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dissertation entitled

PART I
PHOTOINDUCED SULFUR-CARBON BOND CLEAVAGE

PART II
PHOTOCYCLIZATION OF OTHRO-BENZOYL N-ALKYLANILINIUM IONS

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Qunjian Cao

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Major professor

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PART II

PHOTOCYCLIZATION OF ORTHO-BENZOYL N-ALKYLANILINIUM IONS

By

Qunjian Cao

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ABSTRACT

PART I

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PART II

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PART I

The photochemistry of several alkylthiophenyl ketones and alkylthiomethylphenyl ketones has been investigated. Upon irradiation, homolytic sulfur-carbon bond cleavage was observed as a major chemical process. p-(Phenylsulfinyl)methylbenzophenone, p-(phenylsulfonyl)methylbenzophenone and some corresponding (halomethyl)benzophenones and (halomethyl)acetophenones were also studied to compare the reactions of the corresponding ketones. Maximum quantum yields of the photoreactions were obtained by using thiophenol to trap all radicals that escaped from solvent cages. Triplet lifetimes for all the ketones were determined by Stern-Volmer quenching experiments.

Intramolecular charge-transfer to triplet excited carbonyl group from sulfur was observed in o-benzylthiobenzophenone and o-benzylthioacetophenone. The rate constants of carbon-sulfur bond cleavage were

deduced from the triplet lifetimes. The relative rates of substituted p-methylbenzophenones, which is SOPh ~ Br > SPh > Alkyl-S > Cl > SO_2Ph, reveal the stabilities of the radicals that are generated from carbon-sulfur bond cleavage. Meta substituted phenyl ketones exhibited much lower rate constants compared to their para analogs. This may be due to a lack of spin density at the meta position compared to the para position in the excited triplet state.

PART II

The photochemistry of o-benzoyl-N-alkylanilinium salts was investigated. Irradiation of o-benzoyltrimethylanilinium tetrafluoroborate, in acetonitrile solution and in solid state affords 1,1-dimethyl,3-hydroxy-3-phenyl-2,3-dihydroindolium tetrafluoroborate. The quantum yield of the reaction is 0.34. This is in direct contrast to the known inactivity of o-benzoyl-N,N-dimethylaniline. Evidently, a positive charge on the nitrogen changes the nature of the excited state from $^3(\pi,\pi^*)$ to $^3(n,\pi^*)$. The photoreaction proceeds via intramolecular δ-hydrogen abstraction by the triplet carbonyl oxygen followed by 1,5-biradical coupling to form the substituted dihydroindole product. The rate constant was evaluated ($k = 6.8 \times 10^7\ s^{-1}$) and it appears that, compared to o-t-butylbenzophenone ($k = 10^9\ s^{-1}$), the positive charge on the nitrogen deactivates the reaction.

Similarly, irradiation of o-benzoyl-N,N-dibenzylanilinium chloride yielded, in acetonitrile solution, N-benzyl-2,3-diphenylindole. Interestingly, the quantum yield is only 0.0067, plausibly because an unknown process ($k = 10^9\ s^{-1}$) from triplet excited state decays to the ground state ketone. The photocyclization reaction follows the same mechanism.

Stern-Volmer analyses for both systems allowed the calculation of $k_q\tau$ values as well as the estimation of the respective lifetimes (15 and 0.24 ns).

ACKNOWLEDGMENTS

The author wishes to thank Professor Peter J. Wagner for his help, guidance and innumerable entertaining discussions during the course of this work.

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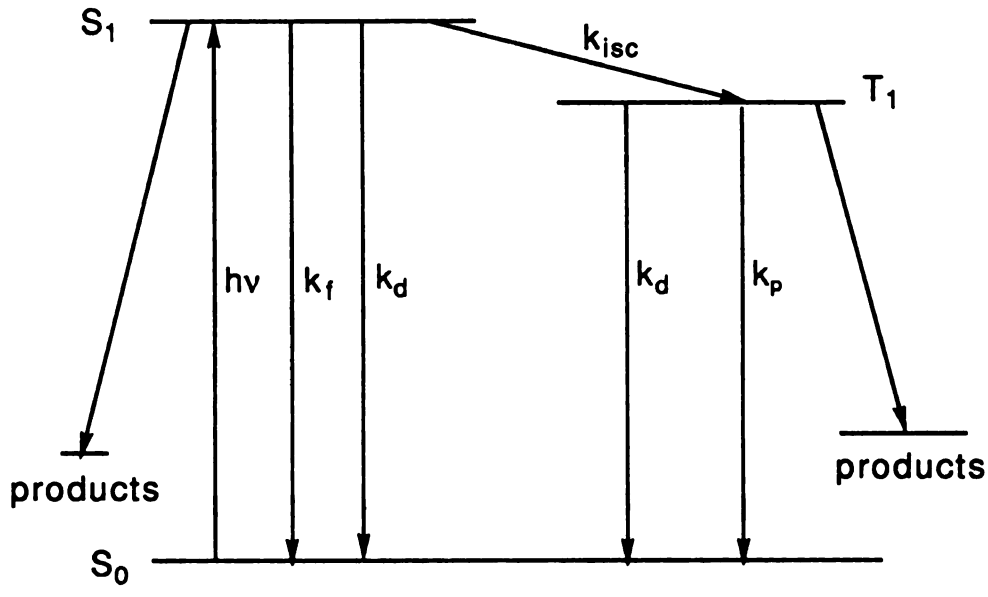
INTRODUCTION

A. Photophysics of Aromatic Carbonyl Compounds

The photochemistry of carbonyl compounds is one of the most active and fundamental fields of research in organic photochemistry. The carbonyl chromophore, especially the aromatic carbonyl chromophore, can be excited by absorption of photons in near ultraviolet light to give products that can be easily isolated and analyzed. A wide variety of photophysical and photochemical reactions can occur via the excited state of the aromatic carbonyl. Hence, it provides a very useful tool in systematic studies of both synthetic and mechanistic organic photochemistry.

To understand carbonyl photochemistry, it is necessary to know the photophysics of the excited state which is described with a modified Jablonski diagram in Scheme 1.[1] Absorption of light by a carbonyl compound promotes a molecule from singlet ground state (S_0) to the singlet excited state (S_n). Internal conversion from S_n to S_1 is very efficient and we only need to consider the S_1 state.[2] The excited S_1 state molecule can decay to the ground state molecule by emission of light (k_f) or by radiationless transition (k_d) to ground state.

The half occupied molecular orbitals in S_1 have paired electron spins. However , the more stable electronic configuration is the one having unpaired

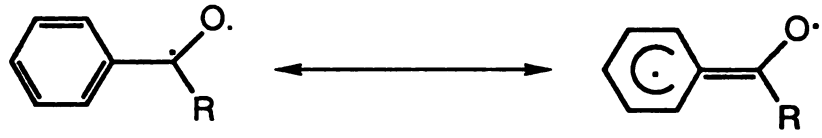


Scheme 1. Modified Jablonski Diagram for an Excited Ketone.

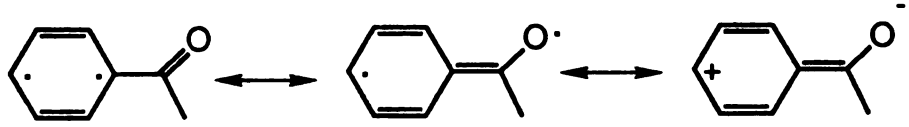
spins. Thus, the excited singlet state S_1 can undergo intersystem crossing to an triplet excited state (T_n). The rate constant of intersystem crossing (k_{isc}) for benzophenone is about 10^{11} s^{-1} and it is believed that this is the case for most of simple phenyl ketones.[4,5] Since the rate constants of intersystem crossing of phenyl ketones ($k_{isc} \sim 10^{11}$ s^{-1}) are so large, compared to rate constants of fluorescence ($k_f \sim 10^6$-10^9 s^{-1}) and rate constants of nonradiative decay ($k_d \sim 10^5$-10^8 s^{-1}), we need only consider the lowest triplet excited state (T_1).[2,6]

The excited triplet state can also decay via phosphorescence ($k_p \sim 10^1$-10^4 s^{-1}) and the low rate of the T_1 to S_0 transition is caused by its spin-forbiddenness.[3] However, radiationless decay from the excited triplet state to ground state is also possible. In addition, singlet and triplet excited states can undergo chemical reactions to products. It ought to be mentioned that direct transitions from S_0 to T_1 are also spin-forbidden and can be ignored for low intensity excitation.

There are two different types of triplet excitation of the aromatic carbonyl compounds with quite different physical and chemistry properties. An n,π* triplet excitation transfers an electron into a π* antibonding orbital from the carbonyl nonbonding orbital and results in an electron poor oxygen. This deficiency gives an n,π* triplet excited state a chemical behavior similar to that of an alkoxy radical.[7] Reactions arising from the n,π* triplet excited state are those expected from the alkoxy radical. A π,π* triplet excited state is the one in which a π orbital electron is promoted into a π* antibonding orbital and results in a shift of electron density from the aromatic π-system to the carbonyl oxygen, producing an electron rich oxygen. The π,π* triplet excited state is less reactive to radical reactions at the carbonyl oxygen than is the n,π* triplet excited state.



$^3(n,\pi^*)$



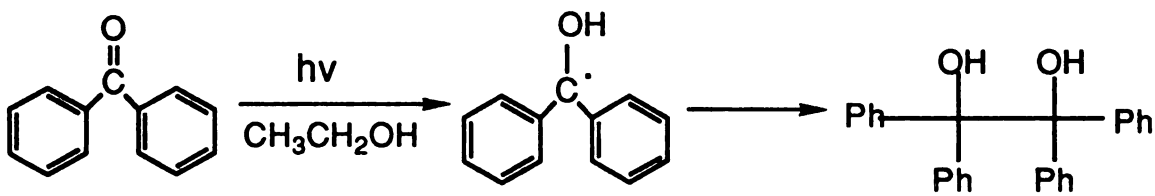
$^3(\pi,\pi^*)$

Phenyl ketones have π,π* triplet energies very close to those of n,π* triplets. Substituents on the benzene ring of phenyl ketones stabilize or destabilize the the two excited states in different way and therefore determine which triplet excited state is the lowest. Usually, electron withdrawing groups stabilize the n,π* transition and electron donating groups stabilize π,π*

transition. The polarity of different solvents also has an effect on the relative triplet energy of the two levels. Thermal equilibrium of the two triplets can be reached if the two triplet state are close to each other within a few kcals and as a result, ketones with a π,π^* lowest triplet can undergo hydrogen abstraction from the n,π^* triplet excited state with low efficiency.[6] A mixture of the two triplets is also possible if the two excited state are close enough.[8]

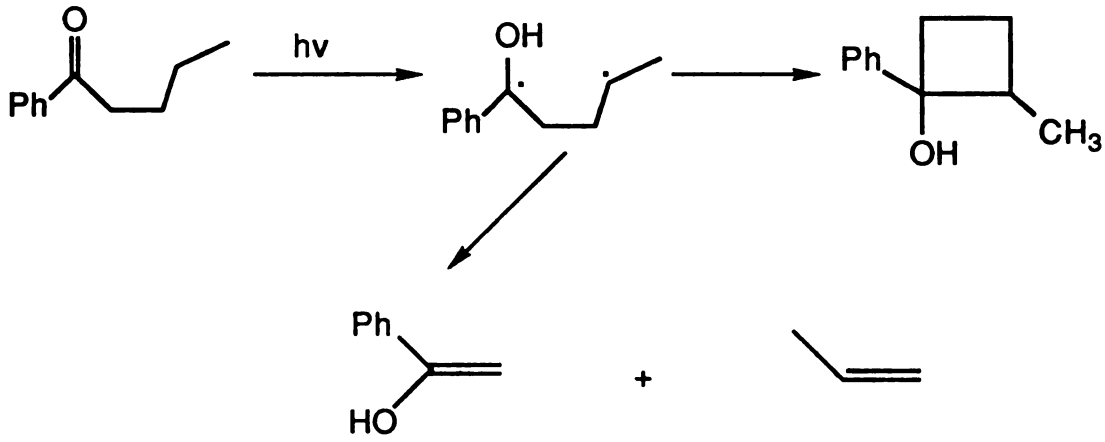
B. δ-Hydrogen Abstraction Reaction and 1,5-Biradicals

Photoexcited ketones undergo characteristic hydrogen abstraction from suitable donors having reactive hydrogens. This reaction was first reported by Ciamician and Silber in 1900.[9] Excited benzophenone abstracts hydrogen from ethanol to generate benzophenone ketyl radicals. Benzpinacol is formed by coupling of radicals.



Hydrogen abstraction can also occur from a position within the ketone molecule. Intramolecular hydrogen abstraction was first observed by Norrish.[10] This reaction is known as the Norrish II reaction, which involves formation of a 1,4-biradical[11] via abstraction of a γ-hydrogen by the excited carbonyl oxygen.

The biradical can either cleave into a smaller ketone and an olefin, or cyclize to cyclobutanol:[12]

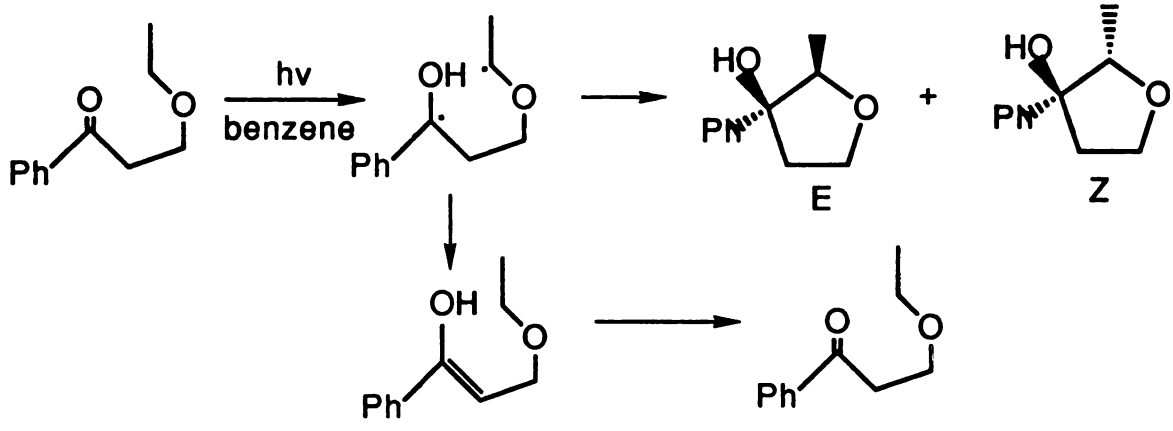


The reactivity for internal hydrogen abstraction depends largely on the nature and multiplicities of the excited state. It has been well accepted that hydrogen abstraction occurs more efficiently from n,π^* excited ketones.[7] The radical-like oxygen of an n,π^* excited ketone behaves in the same way as an alkoxy radical. Ring substituents that lower the π,π^* excited state energies will decrease the reactivity of the reaction.

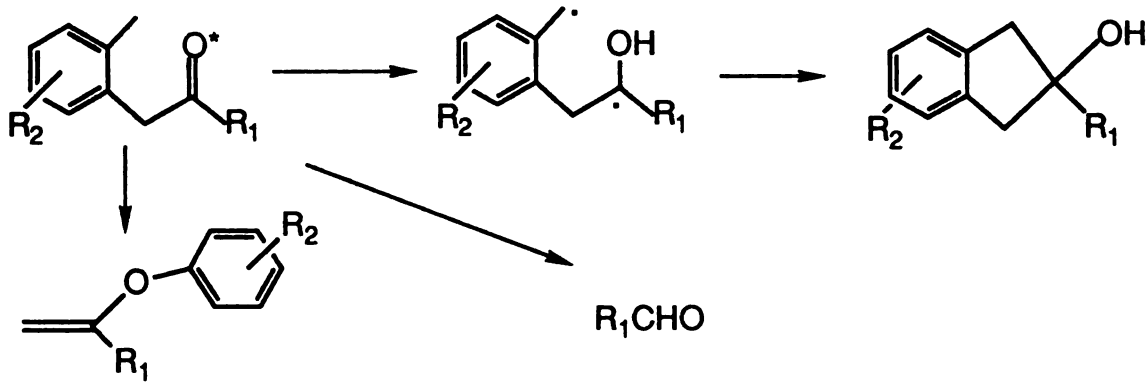
In an unconstrained system, an excited ketone shows a preference for abstraction from the γ–position. It was believed that the reaction proceeds via a six-membered cyclic intermediate.[13] Later studies showed that δ-hydrogen abstraction is competitive with γ-hydrogen abstraction in a system with activated δ-hydrogen and inactive γ-hydrogens.[14] Both entropy and enthalpy factors determine the ratio of the formation of 1,4-biradical and 1,5-biradical. The preference for 1,4-biradical formation over 1,5-biradical formation is because of the lower entropy for forming a smaller six-membered transition

state in γ-hydrogen abstraction. Introducing substituents on the δ-carbon may change the γ / δ-hydrogen abstraction ratio but cannot prevent the formation of a 1,4-biradical because of a strong entropy effect. Therefore, to study δ-hydrogen abstraction, systems with no γ-hydrogen have to be used.

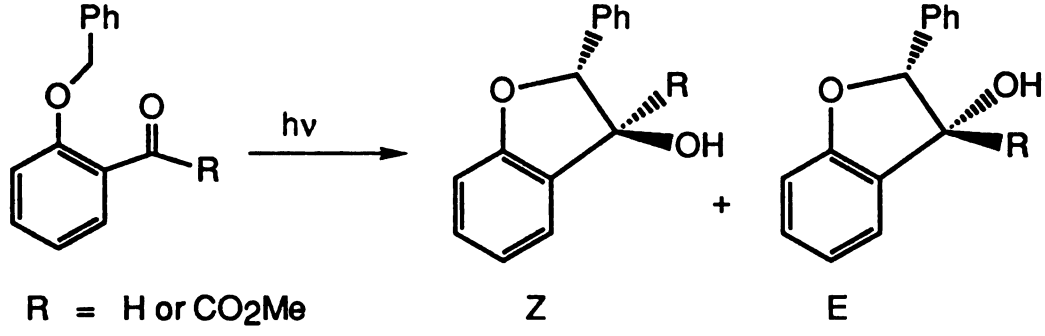
Reactions of acyclic β-alkoxy ketones were reported.[15-25] The biradicals generated from δ-hydrogen abstraction undergo cyclization to cis- and trans-cyclopentanols and disproportionation to enol of the starting ketone, which was confirmed by isotope experiments. Solvents strongly influence the distribution of the products and influence the cis/trans ratio of the cyclization products. A nonpolar solvent such as benzene favors the product with methyl group trans to phenyl group (E) and polar solvents such as t-BuOH favor the product with methyl group cis to phenyl group (Z):[15]



The photochemistry of α-(o-tolyl)ketones were investigated.[16] Three competing reactions were found. They were δ-hydrogen abstraction followed by cyclization, α-cleavage and 1,3-aryl migration:



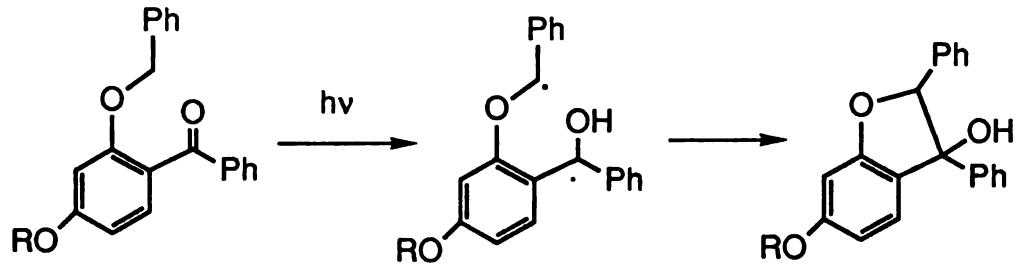
The photocyclyzation of o-benzyloxybenzaldehyde was reported by Pappas.[17] Z and E-2-phenyl-3-hydroxy-2,3-dihydrobenzofuran were obtained.[18] Photolysis of several methyl o-aryloxyphenyl glyoxylates also gave Z and E 3-hydroxy-2,3-dihydrobenzofurans.[19] Dependency of stereoselectivity



on temperature and solvents was investigated. The Z isomer with the phenyl and carbomethoxy groups trans to each other are more favored at low temperatures than at higher temperatures and preferred more in the nonpolar solvent than in the polar solvent.

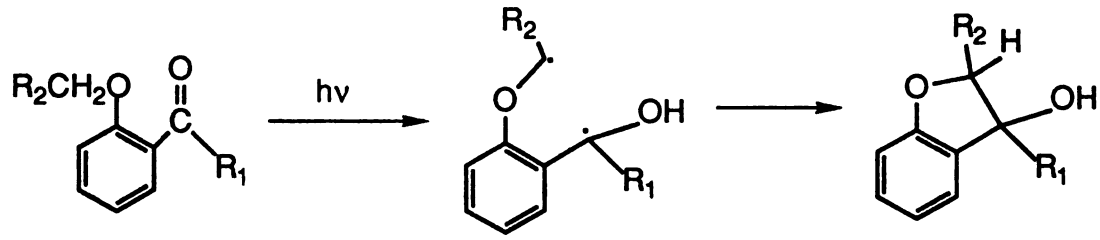
Lappin reported[20] the photolysis of 2-benzyloxy-4-dodecyloxy-benzophenone. The reaction gave 6-dodecyloxy-2,3-dihydro-2,3-diphenyl-3-

benzofuranol as product. The triplet n,π^* excited state was believed to be involved in the process and the lifetime of the excited state was measured (30 ns).

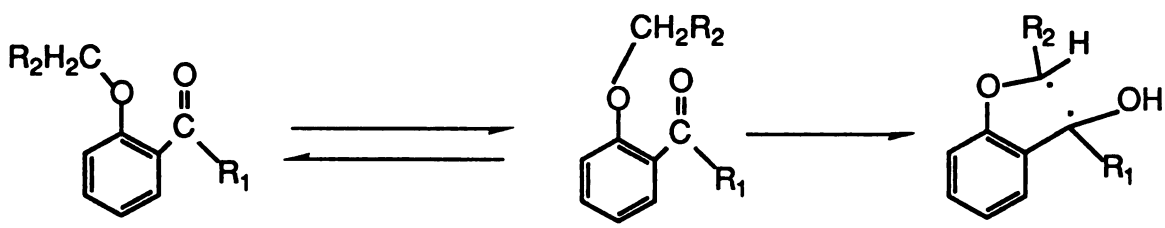


R = $C_{12}H_{25}$

Wagner and Meador[21] studied the photochemistry of o-alkoxyphenyl ketones which undergo photocyclization to benzodihydrofuranols via δ-hydrogen abstraction:



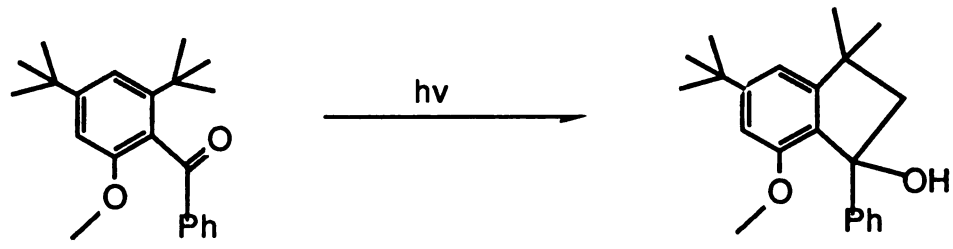
The rate constants of o-methoxybenzophenone (5 x 10^5 s^{-1}), 2,6-diacylmethoxybenzene (1 x 10^7 s^{-1}), o-benzyloxybenzophenone (2 x 10^7 s^{-1}) and 2,6-dimethoxybenzophenone (2 x 10^5 s^{-1}) were measured. The low rate constants for δ-hydrogen abstraction are caused by conformational factors, especially by an equilibrium between syn and anti rotamers of the o-alkoxy group. The rate difference between o-methoxybenzophenone and o-benzylbenzophenone indicates that C-H bond strengths are also important. The relatively low rate constant of 2,6-dimethoxybenzophenone shows that the triplets reach rotational equilibrium about the benzene-carbonyl bond before reaction.



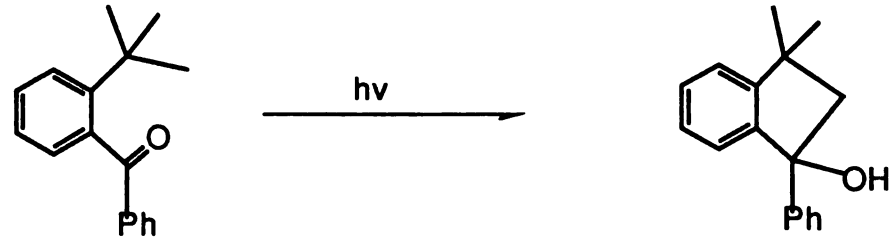
anti syn

The lower rate constants of o-methoxyacetophenone ($<10^5$) and o-benzyloxyactophenone (2 x 10^6 s^{-1}) relative to the corresponding benzophenone derivatives reflect the low reactivity of π,π^* lowest triplets in hydrogen abstraction.[22]

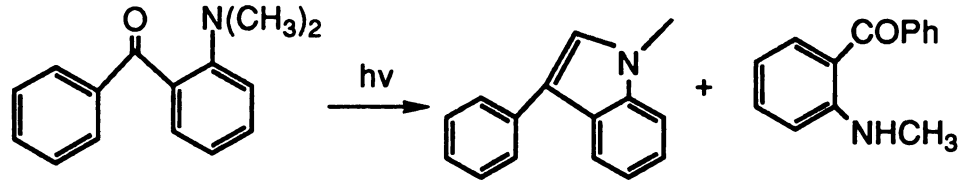
O'Connell[23] reported that photolysis of 2,4-di-tert-butyl-6-methoxy-benzophenone gave a cycloaddition product that is a 3,3-dimethyl-1-indanol derivative. This result indicated that δ-hydrogen abstraction from the tert-butyl group was much faster than that from methoxy group.



Wagner and Scaiano[24] reported the rate constant for δ-hydrogen abstraction in 2-t-butylbenzophenone ($k = 10^9$). X-ray analysis indicated that this fast δ-hydrogen abstraction was due to a suitable conformation with tert-butylphenyl ring twisted 69^o from coplanarity with the carbonyl which holds tert-butyl hydrogens within the bonding distance of the oxygen:



Aoyama[25] reported the photolysis of 2-dimethylamino-benzophenone.



1-Methyl-3-phenylindole was obtained in a very low yield together with 2-methylaminobenzophenone. This low yield is expected because the lowest triplet excited state is π,π^* and is because of conformational restriction. Intramolecular charge-transfer quenching by nitrogen atom also accounts for the low yield.

C. Intramolecular Charge-transfer Quenching By Sulfur and Nitrogen

Photochemical charge-transfer reaction was first observed by Cohen[26] in the photoreduction of benzophenone. The reduction is 1000 times faster by Et_3N than by isopropanol. The mechanism was suggested to involve a rapid electron transfer from nitrogen to the triplet excited carbonyl followed by a proton shift.

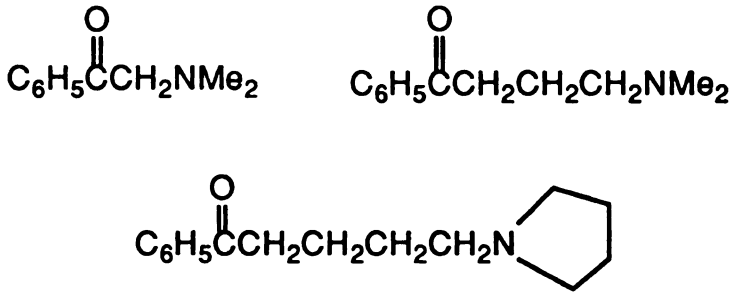
$$^3(R_2C{=}O)^* + RCH_2\ddot{N}R_2 \longrightarrow {}^3(R_2\dot{C}{-}O^-\ \ \dot{N}^+CH_2R)^*$$

$$\longrightarrow R_2\dot{C}OH + R\dot{C}HNR_2$$

Wagner[27] studied the quenching of triplet valerophenone by triethylamine and dimethyl tert-butylamine. Both amines quench the triplet state with the same rate constant and no difference was observed for the rate constants in benzene and acetonitrile. On the other hand, the rate constants in

benzene and acetonitrile are 10 times faster than in methanol. The facts indicated that a charge transfer complex was involved rather than radical ions.

Wagner, Kemppainen and Jellinek investigated the intramolecular charge-transfer quenching of α-dimethylaminoacetophenone, γ-dimethylaminobutyrophenone and δ-pyrrolidinovalerophenone.[27] The results

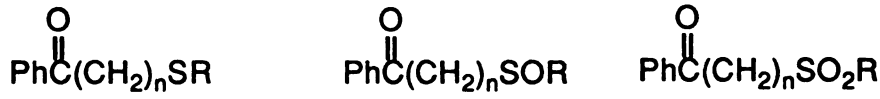


indicated that tertiary amines can quench singlet excited states of phenyl ketones although the rate constants of intersystem crossing for phenyl ketones are very high (kisc ~ 10^{11} s^{-1}). The singlet quenching efficiency decreased as the distance of the amino substituent increased. Charge transfer complexes are also involved in the triplet excited state of γ- and δ-aminoketones and the rate constants for intermolecular quenching also decreased as the distance increased. The charge transfer complexes formed from γ- and δ-aminoketones cannot form biradicals by hydrogen abstraction because of the conformational restrictions that results in low quantum yields for type II reaction (0.046 for δ-pyrrolidinovalerophenone and 0.015 for γ-dimethylaminobutyrophenone in benzene). The slow formation of the triplet charge-transfer complex of α-aminoketone is caused by conformational factors for approach of the lone pair on nitrogen to the oxygen. The high efficiency of type II products for the

hydrochloride salt of the δ-aminoketone(0.38 compared to 0.08 for δ-amino ketone) indicates the absence of competing charge transfer quenching from both singlet and triplet excited states. The large kqτ values for the hydrochloride salts of δ- and γ-aminoketones(570 and 720 compared to 33 and 4.5 for free amino ketone) reflect the lack of competing charge transfer quenching from triplet excited states and very slow H-abstraction.

Other heteroatoms such as sulfur, phosphorous, antimony and arsenic can also form C-T complexes with excited carbonyl groups.[28]

Wagner and Lindstrom investigated α-, β- , γ-, δ- and ε-phenacyl sulfides, sulfoxides and sulfones.[29] They found that the rate constants for charge-transfer (k_{CT}) are maximum for n = 2 and decrease for n > 3. Since the C-T quenching



R = n-butyl, phenyl n = 1, 2, 3, 4, 5

is a through-space process and controlled by conformational factors, five or six atom cycles are the most favorable. SR is a better quencher than NR_2 for n = 1 - 3 is because of the longer reach of sulfur 3p orbital compared to a nitrogen sp^3 orbital. The rate constants k_{CT} for intramolecular quenching of $PhCO(CH_2)_n$-SBu are 160, 550, 290, 17, <2 (x 10^7 s^{-1}) for n = 1, 2, 3, 4, 5 respectively.

D. Photoinduced Sulfur-Carbon Bond Cleavage

The photoinduced homolytic cleavage of carbon-sulfur bonds is of interest to a wide range of physical and organic chemists. Compounds which undergo photochemically-induced carbon-sulfur bond cleavage are useful as synthetic intermediates[30] and as initiators for free radical polymerization.[31]

Photolysis of sulfides, sulfoxides and sulfones results in the production of radical species via homolytic cleavage of the carbon-sulfur bond. These free radicals have been studied with physical methods, such as CIDNP[32], EPR,[33] and flash photolysis[34] as well as with chemical methods.

Haines[35] first reported the decomposition of simple alkylsufides upon irradiation at 254 nm for 65 hours. H_2 and saturated hydrocarbon related to the alkyl on the sulfur were found. Later, Milligan[36] found CH_4, C_2H_6 and CH_3SSCH_3 by irradiation of methylsulfide in gas phase. Callear and Dickson[34] established that the carbon-sulfur bond cleavage was the primary process which generated methyl and methylthiyl radical by using flash photolysis at 195 nm:

$$R'SR \xrightarrow{h\nu} \dot{R}' + \dot{S}R$$

Adam and Elliot[33] investigated the photolysis of several simple alkyl sulfides at 254 nm in dilute glasses of 3-methylpentane. The radical pairs that

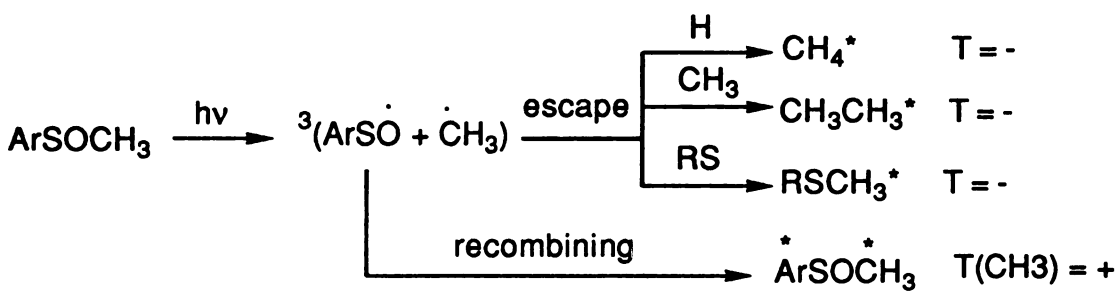
$$EtSEt \xrightarrow{h\nu} \dot{E}tS + \dot{E}t$$

$$(CH_3CH_2CH_2)_2S \xrightarrow{h\nu} CH_3CH_2CH_2\cdot + \cdot SCH_2CH_2CH_3$$

reacted with each other gave rise to the main diamagnetic products .

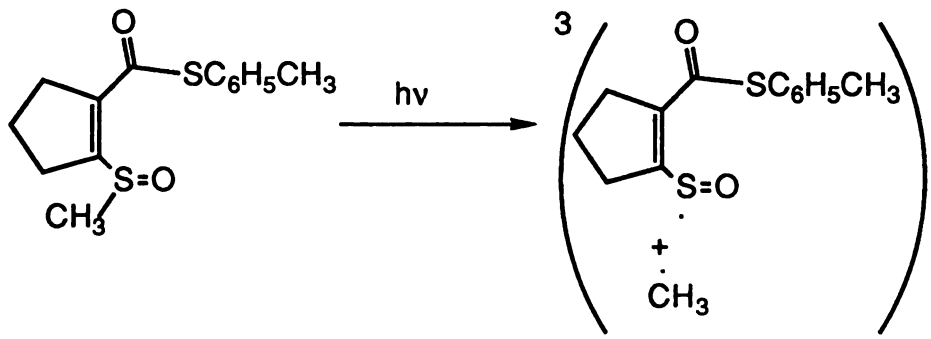
Knight[37] reported the photolysis of simple alkyl sulfides in the gas phase using 229 nm light or sensitization by triplet mercury.[38] Quantum yields were pressure dependent. In the case of methy lethyl sulfide, the products of photolysis are C_2H_6, $CH_3SSC_2H_5$, $C_2H_5SSC_2H_5$, CH_4, CH_3SCH_3, $C_2H_5SC_2H_5$, C_3H_8, C_2H_4, C_2H_5SH and CH_3SH.[37] All of the products are formed from radical recombination, hydrogen abstraction and radical disproportionation. Quantum yields for decomposition of methyl sulfide, methylethyl sulfide and ethyl sulfide at 254 nm were also determined (0.51, 0.46 and 0.49 respectively).[38]

The nature of the C-S α-cleavage in photochemical reactions of sulfoxides has been studied in detail with the CIDNP technique by Muszkat.[32] In the photoreactive ortho-substituted phenyl methyl sulfoxides, the triplet spin

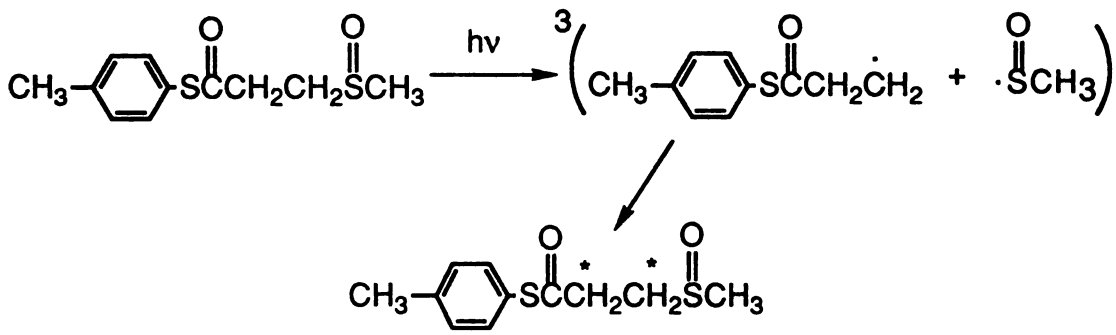


correlated methyl- arylsulfinyl radical pair, CH_3 + ArSO, was formed and detected by CIDNP method.

