minutes, as indicated by the disappearance of the singlet at 4.02 ppm and formation of two new singlets at 4.75 ppm and 2.2 ppm (broad). The product had the same ^{1}H-NMR as BZBP-ECB (on the basis of previous ^{1}H-NMR characterization by Sobczak, in which he had washed the sample with D_2O, upon which the broad peak at 2.2 ppm disappeared indicating it was a hydroxy group). The solution in the NMR tube was a fluorescent yellow-green color.



Experiment 2

Irradiation of Solid BZBP

In an ampoule, prepared similar to those for quantum yield studies, a finely powdered, 10 mg sample of solid BZBP was weighed out. The sample was dispersed evenly at the bottom of the tube. The solid was then degassed on the vacuum setup for an hour and the ampoule sealed while still under vacuum. Several such ampoules were prepared. The samples were irradiated at room temperature with Pyrex filtered light from a medium pressure mercury lamp. The color of the solid turned lemon yellow on irradiation almost within the first 30 minutes. The ampoules were opened in a dry box, the sample dissolved in $CDCl_3$ and transferred to NMR tubes. The NMR tubes were kept at 0°C, till spectrum was achieved. The sample was irradiated in increments of one hour for the first four hours, with no significant change in the ^{1}H-NMR. On irradiation for 20 hours, the ^{1}H-NMR showed formation of both the isomers BZBP-ECB and BZBP-ZCB.

On irradiating it for upto 48 hours, no more change was observed. The two isomers were characterized by Sobczak earlier, and assignments of the peaks were based on that characterization. Formation of benzoyl benzophenone was confirmed by isolating on HPLC using a 95:10 mixture of hexane:ethyl acetate (the retention time for the peak was 10 mins. on a Si80-125-CS column), followed by ^{1}H-NMR spectroscopy and LRMS. The ^{1}H-NMR sample shows only aromatic hydrogens, the same sample when submitted for mass spectral analysis gave an m/z peak at 286 which is consistent with benzoyl benzophenone.

REFERENCES

1. Cowen, D.O.; Drisco, R. L. *Elements of Organic Photochemistry*; Academic Press: New York, **1969**.
2. Wagner, P. J. *Topics In Current Chemistry* **1976**, 66.
3. a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. b) Wagner, P. J.; Meador, M. A.; Park, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 5199. c) Wagner, P. J.; Zhou, B.; Hasegawa, T; Ward D. L. *J. Am. Chem. Soc.* **1991**, *113*, 9640. d) Wagner, P.J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.
4. a) Dewar, M. J. S.; Doubleday, C. *J. Am. Chem. Soc.* **1978**, *100*, 4935. b) Wagner, P. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 4009.
5. Turro, N. J.; Weiss, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 2185.
6. Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2163.
7. Shaffner, J. R. *Organic Photochemistry*, **1987**, *8*, 249.
8. Wagner, P. J.; Kelso, P.; Kemppainen, A. K.; Zepp, R. *J. Am. Chem. Soc.* **1972**, *94*, 7500.
9. Small, R. D.; Sciano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431.
10. Shimizu, N.; Ishikawa, M.; Ishikura, K.; Nishida, S. *J. Am. Chem. Soc.* **1974**, *96*, 6456
11. Caldwell, R.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.
12. Freilich, S.; Peters, K. *J. Am. Chem. Soc.* **1981**, *103*, 6255.
13. Wagner, P. J.; Zepp, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4958.
14. Horspool, W. M. Photochemistry in Organic Synthesis, J. D. Coyle Ed, 1986, No. 57.
15. Wagner P. J. *Acc. Chem. Res.* **1989**, *22*, 83.

16. Wagner, P. J.; Giri, B.P.; Scaiano J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5484.

17. Wagner, P. J.; Jang, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7914.

18. a) Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134. b) Wagner, P.J.; Liu, K-C, Noguchi, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3837. c) Doubleday, C.; Turro, N. J.; Wang, J.-F. *Acc. Chem Res.* **1989**, *22*, 199. d) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896.

19. a) Meador, M. A.; Wagner, P. J. *J. Org. Chem.* **1985**, *50*, 419. b) Winnik, M. A.; Lee, C. K.; Basu, S.; Saunders, D. S. *J. Am. Chem. Soc.* **1974**, *96*, 6182.

20. Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *58*, 2038.

21. Sammes, P. G. *Tetrahedron* **1976**, *32*, 405.

22. Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *58*, 2051.

23. Yang, N. C.; Rivas, C. J. *J. Am. Chem. Soc.* **1961**, 2213.

24. Matsurra, T.; Kitaura, Y. *Tetrahedron* **1971**, *27*, 1597-1606.

25. Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc. Perkin 1* **1974**, 410.

26. a) Wagner, P. J.; Sobczak, M. *Tetrahedron Lett.*, **1998**, *39*, 2523- 2526. b) Wagner P. J.; Subrahmanyam, D.; Park, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 709.

27. Bowry, V.; Lusztyk, J.; Ingold, K. *J. Am. Chem. Soc.* **1991**, *113*, 5687.

28. a) Kim, J.; Bogdan, M.; Mariano, P. *J. Am. Chem. Soc.* **1991**, *113*, 9251. b) Sobczak, M., *Ph.D. dissertation*, Michigan State University, **1997**. c) Bradsher, C. K. *J. Am. Chem. Soc.* **1940**, *62*, 486.

29. Hale, W. J.; Britton, E. C. *J. Am. Chem. Soc.* **1919**, *41*, 841.