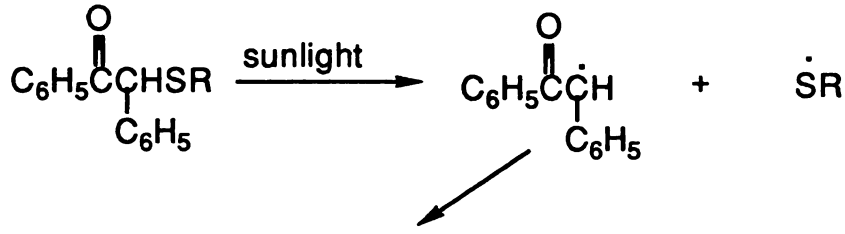
The photochemical behavior of some methyl vinyl sulfoxides such as cyclopent-1-enyl sulfoxide and cyclohex-1-enyl sulfoxide were similar to that of the ortho-substituted methyl phenyl sulfoxides.[32]



Photolysis of methyl β-substituted ethyl sulfoxide caused sulfur-carbon bond cleavage only at the ethyl-sulfinyl bond.[32]



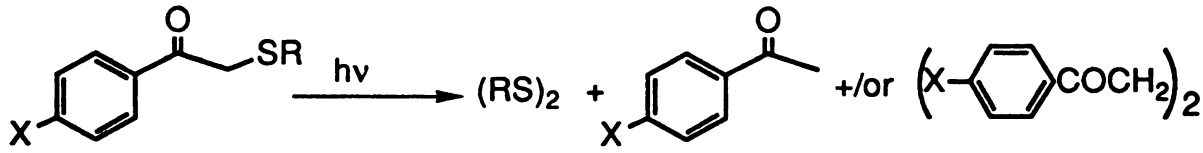
In 1956, Schonberg[39] reported photochemical reactions of desoxybenzoin derivatives in sunlight. Didesyl cystal was obtained in each reaction from sulfur-carbon bond cleavage followed by radical coupling reaction.



$(C_6H_5COHC_6H_5)_2$

R = C_6H_5, o-$C_6H_4CH_3$, m-$C_6H_4CH_3$, p-$C_6H_4CH_3$, COC_6H_5

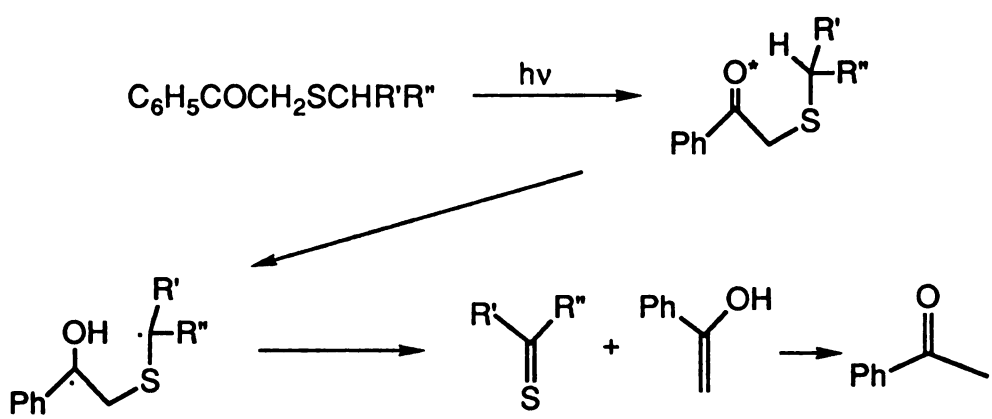
Hill[40] et al described the photoprocesses of aryl phenacyl sulfides and benzyl phenacyl sulfides and related ketosulfides. The products obtained are generated from carbon-sulfur bond cleavage. The C-S bond cleavage may be



a; x = H, R = p-tolyl
b; x = H, R = 2,4,6-$Me_3C_6H_2$
c; x = Cl, R = p-tolyl
d; x = OH, R = p-tolyl
f; x = OMe, R = p-tolyl
g; x = Ph, R = p-tolyl
h; x = H, R = benzothiazol-2-yl
j; x = H, R = PhCO
k; x = H, R =SO_3Na
l; x = H, R = $PhCOCH_2S$
m; x =Cl, R = $PhCH_2$
n; x = OH, R = $PhCH_2$
p; x = OMe, R = $PhCH_2$

direct in the case that there is no active γ-hydrogen available in those molecules or may happen via γ-hydrogen abstraction as in the case of compounds m, n and p.

Caserio[41] reported the the photolysis of β-keto sulfides with γ-hydrogen. Labelling experiments proved that C-S bond cleavage ocoured via intramolecular hydrogen abstraction. Photolysis of phenacyl alkyl sulfides in deuterochloroform did not give the deuterated acetophenone product, a result that excluded primary C-S bond homolytic cleavage.



R' = R" = H

R' = CH_3, R" = C_6H_5

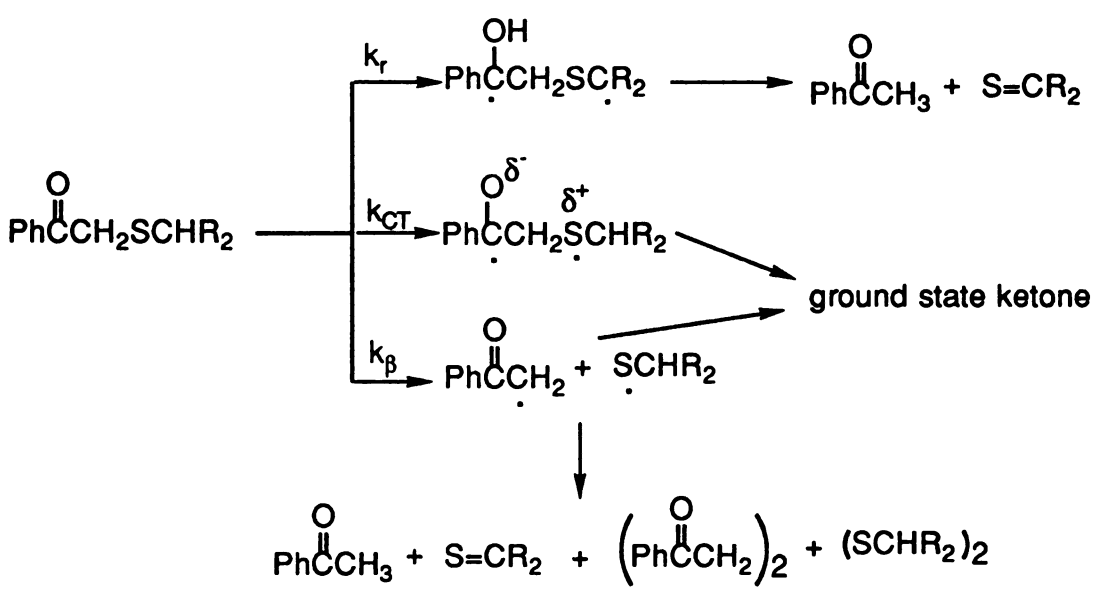
R' = CH_3, R" = H

Padwa[42] investigated the photolysis of α-benzylthioacetophenone and α-benzylthio-4-acetylbiphenyl. The quantum yield of acetophenone product and $1/\tau$ for α-benzylthioacetophenone in benzene were reported as 0.35 and 7 x 10^9 s^{-1}, respectively. For α-benzylthio-4-acetylbiphenyl, the values are 0.04 and > 10^{10} s^{-1}. The difference reflects the different natures of the triplet excited states of the two β-keto sulfides. α-Benzylthioacetophenone has a lowest n,π*

triplet excited state and α-benzylthio-4-acetylbiphenyl has a lowest π,π^* triplet excited state. The low quantum yield and short lifetime (τ) of α-benzylthio-4-acetylbiphenyl suggest the formation of a charge transfer complex which generates the starting ketone with a rate much faster than hydrogen abstraction.

More detailed work on phenyl ketosulfides has been done by Wagner and Lindstrom[43]. Phenyl ketones have two different low lying triplets, n, π^* and π, π^*. Absorption and phosphorescence spectra indicate that the n, π^* and π, π^* transitions both involve some population of the C-S σ^* orbital. This mixing, together with the free spin density on the excited carbonyl carbon, appeared to determine the rate constant for cleavage.

The photochemistry of ketones of the structures $PhCOCH_2SR$, $PhCOCH_2SOR$, $PhCOCH_2SO_2R$, and p-X-$PhCOCH_2SPh$ gave primarily



acetophenone when irradiated in the presence of thiophenol.

According to related work,[43] ketosulfides in general undergo two competitive intramolacular triplet reactions: CT quenching and γ-hydrogen abstraction. These β-ketosulfides undergo β-cleavage only to the extent that its rate competes with those of the other two reactions.

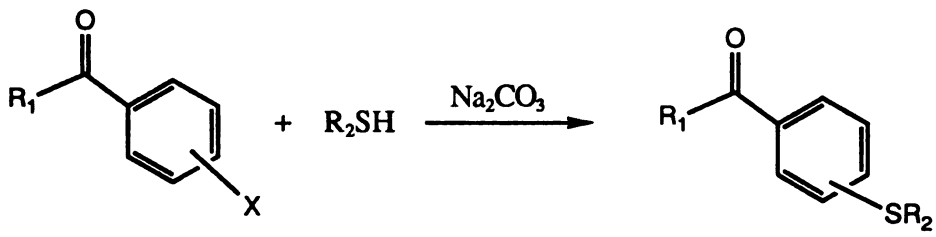
Kinetic studies of β-cleavage reactions of ketones have been done. Oxidation of the sulfur decreased both k_γ and k_{CT}. However, the RS(O) radical was eliminated much more rapidly than either RS or RSO_2, such that β-cleavage becomes a dominant reaction for the ketosulfoxides and a major reaction for the ketosulfones. α-Alkyl substitution resulted in sharp increase of the yield of phenyl ketone which indicates that the more substituted α-keto radicals undergo more disproportionation.

PART I. PHOTOINDUCED SULFUR-CARBON BOND CLEAVAGE AND PHOTOGENERATED SULFUR RADICALS

Results

A. Preparations of the Ketones

Substituted alkylthiophenylketones were prepared[44] by Sn2 reaction of



$R_1 = CH_3$, $R_2 = CH_2Ph$, ortho, o-(benzylthio)acetophenone (o-BzSAP)

$R_1 = CH_3$, $R_2 = CH_2Ph$, para, p-(benzylthio)acetophenone (p-BzSAP)

$R_1 = CH_3$, R_2 = n-octyl, ortho, o-(octylthio)acetophenone (o-C8SAP)

R_1 = Ph, $R_2 = CH_2Ph$, ortho, o-(benzylthio)benzophenone (o-BzSBP)

R_1 = Ph, $R_2 = CH_2Ph$, para, p-(benzylthio)benzophenone (p-BzSBP)

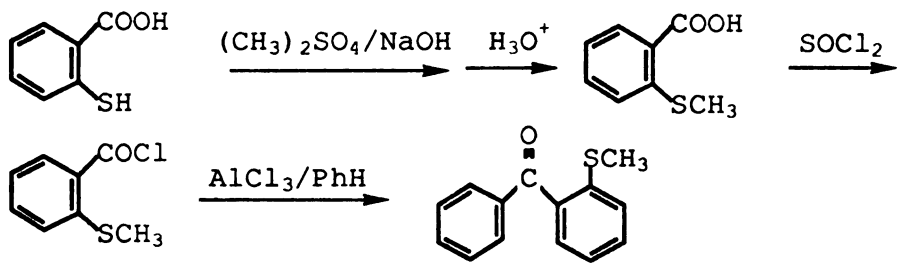
R_1 = Ph, R_2 = n-Bu, para, p-(n-butylthio)benzophenone (p-n-BuSBP)

R_1= Ph, R_2 = t-Bu, para, p-(t-butylthio)benzophenone (p-t-BuSBP)

R_1 = Ph, R_2 = sec-Bu, para, p-(sec-butylthio)benzophenone (p-sec-BuSBP)

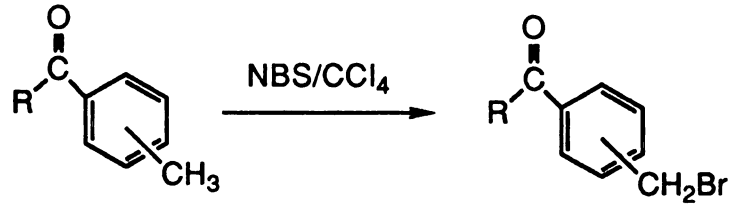
the corresponding halophenyl ketones with alkyl mercaptan in the presence of sodium carbonate or potassium hydroxide.

o-(Methylthio)benzophenone (o-MeSBP) was prepared[45] by the methylation of o-mercaptobenzoic acid with dimethyl sulfate and then treated with thionyl chloride followed by Friedel-Crafts acylation of benzene:



o-MeSBP

Bromomethylphenyl ketones were prepared by bromination of the corresponding tolyl ketones with NBS:



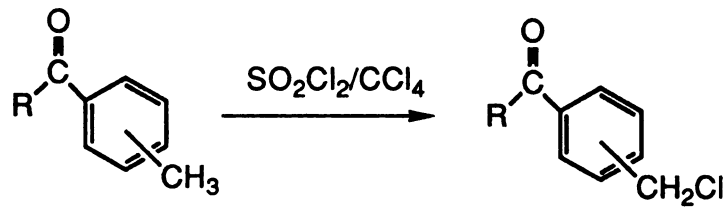
R = CH_3, para, p-bromomethylacetophenone (p-$BrCH_2AP$)

R = Ph, para, p-bromomethylbenzophenone (p-$BrCH_2BP$)

R = Ph, meta, m-bromomethylbenzophenone (m-$BrCH_2BP$)

R = CH_3, meta, m-bromomethylacetophenone (m-$BrCH_2AP$)

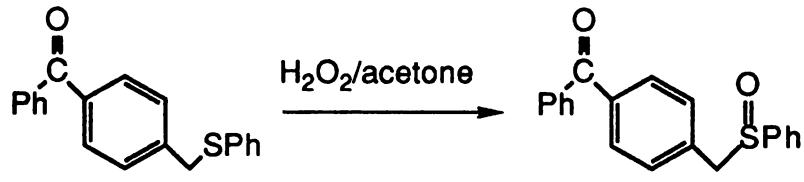
Chloromethylphenyl ketones were prepared by chlorination of the corresponding tolyl ketones with sulfuryl chloride:



R = Ph, para, p-chloromethylbenzophenone (p-$ClCH_2$BP)

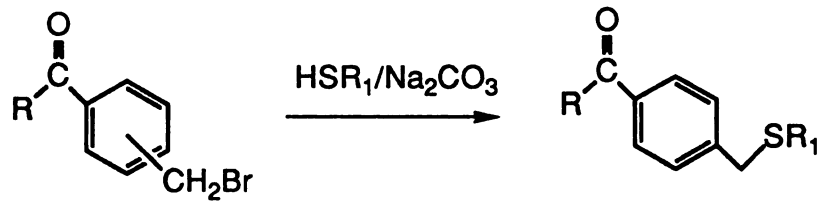
R = CH_3, mata, m-chloromethylacetophenone (m-$ClCH_2$AP)

para-(Phenylsulfinyl)methylbenzophenone (p-$PhSOCH_2$BP) was prepared by oxidation of the ketosulfide in acetone.with excess 30% aqueous hydrogen peroxide:



Alkylthiomethylacetophenones and alkylthiomethylbenzophenones were prepared by nucleophilic substitution reactions of the corresponding

bromomethyl-phenyl ketones with the appropriate mercaptan in the presence of sodium carbonate:



R = CH_3, R_1 = Ph, para, p-(phenylthio)methylacetophenone (p-$PhSCH_2AP$)

R = Ph, R_1 = Ph, para, p-(phenylthio)methylbenzophenone (p-$PhSCH_2BP$)

R = Ph, R_1= n-butyl, para,p-(n-butylthio)methylbenzophenone (p-n-$BuSCH_2BP$)

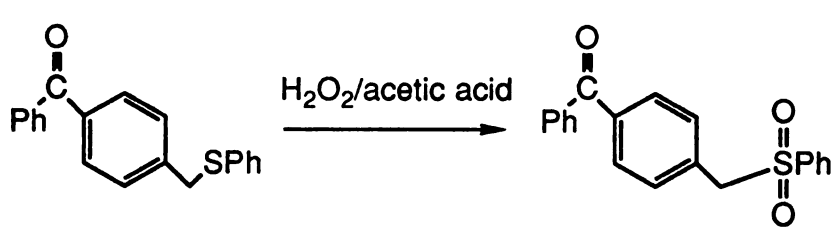
R = Ph, R_1 = Ph, mata, m-(phenylthio)methylbenzophenone (m-$PhSCH_2BP$)

R = CH3, R_1 = Ph, mata, m-(phenylthio)methylacetophenone (m-$PhSCH_2AP$)

R = Ph, R_1 = t-butyl, para, p-(t-butylthio)methylbenzophenone (p-t-$BuSCH_2BP$)

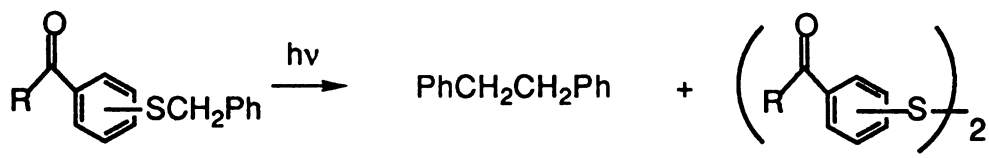
R = Ph, R_1 = sec-butyl, para, p-(sec-butylthio)methylbenzophenone (p-sec-$BuSCH_2BP$)

para-(Phenylsulfonyl)methylbenzophenone (p-$PhSO_2CH_2BP$) was prepared by oxidation of the ketosulfide in acetic acid with excess 30% aqueous hydrogen peroxide:



B. Identification of Photoproducts

Irradiation of 0.1-0.2 g of p-BzSBP, p-BzSAP and o-BzSAP in 50 ml benzene afforded a mixture of C-S bond cleavage products: toluene, bibenzyl and disulfides. The disulfide products were separated by silica gel column chromatography with hexane and ethyl acetate as eluent. Their structures were confirmed based on NMR, IR, and Mass spectrometry. Bibenzyl was identified by GC retention time in comparison with commercially available authentic samples:

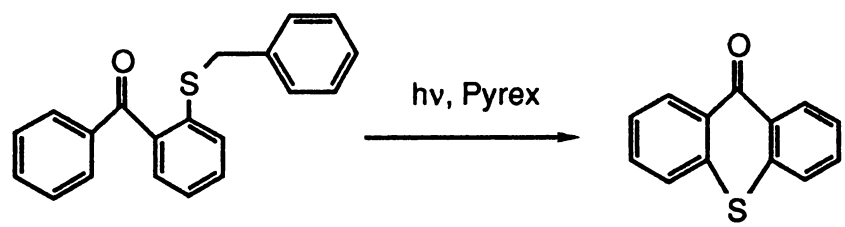


R = Ph, para position, 4,4'-(dithio)dibenzophenone $(p\text{-BPS})_2$

R = CH_3, para position, 4,4'-(dithio)diacetophenone $(p\text{-APS})_2$

R = CH_3, ortho position, 2,2'-(dithio)diacetophenone $(o\text{-APS})_2$

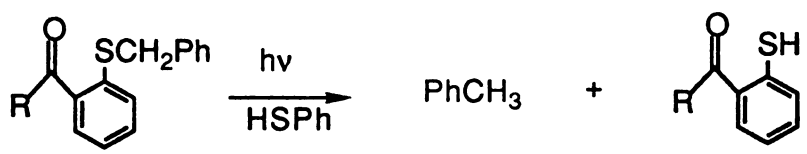
Irradiation of 0.2 g of o-BzSBP in 50 ml benzene with a Pyrex filter until



o-BzSBP thioxanthen-9-one

100% conversion afforded a product that was isolated on silica gel column with hexane and ethyl acetate as eluent. The structure was identified by NMR, IR and Mass spectra as thioxanthen-9-one. The product could not be detected by GC in experiments run to under 10% conversion.

Irradiation of 0.1-0.2 g o-BzSBP or o-BzSAP in 50 ml benzene in the presence of 0.1 M thiophenol afforded a mixture of C-S bond cleavage products, namely toluene and o-mercaptobenzophenone(o-HSBP) or o-mercaptoacetophenone(o-HSAP). Both o-HSBP and o-HSAP were separated by silica gel chromatography using hexane and ethyl acetate as eluent. The structures of mercaptans were confirmed by NMR, IR and Mass spectrometry and toluene was identified by comparing its retention time with authentic sample.



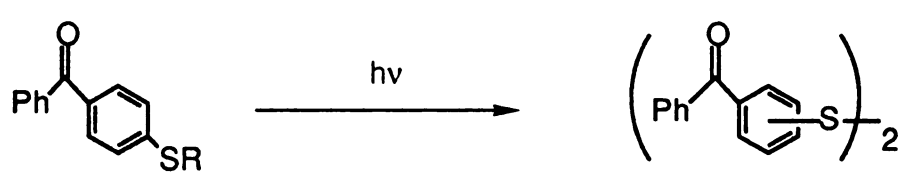
o-BzSBP

o-BzSAP

o-HSBP

o-HSAP

Irradiation of p-t-BuSBP and p-sec-BuSBP at 313 nm or 366 nm gave $(p\text{-}BPS)_2$ as product. The products were identified by HPLC retention time using authentic sample.



p-t-BuSBP

p-sec-BuSBP

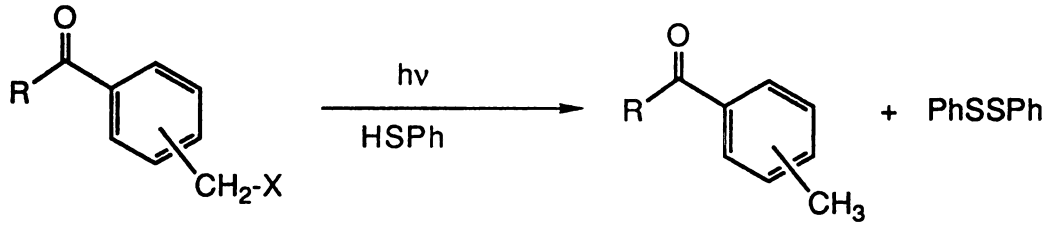
$(p\text{-}BPS)_2$

Irradiation of p-PhSCH$_2$BP, p-BuSCH$_2$BP, p-BrCH$_2$BP, p-ClCH$_2$BP, p-PhSOCH$_2$BP, p-PhSO$_2$CH$_2$BP, p-t-BuSCH$_2$BP and p-sec-BuSCH$_2$BP in the presence of 0.05-0.1 M thiophenol at 313 nm or 366 nm gave as products p-methylbenzophenone (p-MeBP) and phenyldisulfide (PhSSPh). The products were identified by GC using commercially available authentic samples.

Irradiations of p-PhSCH$_2$AP and p-BrCH$_2$AP in the presence of 0.05 - 0.1 M thiophenol at 313 nm or 366 nm gave as products p-methylacetophenone (p-MeAP) and PhSSPh. The products were identified by GC using commercially available authentic samples.

Irradiation of m-PhSCH$_2$BP and m-ClCH$_2$BP in the presence of 0.05-0.1 M thiophenol at 313 nm or 366 nm gave as products m-methylbenzophenone (m-MeBP) and PhSSPh. The products were identified by GC using commercially available authentic samples.

Irradiation of m-PhSCH$_2$AP in the presence of 0.05-0.1 M thiophenol at 313 nm or 366 nm gave as products m-methylacetophenone (m-MeAP) and PhSSPh. The products were identified by GC using commercially available authentic samples:



R= CH3, Ph

X = PhS, Cl, Br, t-Bu, n-Bu, Sec-Bu, SOPh, SO2Ph

Irradiations of o-MeSBP, o-C_8SAP or p-n-BuSBP in the presence of thiophenol, for more then 48 hours, gave no significant products.

C. Molecular Mechanics Calculations

A molecular modeling software, PCMODEL, distributed by Serena Software, Box 3076, Bloomington, IN 47402-3076, was used to calculate the minimum energy of different conformations of molecules. The MMX force field is used in this program which is derived from the MM2 1987 force field.

The energies listed in Table 1 are the total energies of special conformations of the molecules. The total energy is the sum of the π system, bond stretching, bond bending, torsional, and non-bonding interaction energies.

The energies of different conformations of p-t-BuSBP, p-sec-BuSBP, p-n-BuSBP and p-BzSBP were calculated using the dihedral drive method. For the comformation in Table 1, the solid line is a benzene ring: the sulfur atom attached on the benzene is toward us and α is the dihedral angle between R-S and the benzene ring. Minimum energies were calculated for every 15^o from α = 0 to 360^o (Table 1).

D. Spectroscopy

The UV absorption spectra were recorded for all the ketones. The wavelengths of the absorption maxima and their corresponding extinction coefficients are reported in Table 2.

Phosphorescence spectra were taken for all the ketones at 77K in 2-methyltetrahydrofuran with ketone concentrations of about 0.04 M. The triplet energies of the ketones were calculated from the highest energy (0,0) band and are given in Table 3.

E. Kinetic results

1. Quantum Yields - Quantum yields for product formation and for ketone disappearance were determined by irradiation at 313 nm or 366 nm in a merry-go-round apparatus at room temperature. Solutions containing 0.005-0.02 M ketone in benzene were irradiated in parallel with degassed benzene solutions of 0.1 M valerophenone as an actinometer.[48] The ketone conversion was controlled at about 10%. All samples were degassed by three freeze-thaw cycles prior to irradiation. Compound to internal standard ratios were measured by GC or HPLC. Quantum yields are calculated by equation 1 and 2.

$$\Phi = [C] / \{I_o \times (1-10^{-Ak})\} \qquad (1)$$

$$I_o = [AP] / \{ 0.33 \times (1 - 10^{-Avp}) \} \qquad (2)$$

where [C] is the concentration of the products, Io is the intensity of the light absorbed by the ketone solution. [AP] is the concentration of acetophenone from the valerophenone actinometer, Ak and Avp are the optical densities of ketone and valerophenone under the irradiation condition. When the A is larger

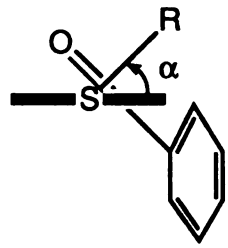
than 2, the term ($1-10^{-A}$) can be ignored and the error is less than 0.01. Product quantum yields were obtained by adding 0.05 M thiophenol to the photolysis solutions. A plot of Quantum yields vs. the concentrations of HSPh are given in figure 1. The values of the quantum yields are listed in Tables 4-5.

2. Triplet Lifetime - Stern-Volmer quenching analysis was performed by 366 nm irradiation of the ketone solutions containing varying amounts of either naphthalene or 1-methylnaphthalene. Conversions were kept below 10% for the sample without quencher and the plots of $\Phi o / \Phi$ vs concentrations of quenchers were linear up to quantum yield ratios of 3-5.

$$\Phi o / \Phi = 1 + k_q\tau[\text{Quencher}] \qquad (3)$$

According to equation 3, $k_q\tau$ values are obtained from the values of slopes of the plots. They are listed in Tables 4-5. All the Stern-Volmer plots are presented in figures 2-12.

Table 1. Minimized Energies of Different Conformations of p-(Alkylthio)benzophenones in kcal/mole.



α	p-t-BuSBP	p-sec-BuSBP	p-n-BuSBP	p-BzSBP
0	38.94	35.79	33.81	40.42
15	38.31	35.45	33.50	40.07
30	36.76.	34.42	32.64	39.36
45	34.79	33.18	31.67	38.40
60	32.90	32.08	30.87	37.49
75	31.53	31.43	30.38	36.95
90	30.84	31.33	30.22	36.80
105	31.34	31.50	30.40	36.95
120	32.63	32.04	30.97	37.62
135	34.54	33.06	31.67	38.90
150	36.70	34.38	32.68	39.99
165	38.37	35.44	33.59	40.48
180	38.97	35.85	33.93	40.52
195	38.37	35.49	33.48	40.19
210	36.72	34.50	32.61	39.37
225	34.57	33.19	31.60	38.32
240	32.66	32.00	30.77	37.40
255	31.36	31.36	30.31	36.87
270	30.85	31.31	30.21	36.75
285	31.61	31.50	30.45	36.95
300	32.88	32.06	31.16	37.66
315	34.76	33.07	31.60	38.94
330	36.74	34.31	32.55	40.07
345	38.30	35.36	33.44	40.51
360	38.91	35.80	33.81	40.47

Table 2. UV Absorption Data for Various Ketones

Ketones	π,π^*_1 λ max (ε)	π,π^*_2 λ max (ε)	n,π^* λ max (ε)	313 nm ε	366 nm ε
p-BzSBP(H[a])	242(17732)		311(20315)	17500	
P-BzSBP(B[b])			315(18850)		334
p-BzSAP(H)	297(15871)		304(18340)	8900	
p-BzSAP(B)	305(19557)			16200	15
p-t-BuSBP(H)	255(21680)	309(4580)	348(235)		
p-t-BuSBP(B)		312(4345)		4300	170
p-n-BuSBP(H)	244(14525)		315(18341)		
o-BzSBP(H)	243(20934)	279(5172)	334(855)		
o-BzSBP(B)			336(1077)	970	530
o-BzSAP(H)	230(16872)	270(5970)	334(2308)		
o-BzSAP(B)			338(1930)	1450	790
p-$BrCH_2$BP(H[a])	257(24027)		348(59)	81	110
p-$BrCH_2$BP(B[b])			344(181)	130	105
p-$ClCH_2$BP(H)	253(23615)		348(142)	64	91
p-$ClCH_2$BP(B)			344(158)	92	93
p-$PhSOCH_2$BP(H)	253(14470)	274(10925)			
p-$PhSOCH_2$BP(B)			343(212)		111
p-$PhSO_2CH_2$BP(H)	255(19161)				
p-$PhSO_2CH_2$BP(B)			344(169)	110	99
Valerophenone(H)			323(49)	45	4.8
Valerophenone(B)			321(54)	51	3.8
p-$PhSCH_2$AP(B)				510	12
p-$PhSCH_2$BP(B)				1090	96
p-n-$BuSCH_2$BP(B)					99
m-$PhSCH_2$AP(B)				240	23
m-$PhSCH_2$BP(B)				490	84
p-t-$BuSCH_2$BP(B)			342(234)	400	134
p-sec-$BuSCH_2$BP(B)			344(234)	460	97
m-$ClCH_2$BP(B)			343(131)	77	70
p-$BrCH_2$AP(B)					12
p-$BrCH_2$AP(H)	250(3597)	289(286)			

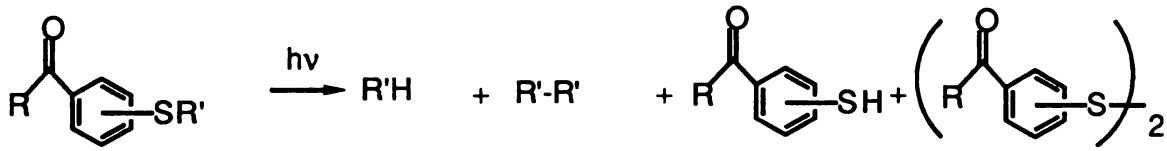
[a]in cyclohexane. [b]in benzene.

Table 3. Spectroscopic data for phenyl ketones.

Ketone	$\lambda_{0,0}$(nm)[a]	$E_{T(0,0)}$ (kcal/mol)[a]	$\lambda_{0,1}$(nm)	ΔE_T(cm^{-1})	State
BP	417.6 (s)	68.5 (68.6)[46]	455.0	1469	n,π*
AP	391.2 (s)	73.1 (73.7)[46]	416.4	1539	n,π*
p-MeBP	415.2 (s)	68.9 (68.7)[47]	444.0	1574	n,π*
p-MeAP	397.2	72.0 (72.9)[47]	---[b]	—	π,π*
m-MeBP	416 (s)	68.8	445	1574	n,π*
m-MeAP	393	72.8 (73.1)[47]	420	1644	π,π*
p-BzSBP	446	64.1	—	—	π,π*
p-t-BuSBP	421 (s)	67.9	452	1504	n,π*
p-sec-BuSBP	446	64.1	—	—	π,π*
p-n-BuSBP	440	65.0	—	—	π,π*
p-BzSAP	438	65.3	—	—	π,π*
o-BzSBP	437	65.4	—	—	π,π*
o-BzSAP	437	65.4	—	—	π,π*
p-PhSCH$_2$BP	416 (s)	68.7	447.0	1644	n,π*
p-t-BuSCH$_2$BP	419(s)	68.3	449.0	1609	n,π*
p-n-BuSCH$_2$BP	417 (s)	68.6	447.0	1609	n,π*
p-ClCH$_2$BP	417 (s)	68.6	447.0	1609	n,π*
p-PhSCH$_2$AP	397.0	72.0	—	—	π,π*
m-PhSCH$_2$BP	416 (s)	68.8	447.0	1644	n,π*
m-PhSCH2AP	395	72.4	—	—	π,π

[a]Phosphorescence Spectra at 77°K in 2-Methyltetrahydrofuran in kcal/mol.
Triplet energy: $E_T = 2.86 \times 10^4 / \lambda$(nm).
[b]no vibrational structructure.

Table 4. Kinetic Data for Various Alkylthiophenylketones in Benzene.



1 2 3 4

Compound	Φ_{-k}[a]	Φ_1[a]	Φ_2[a]	Φ_3[a]	Φ_4[a]	$k_q\tau$[b]
p-BzSBP	0.40	---	0.15	---	0.17	125
p-t-BuSBP	0.37	---	---	---	0.18	683
p-sec-BuSBP	0.019	---	---	---	0.0052	7670
p-BzSAP	0.47	---	0.16	---	0.24	70
o-BzSBP[c]	0.0041	0.0041	---	0.0026	---	2.1
o-BzSAP	0.036	---	0.018	---	0.019	11.6
o-BzSAP[c]	0.081	0.081	---	0.064	---	

[a]Irradiation at 313 nm. [b]Irradiated at 366 nm. Naphthalene was used as quencher. [c]in the presence of 0.05 M thiophenol.

Table 5. Kinetic Data for Various Para Substituted Methylbenzophenones in Benzene in the Presence of 0.05-0.1M Thiophenol.

Compound	Φ-k[a]	Φ_p	ΦPhSSPh	$k_q\tau$[b]
p-PhSCH$_2$BP	0.27	0.19[c]	0.18	0.74
p-t-BuSCH$_2$BP	0.35	0.18[c]		27.6
p-2-BuSCH$_2$BP	0.34	0.19[c]		16.9
p-BuSCH$_2$BP	0.36	0.20[c]		16.5
p-BrCH$_2$BP	0.45	0.30[c]		<0.1
p-ClCH$_2$BP	0.48	0.48[c]		11
p-PhSOCH$_2$BP	0.33	0.35[c]		<0.1
p-PhSO$_2$CH$_2$BP	0.35	0.29[c]		515
p-PhSCH$_2$AP	0.31	0.35[d]		0.24
p-BrCH$_2$AP	0.22	0.25[d]		<0.1
m-PhSCH$_2$BP	0.47	0.39[e]		40
m-ClCH$_2$BP	0.036	0.034[e]		311
m-PhSCH$_2$AP	0.36	0.32[f]		1.9

[a]Irradiated in benzene at 313 nm. [b]Irradiated in benzene at 366 nm. Naphthalene was used as quencher. [c]Quantum yield of p-MeBP. [d]Quantum yield of p-MeAP. [e]Quantum yield of m-MeBP. [f]Quantum yield of m-MeAP.

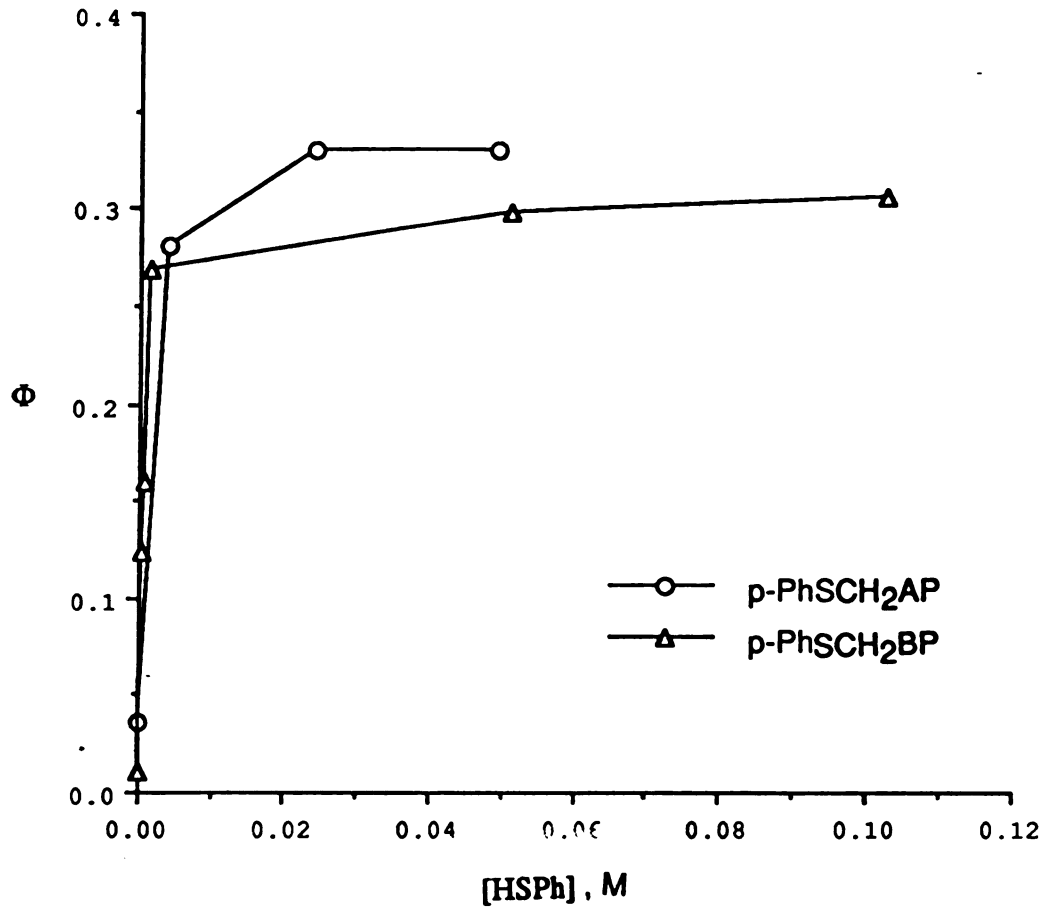


Figure 1. Quantum Yields of Irradiation of p-(Phenylthio)-methylbenzophenone and p-(Phenylthio)methylacetophenone vs. the Concentrations of Thiophenol.

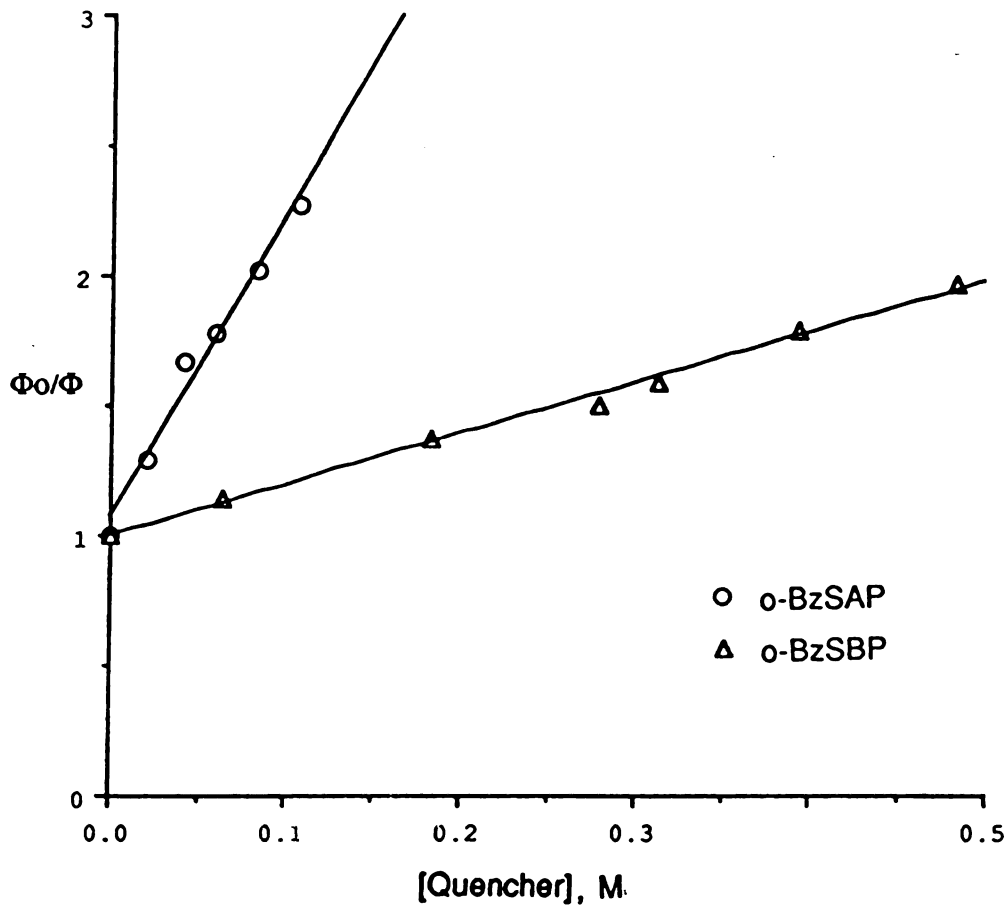


Figure 2. Stern-Volmer Plot of o-(Benzylthio)acetophenone with 1-Methylnaphethalene and of o-(benzylthio)benzophenone with Naphthalene in Benzene Solution.

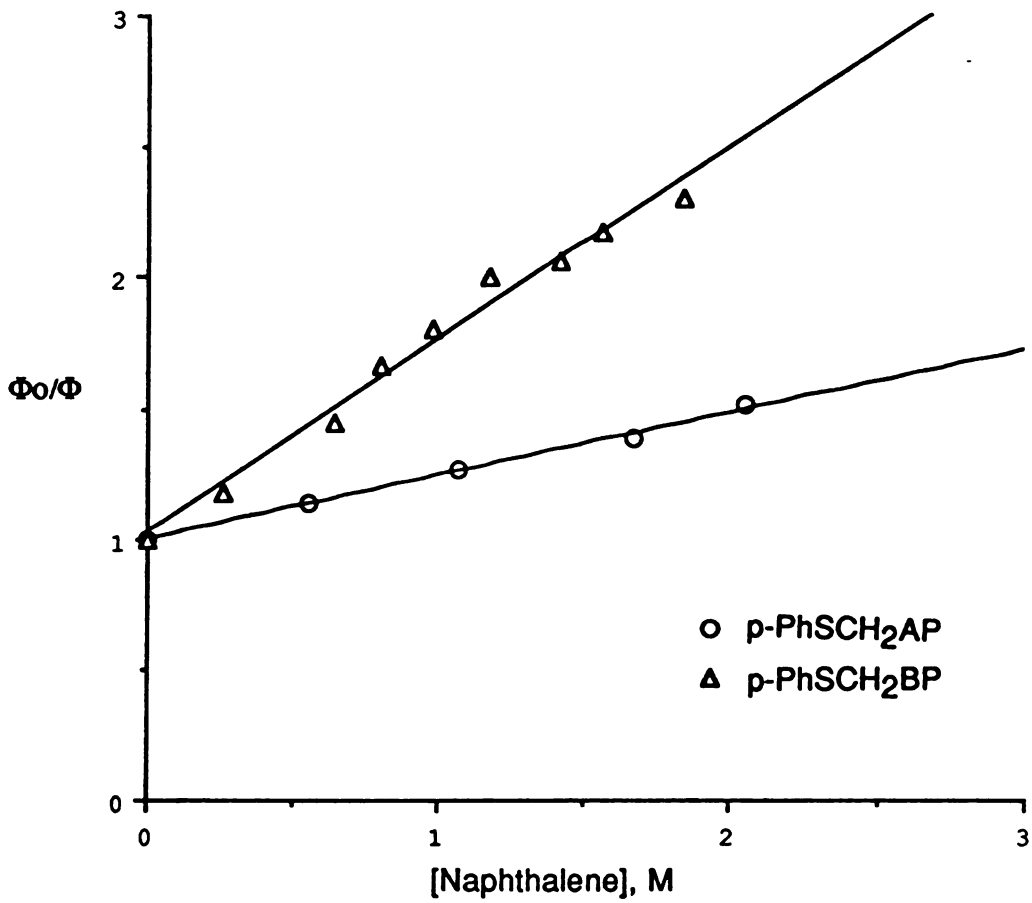


Figure 3. Stern-Volmer Plot of p-(Phenylthio)methylacetophenone and of p-(Phenylthio)methylbenzophenone with Naphthalene in Benzene Solution.

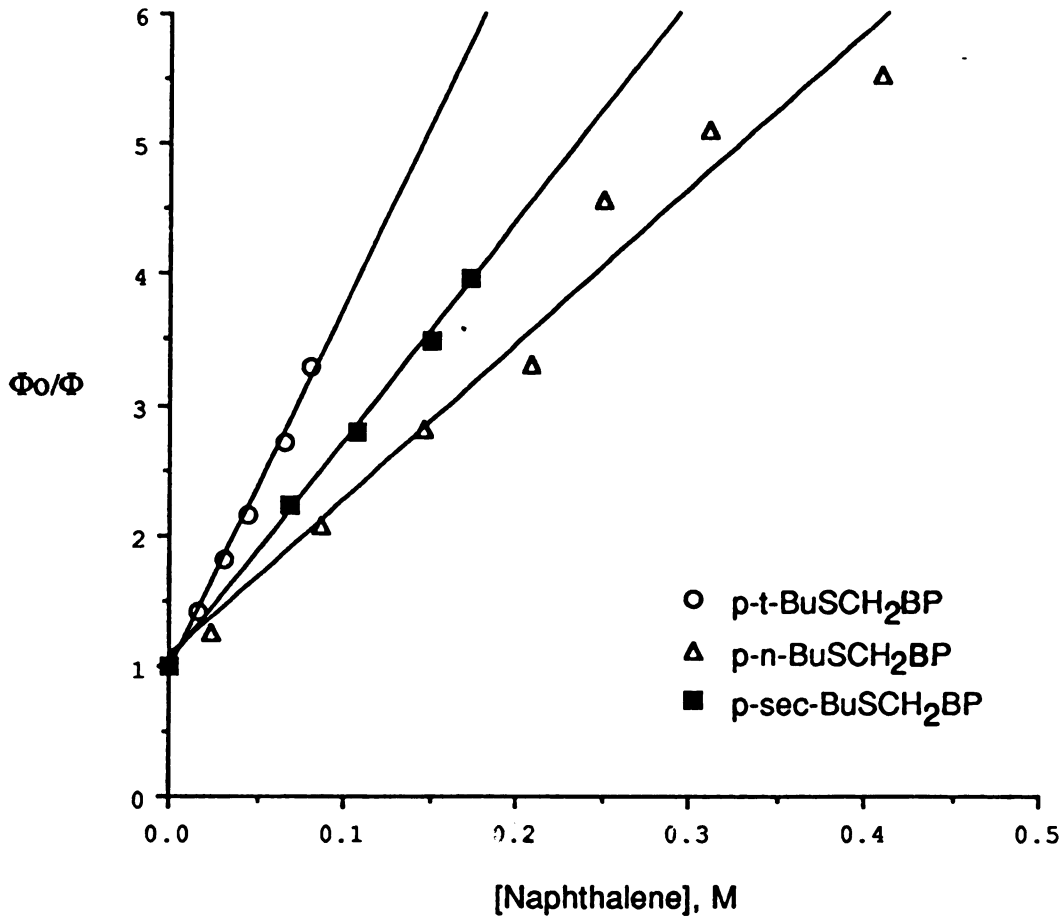


Figure 4. Stern-Volmer Plot of p-(n-Butylthio)methylbenzophenone, p-(sec-Butylthio)methylbenzophenone and p-(t-Butylthio)methylbenzophenone by Naphthalene in Benzene Solution.

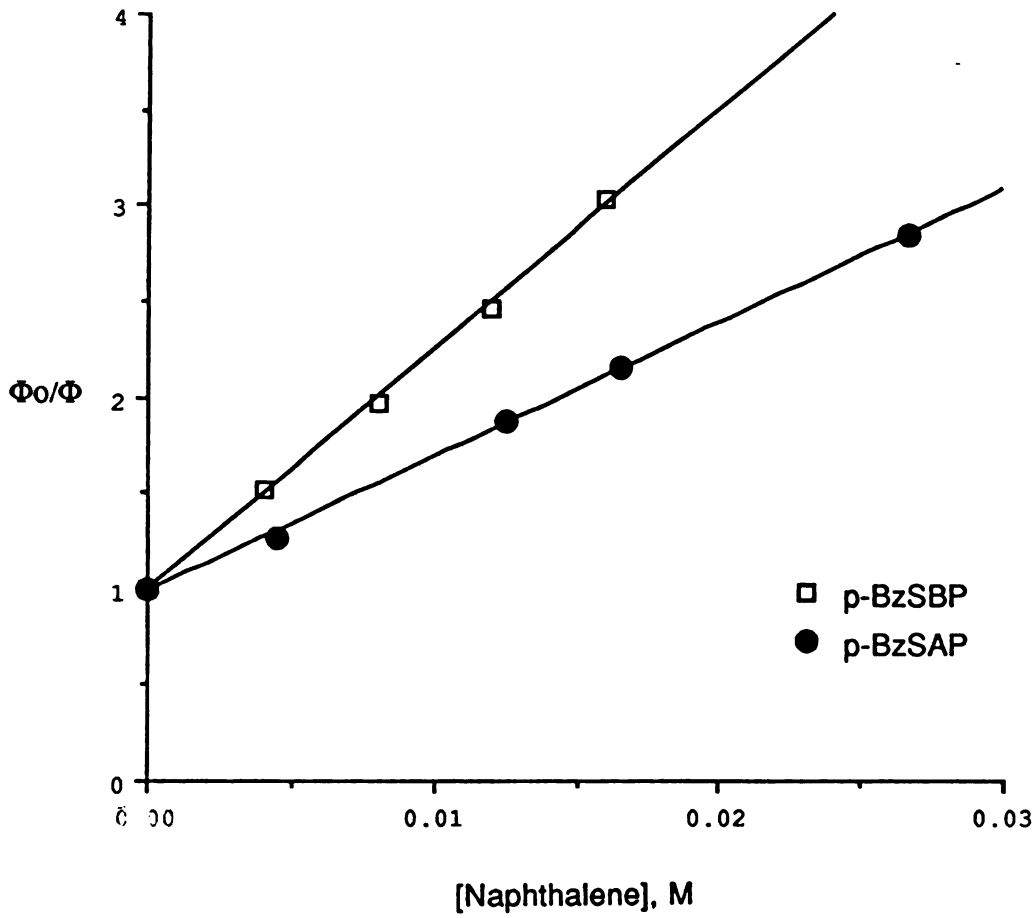


Figure 5. Stern-Volmer Plot of p-(Benzylthio)acetophenone with 1-Methylnaphthalene and of p-(Benzylthio)benzophenone by Naphthalene in Benzene Solution.

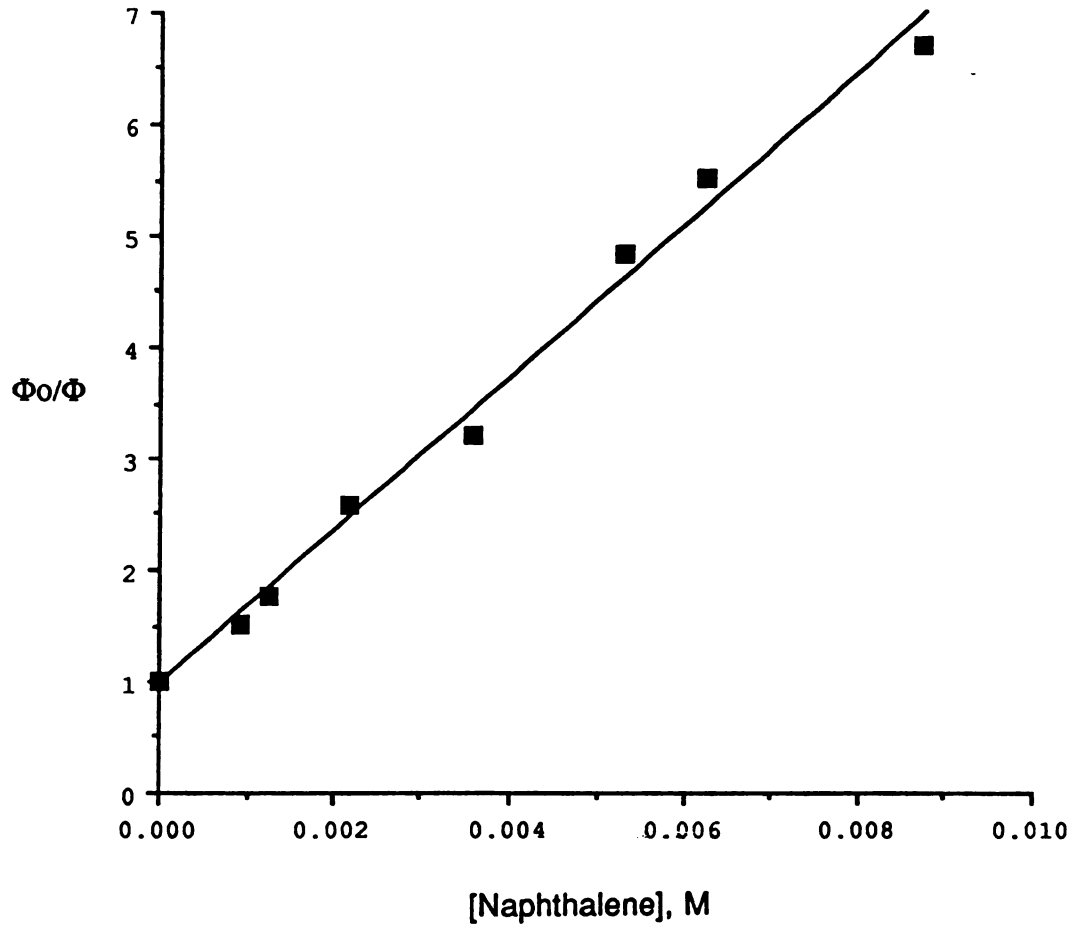


Figure 6. Stern-Volmer Plot of p-(t-Butylthio)benzophenone with Naphthalene in Benzene Solution

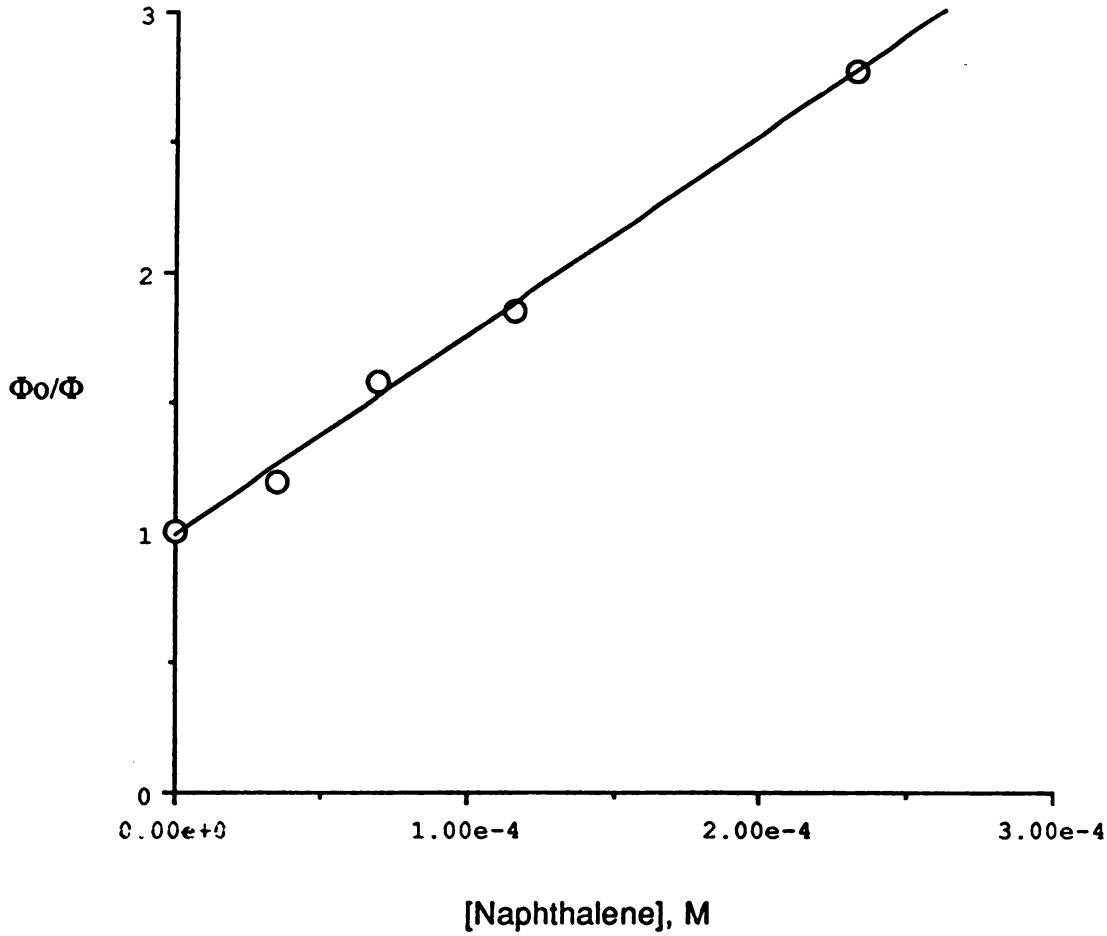


Figure 7. Stern-Volmer Plot of p-(sec-Butylthio)benzophenone with Naphthalene in Benzene Solution.

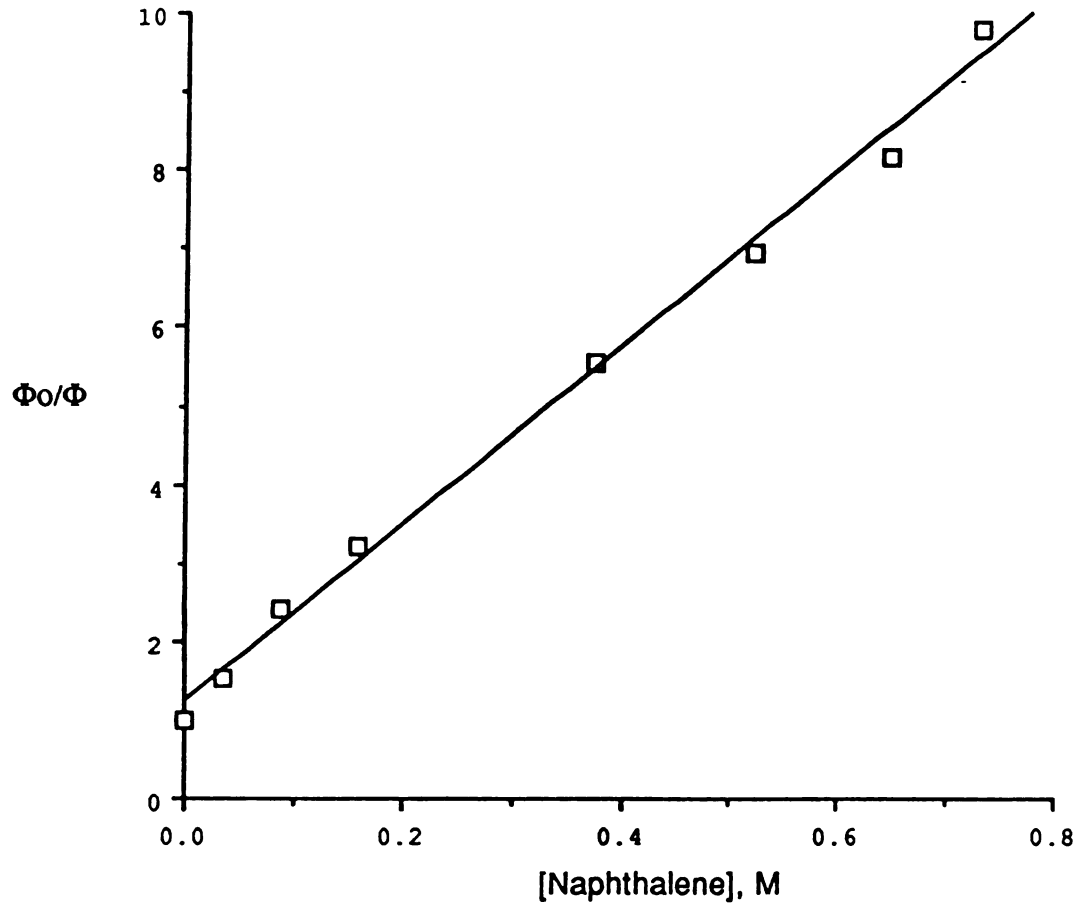


Figure 8. Stern-Volmer Plot of p-Chloromethylbenzophenone with Naphthalene in Benzene Solution

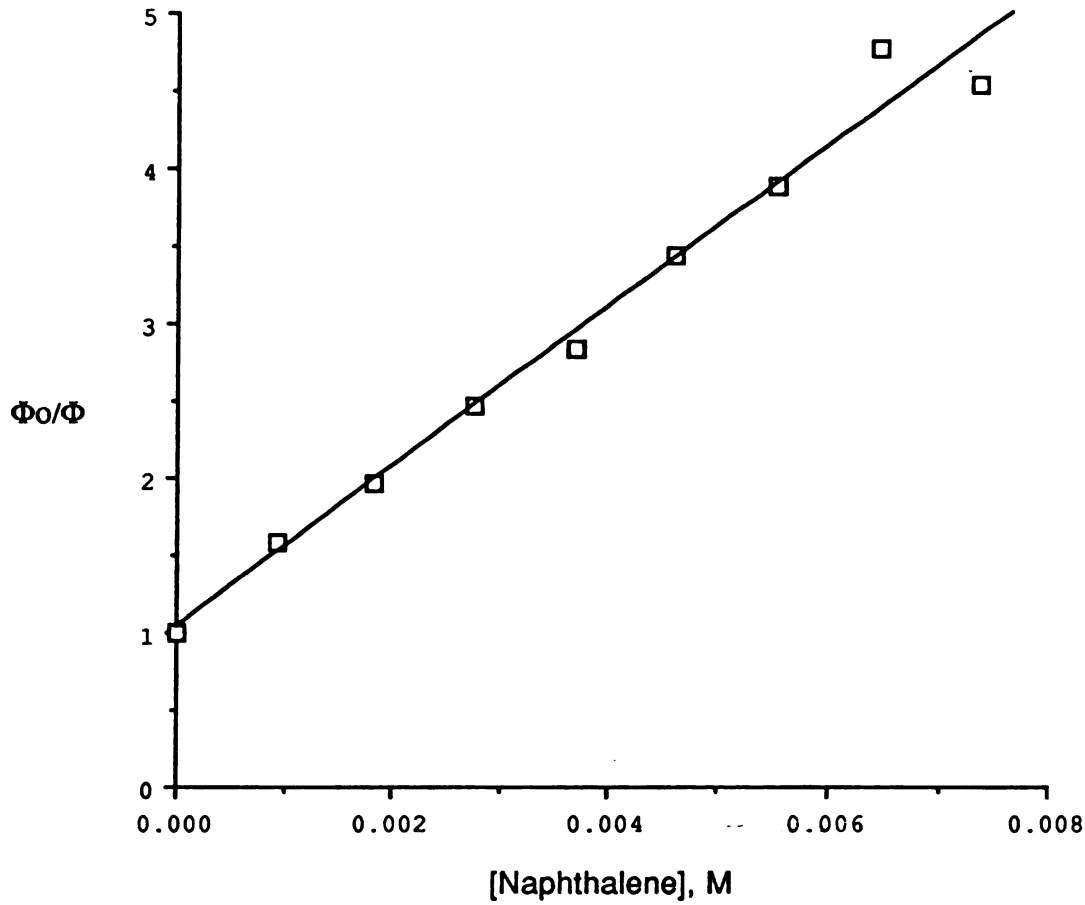


Figure 9. Stern-Volmer Plot of p-Phenylsulfonylmethylbenzophenone with Naphthalene in Benzene Solution

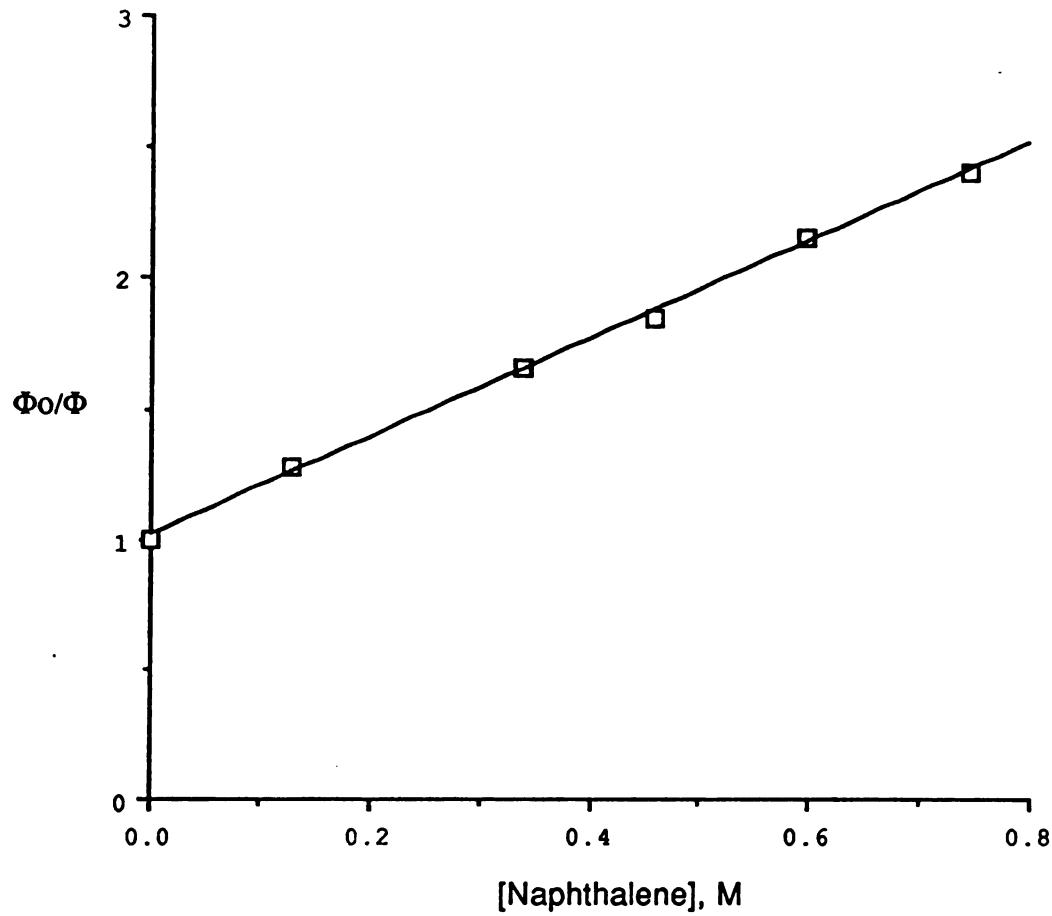


Figure 10. Stern-Volmer Plot of m-(Phenylthio)methylacetophenone with Naphthalene in Benzene Solution

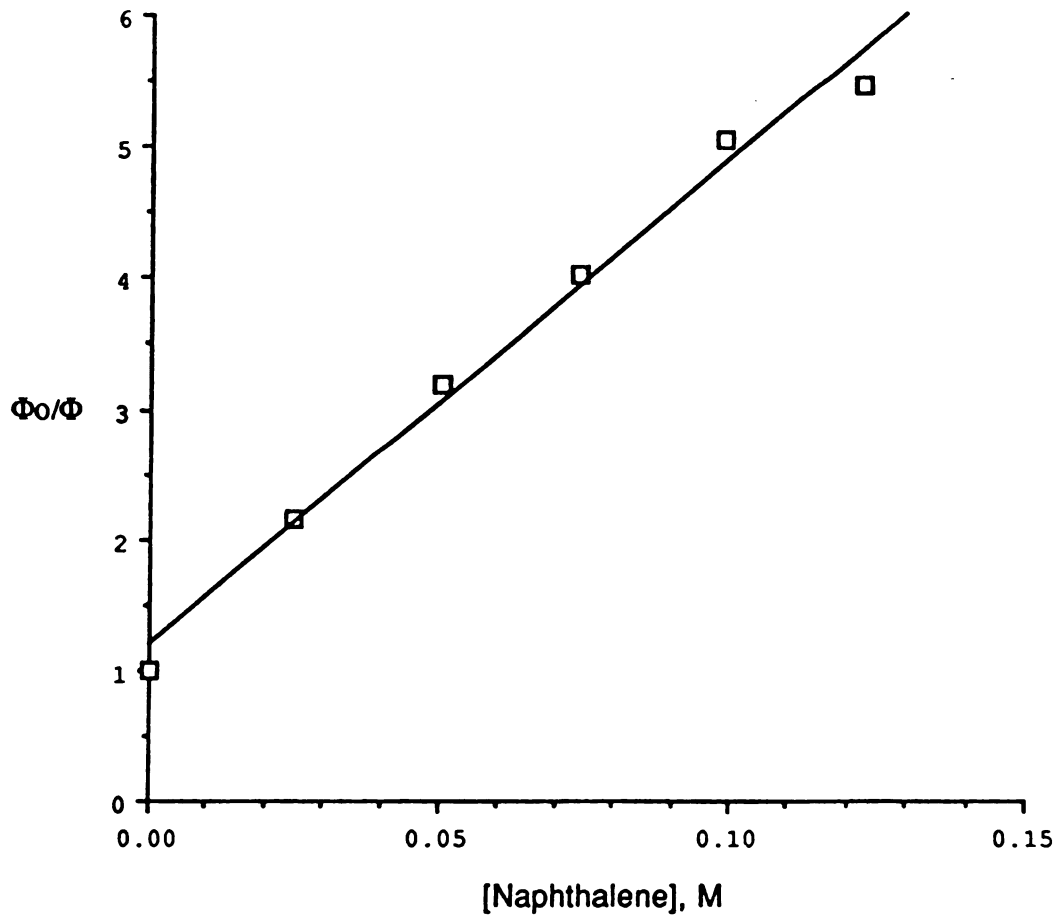


Figure 11. Stern-Volmer Plot of m-(Phenylthio)methylbenzophenone with Naphthalene in Benzene Solution

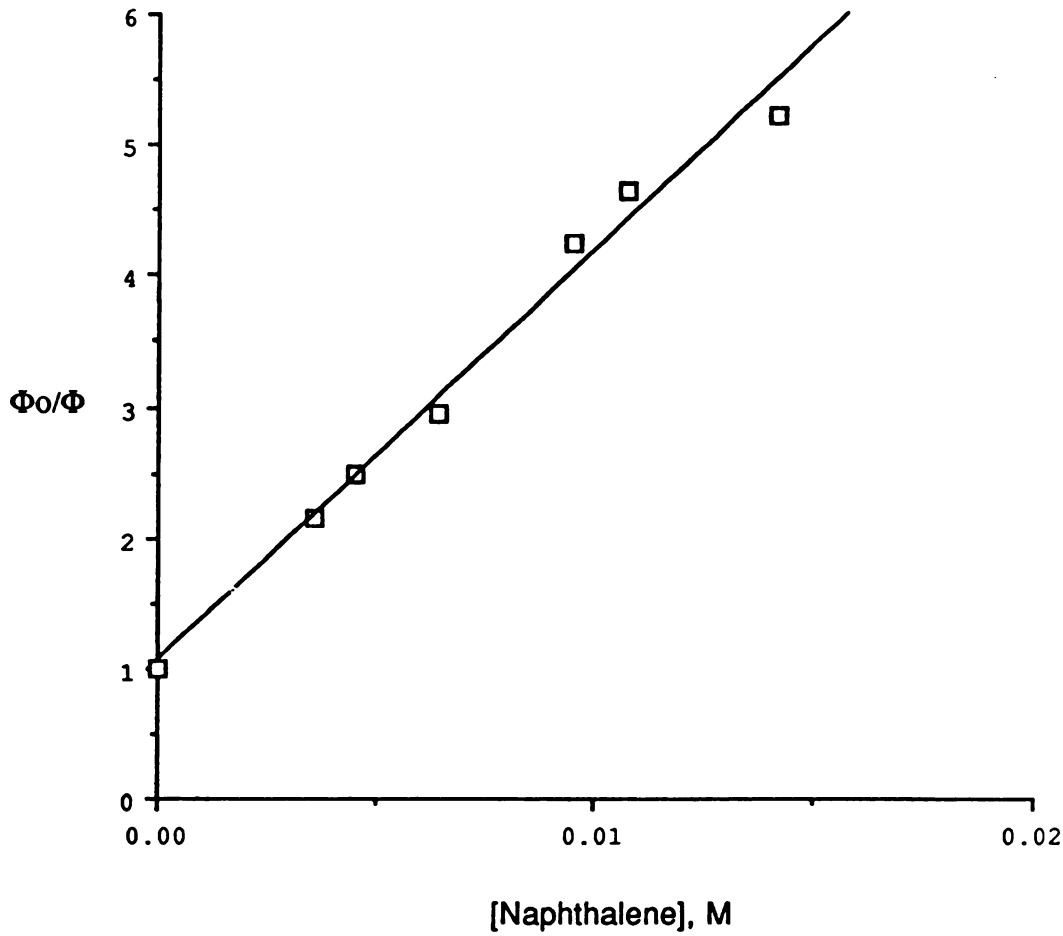
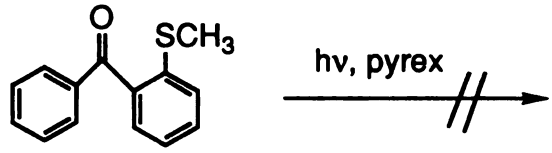


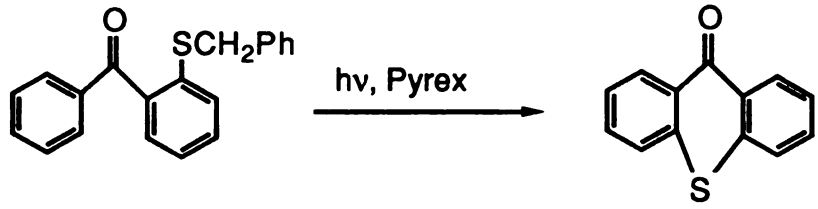
Figure 12. Stern-Volmer Plot of m-Chloromethylbenzophenone with Naphthalene in Benzene Solution

Discussion

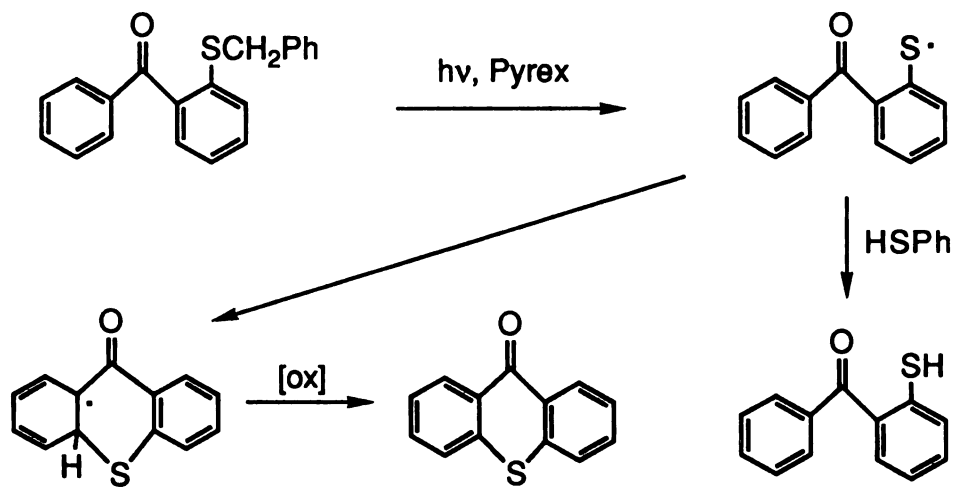
A. Mechanism

The original objective of this study was to investigate the photochemistry of ortho-alkylthio substituted benzophenone and acetophenone. Since the reaction of their oxygen analogs is well-documented,[18-22,49] we expected that the reactions would proceed via δ-hydrogen abstraction to form a biradical followed by coupling to give a cyclization product. Surprisingly, o-(methylthio)-benzophenone was stable to light in benzene and the irradiation of o-benzylthiobenzophenone afforded only thioxanthen-9-one without any alcohol products. Further investigation of the reaction by adding 0.1 M thiophenol to the





o-(benzylthio)benzophenone solution gives only o-mercaptobenzophenone without thioxanthen-9-one product. This suggested that the thioxanthen-9-one is formed via a homolytic carbon-sulfur bond cleavage to give a thiyl radical followed by radical cyclization. There are only a few papers[50,43] that mention cleavage of a S-C or X-C bond attached to the benzene ring of phenyl ketones. No systematic work has yet been done to understand how the energy transfers from the carbonyl chromophore to the S-C bond.

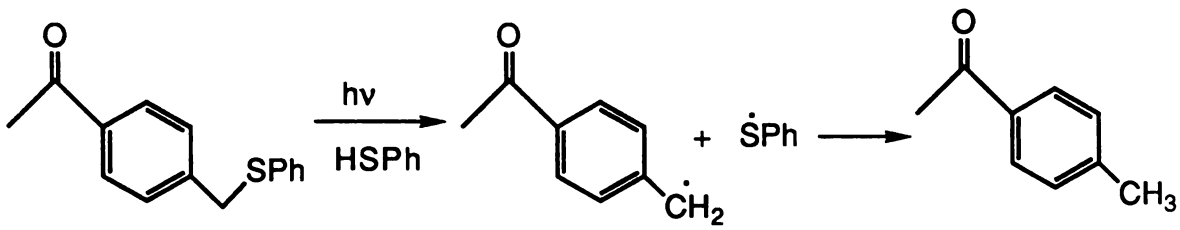


We investigated several derivatives of acetophenone and benzophenone with sulfur-carbon bonds attached to the phenyl ring. To compare the results, several para and meta substituted halomethyl-benzophenones and halomethylacetophenones were also investigated.

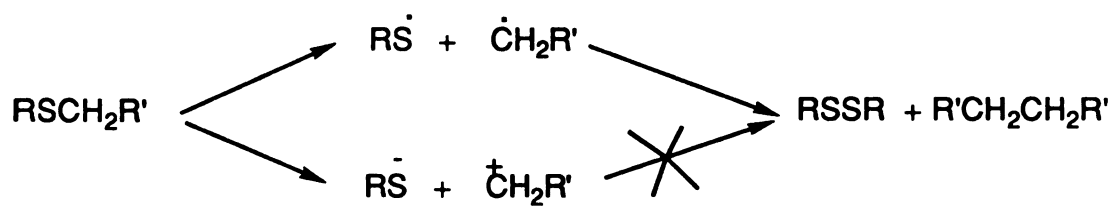
The results of photolysis of a variety of acetophenone and benzophenone derivatives are shown in Tables 4-8. All the compounds studied afford carbon-hetero atom homolytic bond cleavage products except for o-

(methylthio)benzophenone, p-(n-butylthio)benzophenone, and o-(octylthio)-acetophenone which are inert to the light.

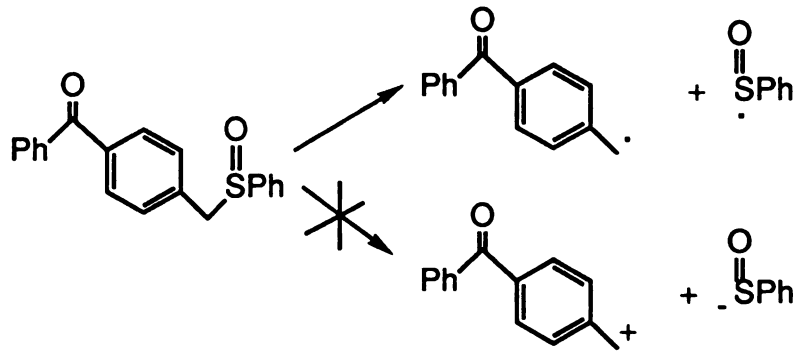
Wagner and Lindstrom[43,51] reported the photolysis of p-(phenylthio)-methylacetophenone. The reaction afforded p-methylacetophenone as product. This reaction was suggested to occur via a homolytic carbon-sulfur bond cleavage process to generate radicals:



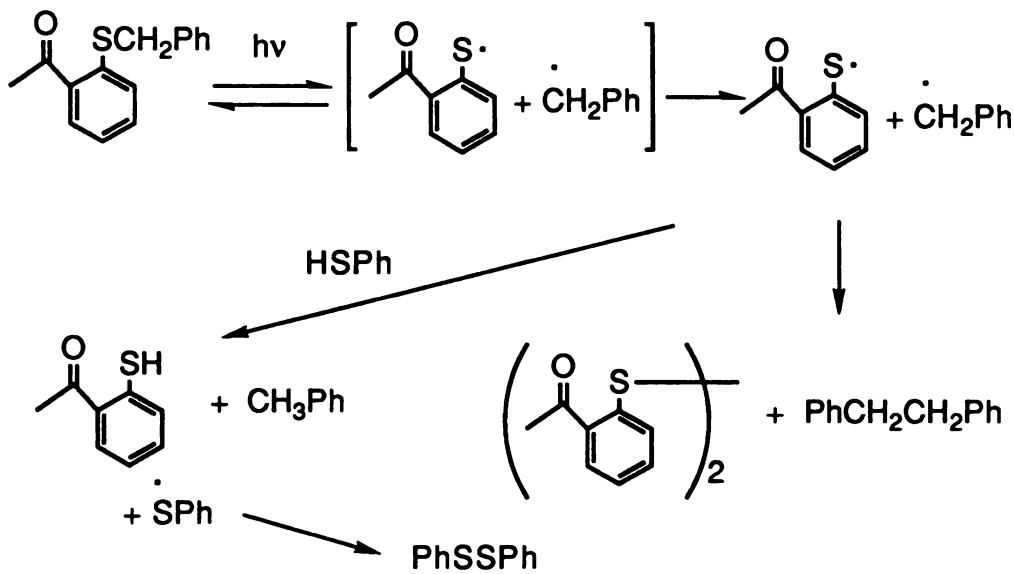
In the present system, evidence for a reaction mechanism which involves free radicals as intermediates is given below. First, the formation of coupling products - disulfides and bibenzyls - can be well explained by the radical process which rules out heterolytic cleavage as a possible mechanism:



Also the reactivity of sulfoxide is much higher than that of sulfone in spite of the fact that SOPh is a poorer anionic leaving group compared to SO_2Ph:[52]



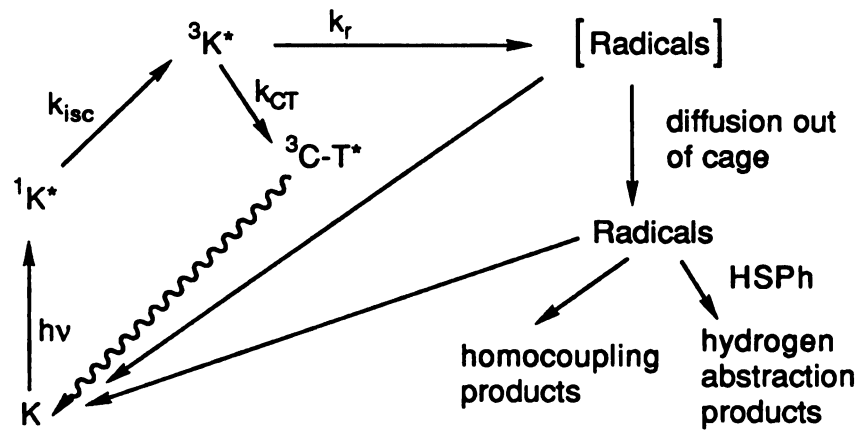
Secondly, the trapping experiment of the reaction by thiophenol[29,53] supported the radical process. In the absence of hydrogen donor, the reaction



gives only radical coupling products. In presence of thiophenol, most of the radicals that escape the radical cage are trapped and hydrogen abstraction products are preferred. For example, the products of photolysis of o-(benzylthio)acetophenone are dibenzyl and 2,2'-dithiodiacetophenone, while

the products in the presence of HSPh are toluene, o-thioacetophenone and phenyldisulfide. The increase of the quantum yields indicates that the decrease of the coupling of the radicals back to ground state starting ketone. The change of the distribution of the products indicated that the radicals generated by homolytic S-C bond cleavage are intercepted by thiol before they can find each other.

Based on the radical process, a mechanism of photoinduced homolytic sulfur-carbon bond cleavage of ketosulfides is presented in Scheme 2. All the detail of the mechanism will be discussed:



Scheme 2. Mechanism of S-C Bond Cleavage of Ketosulfides

B. Radicals

It is well established that a radical cleavage processes involve initial formation of caged radical pairs which can diffuse apart or couple back to ground state starting compounds.[43,54,55] The radicals that escape from the cage can then form coupling products or hydrogen abstraction products if there is a hydrogen donor in the reaction system. Wagner and Lindstrom studied the photolysis of some substituted phenacyl phenyl sulfides.[43] The quantum yields of phenyl alkyl ketone formation increased to a maximum of about 0.4 in the presence of 0.05 M thiophenol. They concluded that about 40 % of the initial radicals escape from the radical cage before they couple to the starting ketones. The experimental data we obtained for the quantum yields vs. the concentration of thiophenol reach maximum value when the concentration increases to 0.02 M. The highest value for this maximum quantum yield is around 0.40. Similar results have also been reported for other triplet radical pairs.[55] Therefore, we conclude that 40 % of the radicals escape from solvent cages. The photolysis of p-BzSBP or p-t-BuSBP in the presence of 0.1 M thiophenol gives only 4,4'-dithiodibenzophenone and p-thiobenzophenone since the p-benzoylphenylthiyl radical is more stable than phenylthiyl radical and thiophenol cannot trap all the radicals. The quantum yield of 4,4'-dithiodibenzophenone from irradiation of p-BzSBP and p-t-BuSBP is 0.17 and 0.18 (corresponding to 34% and 36% for the quantums yield for free radicals). Photolysis of p-BzSAP gave quantum yields of 4,4'-dithiodiacetophenone of 0.24(corresponding to 48% quantum yield for free radical). Therefore, we conclude that nearly all the thiyl radicals that escape the solvent cage are couple to disulfides for the para substituted (alkylthio)benzophenone or (alkylthio)acetophenone and we can apply this result to the photolysis of p-sec-BuSBP.

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Table 6 presents the maximum quantum yields for the photoproducts of a variety of keto sulfides together with some keto halides. Since the S-C bond cleavage is the only reaction that the photolysis of these sulfides undergo, the maximum of the quantum yields represent a measurement of the cage effect of S-C bond cleavage reaction. This indicates that 40% of the initially formed radicals are able to escape from the solvent cage to form products and the other 60% of the radicals couple back to starting ketones in the solvent cage.

C. Triplet lifetimes of ketones

That the radicals are formed exclusively from triplet excited states is confirmed by quenching studies. Naphthalene and α-methylnaphthalene are well-known triplet quenchers with triplet excited state energy at 60.9 and 60.8 kcal/mol,[56] respectively, and can quench the triplet excited states of phenyl ketones (64-74 kcal/mol) with a diffusion controlled rate constant. Straight lines and unity intercepts obtained from the Stern-Volmer plot exclude any products directly from singlet excited states.

The triplet lifetime of ketones can be obtained from the following equation:

$$\tau = \text{Slope} / k_q$$

where τ is the triplet lifetime of ketone, slope is calculated from Stern-Volmer plot and k_q is the rate constant of quenching reaction. It is widely accepted that the quenching of triplet ketones by energy transfer in the benzene solution at 25°C is diffusion-controlled and kq is about 6×10^9 M^{-1} s^{-1}.[57] Scaiano and

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Wagner measured rate constants of several quenching reactions of various organic molecules with a number of triplet quenchers and found the value above was accurate.[58] Table 7 gives the $1/\tau$ value deduced from Stern-Volmer plot.

The triplet lifetime is a measurement of how fast the excited triplet states can decay. The reciprocal of the triplet lifetime is generally expressed as the sum for rate constants of all the physical and chemical decay reactions which the excited state undergoes, i.e.

$$1/\tau = \Sigma k_r + \Sigma k_d$$

where k_r is the rate constant for a chemical reaction and k_d is the rate constant for physical decay. For a reaction involving more than one process, it is necessary to estimate the individual contribution of each process to the overall triplet lifetime.

Radiative deactivation (phosphorescence) usually has a rate constant k_p of the order of 10^1- 10^4 s^{-1}.[59] It can not compete with other physical and chemical processes and therefore can be ignored in this system.

The typical value for the rate constant k_d of the radiationless decay of triplet phenyl ketones is in the order of 10^5 -10^6 s^{-1}.[60] Wagner and Truman[61] measured k_d's for substituted acetophenones and benzophenones and the results fit this range very well. Therefore, it is reasonable to assume that the sulfur substituted benzophenones, acetophenones, p-methylacetophenones

Table 6 Maximum Quantum Yields for photoproducts of Ketones

ketones	Product	Φ_{max}
p-BzSBP	$(p\text{-BPS})_2$	0.17
p-t-BuSBP	$(p\text{-BPS})_2$	0.18
p-sec-BuSBP	$(p\text{-BPS})_2$	0.0052
p-BzSAP	$(p\text{-APS})_2$	0.24
o-BzSBP	o-HSBP	0.0041
o-BzSAP	o-HSAP	0.081
p-PhSCH$_2$BP	p-MeBP	0.19
p-t-BuSCH$_2$BP	p-MeBP	0.18
p-sec-BuSCH$_2$BP	p-MeBP	0.19
p-n--BuSCH$_2$BP	p-MeBP	0.20
p-BrCH$_2$BP	p-MeBP	0.30
p-ClCH$_2$BP	p-MeBP	0.48
p-PhSOCH$_2$BP	p-MeBP	0.35
p-PhSO$_2$CH$_2$BP	p-MeBP	0.29
p-PhSCH$_2$AP	p-MeAP	0.35
p-BrCH$_2$AP	p-MeAP	0.25
m-PhSCH$_2$BP	m-MeBP	0.39
m-ClCH$_2$BP	m-MeBP	0.034
m-PhSCH$_2$AP	m-MeAP	0.32

Table

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p-Ph
p-Br
m-Ph
m-Cl
m-PhS

Table 7. Triplet lifetimes of Ketones

Compound	$k_q\tau$, M^{-1}	τ, sec	$1/\tau$, s^{-1}
p-BzSBP	125	2.1×10^{-8}	4.8×10^{7}
p-t-BuSBP	683	1.1×10^{-7}	8.8×10^{6}
p-sec-BuSBP	7668	1.3×10^{-6}	7.8×10^{5}
p-BzSAP	69.9	1.2×10^{-8}	8.6×10^{7}
o-BzSBP	1.97	3.2×10^{-10}	2.9×10^{9}
o-BzSAP	11.6	1.9×10^{-9}	5.5×10^{8}
p-$PhSCH_2$BP	0.74	1.2×10^{-10}	8.3×10^{9}
p-t-BuSCH_2BP	27.6	4.6×10^{-9}	2.2×10^{8}
p-sec-BuSCH_2BP	16.9	2.8×10^{-9}	3.6×10^{8}
p-n-BuSCH_2BP	16.5	2.8×10^{-9}	3.6×10^{8}
p-$PhSOCH_2$BP	<0.1	$> 1.7 \times 10^{-11}$	$> 5.8 \times 10^{10}$
p-$PhSO_2CH_2$BP	515	8.6×10^{-8}	1.2×10^{7}
p-$BrCH_2$BP	<0.1	$> 1.7 \times 10^{-11}$	$> 5.8 \times 10^{10}$
p-$ClCH_2$BP	11	1.8×10^{-9}	5.5×10^{8}
p-$PhSCH_2$AP	0.24	4.0×10^{-11}	2.5×10^{10}
p-$BrCH_2$AP	<0.1	$> 1.7 \times 10^{-11}$	$> 5.8 \times 10^{10}$
m-$PhSCH_2$BP	40	6.7×10^{-9}	1.5×10^{8}
m-$ClCH_2$BP	311	5.2×10^{-8}	1.9×10^{7}
m-$PhSCH_2$AP	1.9	3.2×10^{-10}	3.2×10^{9}

and p-methylbenzophenones have similar k_d values. Since the triplet decay rates of most ketosulfides measured in this study are in the order of 10^7 -10^{10} s^{-1}, the k_d accounts only less than 1% of the overall triplet decay of the compounds. Thus, the contribution of radiationless decay to the lifetimes can be ignored in most cases.

As indicated in the Introduction,[28,29] the sulfur atom of sulfides quenches the triplet ketone intermolecularly or intramolecularly through charge-transfer(CT) interactions. Cohen and Guttenplan[62] have measured intermolecular CT quenching of phosphorescence of benzophenone triplet by sulfides by charge-transfer in benzene. The k_{CT} values for phenyl methyl sulfide and p-chlorophenyl methyl sulfide are 6.0×10^7 and 2.2×10^7 M^{-1} s^{-1} respectively. If we assume that the intermolecular CT process in our system is on the same order, and consider that the concentration of ketosulfides used in the experiment is usually about 2×10^{-2} M, the contribution of intermolecular charge-transfer ([K] x k_{CT}) to triplet decay is calculated to be about 10^5-10^6 M^{-1} s^{-1}. The low quantum yield of the photolysis of p-sec-BuSBP indicated an intermolecular charge-transfer process. Since the $1/\tau$ of p-sec-BuSBP is only 7.8×10^5 M^{-1} s^{-1}, the charge-transfer process is fast enough to compete and causes low quantum yield.

Singer[85] measured triplet self quenching in derivatives of benzophenone. A charge transfer process via exciplex intermediate was proposed. The rate constants of self quenching k_{sq} are 2.8×10^8, 2.2×10^7 and 1.8×10^6 M^{-1} s^{-1} for 4,4'-bis(dimethylamino)benzophenone, 4,4'-*dime*thoxybenzophenone and 4,4'-dimethylbenzophenone, respectively. He found that log k_{sq} is linear in σ_p^+ (-1.7, -0.778 and -0.311 for dimethylamino, methoxy and methyl, respectively[86]). Since σ_p^+ of methylthio is -0.604[86], the k_{sq} value of alkylthiophenyl ketones is expected to be around 10^7 M^{-1} s^{-1}.

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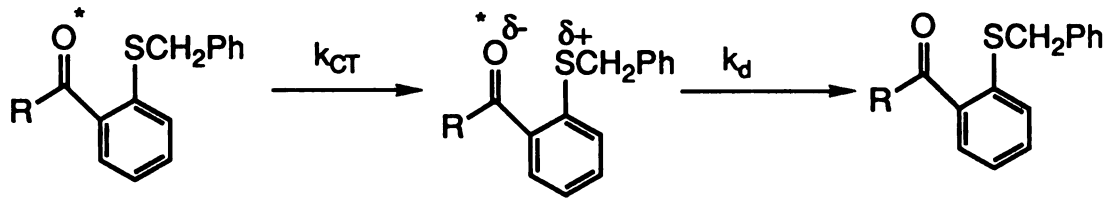
Another physical decay process of triplet excited states of ketones is the intramolecular quenching by sulfur atom through a CT process. Wagner and Lindstrom[29] measured several CT rate constant values (k_{CT} = 5.5 x 10^9 s-1) of β-(n-butylthio)propiophenone in benzene. They also indicated that the phenylthio group is a less active quencher than the alkylthio group (for example k_{CT} = 2.9 x 10^9, 2.5 x 10^9, 0.8 x 10^9 s^{-1} for γ-(n-butylthio)butyrophenone, γ-(t-butylthio)butyrophenone and γ-(phenylthio)butyrophenone respectively). The results we obtained for the photolysis of alkylthiophenyl ketones are unusual since the photolysis of p-BzSAP and p-BzSBP gave higher quantum yields(0.18 and 0.17, respectively) and low triplet reactivities(τ = 1.2 x 10^{-8} s and 2.1 x 10^{-8} s, respectively) while their ortho analogs gave low quantum yields(0.064 for o-BzSAP and 0.0026 for o-BzSBP) and high triplet reactivities(τ = 1.9 x 10^{-9} s for o-BzSAP and 3.2 x 10^{-10} s for o-BzSBP). The unusual results are similar to the study reported by Padwa in the reactions of β-keto sulfides.[42] The different behavior of o-BzSAP and o-BzSBP being relative to p-BzSAP and p-BzSBP suggests a different mechanism for the ortho substituted ketones. The low quantum yields and short lifetimes suggest a rapid decay competing with radical cleavage, the formation of an intramolecular CT complex by the interaction of the excited carbonyl group and sulfur. The CT complex can undergo reverse charge-transfer process to generate a ground state starting ketone.[42,43] Since the intramolecular charge-transfer process occurs through-space,[63] in which five or six atom cyclic conformations are the most favorable, it is not feasible for the para substituted ketones to achieve a conformation that can form a CT complex:



In the present system, the only products detected are the C-S bond cleavage products. Therefore, there is only one rate constant k_r for the chemical process. The equation then can be written as

$$1 / \tau = k_r + \Sigma k_d \qquad (4)$$

where k_r is the rate constant of the chemical process and Σk_d is the sum total contribution of physical decay process. We already concluded that 40 % of the original radical pairs diffuse from solvent cages. By dividing the maximum quantum yields by 0.40, we obtained the quantum yields Φ_r for the S-C bond cleavage.

Table 8 contains k_r and Σk_d for alkylthiophenyl ketones. In the case of o-BzSBP and o-BzSAP, Σk_d equals the rate constant of intramolecular CT by sulfur atom(k_{CT}) and the other decay processes can be ignored. The results are close to results reported by Wagner and Lindstrom.[29] Intramolecular C-T in o-BzSAP is 7 times slower than in o-BzSBP.

In the case of p-BzSBP, p-t-BuSBP and p-sec-BuSBP, Σk_d is the sum of contributions via intermolecular C-T by sulfide and nonradiative decay. Intermolecular C-T reaction and nonradiative decay cannot be detected within the experimental error for p-BzSAP. The result is reasonable, since $1/\tau$ is 8.6 x 10^7 s^{-1} and Σk_d is $<10^6 s^{-1}$.

Table 8 Kinetic Data for Alkylthiophenyl Ketones

Compound	Φ_{max}	Φ_r	$1/\tau$, s^{-1}	k_r, s^{-1}	Σk_d, s^{-1}
p-BzSBP	0.17	0.85	4.8×10^7	4.1×10^7	7.0×10^6
p-t-BuSBP	0.18	0.90	8.8×10^6	7.9×10^6	9.0×10^5
p-sec-BuSBP	0.0052	0.026	7.8×10^5	2.0×10^4	7.6×10^5
p-BzSAP	0.24	1.00	8.6×10^7	8.6×10^7	$< 10^6$
o-BzSBP	0.0041	0.0103	2.9×10^9	3.0×10^7	2.9×10^9
o-BzSAP	0.081	0.203	5.5×10^8	1.1×10^8	4.4×10^8

Table 9 contains values for k_r and Σk_d for alkylthio- ,chloro- and bromo-substituted methylphenyl ketones. The percentage that k_r's contribute to the τ^{-1} values were obtained by dividing the maximum quantum yield by 0.40. The Σk_d obtained represents total decay from the triplet excited state and is in a range of 10^8-10^{10} s^{-1} for most ketones. We already indicated that the rate constant of intramolecular C-T is in the range of 10^7-10^8 M^{-1} sec^{-1} for p-BzSBP, p-t-BuSBP and p-sec-BuSBP. If we use the same range for alkylthiomethylphenyl ketones, the contribution of C-T to $1/\tau$ lies in the range of 10^5-10^6 s^{-1}, considering that sulfide concentration is only 0.01-0.02 M. Therefore, intermolecular C-T reaction can be ignored. Since no products other than the S-C bond cleavage products were detected, Σk_d may represent some unknown processes that occurs from triplet excited states.

Table 9 Kinetic Data for Methylphenyl Ketones Derivatives.

Compound	Φ_{max}	Φ_r	$1/\tau$ (s^{-1})	k_r (s^{-1})	Σk_d (s^{-1})
p-PhSCH$_2$BP	0.19	48%	8.3×10^9	4.0×10^9	4.3×10^9
p-t-BuSCH$_2$BP	0.18	45%	2.2×10^8	1.0×10^8	1.2×10^8
p-sec-BuSCH$_2$BP	0.19	48%	3.6×10^8	1.7×10^8	1.9×10^8
p-n-BuSCH$_2$BP	0.20	50%	3.6×10^8	1.8×10^8	1.8×10^8
p-BrCH$_2$BP	0.30	75%	$> 5.8 \times 10^{10}$	$> 4.4 \times 10^{10}$	$> 1.4 \times 10^{10}$
p-ClCH$_2$BP	0.48	100%	5.5×10^8	5.5×10^8	$< 10^7$
p-PhSOCH$_2$BP	0.35	88%	$> 5.8 \times 10^{10}$	$> 5.1 \times 10^{10}$	$> 7.0 \times 10^9$
p-PhSO$_2$CH$_2$BP	0.29	73%	1.2×10^7	8.7×10^6	3.3×10^6
p-PhSCH$_2$AP	0.35	88%	2.5×10^{10}	2.2×10^{10}	3.0×10^9
p-BrCH$_2$AP	0.25	63%	$> 5.8 \times 10^{10}$	$> 3.7 \times 10^{10}$	$> 2.1 \times 10^{10}$
m-PhSCH$_2$BP	0.39	98%	1.5×10^8	1.5×10^8	3.0×10^6
m-ClCH$_2$BP	0.034	8.5%	1.9×10^7	1.6×10^6	1.7×10^7
m-PhSCH$_2$AP	0.32	80%	3.2×10^9	2.6×10^9	6.0×10^8
p-BrCH$_2$VP^{50}	0.25	63%	$> 5.8 \times 10^{10}$	$> 3.7 \times 10^{10}$	$> 2.1 \times 10^{10}$
p-ClCH$_2$VP^{50}	0.43	100%	$> 5.8 \times 10^{10}$	$> 5.8 \times 10^{10}$	----
m-ClCH$_2$VP^{50}	0.22	55%	2.9×10^8	1.6×10^8	1.3×10^8

[a]percentage of contribution to k_r.

D. Reactivities of C-S bond cleavage

Several factors seem to affect the rates of the S-C bond cleavage reaction: the stability of the radicals, the S-C bond energy and the nature of the triplet excited state.

In free radical chemistry, some of the early work[64] suggested the order of stability for sulfur radicals to be SPh > SOR > SR > SO_2R. This was confirmed by Wagner and Lindstrom[43,65] in their study of β-cleavage in phenacylsulfides. The relative rates they obtained are > 196 : 44 : 1 : 0.0078 for SPh, SOMe, S-t-Bu and SO_2Me, respectively.

The relative rates listed in Table 10 are determined by the feature of the leaving groups-- the well known relative stabilities[66] of the radicals, Bz > t-Bu > sec-Bu > n-Bu.

Table 10. Relative Rate for C-S Bond Cleavage of Alkylthiobenzophenone

Compound	k_r (s^{-1})	k_{rel}
p-BzSBP	4.1×10^7	5.2
p-t-BuSBP	7.9×10^6	1
p-sec-BuSBP	2.0×10^4	0.0025
p-n-BuSBP	$< 10^3$	< 0.0001

Table 11 Relative Rate for C-S and C-X Bond Cleavage of p-Methylbenzophenone Derivatives.

Compound	k_r (s^{-1})	k_{rel}
p-$PhSCH_2BP$	4.0×10^9	40
p-t-$BuSCH_2BP$	1.0×10^8	1
p-sec-$BuSCH_2BP$	1.7×10^8	1.7
p-n-$BuSCH_2BP$	1.8×10^8	1.8
p-$PhSOCH_2BP$	$> 5.3 \times 10^9$	> 510
p-$PhSO_2CH_2BP$	8.7×10^6	0.0087
p-$BrCH_2BP$	$> 4.5 \times 10^9$	> 440
p-$ClCH_2BP$	5.5×10^8	5.5

The relative rates listed in Table 11 give as relative stabilities of sulfur and halogen radicals: PhSO ~ Br > PhS > Cl > Alkyl-S > $PhSO_2$. The order, SOPh > SPh > S-Alkyl > SO_2Ph, obtained in this study is what was expected and matches Lindstrom's[65] data very well. Since bromine is a much more stable radical than chlorine, it is no surprise that p-$BrCH_2BP$ reacts much faster than p-$ClCH_2BP$.

Table 12 contains relative rates of C-SPh and C-X bond cleavage for meta and para substituted phenyl ketones. The cleavages of p-$PhSCH_2AP$, p-$BrCH_2AP$, p-$BrCH_2VP$ and p-$ClCH_2VP$ are too fast to be quenched and the rate constants for bond cleavage are larger than 10^{10} s^{-1}. The extremely fast rate for bromides may also be caused by a heavy-atom effect. The ratio of rate

Table 12. Relative Rate for C-S and C-X Bond Cleavage of Methylphenyl ketone Derivatives.

Compound	k_r (s^{-1})	k_{rel}
p-$PhSCH_2AP$	2.5×10^{10}	---
p-$BrCH_2AP$	$> 3.7 \times 10^{10}$	---
p-$BrCH_2VP^{50}$	$> 3.7 \times 10^{10}$	---
p-$ClCH_2VP^{50}$	$> 5.8 \times 10^{10}$	---
m-$PhSCH_2BP$	1.5×10^{8}	94
m-$ClCH_2BP$	1.6×10^{6}	1
m-$PhSCH_2AP$	2.6×10^{9}	16
m-$ClCH_2VP^{50}$	1.6×10^{8}	1
p-$PhSCH_2BP$	4.0×10^{9}	7.3
p-$BrCH_2BP$	$> 3.7 \times 10^{10}$	> 67
p-$ClCH_2BP$	5.5×10^{8}	1

constants for m-$PhSCH_2BP$ / m-$ClCH_2BP$ and m-$PhSCH_2AP$ / m-$ClCH_2VP$ are 94:1 and 16:1 respectively. The relative rates of p-$PhSCH_2BP$ and p-$ClCH_2BP$ are in the same order (7.3 : 1). The relatively smaller rate constants for the meta substituted methylphenyl ketones show that a para-carbonyl stabilizes the benzyl radical by spin delocalization while a meta substituent cannot.[87]

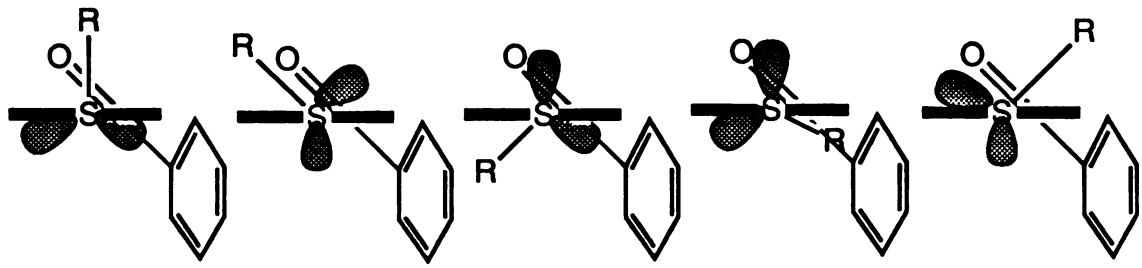
That the ring substituents on benzophenone and alkyl phenyl ketones strongly affect the n,π^* and π,π^* triplet excited states and excitation energies has been reported by several groups.[67] Generally, a strong electron withdrawing group such as CF_3 stabilizes the n,π^* excited state[68] and an electron donating group stabilizes the π,π^* state[67d]. Both benzophenone and acetophenone have n,π^* lowest excited states. Methylacetophenone and methoxyacetophenone have lowest π,π^* triplet excited states, but methylbenzophenone and methoxybenzophenone retain n,π^* lowest excited triplet states. This is because the energy gap between lowest n,π^* and π,π^* triplets is larger for benzophenone than for acetophenone and the electron donating groups -- methyl and methoxy -- are not strong enough to bring the energy of the triplet π,π^* excited state lower than that of the n,π^* excited state.[69] The thiomethoxy group can stabilize the π,π^* triplet much more than a methoxy group.[67d] In our system, the molecules with a sulfur atom attached to the aromatic rings of both acetophenone and benzophenone have π,π^* lowest triplet excited states, because the sulfur atom is a much better electron donor than an alkoxy group. The triplet energies of p-BzSBP, p-sec-BuSBP, p-n-BuSBP and o-BzSBP are in the range of 64.1 - 65.4 Kcal/mole and are about 3.0 - 4.4 kcal / mole lower than the energy of the n,π^* triplet excited state of benzophenone.

The only exception is p-t-BuSBP, which has an n,π^* lowest triplet excited state energy of 67.9 kcal / mole, only 0.6 kcal / mole below the n,π^* lowest triplet energy of benzophenone. Molecular mechanics calculations show that the most stable structure is structure 1 (p. 68) with the S-C bond plan perpendicular to the benzene ring. In this structure, the lone pair orbital of sulfur is only 30^o out of plane with respect to the benzene ring and cannot provide enough overlap for the sulfur atom to donate electron density and stabilize the π,π^* triplet.

To achieve the best overlap, there are four possible conformations, 2, 3, 4 and 5 (p. 68), with one of lone pair orbitals perpendicular to the benzene ring. The calculated energies for each conformations are different depending on what R is. With the large t-butyl, the energy needed to achieve conformation 2,3, 4 and 5 is about 5.9 kcal / mole and the energy barrier for the bond rotation is 8.10 kcal / mole. This keeps p-t-BuSBP in conformation 1. The corresponding energy parameters are: 3.1 kcal / mole and an energy barrier of 4.49 Kcal/ mole for p-sec-BuSBP, 2.4 and 3.79 kcal / mole for p-n-BuSBP, and 2.5 and 3.72 kcal / mole for p-BzSBP. Therefore, it is unlikely for p-t-BuSBP to donate as much electron density as the primary and secondary alkylthio compounds.

On the other hand, the substituents on the methyl group of methylbenzophenone or methylacetophenone have little effect on the triplet excited states. Methylbenzophenone and all of its derivatives retain an n,π^* lowest triplet excited states while methylacetophenone and all of its derivatives have π,π^* lowest triplet excited states.

Table 13. Relative Energies for Conformations of Alkyl Thiobenzophenone.[a]



1 2 3 4 5

R	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5
n-Butyl	0	2.44	2.39	2.33	2.42
sec-Butyl	0	3.02	3.14	3.00	3.11
t-Butyl	0	5.86	5.98	5.90	5.92
Benzyl	0	3.11	2.57	3.35	2.56

[a]kcal/mol

It has been reported that coupling of the S-C σ^* orbital and benzoyl π^* orbital has a strong stabilizing effect on the triplet excited state and weakens the C-S bond [43] for phenacyl alkyl sulfides and phenacyl phenyl sulfides. Electron transfer to the C-S bond can cause rapid β-cleavage.[70] A similar situation occurs in our system. With a C-S bond attached to the benzene ring of the phenyl ketones, the C-S σ^* orbital can couple to the benzoyl π^* orbital to stabilize both n,π^* and π,π^* triplet excited states. The mixing of the benzoyl π^* orbital with the C-S σ^* orbital also weakens the C-S bond and causes rapid bond cleavage.

Photochemically induced carbon-sulfur bond cleavage of both n,π* and π,π* triplet excited states has been reported.[42,43,71] But there is a lack of examples to compare the reactivities of the two excited states. In the present system, both π,π* and n,π* excited states undergo S-C bond cleavage. The kinetic results show that π,π* triplet excited states undergo C-S bond cleavage faster than the corresponding n,π* triplet excited states: m-PhSCH$_2$AP is about 17 times faster than m-PhSCH$_2$BP, m-ClCH$_2$VP is 100 times faster than m-ClCH$_2$BP and p-ClCH$_2$VP is at least 10 times faster than p-ClCH$_2$BP. It is hard to compare p-PhSCH$_2$AP with p-PhSCH$_2$BP since both reactions are too fast to be quenched. The reason for this is that π,π* triplet excited states have about 4 kcal / mole higher energies than n,π* triplet excited states and different spin distributions.

To break the S-C bond, bond dissociation energy must be less than the lowest triplet energy of ketosulfides. The sulfides we studied have the basic structures, ArS-CH$_2$Ar, ArS-n-Alkyl, ArS-sec-Alkyl, ArS-t-Alkyl, n-AlkylS-CH$_2$Ar, sec-AlkylS-CH$_2$Ar and t-AlkylS-CH$_2$Ar and BrCH$_2$Ar and ClCH$_2$Ar. Several bond dissociation energies for some similar compounds have been reported[72] by several groups. Table 14 lists some bond dissociation energies for some C-X bonds. The energy required for breaking a S-C bond to form radicals is 67.4 kcal / mole for C$_6$H$_5$S-CH$_3$, about 10 kcal / mole lower than AlkylS-CH$_3$. If the behavior of ArS-Alkyl is paralleled by AlkylS-Alkyl, the bond dissociation energy of ArS-Alkyl should be about 10 kcal / mole lower than AlkylS-Alkyl. Therefore, the bond dissociation energy for ArS-t-Bu would be about 56 Kcal / mole, ArS--sec-Alkyl ~ 60 Kcal / mole, and for ArS-n-Alkyl ~ 65 kcal / mole which is little below the lowest triplet excited state. These data can explain why there is no reaction for the o-MeSBP, o-n-octyl-SAP, and p-n-BuSBP and why the reactivity of p-t-BuSBP is 400 times higher than that of p-sec-BuSBP. It is no surprise to

see the high reactivities of ArS-CH2Ph and Br-CH2Ar since their bond dissociation energies are much lower than that of ArS-Alkyl. One exception is the compound p-$PhSO_2CH_2BP$. Although the bond dissociation energy is very low (lower than that of p-$PhSCH_2BP$), the rate constant for this compound is small.

Table 14 Bond dissociation energies.

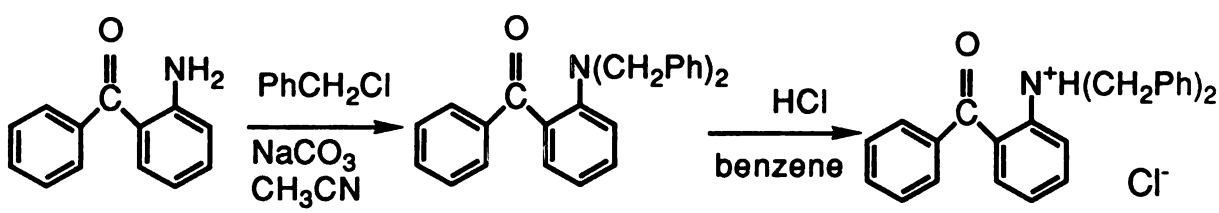
RS-C	Bond dissociation energy, kcal/mole
$PhS-CH_3$	67.4
C_2H_5S--t-Bu	66
$C_2H_5S-CH_2Ph$	53
$CH_3SO_2-CH_2Ph$	48
C_2H_5S-Ph	77
Alkyl$S-CH_3$	77
C_2H_5S-n-Bu	75
C_2H_5S-i-Pr	70
$Cl-CH_2Ph$	68
$Br-CH_2Ph$	51

PART II PHOTOCYCLIZATION OF ORTHO-BENZOYL N-ALKYLANILINIUM IONS

Results

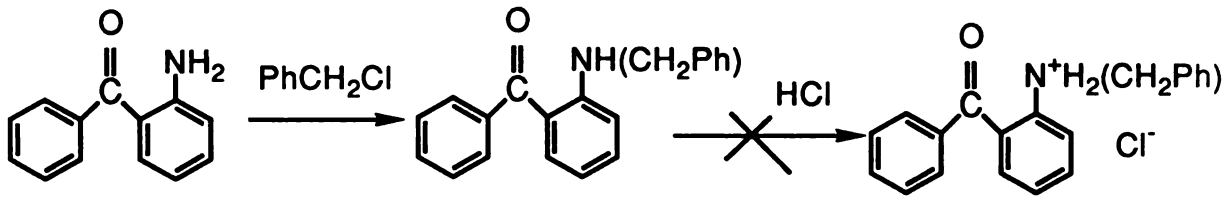
A. Preparation and Identification

o-Benzoyl-N,N-dibenzylaniline hydrochloride (Bz_2NBP:HCl) was prepared by Sn2 reaction of o-aminobenzophenone and excess benzyl chloride followed by bubbling dry HCl gas into the benzene solution of o-benzoyl-N,N-dibenzylaniline.

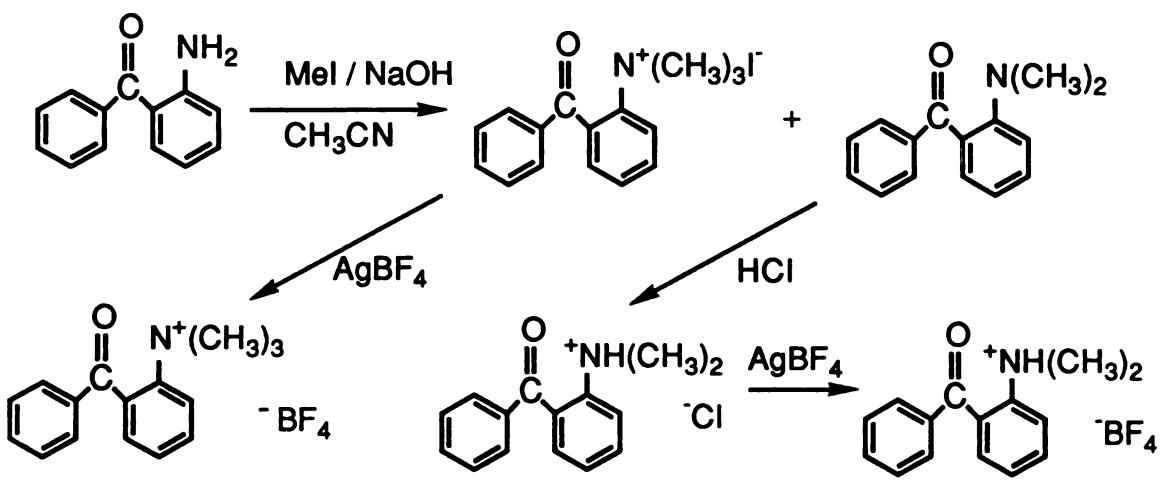


o-Benzoyl-N-benzylaniline was prepared by Sn2 reaction of o-aminobenzophenone and one equivalent benzyl chloride. The attempt to separate its hydrochloride salt failed. By bubbling HCl through a benzene solution of o-(N-benzylamino)benzophenone, a liquid layer separarated at the bottom of the solution. NMR spectra of the liquid in CD_3CN showed that the NH

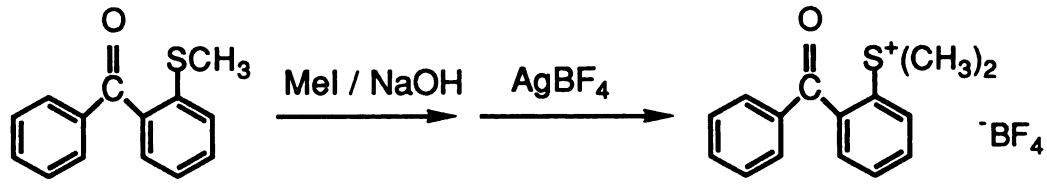
peak shifted down field which indicated a protonated o-(N-benzylamino)benzophenone. The effort to separate the protonated compound by removing solvent under reduced pressure failed and only o-(N-benzylamino)benzophenone was recovered.



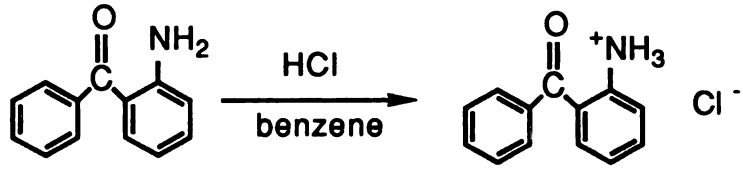
o-Benzoyltrimethylanilinium tetrafluoroborate ($Me_3NBP:BF_4$) and o-benzoyl-N,N-dimethylaniline hydrochloride and hydrotetrafluoroborate were prepared by methylation of o-aminobenzophenone with iodomethane followed by ion exchange.



S,S-Dimethyl-o-Benzoylphenylsulfonium tetrafloroborate was prepared by methylation of o-(methylthio)benzophenone with iodomethane followed by ion exchange:



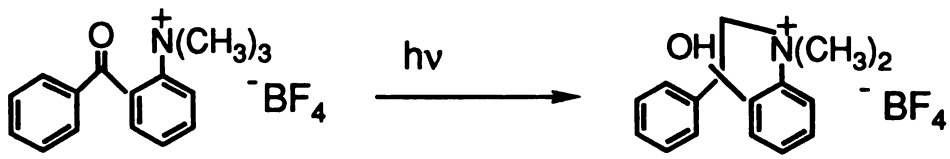
o-Benzoylanilinium chloride was prepared by bubbling HCl through a benzene solution of o-aminobenzophenone:



B. Photocyclization and Identification of Photoproducts

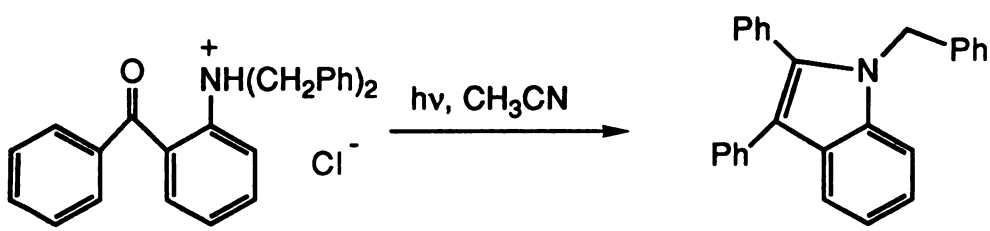
1. Photoproduct from o-Benzoyltrimethylanilinium Tetrafluoroborate ($Me_3NBP:BF_4$) Irradiation of a degassed acetonitrile solution of $Me_3NBP:BF_4$ at 313 nm afforded one product. After 100% conversion (monitored by NMR), the solvent was evaporated at room temperature under reduced pressure. The product was recrystallized from MeOH and identified as 1,1-dimethyl-3-hydroxy-3-phenyldihydroindolium tetrafluoroborate by NMR, IR and mass spectrometry.

Irradiation of o-benzoyltrimethylanilinium tetrafluoroborate in the solid state for 24 hours also gave the same product in 100 % conversion:



2. Photoproducts from o-Benzoyl-N,N-dibenzylaniline Hydrochloride

Irradiation of degassed an acetonitrile solution of o-benzoyl-N,N-dibenzylaniline hydrochloride at 313 nm produced two products. After 100 % conversion, the solvent was evaporated at room temperature under reduced pressure. N-benzyl,2,3-diphenylindole and an unknown product were separated by silica gel column chromatography. The product structure was confirmed by X-ray crystallography, NMR, IR and Mass spectra. The indole was totally converted to the unknown product after 24 hours irradiation at the same condition:



3. Irradiations of Some Other Anilinium Ions Irradiations of degassed CD_3CN solutions of o-benzoyl-N,N-dimethylaniline hydrochloride or hydrotetrafluoroborate, o-dimethylthiobenzophenone tetrafluoroborate and o-aminobenzophenone hydrochloride for more than 48 hours gave no significant change as monitored by NMR.

4. Irradiation of o-benzoyl-N-benzylaniline Irradiation of a degassed solution of o-benzoyl-N-benzylaniline and trifluoromethanesulfonic acid in CD_3CN for more than 48 hours gave no significant reaction as monitored by NMR.

C. Kinetic Results

1. Quantum Yields: Quantum yields for photoproduct formation and starting ketone disappearance were measured. Ketone solutions 0.01-0.02 M in acetonitrile were irradiated at 366 nm or 313 nm in parallel with degassed benzene solutions of 0.1 M valerophenone as actinometer. All samples were degassed by three freeze-thaw cycles prior to irradiation. For o-benzoyl-N,N-dibenzylaniline hydrochloride, the percent conversion of ketone was controlled below 10%. Concentrations of ketone and product were measured by HPLC with reverse phase column. For o-benzoyltrimethylanilinium tetrafluoroborate, the quantum yield for starting ketone disappearance was measured both by UV spectroscopy at 340 nm or IR Spectroscopy at 1674.5-1664.5 cm^{-1}. The following equations were used to calculate the quantum yields. The symbols in the equations 1 and 2 are the same as in part I. The quantum yields are listed in tables 16 and 17. The IR measurements are considered more accurate, since

we detected a minor byproduct which had strong UV absorption in the spectra region to be measured.

$$\Phi_C = [C] / \{ Io \times (1-10^{-Ac}) \} \quad (1)$$

$$Io = [AP] / \{0.33 * (1-10^{-Avp})\} \quad (2)$$

2. Triplet Lifetime: Stern-Volmer quenching analysis was performed at 366 nm by irradiation of ketone solutions containing varying amounts of quenchers. Ethyl sorbate, sodium sorbate and 1-naphthylamine hydrochloride were used for quenching the photoreaction of o-benzoyl-N,N-dibenzylaniline hydrochloride in dry acetonitrile and aqueous acetonitrile. Conversions were controlled under 10% for the zero quencher sample and the highest value of $\Phi o / \Phi$ was about 5. Ethyl sorbate and 2,4-dimethyl-2,4-hexadiene were used for quenching the reaction of o-benzoyltrimethylanilinium tetrafluoroborate. The conversion of the starting ketone was 18 % for ethyl sorbate quencher, as measured by UV spectra and is 34 % for 2,4-dimethylhexadiene as measured by IR spectra. Since the UV absorbance of the photolysis solution increased slowly in dark after irradiation, indicating some thermal reaction is taking place, we consider the IR method for analysis to be more accurate.

D. Spectroscopy

The x-ray structure of 1-benzyl,2,3-diphenylindole is given in Figure 18 (p. 84). The sample was recrystallized from methanol. Detailed crystallographic parameters are given in the Appendix at the end of the thesis.

Table 15. Ultraviolet[a] and Phosphoresence[b] Spectra of the Derivatives of o-Benzoylaniline.

Ketone	$\lambda_{0,0}$ nm	E_T kcal/mole	π,π^* $\lambda max_{(\varepsilon)}$	n,π^* $\lambda max_{(\varepsilon)}$
o-Me3NBP:BF4	401.2	71.3	256(17100)	333(95)
o-Bz_2NBP	446.0	64.1	256(21100)	353(1090)
o-Bz_2NBP:HCl	452.0	63.3	249(18300)	359(730)
BP	413.8	69.1		

[a]in acetonitrile. [b]in MeOH/EtOH.

Table 16. Quantum Yields and $k_q\tau$ Values for Disappearance of o-Benzoyltrimethylanilinium Tetrafluoroborate upon Irradiation in Acetonitrile solution.

Method	Φ-k	$k_q\tau$, M^{-1}
UV	0.56	86
IR	0.34	146

The UV absorption spectra were recorded for the starting ketones in MeOH/EtOH(100:10). The wavelengths of the absorption maxima and their corresponding extinction coefficients are reported in table 15.

Phosphorescence spectra were taken for all the ketones at 77K in MeOH/EtOH(100:10) with ketone concentrations of about 10^{-4} M. The triplet energies of these ketones were calculated from the highest energy (0,0) band and are given in Table 15.

Table 17. Quantum Yields and $k_q\tau$ Values for N-benzyl,2,3-diphenylindole upon Irradiation of o-Benzoyl-N,N-dibenzylaniline Hydrochloride in Acetonitrile Solution.

H_2O(%) in CH_3CN	Φ_k	Φ_p	$k_q\tau^a$	$k_q\tau^b$
0	0.0145	0.0067	2.4	
2	0.0112	0.0033		
4	0.0046	0.0029		347
6	0.00099	0.0017		
8	0.00099	0.00090	7.0	220
10	——	0.00059		

[a] Ethyl Sorbate as quencher. [b] Sodium Sorbate as quencher.

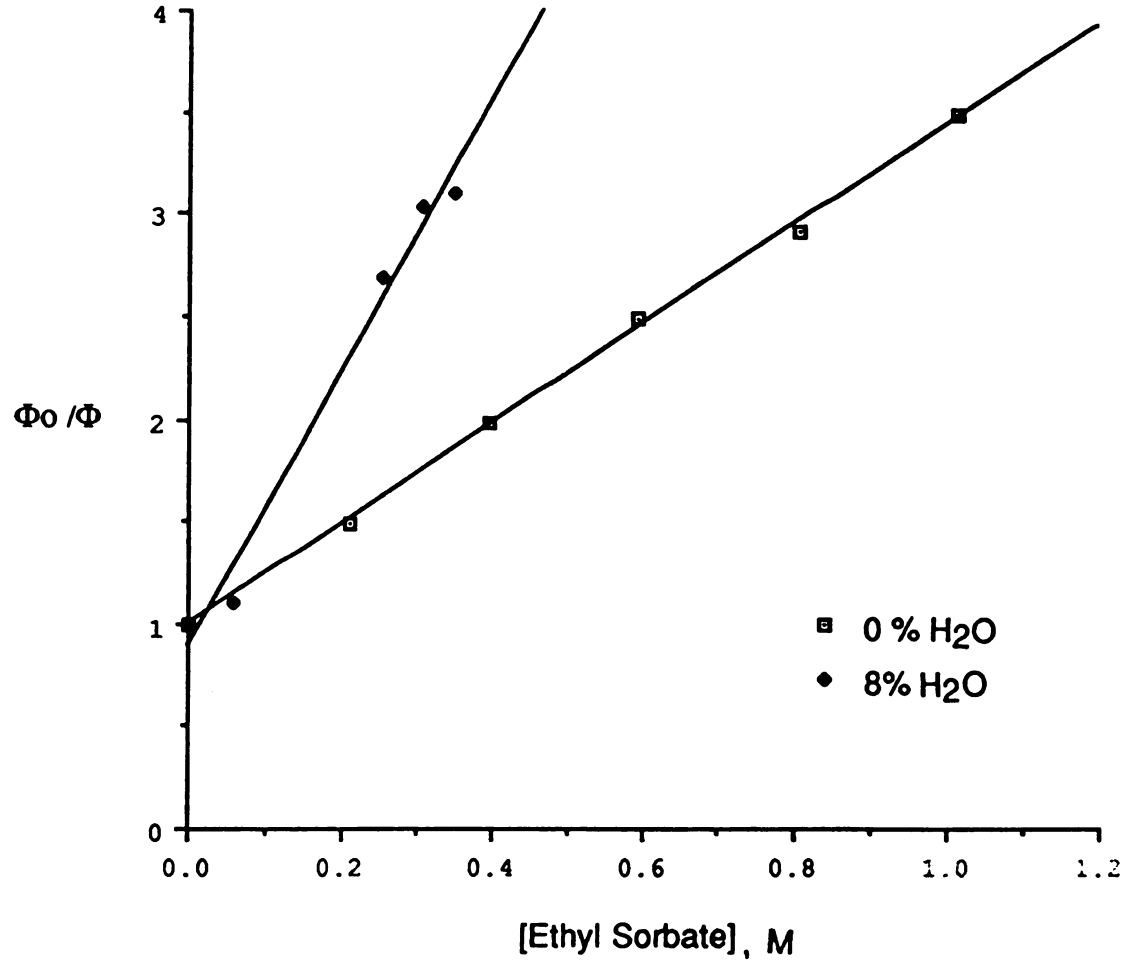


Figure 13. Stern-Volmer Plot of o-Benzoyl-N,N-dibenzylaniline Hydrochloride by Quenching Formation of N-benzyl,2,3-diphenylindole with Ethyl Sorbate in 0 % and 8% Aqueous Acetonitrile Solution.

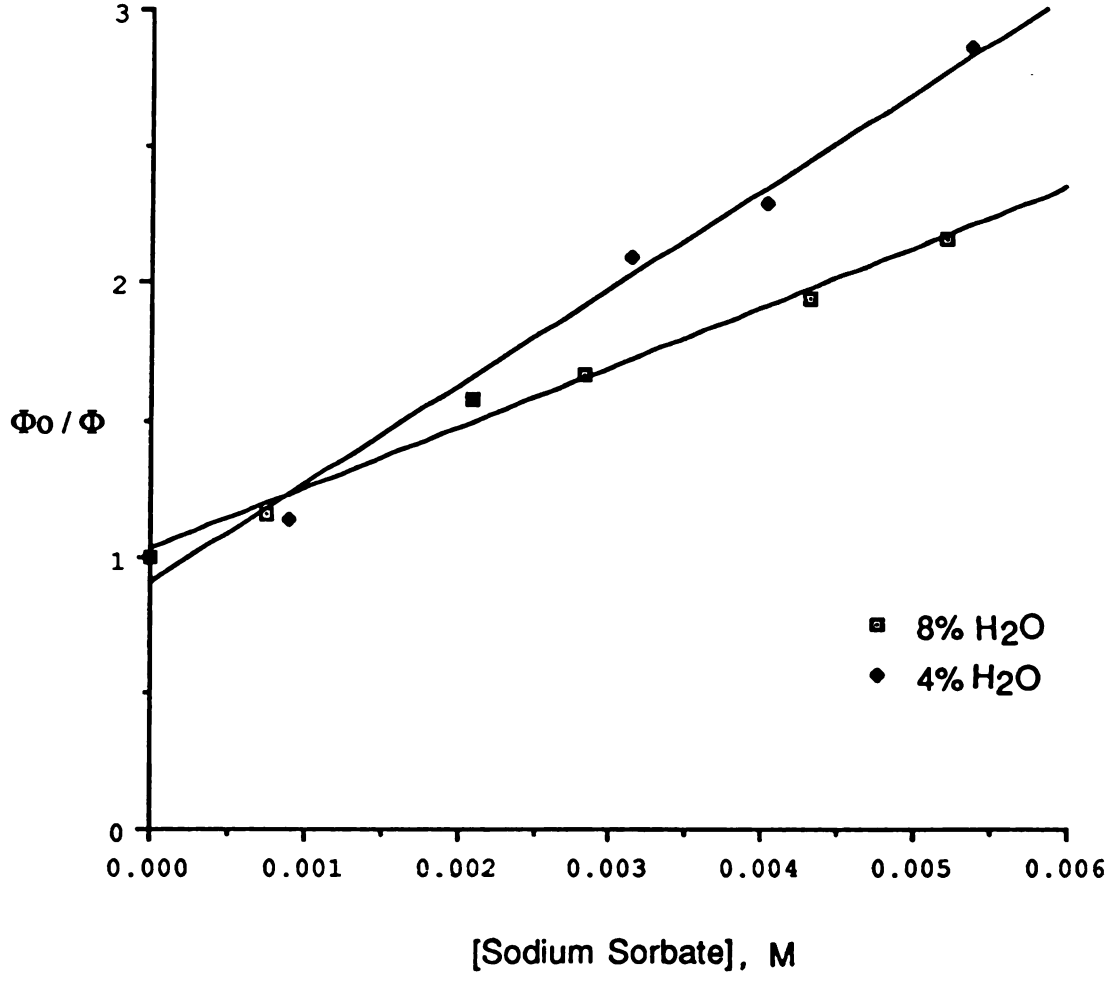


Figure 14. Stern-Volmer Plot o-Benzoyl-N,N-dibenzylaniline Hydrochloride by Quenching Formation of N-benzyl,2,3-diphenylindole with Sodium Sorbate in 4 % and 8% Aqueous Acetonitrile Solution.

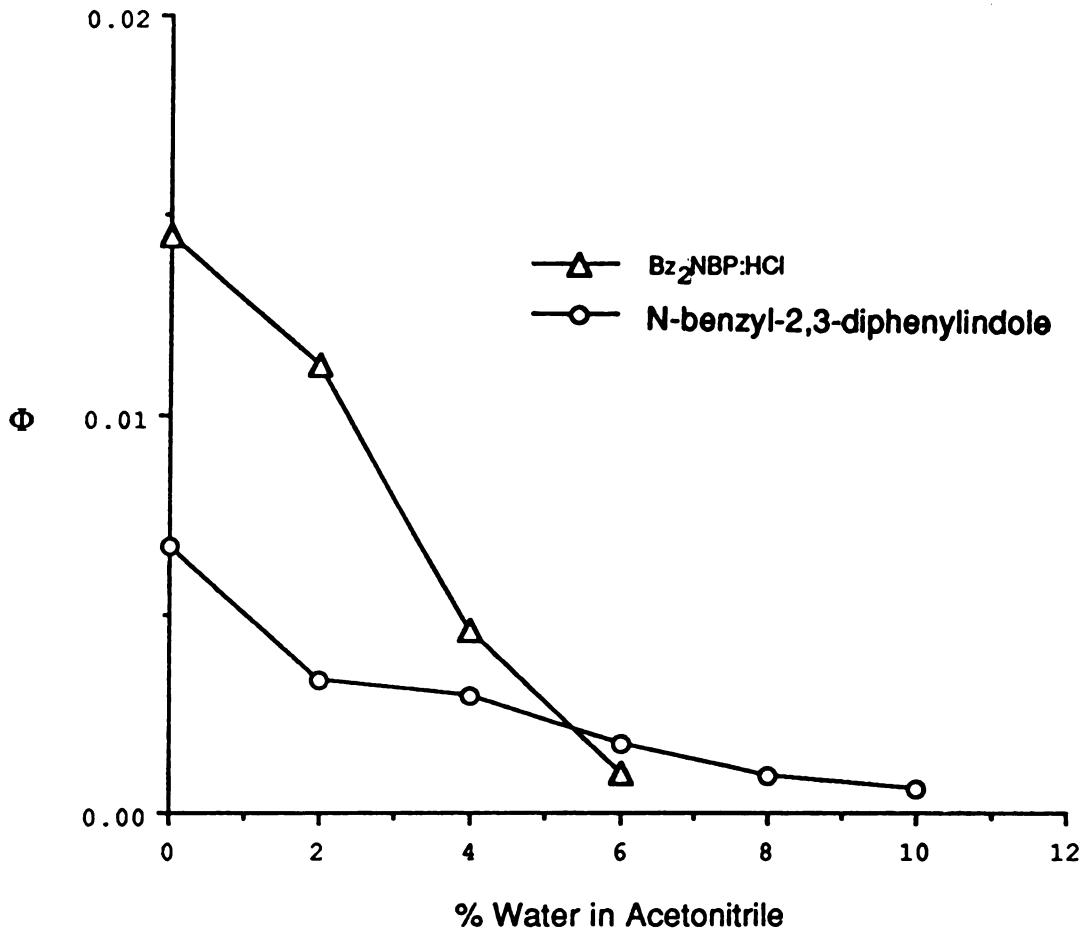


Figure 15. Effect of Water in Acetonitrile Solution on Quantum Yields of o-Benzoyl-N,N-dibenzylaniline Hydrochloride Disappearance and of N-Benzyl-2,3-diphenylindole formation.

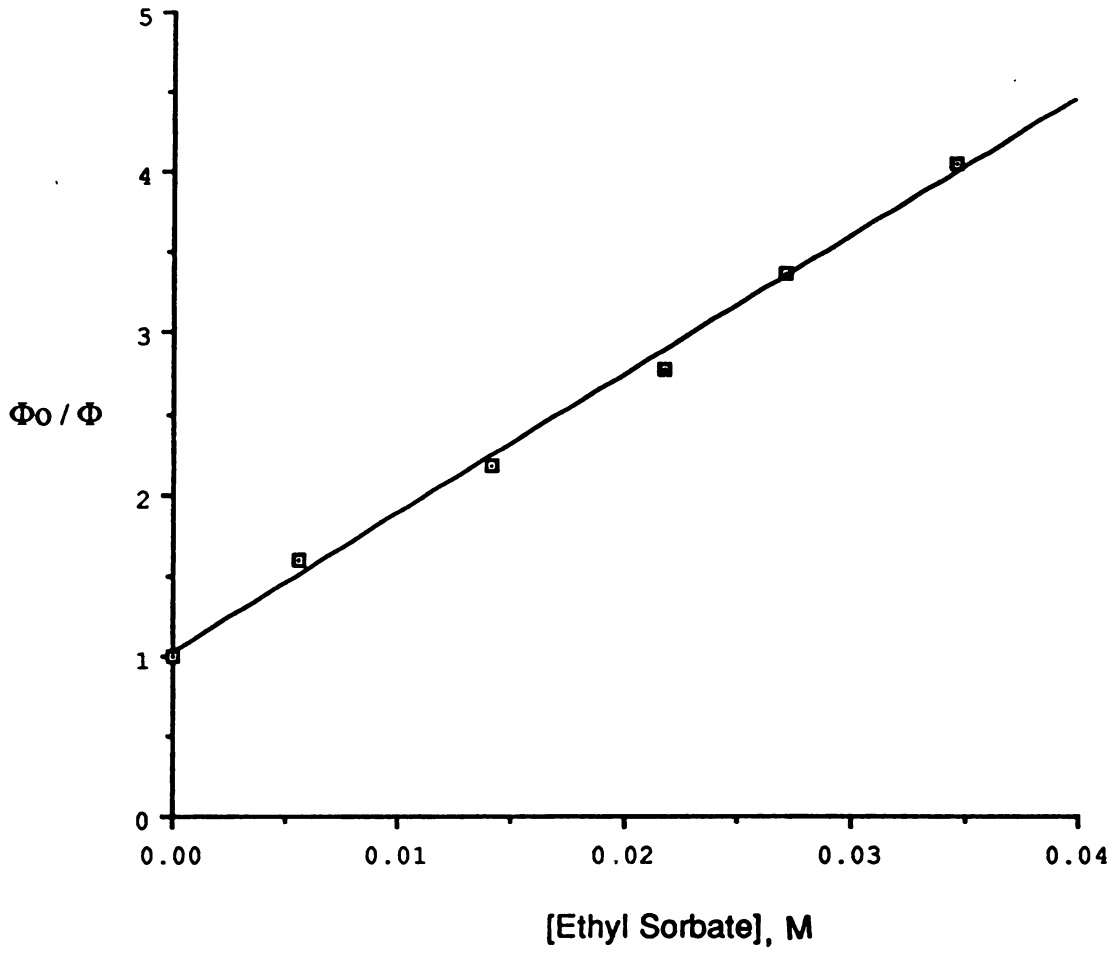


Figure 16. Stern-Volmer Plot of o-Benzoyltrimethylanilinium Tetrafluroborate by Quenching Disappearance of o-Benzoyltrimethylanilinium Tetrafluroborate in Acetonitrile with Ethyl Sorbate Monitored by UV at 340 nm.

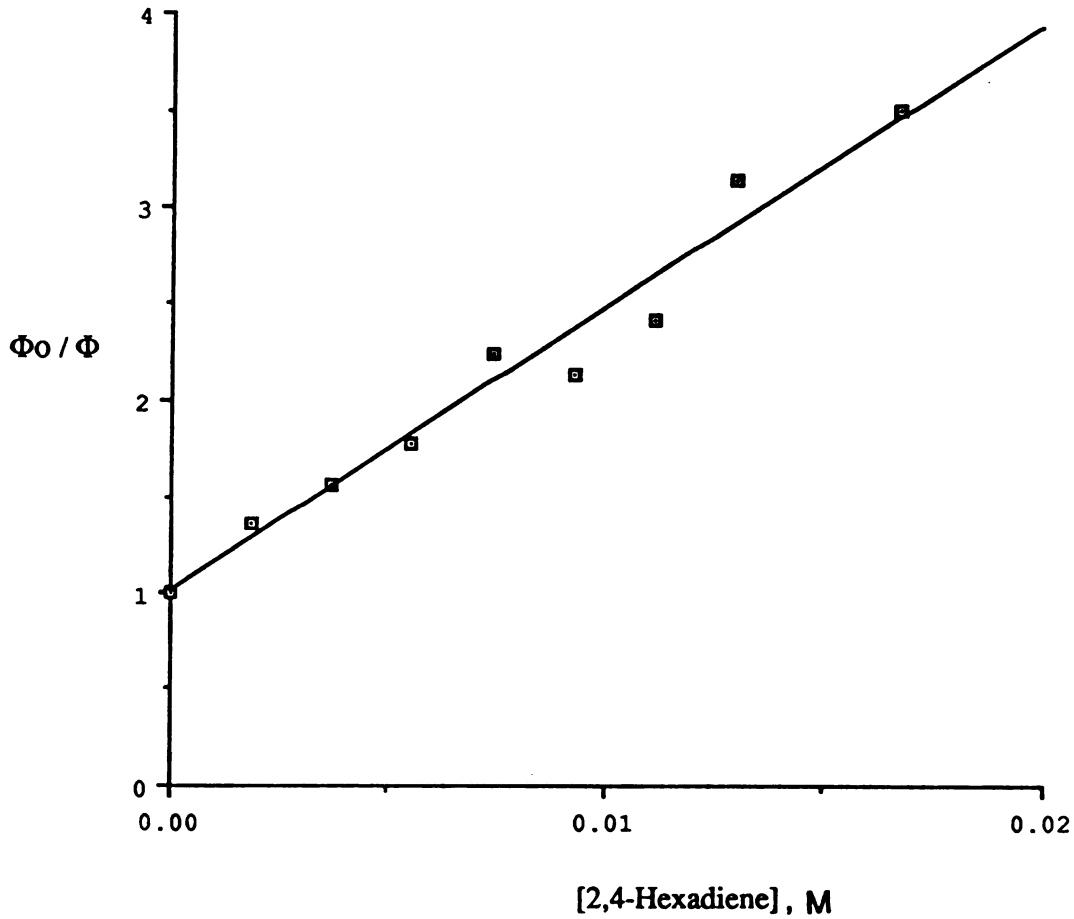


Figure 17. Stern-Volmer Plot of o-benzoyltrimethylanilinium Tetrafluroborate by Quenching Disappearance of o-Benzoyltrimethylanilinium Tetrafluroboratewith 2,4-hexadiene in Acetonitrile Monitored by IR at 1674.5-1664.5 cm^{-1}.

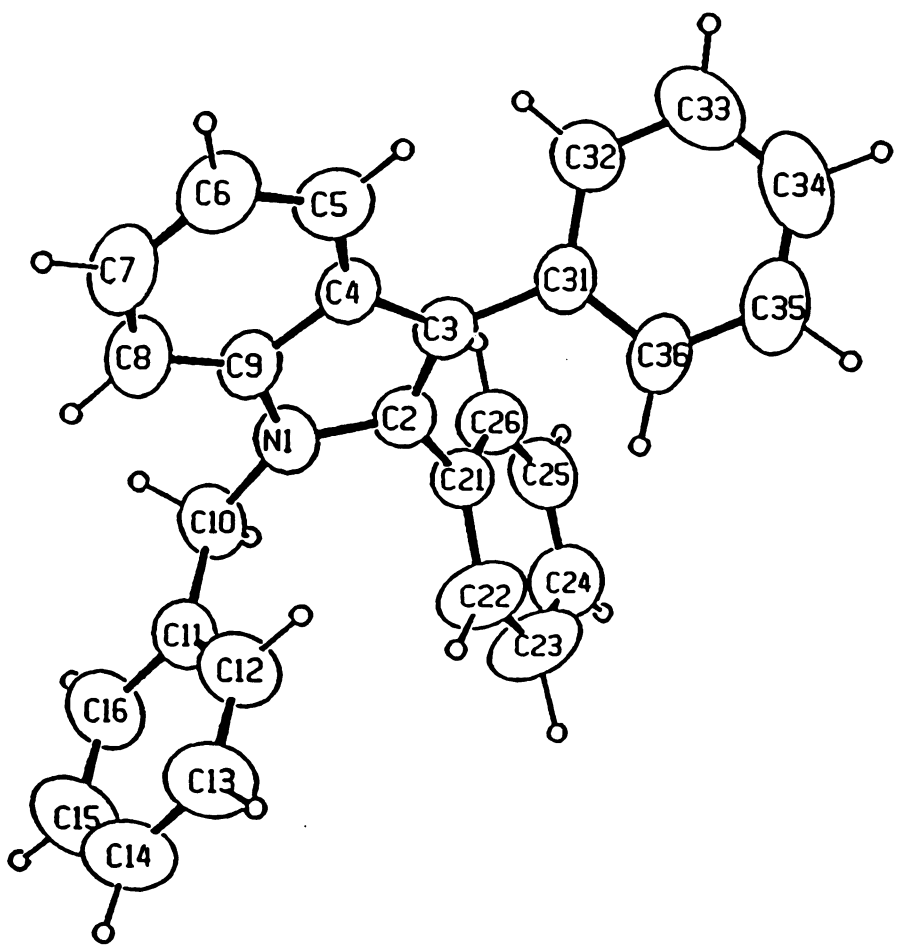


Figure 18. X-ray Structure of N-benzyl,2,3-diphenylindole

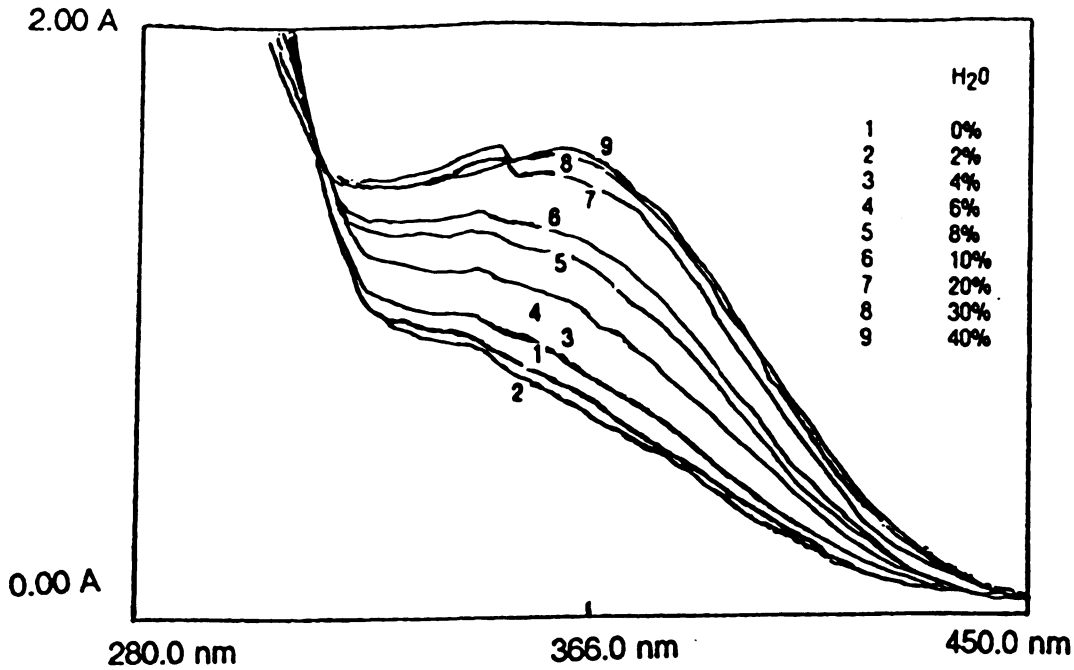


Figure 19. UV Spectra of 0.00203 M o-Benzoyl-N,N-dibenzylaniline Hydrochloride in Acetonitrile

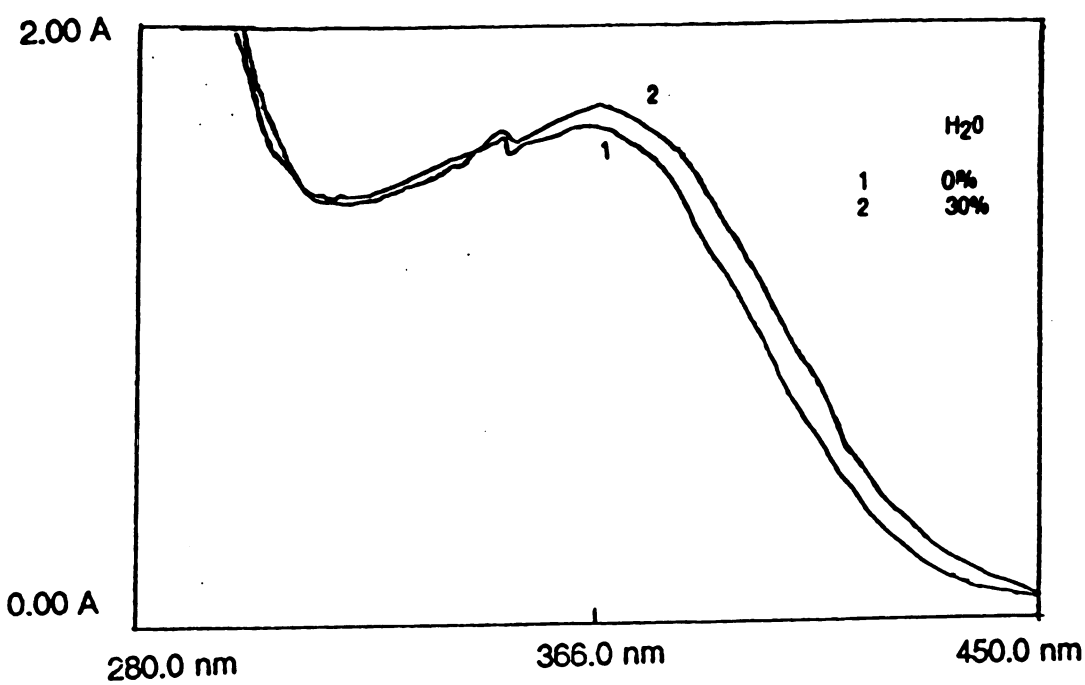
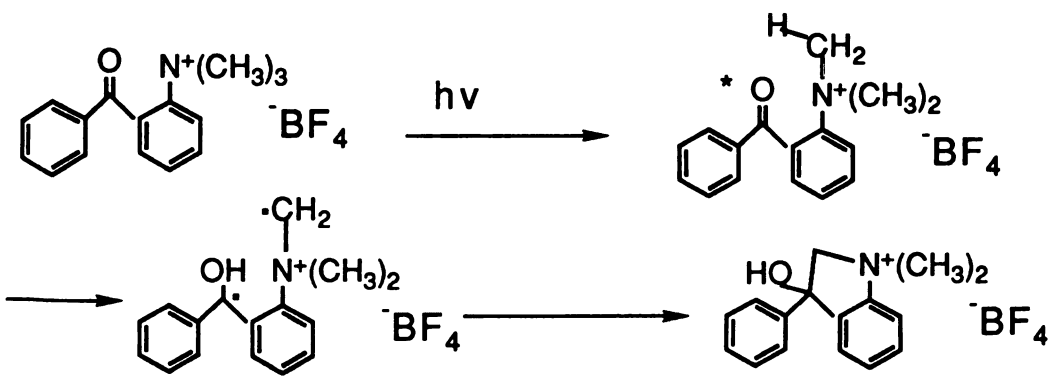


Figure 20 UV Spectra of 0.0017 M o-Benzoyl-N,N-dibenzylaniline in Acetonitrile

DISCUSSION

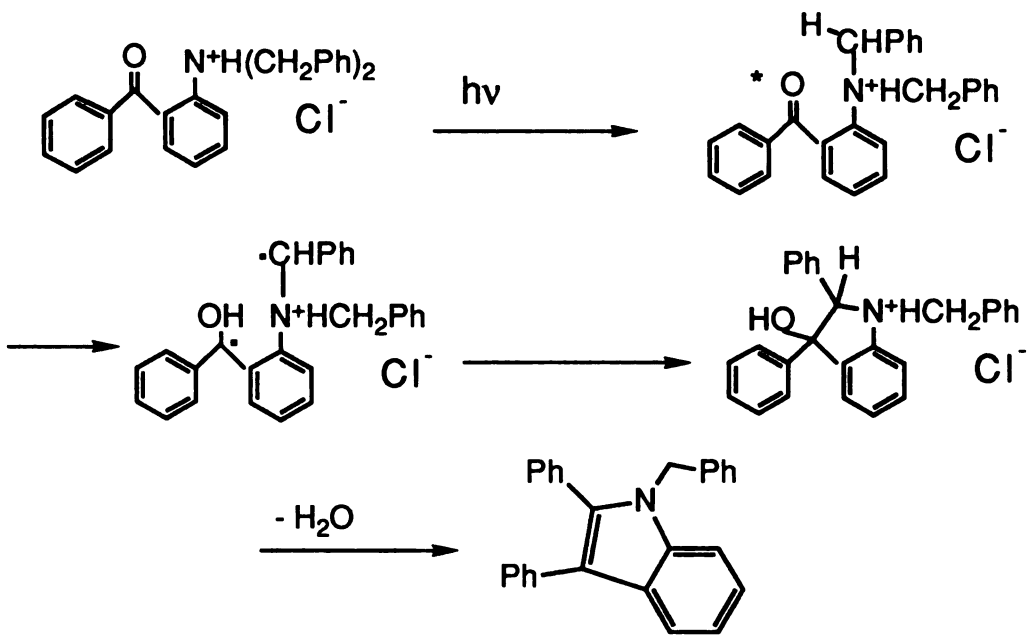
A. Biradical Process

Irradiation (hv> 313 nm) of o-benzoyltrimethylanilinium tetrafluoroborate in both solution and solid state yielded 1,1-dimethyl-3-hydroxy-3-phenyl-2,3-dihydroindolium tetrafluoroborate. The photochemistry of ketones with active δ-C-H bond has been studied systematically and the mechanism of the reaction is well established.[13,19b,23,73] The reaction proceeds via δ-hydrogen abstraction to generate a 1,5-biradical followed by cyclization to give products. The suggested photoreaction pathway of o-benzoyltrimethylanilinium tetrafluoroborate is shown in scheme 3.



Scheme 3. Hydrogen Abstraction Pathway for o-Benzoyltrimethylanilinium tetrafluoroborate.

Photolysis of o-benzoyl-N,N-dibenzylaniline hydrochloride afforded N-benzyl-2,3-diphenylindole. The cyclization products from o-benzoyl-N,N-dibenzylaniline hydrochloride suggested the same biradical process. The reaction pathways are summarized briefly in Scheme 4. Since the solution is acidic, the initial cyclization product N-benzyol-2,3-diphenyl-2,3-dihydroindole hydrochloride eliminates a water molecule to give the final product.



Scheme 4. Hydrogen Abstraction Pathway for o-Benzoyl-N,N-dibenzylaniline Hydrochloride.

B. Lifetimes of Triplet Excited State

Since the ammonium salts used for this study are not very soluble in benzene, we chose acetonitrile as solvent in which benzoyl anilinium salts dissolve easily.

To determine the lifetime of triplet excited state by Stern-Volmer quenching experiment, it is extremely important to obtain accurate values of rate constants of quenching (k_q). It is widely accepted that exothermic quenching process is a diffusion controlled reaction.[74] Several work[76-78] has been done to determine the k_q value of energy transfer quenching in a number of solvents. Hammond[75] used eq. 5 to estimate the lifetime of triplet excited state from $k_q\tau$ values by assuming k_q as given by equation 5:

$$k_{dif} = 8RT/\alpha\eta \qquad (5)$$

where η is viscosity of the solvent and α is a constant obtained from the Debye equation. A widely accepted rate constant for triplet quenching in benzene at 25°C is 6×10^9 M^{-1} s^{-1}.[57] Since acetonitrile is a less viscous solvent than benzene, it is expected that the k_q value for energy transfer quenching in acetonitrile is larger than that in benzene. A k_q value in acetonitrile of 1.0×10^{10} $M^{-1}s^{-1}$ is reported and widely accepted.[76,77] Saltiel[78] undertook a extensive study of energy transfer quenching of indeno[2,1-a]indene with azulene as a function of temperature in n-pentane, toluene, acetonitrile and t-butyl alcohol. He found that the k_q values in acetonitrile fall in the same range.

Therefore, triplet lifetimes in acetonitrile were calculated from the slopes of Stern-Volmer quenching plots ($k_q\tau$) assuming that $k_q = 1.0 \times 10^{10}$ $M^{-1}s^{-1}$ for

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both o-benzoyltrimethylanilinium tetrafluroborate and o-benzoyl-N,N-dibenzylaniline hydrochloride. The results are listed in the Table 18.

Table 18. Kinetic data for o-benzoyltrimethylanilinium tetrafluoroborate and o-benzoyl-N,N-dibenzylaniline Hydrochloride.

Compound	Φ_{-k}	Φ_p	$k_q\tau$	τ (ns)
$Me_3NBP:BF_4$	0.34		146	15
$Bz_2NBP:HCl$	0.020	0.010	2.44	0.24

C. δ-Hydrogen Abstraction Rate Constants

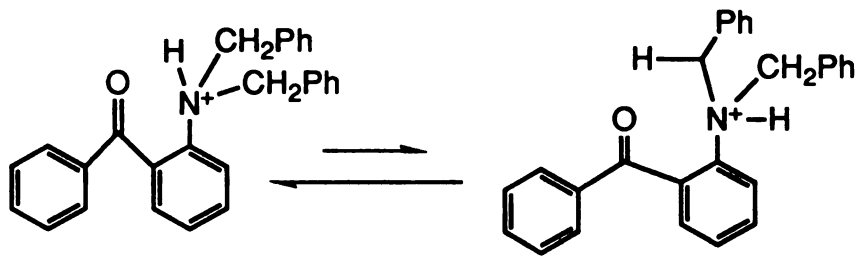
The reciprocal of the triplet lifetime, τ^{-1}, is the sum of rate constants for all the activities that take place from the triplet excited state. Since the rate of intersystem crossing is very fast,[5] only the triplet excited states needs to be considered for the phenyl ketones.

The rate constant (k_H) of δ-hydrogen abstraction for o-benzoyltrimethylanilinium tetrafluroborate is calculated to be 6.7×10^7 s^{-1}. Ortho-alkoxyphenyl ketones[22] and o-t-butylphenyl ketones[80] have been reported to undergo similar δ-hydrogen abstraction reaction. The photoreaction of $Me_3NBP:BF_4$ is 100 times faster than the photocyclization of o-methoxybenzophenone whose rate constant is 5×10^5 s^{-1}.[22] The result is expected by

the conformational factors, there is a high population of the conformation in which one of the methyl groups points to the carbonyl group for $Me_3NBP:BF_4$, whereas the methyl group in o-methoxybenzophenone points away from the carbonyl group. The positive charge on the nitrogen is expected to slow down the hydrogen abstraction.[79] The cyclization of $Me_3NBP:BF_4$ is about 40-fold slower than that of o-t-butylbenzophenone ($k = 10^9\ s^{-1}$).[80] The factor of 40 seems too small compared to the 1000 fold difference between protonated γ-dimethylamino-butyrophenone and valerophenone.[81] Wagner reported an increase of the triplet reactivity upon protonation of pyridyl ketones by one order of magnitude.[82] Therefore, the factor of 40 is a combination of positive charge effects: deactivating the adjoining C-H bond towards an electron-deficient reagent and enhancing the reactivity of the conjugated carbonyl.

On the other hand, the quantum yield for the cyclization of o-benzoyl-N,N-dibenzylaniline hydrochloride is very low(0.067 in dry acetonitrile and 0.033 with 2% water present). The low quantum yield is clearly caused by the equilibrium between o-benzoyl-N,N-dibenzylaniline hydrochloride and its conjugate base, which absorbs more light at 366nm as shown by the UV spectra in Figure 19 and 20. UV spectra indicate that in solution the anilinium cation is in equilibrium with its conjugate base. It is also possible that a rapid decay takes place by deprotonation because of the strong acidity of triplet anilinium ion. The presence of water increases the deprotonation and therefore decreases the quantum yield. The lifetime of 0.24 ns indicated a rate constant for hydrogen abstraction of $4.2 \times 10^7\ s^{-1}$. The rate constant is at the same magnitude as that of o-benzoyltrimethylanilinium tetrafluoroborate. Obviously the result is a combination of two opposite factors. One of the factors which affects the reaction activity is the conformational effect. The conformation with N-H bond pointing to the carbonyl group is the most stable conformation. The

conformation for δ-hydrogen abstraction requires an N-C bond rotation so that H and O is within bonding distance, a much less stable conformation. A well known example is o-methoxybenzophenone[22] with rate constant (5×10^5 s^{-1})1000 times smaller than the rate constant (10^9 s^{-1}) of o-t-butylbenzophenone[80]. Another factor is the C-H bond strength which favors abstraction of a hydrogen of the benzyl group over a hydrogen of the methyl group. The rate constant for the δ-hydrogen abstraction of o-benzyloxybenzophenone[22] is 2×10^7 s^{-1}.



Photolysis of o-benzoyl-N-benzylaniline in acetonitrile with strong acid such as triflic acid does not afford any photocyclization product. The result is the combination of bad conformation[22c] for δ-hydrogen abstraction, the positive charge on the nitrogen, rapid deprotonation and absorption of light by unprotonated free amine.

D. Nature of the triplet excited states

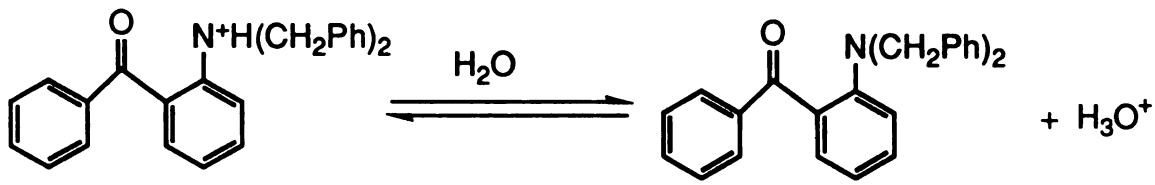
The difference between the reactivities of $Me_3NBP:BF_4$ and o-dimethylaminobenzophenone can be explained partially by the nature of the

excited states. Photolysis of o-dimethylaminobenzophenone afforded a mixture of several products with low quantum yield[25] and the hydrogen abstraction-cyclization product is only a minor part. While the lowest triplet excited state of o-dimethylaminobenzophenone is π,π^*, the lowest triplet excited state of o-benzoyltrimethylanilinium tetrafluoroborate is n,π^*. Very slow hydrogen abstraction of π,π^* triplet excited state has been reported[22,49]. For example, o-methoxyacetophenone does not undergo photocyclization and o-benzyloxyacetophenone does at the rate of only 2×10^6 s^{-1}. Charge-transfer quenching also plays an important role and produces the low quantum yield of o-dimethylaminobenzophenone. Nitrogen is a good intramolecular charge donor[27] and therefore quenches hydrogen abstraction in o-dimethylaminobenzophenone. On the other hand, the positive charge on the nitrogen of the o-benzoyltrimethylanilinium tetrafluroborate eliminates the electron donating ability of the nitrogen; the intramolecular charge-transfer quenching for o-benzoyltrimethylanilinium tetrafluroborate is therefore eliminated.

E. Effect of Water on Quantum Yield

With the presence of H_2O in the solution, the quantum yield drops dramatically from 0.0067 for dry acetonitrile solution to 0.00059 with 10% H_2O in acetonitrile solution. Further increasing of H_2O does not further decrease quantum yield. UV spectra in figure 19 and 20 indicate that the increase in absorption for o-benzoyl-N,N-dibenzylaniline occurs with increasing H_2O. The maximum absorption was obtained with 10% H_2O in acetonitrile. It is obvious

that there is an equilibrium between Bz_2NBP:HCl and o-benzoyl-N,N-dibenzylaniline.



The agreement between UV spectroscopy and quantum yields indicates that free amine in the reaction system causes the low quantum yield. o-Benzoyl-N,N-dibenzylaniline has a similar structure to o-N-dimethylaminobenzophenone. Therefore, it is expected that this free amine has a low reactivity to hydrogen abstraction reaction. The free amine existing in reaction solution absorbs light and causes the decrease of the quantum yield.

F. The Charge Effect on Quenching Experiment

The photoreaction of positively charged Bz_2NBP:HCl allowed us to design experiments to compare effects of differently charged or neutral quenchers on energy transfer. The reaction was studied in 8 : 92 H_2O-acetonitrile solution to allow solubility of all materials in a common medium. Ethyl sorbate gave a $k_q\tau$ value of 7.0 in this solution which is 2 times higher than that in dry acetonitrile solution. The difference may be caused by the presence of water and its effect on the diffusion of ethyl sorbate. The negatively charged quencher sodium sorbate quenched the triplet and gave a $k_q\tau$ value of

220. Assuming that the lifetime of the triplet is the same, the k_q value must be increased which may be caused by electrostatic attraction between the negative charge on quencher and the positive charge on substrate ketone. The positively charged 1-naphthylamine hydrochloride gave no quenching effect and this may be caused by electrostatic repulsion of the positive charges on the two species which prevent them from coming close to each other.

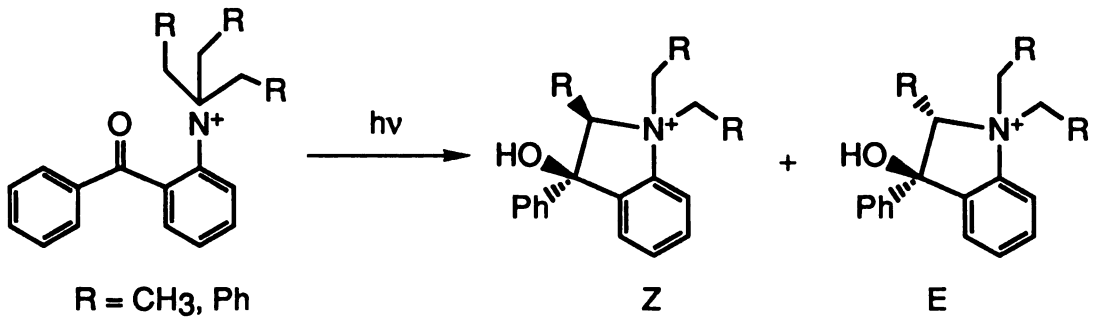
G. Suggestions for Further Investigation

1. Solvent effect on biradical Behavior: Solvent effects on biradical behaviors have already been reported.[67b,22c,83,84] The quantum yields, diastereoselectivities and lifetimes are strongly dependent on the solvent for the biradicals generated from δ-hydrogen abstraction of o-t-butylbenzophenone, o-alkoxyphenyl ketones and acyclic β-alkoxyketones.

It is of interest to investigate the solvent effect on the behavior of biradicals generated from o-benzoylanilinium ions.

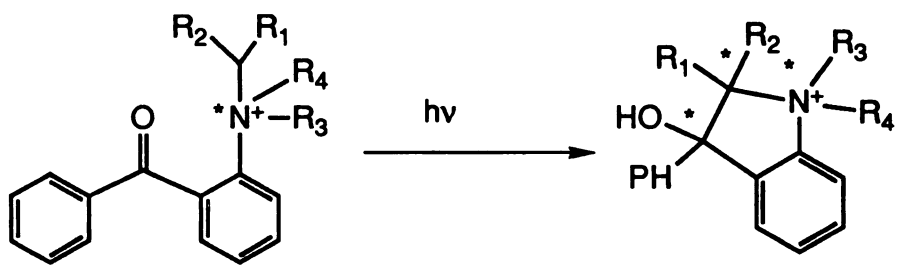
o-Benzoyltrimethylanilinium tetrafluoroborate can be used to explore the solvent effect on biradical lifetimes and quantum yields. t-Butanol or other alcohol solvents will be chosen to compare with results from acetonitrile. A Lewis base such as pyridine may affect quantum yields too.

o-Benzoyltriethylanilinium tetrafluoroborate or o-benzoyltribenzyl-anilinium tetrafluoroborate will be synthesized. These compounds may afford two diastereomers. Basic solvent and Lewis base can form hydrogen bonding to the hydroxy of 1,5-biradical and therefore induce diastereoselectivity in the cyclization. We expect that the cyclization will strongly favor the isomer with R group trans to the large phenyl group in a nonpolar solvent, while in the basic

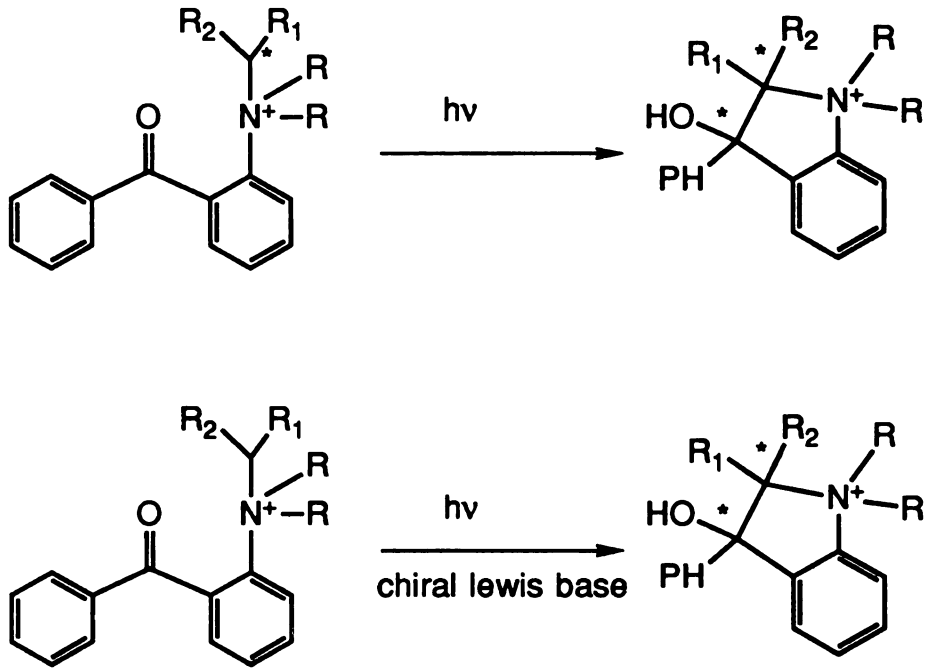


solvent, the stereoselectivity is expected to decrease due to hydrogen bonding.

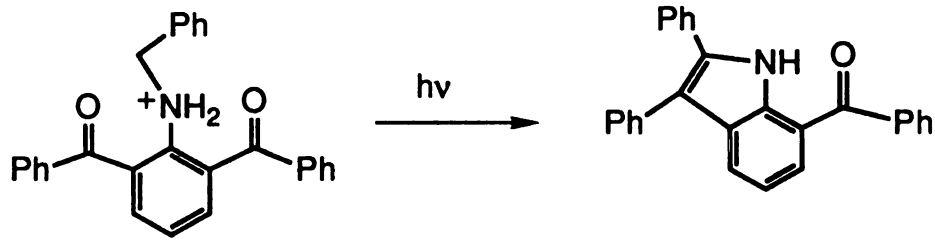
2. Synthetic Applications: The remarkably high chemical yield for 1,1-dimethyl-3-hydroxy-3-phenyl-2,3-dihydroindolium tetrafluoroborate generated from the photocyclization of o-benzoyltrimethylanilinium salt prompted us to investigate the potential application of the synthesis to indole compounds. o-Benzoyltrialkylanilinium ions will give two diastereomers with a ratio that favors the isomer with alkyl group trans to the large phenyl group. Solvent and Lewis base may change the stereoselectivity and therefore provide a pathway to selectively synthesize one of the diastereomers. Another interesting aspect is



asymmetric induction which can proceed by introducing a chiral center in the starting ketone or by using chiral Lewis bases. Three or two contiguous chiral centers may be generated from cyclization:

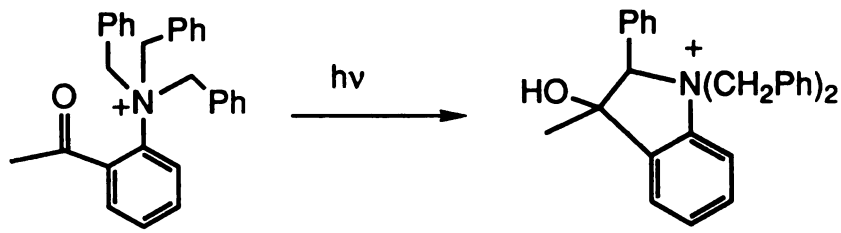


3. Kinetic study: More extensive investigations on the kinetics of photocyclization of o-benzoylanilinium derivatives are of future interest. We

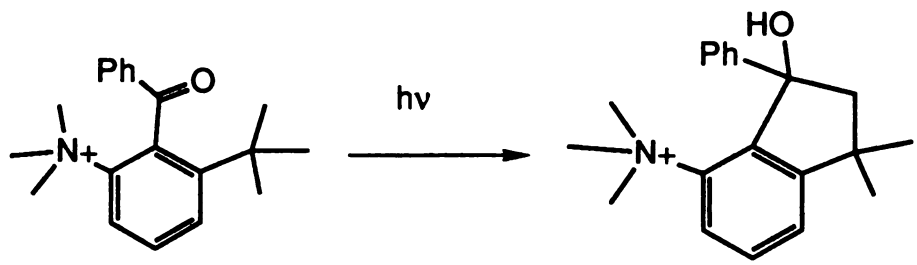


indicated that the o-benzoyl-monobenzylanilinium ion does not photocyclize mainly because of inappropriate conformation. 2,6-Dibenzoyl-N-benzylanilinium salts may solve this problem and cyclize to give indole compound.

Therefore, o-acyltribenzylanilinium salt may photocyclize since the lowest triplet excited state of o-acyltribenzylanilinium salt should be n,π^* state:



Several models may be used to compare the relative rate of the cyclization for different groups. The relative rate for the cyclization is t-Bu > Me_3N^+ > MeO and compounds 1 and 2 are expected to be major products. For benzyloxy and dibenzylamonium groups, the reactivities are comparable and a mixture of two isomers is expected:



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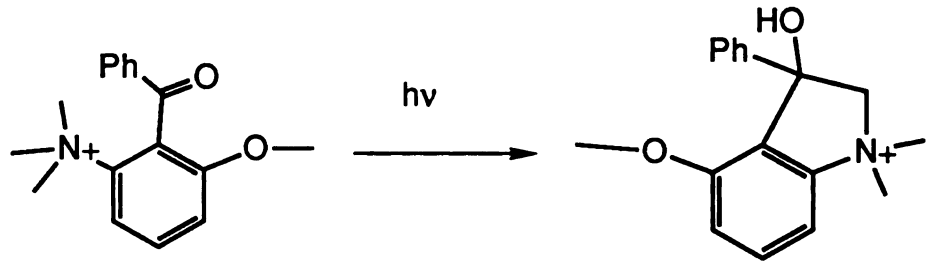

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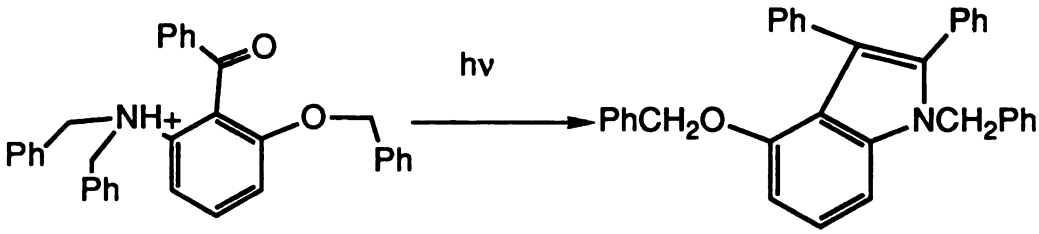
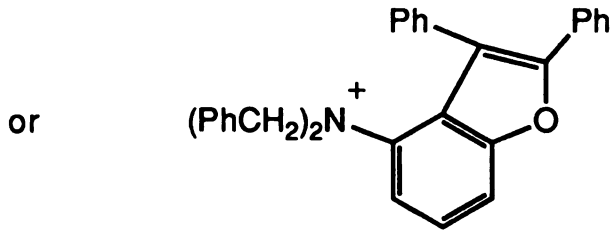
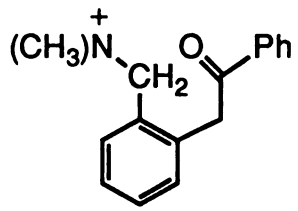




Several of the following compounds are very useful to investigate. We indicated that the positive charge on the nitrogen will deactivate the adjacent C-H bond and compound 1 may indicate to what extent the positive charge may slow down the reaction. Compound 2 may give a cyclization product 5 which is a very common structure in the natural products. Compounds 3 and 4 may also give cyclization products since the positive charge on the nitrogen may reduce

the π,π^* characters of the triplet excited state and make the δ-hydrogen abstraction possible:



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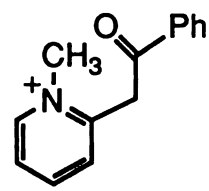

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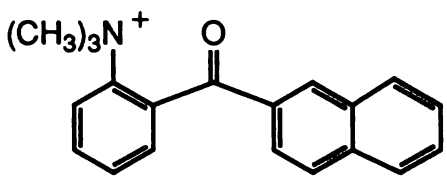

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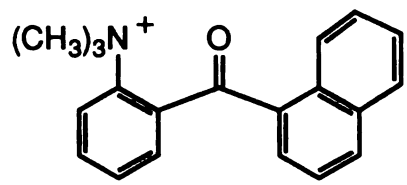

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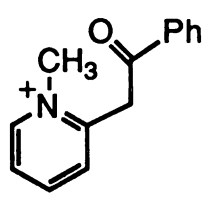

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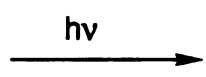

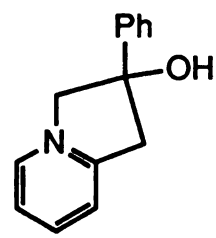

5

EXPERIMENTAL

A. Preparation and Purification of Materials

1. Solvents

Benzene: One gallon of reagent grade benzene was repeatedly stirred with 200 ml portions of concentrated sulfuric acid for 24 hour periods until the sulfuric acid remained white. The benzene and the sulfuric acid were separated and the benzene was washed with distilled water and then saturated aqueous sodium bicarbonate solution. The benzene was separated, dried over sodium sulfate and filtered into a 5 l round bottom flask. Phosphorus pentoxide was added and the solvent was refluxed overnight.The benzene was distilled through an one meter column packed with stainless steel helices. The first and last 10% were discarded.

Acetonitrile: One gallon of reagent grade acetonitrile was distilled from potassium permanganate. Sulfuric acid was added to the distillate and the distillate was decanted from the ammonium salts. It was then distilled through a column packed with glass helices. Only the middle 60% was collected.

Hexanes: Reagent grade hexanes was purified the same way as benzene.

2. Internal Standards

Hexadecane (C_{16}) (Aldrich) was purified by washing with sulfuric acid, then distilled by Dr. Peter J. Wagner.

Eicosane (C_{20}) (Aldrich) was purified by recrystallization from ethanol.

Cycloheptane (C_7) (Aldrich) was purified by washing with sulfuric acid, then distilled by Dr. Peter J. Wagner.

1-Phenyltridecane ($C_{13}Ph$) (Aldrich) was purified by washing with sulfuric acid, then distilled by Dr. Peter J. Wagner.

Hexacosane (C_{26}) (Aldrich) was purified by recrystallization from ethanol.

Tetracosane (C_{24}) (Aldrich) was purified by recrystallization from ethanol.

Docosane (C_{22}) (Aldrich) was purified by recrystallization from ethanol.

Methyl benzoate (MeBz) (Aldrich) in ether was washed with aqueous sodium bicarbonate solution and water, then dried over anhydrous sodium sulfate, finally distilled under reduced pressure.

Decyl benzoate ($C_{10}Bz$) was prepared by the reaction of benzoyl chloride with n-decyl alcohol. n-decyl alcohol (50 g) was added to benzoyl chloride (50 g) in 220 ml ether in a 500 ml round bottom flask. The solution was refluxed overnight with stirring. Then it was cooled, washed with water, extracted with ether, dried over anhydrous sodium sulfate, finally concentrated in vacuo. Distillation under reduced pressure; B.p. 135^{o} C / 0.7 mm; MS 262 (M+).

n-Octyl benzoate (C_8Bz) was prepared by the same procedure as decyl benzoate.

2,6-Dichlorobenzonitrile (Cl2CNPh) (Aldrich) was purified by recrystallization from ethanol.

3. Quenchers

Naphthalene: (Eastman) was recrystallized from Ethanol.

1-methylnaphthalene: was distilled under reduced pressure.

Ethyl sorbate: (aldrich) was used as received.

Sodium sorbate: Sorbic acid (Aldrich) was dissolved in ethanol. A solution of 1 equivalent NaOH in ethanol was added into the solution dropwise. The solvent was removed under reduced pressure. The residue was recrystallized from ethanol. mp > 250°C.

1-Naphthylethylamine hydrochloride 1-Naphthylethylamine (Aldrich, 2g) was dissolved in 40 ml EtOH in an 100 ml round bottom flask. HCl (37%, 1.15g) in 10 ml H_2O was added into the solution dropwise. The solvent was removed under reduced pressure. The residue was recrystallized from CH_3CN/H_2O. A white crystal (0.69g) was obtained. mp 255°C.

4. Ketones

o-(Methylthio)benzoic acid[45a] A mixture of thiosalicylic acid (Aldrich, 9g, 0.058 mole), NaOH (EM, 4.8g, 0.12 mole), dimethyl sulfate (MCB, 11.4g, 0.09 mole) and distilled H_2O (36 ml) in a 100 ml round bottom flask was refluxed for 6 hours. A solution of NaOH (EM, 9g, 0.23 mole) in 25 ml distilled H_2O was added to the reaction mixture. Separation of the solid formed with suction filtration afforded crude product (6g, 60%) which was recrystallized from toluene: mp160-167°C.

o-(Methylthio)benzoyl chloride[45b] A mixture of o-methylthiobenzoic acid (3g, 0.018 mole), thionyl chloride (MCB, 15 ml) and pyridine (Fisher, 4 drops) was refluxed in a 50 ml round bottom flask for 5 hours. The thionyl chloride was removed under reduced pressure. White needles (1.3g, 40%) were recrystallized from ether, 74-78°C.

o-(Methylthio)benzophenone (o-MeSBP)[45c] A mixture of o-methylthiolbenzoyl chloride (1.3g, 0.0069 mole), benzene (EM, 9.2 ml, 0.10 mole) and 1.5g $AlCl_3$ (EM, 1.5g, 0.011 mole) was stirred in a 25 ml round

bottom flask at room temperature for 16 hours. The reaction mixture was then washed with 10% NaOH solution followed by distilled water twice and then dried with $CaCl_2$. Removing the solvent in vacuum yielded a yellow oil which was distilled in vacuum (140°C/0.07mmHg).

NMR: (300 MHz, CDCl3) δ 2.41 (s, 3H), 7.21 (dt, J = 1.38 and J = 6.93 Hz, 1H), 7.35-7.50 (m, 5H), 7.56 (tt, J = 1.34 and J = 7.41 Hz, 1H), 7.77 (dd, J = 1.37 and J = 8.48 Hz,2H).

^{13}C NMR (75 MHz,$CDCl_3$): δ 16.35, 124.36, 127.12, 128.40, 129.76, 130.08, 131.05, 133.03, 137.48, 137.75, 139.14, 196.89.

IR: 1650 (C=O), 1590, 1580, 3030 cm^{-1}.

MS (EI) m/e 228(M+), 213(100), 195, 184, 151, 105, 91, 77.

<u>o-(Benzylthio)benzophenone (o-BzSBP)</u> A mixture of o-fluorobenzophenone (Aldrich, 6.5g, 0.032 mole), K_2CO_3 (Baker, 5g, 0.047 mole) and DMF (MCB, 60 ml) in a 250 ml round bottom flask cooled in an ice bath was stirred with magnetic bar overnight. Benzyl mercaptan (Aldrich, 6.5g, 0.052 mole) was then added dropwise into the solution. The reaction mixture was kept in an ice bath for 0.5 hour and then at room temperature for 12 hours. The reaction mixture was poured into cold water. The mixture was extracted with methylene dichloride (2 x100 ml). The organic layer was washed with saturated K_2CO_3/H_2O solution (2 x100 ml). After removing the solvent under the reduced pressure, the residue was recrystallized from ethanol to afford white crystals (2.46g, 25% yield): mp 68-69°C.

IR (CCl_4) ν 3090, 3065, 3030, 2927,2857,1672 (C=O), 1598, 1449, 1284, 928 cm^{-1}

MS (EI) m/e 304 (M^+), 213(100), 184, 91, 77

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.03 (s, 2H), 7.1-7.2 (m, 5H), 7.25 (td, J = 1.40 and 7.03 Hz, 2H), 7.3-7.5 (m, 5H), 7.56 (tt, J = 1.41 and 7.23 Hz, 1H), 7.73 (qd, J = 1.80 and 7.02 Hz, 2H)

^{13}C NMR (75 MHz,$CDCl_3$): δ 39.61, 125.94, 127.12, 128.35, 128.92, 130.02, 130.38, 131.15, 133.06, 135.39, 136.81, 137.31, 140.68, 197.44 (two missing tertiary aromatic carbon peaks may have been overlaped with other tertiary carbon peaks)

p-(Benzylthio)benzophenone (p-BzSBP) KOH (Baker, 1.7g, 0.030 mole), toluene (Aldrich, 10 ml) and benzyl mercaptan (Aldrich, 3.7g, 0.030 mole) were placed into a 250 ml round bottom flask, . The mixture was then stirred and heated to boil for 5 min. DMF (MCB, 50 ml) and p-chlorobenzophenone (Aldrich, 4.0g, 0.018 mole) were added into the flask. The reaction mixture was refluxed for 27 hours. The reaction mixture was poured into cold water and extracted with methane dichloride (2 x 100 ml). The organic layer was washed with distilled water (2 x 100 ml). After removing the solvent under the vacuum, the residue was recrystallized from methanol to afford white crystals (2.5g, 45%) : mp 80-84 ^{o}C.

IR (CH_2Cl_2): ν 3084, 3063, 3026, 2926,1660 (C=O), 1589, 1448, 1317, 1280, 1089, 937,922 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.22 (s, 2H), 7.2-7.4 (m, 7H), 7.45 (t, J = 7.54 Hz, 2H), 7.56 (t, J = 6.98 Hz, 1H), 7.70 (d, J = 8.10 Hz, 1H), 7.74 (d, J = 7.28 Hz, 1H)

MS (EI) m/e 304 (M+), 185, 91 (100), 77

^{13}C NMR (75 MHz, $CDCl_3$) δ 37.95, 127.45, 128.20, 128.96, 129.38, 129.45, 130.52, 131.30, 132.94, 135.08, 137.00, 138.39, 144.27, 196.43

o-(Benzylthio)acetophenone (o-BzSAP) Sodium hydroxide (Baker, 5g, 0.125 mole) and toluene (Aldrich, 40 ml) were placed in a 500 ml round bottom flask. Benzyl mercaptan (Aldrich, 9g, 0.073 mole) was added dropwise while stirring and DMF (MCB,100 ml) was then added. 2-Chloroactophenone (Aldrich, 10g,0.065 mole) was added. The solution was refluxed for 12 hours. The reaction mixture was poured into cold distilled water (200 ml). The mixture was extracted with methylene dichloride (2 x 100 ml). The organic layer was washed with distilled water (2 x 100 ml). After removed the solvent under the vacuum, the residue was recrystallized with chloroform. White crystals (12g, 76%) were obtained: mp141-144 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57 (s, 3H), 4.11 (s, 2H), 7.15-7.30 (m, 5H), 7.32-7.40 (m, 3H), 7.76 (dt, J = 7.54 and J = 1.11 Hz, 1H)

^{13}C NMR (75 MHz, CDCl3) δ 27.71, 37.08, 123.81, 126.40, 126.93, 128.22, 128.74, 130.36, 131.75, 135.22, 135.95, 140.41, 199.31

IR (CCl_4) ν 3089, 3068, 3031, 2925, 1678 (C=O), 1587, 1246, 1053 cm^{-1}

MS (EI) m/e 242 (M+), 151, 91

p-(Benzylthio)actophenone (p-BzSAP) KOH (Baker, 2.3g, 0.041 mole) and toluene (Aldrich, 10 ml) were placed in a 250 ml round bottom flask. The mixture was heated and stirred for 5 min. DMF (MCB, 50 ml) and benzyl mercaptan (Aldrich, 4g, 0.032 mole) were added. The solution was stirred for 5 min. p-Chloroactophenone (Aldrich, 5g, 0.032 mole) was added dropwise. The reaction mixture was stirred and refluxed for 16 hours. The reaction mixture was poured into cold water. Extracted the mixture with methylene dichloride (2x100 ml). The organic layer was washed with water (2x100 ml). After removed the solvent under the vacuum, the residue was recrystallized with MeOH. A white crystal was obtained: mp 103-105 ^{o}C.

^1H NMR (300 MHz, $CDCl_3$) δ 4.22 (s , 2H), 2.55 (s, 3H), 7.2-7.4 (m, 7H), 7.83 (dt, J = 8.76 and J = 1.99 Hz, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 26.27, 36.94, 126.65, 127.37, 128.54, 128.59, 133.96, 136.08, 144.06, 196.94 (one missing aromatic tertiary carbon peak may overlapped with the peak at 128.59)

MS (EI) m/e 242(M+), 197, 119, 91(100)

IR (CCl_4) ν (CH_2Cl_2): 3089, 3068, 3031, 3010, 2925, 1686 (C=O), 1591, 1263, 1099, 954 cm^{-1}

p-(n-Butylthio)benzophenone (p-n-BuSBP) KOH (Baker, 15g, 0.27 mole) and toluene (Aldrich, 20 ml) were placed into a 50 ml round bottom flask. The mixture was then stirred and heated to boil for 5 min. A solution of p-chlorobenzophenone (Aldrich, 30g, 0.13 mole) in DMF (MCB, 20 ml) were added into the flask and a solution of n-Butyl mecaptan (Aldrich, 15g, 0.17 mole) in DMF (MCB, 10 ml) were added into the flask.. The reaction mixture was refluxed for 24 hours. The reaction mixture was poured into cold water and extracted with methylene dichloride (2 x 200 ml). The organic layer was washed with distilled water (2 x 200 ml). After removed the solvent under the vacuum, white crystals (9.5g, 25% yield) were recrystallized from methanol: mp 80-84 ^oC.

IR (CH_2Cl_2): ν 3084, 3063, 3026, 2926,1660 (C=O), 1589, 1448, 1317, 1280, 1089, 937,922 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$): δ 0.94 (t, J = 7.36 Hz, 3H), 1.47 (hextet, J = 726, 2H), 1.69 (tt, J = 6.70, 2H), 2.99 (t, J = 7.50 Hz, 2H), 7.35 (d, J = 8.65 Hz, 2H), 7.46 (t, J = 6.98 Hz, 2H), 7.56 (t, J = 7.25 Hz, 1H), 7.7-7.8 (m, 4H)

^{13}C NMR (75, $CDCl_3$) δ 14.29, 22.69, 31.50, 32.41, 126.79, 128.90, 130.47, 131.29, 132.83, 134.54, 138.49, 145.03, 196.43

MS (FAB, NBA, Positive) m/e 270, 105

MS (EI) m/e 270 (100, M+), 227, 214, 193, 181, 137, 105, 77

p-(t-Butylthio)benzophenone (p-t-BuSBP) KOH (Baker, 2g, 0.036 mole) and toluene (Aldrich, 10 ml) were placed into a 250 ml round bottom flask. The mixture was then stirred and heated to boil for 5 min. t-butyl mecaptan (Aldrich, 3.0g, 0.033 mole) and DMF (MCB, 20ml) were added. A solution of p-chlorobenzophenone (Aldrich, 4.5g, 0.021 mole) in DMF (MCB, 30 ml) were added into the flask. The reaction mixture was refluxed for 36 hours. The reaction mixture was poured into cold water and extracted with methylene dichloride (2 x 200 ml). The organic layer was washed with saturated Na_2CO_3/H_2O (4 x 100 ml). After removing the solvent under the vacuum, the residue was recrystallized from ethanol to afford white crystals (3.1g):

mp 87-90^{o} C.

IR (CH_2Cl_2): v 3078, 3062, 3026, 2965, 2936, 2894, 2862, 1665, 1591, 1550, 1302,1280, 937 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 9H), 7.50 (tt, J = 1.04 Hz and J = 7.20 Hz, 2H), 7.59 (td, J = 1.37 Hz and J = 7.42 Hz, 1H), 7.63 (td, J = 1.74 Hz and J = 8.46 Hz, 2H), 7.77-7.78 (m, 2H)

^{13}C NMR (75, $CDCl_3$) δ 30.37, 46.17, 127.97, 129.54, 129.63, 132.22 136.28, 136.99, 138.18, 196.12 (one missing aromatic quatenary carbon peak may overlapped with the peak at 136.28)

MS (EI) m/e 270 (M+), 214 (100), 185, 152, 137, 105, 77

p-(sec-Butylthio)benzophenone (p-sec-BuSBP) KOH (Baker, 2g, 0.036 mole) and toluene (Aldrich, 10 ml) were placed into a 250 ml round bottom flask. The mixture was then stirred and heated to boil for 5 min. 2-Butyl

mecaptan (Aldrich, 3.0g, 0.033 mole) and DMF (MCB, 20ml) were added. A solution of p-chlorobenzophenone (Aldrich, 4.5g, 0.021 mole) in DMF (MCB, 30 ml) were added into the flask. The reaction mixture was refluxed for 36 hours. The reaction mixture was poured into cold water and extracted with methylene dichloride (2 x 200 ml). The organic layer was washed with saturated Na_2CO_3/H_2O (4 x 100 ml). After removing the solvent under the vacuum, a yellow liquid (4.0 g) was obtained which was purified by silica gel column chromatography (Hexane). The purity was confirmed by HPLC.

IR (CCl_4): ν 3078, 3062, 3031, 2969, 2925, 2873, 1661, 1590, 1318, 1273, 1089, 937, 922 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$): δ 1.02 (t, J = 7.30 Hz, 3H), 1.33 (d, J = 6.69 Hz, 3H), 1.58 (qdd, J = 7.14, J = 7.14 and J = 7.14 Hz, 1H), 1.72 (qdd, J = 7.50, J = 6.25 and J = 7.49 Hz, 1H), 3.34 (qt, J = 7.38 and J = 7.38 Hz, 1H), 7.35 (dt, J = 8.31 and J = 1.93 Hz, 2H), 7.44 (tt, J = 7.05 and J = 1.22 Hz, 2H), 7.56 (tt, J = 7.60 and J = 1.38, 1H), 7.6-7.8 (m, J = 8.30, 1.68, 1.47 and 6.17 Hz, 4H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 11.14, 20.13, 29.20, 43.16, 128.41, 128.46, 130.00, 130.72, 132.40, 134.60, 137.92, 143.48, 196.22

MS (EI) m/e 270 (M+), 241, 214(100), 137, 105, 77

<u>o-(n-Octylthio)acetophenone (o-C_8SAP)</u> A mixture of o-fluoro-acetophenone (Aldrich, 4.1g, 0.026 mole), K_2CO_3 (Baker, 3.8g, 0.028 mole) and DMF (MCB, 40 ml) in a 250 ml round bottom flask cooled in an ice bath was stirred with magnetic bar. n-octyl mercaptan (Aldrich, 3.5g, 0.023 mole) was then added dropwise into the solution. The reaction mixture was stirred at room temperature for 24 hours . The reaction mixture was poured into cold water. The mixture was extracted with methylene dichloride (2 x100 ml). The organic layer was washed with saturated K_2CO_3/H_2O solution (2 x100 ml). The organic layer

was dried with $MgSO_4$. After removing the solvent under the vacuum, the residue was recrystallized from ethanol to afford white crystals (3.5g, 47% yield). mp 40-41^oC.

IR (CCl_4) ν 3060, 2960, 2930, 2860, 1680 (C=O), 1590, 1465, 1435, 1247, 1055, 955 cm^{-1}

MS (EI) m/e 264 (M+), 249, 151 (100), 137, 109, 91, 77

^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, J = 6.98 Hz, 3H), 1.08-1.18 (m, 8H), 1.44 (quintet, J = 7.26 Hz, 2H), 1.69 (tt, J = 7.54 and J = 7.30 Hz, 2H), 2.87 (t, J = 7.50 Hz, 2H), 7.16 (dt, J = 1.39 and J = 6.98 Hz, 1H), 7.35 (dt, J = 1.40 and J = 8.10 Hz, 1H), 7.41 (dt, J = 1.40 and J = 8.38 Hz, 1H), 7.75 (dd, J = 1.39 and J = 8.81 Hz, 1H)

^{13}C NMR (75 MHz, CDCl3) d 13.74, 22.31, 27.89, 28.27, 28.85, 28.90, 31.51, 32.14, 123.72, 126.29, 130.79, 132.01, 135.64, 141.24, 199.76 (one missing CH_2 peak may overlaped with another CH_2 peak)

p-Bromomethylacetophenone (p-$BrCH_2$AP) 4-Methylacetophenone (Aldrich, 55g, 0.41 mole), N-bromosuccinimide (MC/B, 60g, 0.34 mole), benzoyl peroxide (OR, 0.5g, 0.0021 mole) and 200 ml CCl_4 (Mallinckrodt) were placed in a 500 ml Three neck round bottom flask. The reaction mixture was stirred with magnetic stirring bar and heated to reflux for 4 hours. The hot mixture was filtered with suction filtration. The solid was washed with hot CCl_4 (2x50 ml). The solvent was removed from filtrate under reduced pressure. A yellow liquid (104-110^oC/0.5mmHg) was obtained which turned out to be a white solid after cooled in refrigerator. White crystals were recrystallized from ethanol. mp 44-47 ^oC

^1H NMR (300 MHz, $CDCl_3$) δ 2.58 (s, 3H), 4.48 (s, 2H),7.46 (d, J = 8.40 Hz, 2H), 7.90 (d, J = 8.40 Hz, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 25.93, 31.47, 128.43, 128.86, 136.48, 142.47, 197.26

IR ($CHCl_3$) ν 3036, 3007, 2973, 1691 (C=O), 1608, 1574, 1412, 1358, 1228, 1074, 1018, 956 cm^{-1}

MS (FAB, NBA, Positive) m/e 215, 213 (M + 1). MS (EI) m/e 212 (M+), 197, 133, 118 (100), 105, 90

p-(Phenylthio)methylacetophenone (p-$PhSCH_2$AP) p-Bromomethyl-acetophenone (11g, 0.052 mole) was dissolved in ethanol (50 ml) in a 250 ml round bottom flask. Thiophenol (Aldrich, 5.7g, 0.052 mole) was added in to a flask containing a solution of KOH (Baker, 2.9g, 0.052 mole) in 95% ethanol (50 ml). The latter solution was added to the former one. After 10 minutes' stirring, distilled water (300 ml) was added into the reaction mixture. A white solid was precipitated and the reaction mixture was cooled in an ice bath to 0°C. The reaction mixture was filtered by suction filtration. White crystals (8.5g, 68% yield)were recrystallized from ethanol. mp 90-92 °C

^{13}C NMR (75 MHz, $CDCl_3$) δ 26.55, 39.05, 126.82, 128.55, 128.92, 128.95, 130.47, 135.39, 136.05, 143.27, 197.60

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.58 (s, 3H), 4.13 (s, 2H), 7.2-7.3 (m, 5H), 7.34 (d, J = 11.70 Hz, 2H), 7.86 (d, J = 8.10, 2H)

IR (CCl_4) ν 3060 , 2960, 2920, 1685 (C=O), 1605, 1255, 960 cm^{-1}

MS (EI) m/e 242 (M+), 199, 133 (100), 105, 90

p-Bromomethylbenzophenone (p-$BrCH_2$BP) p-Methylbenzophenone (Aldrich,12g, 0.061 mole), N-bromosuccinimide (MC/B,11g, 0.062 mole), benzoic peroxide (OR, 0.1g, 0.0004 mole) and CCl_4 (Mallinckrodt, 40 ml) were added into a 250 ml round bottom flask. The reaction mixture was stirred and

refluxed for 3 hours. The reaction mixture was filtered by suction filtration. The solvent was removed from filtrate under reduced pressure. A white solid (13 g, 78% yield) was obtained after beingrecrystallized from ethanol. mp 100- 105 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (s, 2H), 7.45-7.55 (m,4H), 7.60 (tt, J = 7.45 and J = 1.34 Hz, 1H), 7.79 (m, 4H)

^{13}C NMR (75 MHz, CDCl3) δ 31.60, 127.99, 128.60, 129.65, 130.19, 132.24, 137.01, 137.08, 141.80, 195.85

MS (EI) m/e 274 (M+), 195 (100), 167,105,77

IR ν 3080, 3060, 3030, 1730,1630 (C=O), 1615, 1600,1275, 980, 950 cm^{-1}

m-Bromomethylbenzophenone (m-$BrCH_2$BP) m-Methylbenzophenone (Aldrich,12g, 0.061 mole), N-bromosuccinimide (MC/B,11g, 0.062 mole), benzoic peroxide (OR, 0.1g, 0.0004 mole) and CCl_4 (Mallinckrodt, 50 ml) were added into a 250 ml round bottom flask. The reaction mixture was stirred and refluxed for 2 hours until red color disappeared. The reaction mixture was allowed to cool to room temperature and the reaction mixture was filtered by suction filtration. The solvent was removed from filtrate under reduced pressure. A liquid (10 g) was obtained by distillation (160-170 ^{o}C/1.0mm). A white solid was recrystallized from ethanol. mp 60-62 ^{o}C

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (s, 2H), 7.50 (t, J = 8.03 Hz, 3H), 7.61 (t, J = 8.43 Hz, 2H), 7.71 (d, J = 7.85 Hz, 1H), 7.78-7.84(m, 3H)

^{13}C NMR (75 MHz, CDCl3) δ 31.82, 128.02, 128.46, 129.68, 130.03, 132.30, 132.59, 136.90, 137.78, 137.84, 195.98 (one missing aromatic quatenary carbon peak may overlapped with another aromatic quatenary carbon peak)

MS (EI) m/e 276, 274, 195, 165, 152, 105, 90, 77

IR (CCl_4) ν 3070, 3064, 3032, 2974, 2927, 2885, 1669, 1599, 1449, 1340, 1224 cm^{-1}

m-(Phenylthio)methylbenzophenone (m-$PhSCH_2BP$) m-Methylbenzophenone (Aldrich, 5g, 0.026 mole), N-bromosuccinimide (MC/B,5g, 0.028 mole), benzoic peroxide (OR, 1g, 0.004 mole) and CCl_4 (Mallinckrodt, 30 ml) were added into a 100 ml round bottom flask. The reaction mixture was stirred and refluxed for 1.5 hours until yellow color disappeared. The solvent was removed under reduced pressure. The residue was transferred to a 100 ml round bottom flask and 40 ml DMF was then added. A solution of 1.4 g KOH and 2.7 g thiophenol in 20 ml 95% EtOH was added dropwise. It was kept stirring at room temperature for 3 hours. The reaction mixture was poured into 100 ml H_2O and extracted with methylene dichloride. Solvent was removed under reduced pressure to give yellow oil (3g). A colorless liquid product was purified by silica gel column chromatography (50:50, hexane/CCl_2H_2).

^1H NMR (300 MHz, $CDCl_3$) δ 4.15 (s, 2H), 7.20-7.35 (m, 4H), 7.40-7.60 (m, 6H), 7.67-7.75 (m, 4H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 38.71, 126.89, 128.44, 128.69, 129.05, 129.08, 130.18, 130.52, 130.60, 132.61, 133.00, 135.65, 137.63, 137.90, 138.15, 196.78

MS (EI) m/e 304, 210, 195, 105,77 (100)

IR (CCl_4) ν 3058, 3032, 2958, 2927, 1664, 1599, 1583, 1481, 1433, 1317, 1309, 1282, 1234 cm^{-1}

m-Bromomethylacetophenone (m-$BrCH_2AP$) 3-Methylactophenone (Aldrich, 8.2g, 0.061 mole), N-bromosuccinimide (MC/B, 11g, 0.062 mole), benzoic peroxide (OR, 0.1g, 0.0004 mole) and 50 ml CCl_4 (Mallinckrodt) were

placed in a 250 ml round bottom flask. The reaction mixture was stirred with magnetic stirring bar and heated to reflux for 25 min until red color disappeared. The solvent was removed under reduced pressure. Distillation afforded a liquid (5.3 g, 90-100°C/0,2mm).

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.58 (s, 3H), 4.50 (s, 2H),7.42 (t, J = 7.54 Hz, 1H), 7.56 (dm, J = 7.82 Hz, 1H), 7.85(d, J = 7.54 Hz, 1H), 7.94(b, 1H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 25.92, 31.86, 127.93, 128.31, 128.80, 133.24, 137.24, 138.07, 197.34

IR (CCl_4) ν 3067, 3030, 3004, 2962, 2925, 2862, 1693, 1603, 1587, 1550, 1441, 1358, 1277, 1217, 1192 cm^{-1}

MS (EI) m/e 214, 212(M+), 199, 197, 171, 133(100), 118, 90

p-(Phenylthio)methylbenzophenone (p-$PhSCH_2$BP) p-Bromomethyl-benzophenone (7g, 0.025 mole) was dissolved in DMF (MCB, 40 ml) in a 250 ml round bottom flask. Thiophenol (Aldrich, 2.7g, 0.025 mole), KOH (Baker, 1.4g, 0.025 mole) and 95% EtOH (40 ml) were added into another 250 ml round flask and stirred for 10 minutes. The latter solution was then added into the former one. The reaction mixture was stirred for 30 minutes. Distilled water (300 ml) was added in the reaction mixture and a white solid was precipitated. The reaction mixture was allowed to cool in an ice bath. The solution was filtered by suction filtration. White crystals (6.5g, 85% yield) were recrystallized from ethanol. mp 49 - 51 °C.

MS (EI) m/e 304 (M+), 195 (100), 167, 105,77

IR (CCl_4) ν 3079, 3058, 3032, 2935, 1664, 1606, 1581, 1277, 937 cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ 4.14 (s, 2H), 7.15-7.30 (m, 5H), 7.36 (d, J = 8.51 Hz, 2H), 7.46 (t, J = 7.69 Hz, 2H), 7.57 (t, J = 7.29 Hz, 1H), 7.71 (d, J = 8.68 Hz, 2H), 7.76 (d, J = 6.93, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 38.89, 126.98, 128.44, 128.88, 129.01, 129.14, 130.16, 130.55, 132.56, 135.70, 136.58, 137.85, 142.79, 196.75

p-(Phenylsulfinyl)methylbenzophenone (p-$PhSOCH_2BP$) p-(Phenylthio)-methylbenzophenone (0.78 g, 0.0026 mole) was dissolved in acetone (Baker,10 ml) in a 50 ml round bottom flask. 30% Aqueous hydrogen peroxide (Baker, 1 ml, 0.0098 mole) was then added to the solution. The reaction mixture was stirred for 48 hours at room temperature until white solid formed. The reaction mixture was filtered by suction filtration. A white solid (0.60g, 72% yield) was obtained. mp152-154 ^oC.

^1H NMR (300 MHz, $CDCl_3$) δ 4.05 and 4.12 (AB q, J = 12.63 Hz, 2H), 7.07 (dt, J = 8.09 and J = 1.92 Hz, 2H), 7.24-7.49 (m, 7H), 7.58 (tt, J = 7.57 and J = 1.40 Hz, 1H), 7.66 (tt, 8.30 and J = 1.77 Hz, 2H), 7.74 (td, J = 7.02 and J = 1.44 Hz, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 62.91, 124.46, 128.49, 129.19, 130.174, 130.21, 130.45, 131.57, 132,75, 133.87, 137.43, 137.59, 142.67, 196.56.

IR ($CHCl_3$) 3456, 3069, 3007, 1658 (C=O), 1606, 1446, 1278, 1043 (S=O), 929, 702.

MS (FAB, NBA, Positive) m/e 321(M+1).

MS (EI) m/e 320 (M+), 304, 195 (100), 167, 105, 90, 77.

p-(Phenylsulfonyl)methylbenzophenone (p-$PhSO_2CH_2BP$) p-(Phenyl-thio)methylbenzophenone (2g, 0.0066 mole) and glacial acetic acid (Mallinckrodt, 25 ml) were placed in a 50 ml round bottom flask. 30% Aqueous hydrogen peroxide (Baker, 3g, 0.026 mole) was then added. The reaction mixture was stirred at room temperature for 17 hours. It was extracted with $CHCl_3$ (3 x 20 ml) followed by H_2O (2 x 20 ml) and saturated $NaHCO_3$ solution (2 x 20 ml). The organic layer was separated and the solvent was removed

under reduced pressure. The solid obtained was recrystallized with ethanol. White crystals (1.5g, 68% yield) was recrystallized from ethanol. mp 155-156 ^{o}C.

MS (EI) m/e 336 (M+),195,167,141,105,77.

^{1}H NMR (300 MHZ, $CDCl_3$) δ 4.39 (s, 2H), 7.23 (d, J = 8.10 Hz, 2H), 7.49 (td, J = 7.53 and J = 1.39, 4H), 7.60 (tt, J = 7.26 and J = 2.51, 2H), 7.70 (dm, J = 8.10, 4H), 7.76 (dd, J = 6.98 and J = 1.67, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) 195.94, 147.86, 137.87, 137.77, 137.23, 133.93, 132.63, 132.41, 130.63, 62.64.

IR ν 3552, 3069, 3026, 1660 (C=O), 1590, 1448, 1302 (S=O), 1278, 1155 (S=O)

p-Chloromethylbenzophenone (p-$ClCH_2$BP) p-Methylbezophenone (Aldrich, 6g, 0.030 mole), sulfuryl chloride (MCB, 4g, 0.030 mole) and CCl4 (Mallinckrodt, 20ml) were placed into a 50 ml round bottom flask. After stirred for 2 minutes, benzoyl peroxide (OR, 100 mg, 0.0004 mole) was added into the reaction mixture. The reaction mixture was refluxed for 24 hours with stirring. The reaction mixture was filtered by suction filtration and the solvent was removed under reduced pressure. White crystals (4.0g, 58% yield) were recrystallized from ethanol. mp 94-97 ^{o}C.

^{1}HNMR (300 MHz, $CDCl_3$) δ 4.64 (s,2H),7.50 (dd, J = 8.51 and J = 1.89, 4H), 7.60 (tt, J = 7.41 and J = 1.38, 1H), 7.80 (dd, J = 8.02 and J = 1.87, 4H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 44.47, 127.99, 128.06, 129.65, 130.12, 132.24, 137.02, 137.13, 141.39,195.94

IR (CCl4) ν 3310, 3084, 3062, 3031, 2957, 2925, 2868, 2857, 1667, 1608, 1549, 1446, 1317, 1277, 1178, 939

MS (FAB, NBA, Positive) m/e 231 (M + 1)

MS (EI) m/e 230 (100, M+), 195, 181, 167, 153, 125, 105, 90, 77

m-Chloromethylbenzophenone (m-$ClCH_2BP$) m-Methylbezophenone (Aldrich, 6g, 0.030 mole), sulfuryl chloride (MCB, 4g, 0.030 mole) and CCl4 (Mallinckrodt, 20ml) were placed into a 100 ml round bottom flask. After stirring for 2 minutes, benzoyl peroxide (OR, 100 mg, 0.0004 mole) was added into the reaction mixture. The reaction mixture was refluxed for 3 hours with stirring. The solvent was removed under reduced pressure. Distillation afforded a liquid (163 oC/1.0 mm, 5.0 g). White crystals were recrystallized from ethanol. mp 43-46 ^oC.

^{1}HNMR (300 MHz)δ 4.65 (s,2H),7.47-7.54 (m, 3H), 7.59-7.67 (m, 2H), 7.76 (tt, J = 7.69 and J = 1.53, 1H), 7.79-7.86(m, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 44.88, 128.01, 128.38, 129.59, 129.68, 132.10, 132.27, 136.95, 137.51,137.76, 196.02 (one missing aromatic tertiary carbon peak may overlapped with the peak at 129.68 ppm)

IR (CCl4) ν 3068, 3031, 2957, 2925, 2867, 1666, 1599, 1587, 1549, 1148, 1319, 1286, 1261, 1211, 984 cm^{-1}

MS (EI) m/e 230 (M+) 195, 181, 165, 153, 125, 105(100), 77

p-(n-Butylthio)methylbenzophenone (p-n-$BuSCH_2BP$) 4-Bromomethyl-benzophenone (6g, 0.022 mole) , n-butylmercaptan (2g, 0.022 mole) and KOH (1.2g, 0.021 mole) were placed into a 250 ml round bottom flask. 95% Ethanol (100 ml) was then added. The reaction mixture was refluxed for 12 hours with stirring. The reaction mixture was poured into a saturated Na_2CO_3 / H_2O solution (100 ml) and extracted with $CHCl_3$ (2 x 100 ml). Organic layer was washed with saturated Na_2CO_3 / H_2O solution (2 x 100 ml). The organic layer was separated and solvent was removed under reduced pressure. A liquid was obtained by distillation (164-165^oC / 0.2 mm).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87(t, J = 7.26 Hz, 3H), 1.36(hextet, J = 8.98Hz, 2H), 1.54(tt, J = 6.98 Hz, J = 8.09 Hz, 2H), 2.42(t, J = 6.32 Hz, 2H), 3.74(s,2H), 7.44(tq, J = 1.68 and 8.37 Hz, 4H), 7.56(tt, J = 1.39 and 7.54 Hz, 1H), 7.76(tt, J = 1.67 and 8.28 Hz, 4H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 14.32, 22.61, 31.89, 31.91, 36.75, 128.91, 129.38, 130.61, 131.03, 132.99, 136.84, 138.349, 144.41, 197.44.

IR (CCl_4) ν 3310, 3080, 3060, 3030, 2961, 2932, 2850, 1664, 1606, 1317, 1277, 937 cm^{-1}

MS (FAB, NBA, Positive) m/e 285 (M+1), 195, 105, 77

MS (EI) m/e 284, 226, 209, 185 (100), 178, 167, 152, 133, 122, 105, 90, 77

m-(Phenylthio)methylacetophenone (m-$PhSCH_2AP$) m-Bromomethyl-acetophenone (4.8g, 0.023 mole) and 95% ethanol (25 ml) were placed into a 250 ml round bottom flask. A solution of thiophenol (aldrich,3.0 g, 0.027 mole) and KOH (0.8 g, 0.014) in 95% Ethanol (25 ml) was then added dropwise. The reaction mixture was refluxed for 1 hour with stirring. The reaction mixture was poured into H_2O (100 ml). The solution was then extracted with $CHCl_3$ (200 ml). The organic layer was washed with saturated Na_2CO_3 / H_2O solution (4 x 50 ml). The organic layer was separated and dried over MgSO4. The solvent was removed under reduced pressure. A liquid (4 g) was obtained by distillation (159 ^oC/0.2 mm). It was purified with silica gel column chromatography (Hexane/AcOEt).

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.55(s, 3H), 4.15(s, 2H), 7.2-7.3(m, 5H), 7.38(tt, J = 7.23 and J = 1.13 Hz, 1H), 7.77(m, 1H), 7.81-7.84(m, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 25.88, 38.31, 126.42, 126.75 128.31, 128.39, 128.56, 130.15, 135.13, 136.92, 137.93, 133.08, 197.78

IR (CCl_4) ν 3078, 3067, 3009, 2957, 2925, 2857, 1691, 1585, 1550, 1481, 1439, 1358, 1275, 1230, 1188, 1026 cm^{-1}

MS (EI) m/e 242 (M+), 218, 133, 109, 91,77

p-(t-Butylthio)methylbenzophenone (p-t-BuSCH$_2$BP) 4-Bromomethylbenzophenone (4.5g, 0.016 mole), 95% ethanol (25 ml) and acetonitrile (25 ml) were placed into a 250 ml round bottom flask. A solution of t-butylmercaptan (aldrich,1.5 g, 0.017 mole) and KOH (1.0g, 0.018 mole) in 95% Ethanol (25 ml) was then added dropwise. The reaction mixture was refluxed for 5 hours with stirring. The reaction mixture was poured into H_2O (100 ml). The solution was then extracted with $CHCl_3$ (200 ml). The organic layer was washed by saturated Na_2CO_3 / H_2O solution (3 x 100 ml) and $NaHCO_3$ / H_2O solution (100 ml). The organic layer was separated and dried over MgSO4. Removed the solvent under reduced pressure. White crystals (4 g) were recrystallized from ethanol. mp 75-77°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37(s, 9H), 3.83(s, 2H), 7.48(tq, J = 6.72 and J = 1.73 Hz, 4H), 7.59(tt, J = 7.24 and J = 1.41 Hz, 1H), 7.77(tq, J = 8.24 and J = 1.28 Hz, 4H)

13C NMR (75 MHz, $CDCl_3$) δ 30.72, 33.09, 43.07, 128.40, 129.04, 130.14, 130.55, 132.48, 136.27, 137.92, 144.02, 196.70

IR (CCl_4) ν 3078, 3062, 3030, 2963, 2941, 2925, 2899, 2862, 1665, 1606, 1549, 1317, 1308, 1277, 1176, 937 cm^{-1}

MS (EI) m/e 284 (M+), 228 (100), 195, 167, 150, 105, 90, 77

p-(sec-Butylthio)methylbenzophenone (p-sec-BuSCH$_2$BP) p-Bromomethylbenzophenone (4.5g, 0.016 mole), ethanol (25 ml) and acetonitrile (25 ml) were placed into a 250 ml round bottom flask. A solution of iso-

butylmercaptan (aldrich,1.5 g, 0.017 mole) and KOH (1.0g, 0.018 mole) in 95% Ethanol (100 ml) was then added dropwise. The reaction mixture was refluxed for 1.5 hours with stirring. The reaction mixture was poured into CHCl3 (150 ml). The solution was then washed with saturated Na_2CO_3 / H_2O solution (3 x 100 ml) and extracted with $CHCl_3$ (2 x 100 ml). The organic layer was washed by saturated Na_2CO_3 / H_2O solution (2 x 100 ml). The organic layer was separated and dried over MgSO4. Solvent was removed under reduced pressure. A liquid (3 g) was obtained by distillation (186^oC / 0.5 mm); The reddish color was removed by run the liquid through silica gel column.

^1H NMR (300 MHz) δ 0.925(t, J = 7.42 Hz, 3H), 1.24(d, J = 6.78 Hz, 3H), 1.56(m, J = 7.11, 2H), 2.59(qt, J = 6.20 and J = 6.20 Hz, 1H), 3.77(s, 2H), 7.45(qq, J = 7.97 and 1.35 Hz, 4H), 7.57(tt, J = 7.53 and J = 1.40, 1H), 7.76(tq, J = 8.27 and J = 1.31 Hz, 4H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 10.94, 20.23, 29.20, 34.49, 41.06, 128.39, 128.85, 130.11, 130.52, 132.48, 136.28, 137.87, 144.15, 196.67

IR (CCl_4) ν 3078, 3062, 3031, 2969, 2928, 2883, 1662, 1606, 1448, 1317, 1302, 1277, 1176, 937 cm^{-1}

MS (EI) m/e 284 (M+, 100), 255, 240, 228, 211, 184, 185, 167, 152, 105, 90, 77

o-Aminobenzophenone (Aldrich, 9g, 0.045 mole) was dissolved in acetonitrile (Baker, 75 ml) in a 250 ml round bottom flask. Iodomethane (Baker, 30g, 0.21 mole) and K_2CO_3 (Baker, 18g, 0.13 mole) were then added into the solution. The solution was refluxed for 17 hours. A white solid was precipitated. The reaction mixture was allowed to cool down to room temperature. The solution was filtered by suction filtration. White solid (4.5g, 27% yield) was obtained and recrystallized from ethanol. The product was identified as o-Benzoyltrimethylanilinium iodide. by its spectroscopic data. The filtrate above

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was poured into 100 ml water and extracted with methylene chloride (3 x 70 ml). The organic layer was washed with distilled water (2 x 50 ml) and finally with saturated sodium bicarbonate solution (2 x 50 ml). The solvent was removed under reduced pressure to afford a yellow liquid. A yellowish liquid (1.5g, 15% yield) was obtained by distillation (117^{o}C/2mm). This product was identified as o-Benzoyldimethylaniline by its spectroscopic data.

o-Benzoyltrimethylanilinium iodide mp 174-176^{o}C.

IR (CH_3CN) ν 3400-3650(broad), 3060, 2926, 1668 (C=O), 1597, 1282, 1063, 949, 925

MS (EI) m/e 225,208,193,142,127,105,91,77 (100)

Mass (NBA + FAB, Positive) 240, 224, 208, 194, 165, 148, 107

^{1}H NMR (300 MHz, CD_3CN) δ 3.63 (s, 9H, CH_3), 7.47(dd, J = 1.71 and J = 7.63 Hz, 1H), 7.58 (tt, J = 1.65 and J = 7.74 Hz, 2H), 7.68(dt, J = 0.95 and J = 7.57 Hz, 1H), 7.78 (m, 2H), 7.90 (dd, J = 1.31 and J = 8.36 Hz, 2H), 8.02 (dd, J = 8.73 and J = 0.76 Hz, 1H)

^{13}C NMR (75 MHz, CD_3CN) δ 198.2 (C=O), 144.38, 137.2, 136.7, 134.4, 133.5, 132.8, 132.4, 131.6, 130.6, 123.6, 59.4 (CH_3)

o-Benzoyldimethylaniline

MS (EI) m/e 225(M^+), 208, 193, 148,105, 91 77

^{1}H NMR (300 MHz, $CDCl_3$) δ2.68 (s, 6H), 6.88(td, J = 7.42 and J = 0.98 Hz, 1H), 6.97 (d, J = 8.30, 1H), 7.30 (dd, J = 7.69 and J = 1.58 Hz, 1H), 7.40 (tt, J = 7.14 and J = 1.16 Hz, 3H), 7.55-7.60 (m, 1H), 7.81 (dt, 7.08 and J = 1.44 Hz, 2H)

IR(nujol): 3060, 1660, 1600, 1500 1460, 1380 cm^{-1}

^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.27, 116.55, 128.17, 128.26, 130.11, 130.89, 131.62, 132.83, 135.23, 135.68, 137.92, 198.62

o-Benzoyltrimethylanilinium tetrafluoroborate (o-Me_3NBP:BF_4)

o-Benzoyltrimethylanilinium iodide (2g, 0.0054 mole) was dissolved in hot distilled water (30 ml) in a 50 ml round bottom flask. A solution of $AgBF_4$ (Aldrich, 1.03g, 0.0053 mole) in distilled water (5 ml) was added dropwise into the flask. White precipitate appeared. The reaction mixture was filtered by suction filtration. The water solution was allowed to cool down to room temperature and white crystals (1.5g, 85% yield) were obtained. Recrystallization from ethanol afforded white crystals. mp 240-241 ^{o}C.

MS (FAB, MF) 240(positive), 208

MS (EI) m/e 225 (positive part - CH_3), 208, 193, 148, 105, 91, 77

IR (CH_3CN) ν 3631 (b), 3544 (b), 3130, 3063, 2987, (C=O) 1669, 1597, 1493,1282,1257,1053,843,771 cm^{-1}

^1H NMR (500 MHz, CD_3CN): δ 3.6 (s, 9H), 7.5 (dd, J = 1.72 and J = 7.76 Hz, 1H), 7.6 (t, J = 7.97 Hz, 2H), 7.7 (t, J = 7.54 Hz, 1H), 7.76 (tt, J = 7.32 and J < 1 Hz, 1H), 7.79 (dt, J = 1.72 and J = 7.32 Hz, 1H), 7.9 (dd, J = 1.51 and J = 8.62 Hz, 2H), 8.0 (d, J = 8.62 Hz,1H)

^{13}C NMR (CD_3CN, 75 MHz) δ 197.4 (C=O), 144.8, 136.7, 136.1, 133.9, 133.1, 132.3, 131.8, 131.1, 130.0, 123.0, 59.2

UV (MeOH/EtOH, 100:10) 256.4_{max}(17120), 295_{sd}(1316), 333_{max}(95), 313(168), 366(22.8)

UV (acetonile) 366(17.9)

<u>o-Benzoyl-N,N-dibenzylaniline (o-Bz_2NBP)</u> 2-Aminobenzophenone (Aldrich,1g, 0.005 mole), benzyl chloride (Fisher, 1.9 g, 0.015 mole) and sodium iodide (CCI, 0.22 g, 0.0015 mole) were placed into a 100 ml round bottom flask. Acetonitrile (Baker, 30 ml) and sodium carbonate (Baker, 1.59 g, 0.015 mole) were then added into the flask. The solution was stirred and refluxed for 20 hours. The reaction mixture was cooled in an ice bath and filtered by suction

filtration. The filtrate was then distilled in vacuum. The residue was a yellow oil. Yellowish crystals (0.5g, 27%) were recrystallized from methanol. mp 59°-60 °C.

IR (CCl_4) ν 3066,3030, 2845, 2816, 1666 (C=O), 1595, 1501,1485,1450,925 cm^{-1}

MS (EI) m/e 377 (M+), 286 (100), 208,180,167,105,91,77

^1H NMR (500 MHz, $CDCl_3$) δ 4.0 (s, 4H), 6.8 (d, J = 6.43 Hz, 4H), 7.0 (d, J = 8.04 Hz, 1H), 7.1 (m, 7H), 7.4 (m, 2H), 7.44 (tt, J = 7.43 and J < 1.0 Hz, 2H), 7.6 (tt, J = 7.43 and J < 1.0 Hz, 1H), 7.8 (dd, J = 8.43 and J = 1.20 Hz, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (C=O), 150.0, 138.3, 137.2, 134.5, 132.8, 130.7, 129.7, 129.6, 128.7, 128.5, 128.0, 127.0, 122.1, 121.6, 56.5 (CH_2)

UV (MeOH/EtOH, 100:10) 256_{max}(21101), 353_{max}(1091), 313(1067), 366(1077).

<u>o-Benzoyl-N,N-dibenzylaniline hydrochloride (o-Bz_2NBP:HCl)</u> o-Benzoyl-N,N-dibenzylaniline (2g, 0.0053 mole) was dissolved in benzene and hydrochloric acid gas generated by heating 37% aqueous hydrochloride (CCl, 30 ml) in a round bottom flask was bubbled through the solution. A solid precipitated and collected by suction filtration. A yellowish solid was recrystallized form ethanol (1.8g, 80% yield). mp 123-125 °C.

IR (CH_3CN): ν 3628 (broad), 3550 (broad), 3065, 3042, (C=O) 1662, 1643,1597 cm^{-1}

MS (FAB, MF) 378 (100, positive part),300,286,270,208,91

MS (EI) m/e 377, 359, 287, 286 (100), 270, 256, 208, 196, 180, 167, 152, 105, 91, 77

^{1}H NMR (500 MHz, CD_3CN) δ 4.78 (b, 4H), 7.16 (q, J = 7.42 Hz, 6H), 7.19-7.43 (m, 9H), 7.42 (t, J = 7.48 Hz, 2H), 7.64 (t, J = 7.41 Hz, 1H), 7.80 (d(b), J = 60.16 Hz, 1H)

^{13}C NMR (75 MHz, CD_3CN) δ 61.86, 125.67, 128.84, 129.76, 129.86, 130.44, 131.00, 131.99, 133.63, 134.99, 137.80, 199.51 (four missing aromatic carbons may overlapped with other aromatic carbons)

UV (MeOH/EtOH, 100:10) 249_{max}(18276), 359_{max}(728), 313(889), 366(720).

UV (acetonitrile) 366_{max}(936).

<u>o-Benzoyl-N-benzylaniline</u> was prepared by Sn2 reaction of o-aminobenzophenone and one equivalent benzyl chloride. o-Aminobenzophenone (Aldrich, 2.0g, 0.01 mole), benzyl chloride (Fisher, 1.3g, 0.01 mole), 0.5g sodium iodide (CCI, 0.5g, 0.003 mole) and 1.0g sodium carbonate (Baker, 1.0g, 0.0094 mole) were added into a 100 ml round bottom flask. Acetonitrile (Baker, 30 ml) was then added. The reaction mixture was stirring and refluxed for 5 hours. The reaction mixture was then cooled in ice bath for 5 min. and filtered by suction filtration. The solvent was removed from filtrate under reduced pressure. Recrystallization of the residue from EtOH yielded white crystals (1.2g, 41% yield). mp 79°-80°C.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.49 (d, J = 5.79 Hz, 2H), 6.51 (td, J = 7.12 and J = 1.04, 1H), 6.72 (d, J = 8.24, 1H), 7.20-7.65 (m,10H), 7.60 (d, J = 8.27 Hz, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ199.4, 151.3, 140.4, 138.3, 135.4, 135.0, 130.8, 129.1, 128.7, 128.0, 127.3, 127.2, 117.7, 114.4, 112.3, 47.2

IR 3320(b), 3085, 3068, 3035, 2936, 2850, 1628 (C=O), 1603, 1576, 1520, 1255, 937(cm^{-1})

MS (EI) m/e 287 (M+),270,210,196,180,167,152,106,91,77

o-Benzoyl-S,S-dimethyl-phenylsulfonium tetrafluoroborate 1.3g o-Methylthiobenzophenone (1.3g, 0.0057 mole), methylene chloride (Mallinckrodt, 20 ml) and iodomethane (Baker, 2.0) were placed in a 100 ml round bottom flask. The solution was cooled to -78°C. $AgBF_4$ (Aldrich, 1.0g, 0.0051 mole) was added and the reaction mixture was kept under N_2 overnight at room temperature. The solution was filtered by suction filtration. The solid was then washed with CH_3CN (30 ml) and filtered. The two filtrates were combined. The solvent was removed under reduced pressure and a white solid (1.1g, 59%)) was obtained. White crystals were recrystallized from EtOH. m.p191°-194°C.

^1H NMR (CD_3CN, 300 MHz) δ3.19 (s, 6H), 7.61 (t, J = 7.42, 2H), 7.77 (tt, J = 7.45 and J = 1.28 Hz, 1H), 7.80-7.90 (m, 4H), 7.92-8.03 (m, J = 3.02 Hz, 1H), 8.18 (d, J = 7.82 Hz, 1H)

MS (NBA + FAB) 243, 213

IR (KBr) ν 3299, 3089, 3026, 3010, 2984, 2973, 2936, 2910, 1645, 1595, 1431, 1280, 1037, 929

^{13}C NMR (75 MHz, CD_3CN) δ 29.38, 128.31, 130.34, 130.66, 132.31, 134.20, 134.76, 135.87, 136.93, 140.59, 196.77 (one missing aromatic tertiary carbon may overlapped with another aromatic tertiary carbon).

o-Aminobenzophenone hydrochloride o-aminobenzophenone (Aldrich, 2.0 g) was dissolved in benzene (EM, 50 ml). HCl gas was bubbled though the solution for 30 min. The reaction mixture was filtered to give a white solid (2.0g). Recrystallization of the solid from ethanol afforded white crystals m.p175-178 °C.

^1H NMR (CD_3CN, 300 MHz) δ3.60 (s), 6.91 (td, J = 7.39 and J = 1.19 Hz, 1H), 7.10 (dd, J = 8.52 and J = 1.22, 1H), 7.40-7.55 (m, 4H), 7.55-7.68 (m, 3H)

MS (FAB, Positive) 198

IR (KBr) n 3036, 3200-2800(b), 2559, 1664, 1626, 1597, 1493, 1298, 93

^{13}C NMR (75 MHz, CD_3CN) δ 124.27(b), 125.70 (b), 129.89, 131.23, 134.23, 134.97, 135.56, 199.15 (three missing aromatic carbons may overlapped in the broad peaks)

B. Techniques

1. Photochemical Glassware

All glassware used were rinsed with acetone, then with distilled water and boiled in a solution of alconox laboratory detergent in distilled water for 24 hours. The glassware was carefully rinsed with distilled water, and boiled in the distilled water for 3 days, with the distilled water changed every 12 hours. After the final distilled water rinse, the glassware was dried in an oven reserved for photochemical glassware at 150°C.

Ampoules used for irradiations were made by heating 13 x 100 mm pyrex test 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.

2. Sample preparations

All solutions were prepared either by directly weighing the desired material into volumetric flask or by dilution of a stock solution. Equal volumes (2.8 ml) of sample were placed via syringes into each ampoule. internal standards used for GC and HPLC analyses were weighed with the ketone starting material.

3. Degassing Procedure

Filled tubes were attached to a vacuum line with a diffusion pump. 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 for 10 minutes. The vacuum was removed and the tubes were allowed to thaw at room temperature with stopcocks closed. This freeze-pump-thaw cycle was repeated three times. The tubes were then sealed with an oxygen-natural gas torch.

4. Irradiation procedure

All samples for kinetic measurements were irradiated in parallel with actinometer solutions in a Merry-Go-Round apparats 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) was used to isolate the 313 nm emission band. A Corning CS 7-37 Filter was used for 366nm emission band.

Preparative scale photolyses were performed using a Hanovia 450-watt medium pressure lamp filtered through a pyrex tube. Ketones were dissolved with the chosen 60 ml solvent in a 25 x 200 test tube. A quartz cooling jacket was inserted. The sample was degassed by bubbled argon through it about 10 minutes and irradiated at room temperature.

5. Analysis procedure

Analysis by HPLC were performed on a Beckman 332 Gradient Liquid Chromatography System equipped with a Perkin-Elmer Lc-75 Ultraviolet-visible detector and a Dupont 860 Column compartment. An altex Ultrasphere Si

absorption Phase column was used. the HPLC system was connected to a Hewlett-Packard 6080 integration Recorder.

Analysis by GC was performed on a Varian Aerograph 1400 or 3400 Gas Chromatography equipped with a flame ionization detector. The GCs were connected to either a Hewlett-Packard 3393a of 3392a integrating Recorder.Three types of columns have been used for GC: Magabore DB-1with 15 meters in length, Magabore DB-210 with 15 meters in length and Magabore DBWAX with 30 meter in length.

6. Calculation of quantum yield

Quantum yields were calculated with the following equation,

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

where [C] is the concentration of the compound being measured and I is the intensity of light absorbed by samples.

The intensity of light was determined by valerophenone actinometry. Thus a degassed 0.1 M valerophenone solution was irradiated in parallel with the samples being analyzed. Upon completion of the irradiation the valerophenone sample was analyzed for acetophenone, using the following equations,

$$[AP] = R_f[Std]A_{ap}/A_{Std}$$

Where [AP] is the concentration of acetophenone, R_f is the response factor for acetophenone, Aap is the integrated area for acetophenone, [Std] is the concentration of the added internal standard, and A_{Std} is the integrated area for the internal standard.

The intensity of light absorbed by each sample, in ein l^{-1} can be calculated from the acetophenone concentration knowing that Φ is 0.33 for acetophenone,

$$I = [\text{acetone}] / 0.33$$

The response factors for each compound on GC or HPLC were obtained by the following equation,

$$R_f = ([C] / [Std]) (A_{Std} / A_C)$$

The R_f values for GC and HPLC are listed in table 21 and 22.

7.Spectroscopic Measurements

^1H NMR and ^{13}C NMR were recorded on VXR 300,500 and Gemini-300. $CDCl_3$ and CD_3CN were used as solvents and as internal standard ($CDCl_3$: d 7.24 ppm for ^1H NMR and.77 ppm for ^{13}C NMR; CD_3CN: 1.93 ppm for ^1H NMR and 1.3 ppm for ^{13}C NMR).

IR spectra were recorded in a FTIR Nicolet IR/42 Spectrometer in CCl_4 solutions or as pressed KBr discs.

Ultraviolet-visible spectra were recorded on a Shimadzu UV-160 Spectrometer in a 1x1 cm cell. Full spectra were taken in cyclohexane or MeOH/EtOH(100:10). The spectra for irradiation condition were taken in the same solvent as irradiation solvents (benzene or acetonitrile) at 313 nm and 366 nm.

Mass spectra were recorded on a Finnigan 4000 GC/MS using EI or FAB methods.

Phosphorescence spectra were recorded on a Perkin-Elmer MPF-44a Fluorescence Spectrometer. 10^{-4} M solution of ketone in 1-methyltetrahydrofuren in a NMR tube was used.The tube was inserted into a liquid nitrogen-filled, quartz-windowed Dewar flask placed in the cell chamber. The sample was irradiated and the spectra was recorded on a HP 3329A Intergrator.

The X-ray crystal structure was measured by Dr. Ward on a Picker FACS-I automatic X-ray diffractometer. Sample of 1-benzyl, 2, 3-diphenylindole was dissolved in methanol in a vial. The resulted solution was then allowed to leave in dark for 3 days until crystal obtained. The data collections were performed with MoKα radiation (λ = 0.71073 A) on a Nicolet P3F diffractometer. The structure were solved by direct methods. The X-ray structure is shown in the result section and the crystallographic parameters are presented in the appendix.

C. Isolation and identification of photoproducts

Most of the photoproducts were prepared by irradiation of 0.01 to 0.1 M solutions of the appropriate ketone in the same solvent as the one used in the analysis procedure. The samples were degassed by bubbling argon gas through the solution. Preparative scale photolyses were performed using a Hanovia 450-watt medium pressure lamp filtered through a pyrex tube. Ketones were dissolved with the chosen 60 ml solvent in a 25 x 200 test tube. A quartz cooling jacket was inserted. The sample was degassed by bubbled argon through it about 10 minutes and irradiated at room temperature.

Products from o-(Benzylthio)benzophenone

A solution of 0.02 M o-benzylthiobenzophenone and 0.1 M thiophenol in benzene was irradiated. Nitrogen gas was bubbled through the solution for all the time during the irradiation. A 450-watt medium-pressure lamp around by a pyrex filter was used. The irradiation was stopped after 10% starting ketone disappearance. One product was identified as o-mercaptobenzophenone by comparing its retention time with authentic sample prepared below. Another product was identified as toluene by comparing its retention time with authentic sample.

o-Mercaptobenzophenone (o-HSBP) o-Fluorobenzophenone (Aldrich, 2.0 g) and sodium sulfide (Mallinckrodt, $Na_2S(H_2O)_9$, 2.4 g) and 60 ml DMF were placed in a 100 ml round bottom flask. it was heated and stirred for 20 hours under argon environment. The reaction mixture was poured into ice water (50 ml)and then 15% HCl aqueous solution was added dropwise until the solution turned acidic. It was extracted with 2 x 100 ml ether. The ether layer was washed by 2 x 100 ml 10 % KOH / H2O solution. The water layer was acidified and extracted with 2 x 100 ml ether. Solvent was removed under reduced pressure. A yellow liquid (1.0 g) was obtained. The product was further purified by passing though silica gel column chromatography (hexane / ethyl acetate).

MS (EI) m/e 214 (100), 197, 184, 149, 137, 105,77

IR (CCl_4) v 3084, 3063, 3026, 2565 (SH), 1655 (C=O), 1599, 1448, 1433, 1317, 1298, 937, 923.

1H NMR (300 MHz, CDCl3) δ 4.20 (s, 1H), 7.22 (td, J = 7.51 and J = 1.13 Hz, 1H), 7.30-7.50 (m, 4H), 7.59 (tq, J = 7.54 and J = 1.35 Hz, 1H), 7.78 (m, 2H), 7.86 (dd, J = 7.94 and J = 0.95 Hz, 1H)

^{13}C NMR (75 MHz, CDCl3) δ 125.77, 128.14, 128.66, 130.41, 131.25, 132.15, 133.224, 136.92, 137.54, 139.59, 196.31

o-(Benzylthio)benzophenone (0.5 g) was dissolved in 100 ml benzene. The solution was irradiated 72 hours until 100% ketone conversion by GC. One product was identified as toluene by comparing its retention time with authentic sample.The solvent was removed under reduced pressure. The product was separated by silica gel chromatography column with hexane and ethyl acetate as eluent. The product was identified as thioxanthen-9-one by its spectrometric data. mp 208-210^{o}C.

Thioxanthen-9-one

^{1}H NMR (300 MHZ, $CDCl_3$) δ 7.48(t, J = 6.53 Hz, 1H), 7.58(m, 2H), 8.60 (d, J = 8.06 Hz, 1H)

^{13}C NMR (75 MHz, CDCl3) δ 125.98, 126.30, 129.24, 129.86, 132.26, 137.27, 200.96

IR (CCl_4) ν 1650,1590, 1460, 1340 cm-1

MS (EI) m/e 212 (100), 184, 139, 108, 79, 69

Products from o-(Benzylthio)acetophenone

o-(Benzylthio)acetophenone (3g) in 500 ml purified benzene was irradiated after bubbling with argon for 10 min. The irradiation underwent for 24 hours. A 450-watt medium-pressure lamp around by a pyrex filter was used. Toluene and bibenzyl were identified by comparing the retention times with authentic samples. Two products were collected by flash column

chromatography. The products were identified by their spectrometric data as o-mercaptoacetophenone and 2,2'-dithiodiacetophenone.

o-Mercaptoacetophenone (o-HSAP)

^{1}H NMR (300 MHz,$CDCl_3$) δ 2.61(s, 3H), 4.44 (s, 1H), 7.18(m, 1H), 7.29 (m, 2H),7.86 (d, J = 7.72 Hz, 1H)

^{13}C NMR (75 MHz, CDCl3) δ 27.73, 124.67, 131.64, 131.75, 132.30, 132.71, 137.57, 198.85

MS (EI) m/e 152,137,109

IR (CCl_4) ν 1670, 1590, 1560, 2300, 2690(SH), 3030 cm^{-1}

2,2'-dithiodiacetophenone ((o-APS)$_2$)

1H NMR (300 MHz,CD_3CN) δ 2.45(s,6H), 7.34(dt, J = 1.46 and J = 7.54 Hz, 2H), 7.45(dt, J = 1.44 and J = 8.03 Hz, 2H), 7.74(dd, J = 1.56 and J = 7.78 Hz, 2H), 8.06(dd, J = 1.47 and J = 7.69 Hz, 2H)

^{13}C NMR (75 MHz, CDCl3) δ 27.45, 125.29, 126.47, 131.44, 132.98, 134.54, 140.65, 199.04

MS (EI) m/e 302,151

IR (CCl_4)3050, 2300, 1670, 1590, 1560, 900 cm^{-1}

Products from p-(Benzylthio)benzophenone

p-(Benzylthio)benzophenone (6.2g) was added into a quartz immerssion well. 500 ml 1:1 benzene/hexane mixture was added. Nitrogen gas was bubbled through the solution for all the time during the irradiation. A 450-watt medium-pressure lamp around by a pyrex filter was used. After 1.5 hours irradiation, HPLC shown that 90% of the starting ketone was converted. Two products were detected by GC and HPLC. The solvent was removed under

reduced pressure. A yellow solid was separated by using silica gel column chromatography with hexane/methylene dichloride. The product was identified by its spectroscopic data as 4,4'-dithiodibenzophenone. Another product was identified by comparing the retention time with authentic sample on GC as bibenzyl.

4,4'-dithiodibenzophenone ((p-BPS)$_2$)

^{1}H NMR (300 MHz, CDCl3) δ 7.46 (t, J = 7.90 Hz, 2H), 7.57 (m, 3H), 7.76 (d, J = 8.27 Hz, 4H)

^{13}C NMR (75 MHz, CDCl3) δ 126.07, 128.53, 130.08, 131.07, 132.73, 136.39, 137.55, 141.90, 196.02

MS (EI) m/e 426(M+), 394, 349, 245, 214, 185,152,136,108,77(base)

IR (CCl_4) ν 3089, 3062, 3031, 2957, 2925, 2857, 1662, 1587, 1550, 1273, 937, 922

p-(Benzylthio)benzophenone (0.4422g) was added into 50 ml volumetric flask and benzene was added to the volume. 3 ml of the solution and 0.1 ml HSPh were transferred to each of 10 photolysis tubes . The samples was degassed and sealed using the same degassing procedure described above. The samples was then irradiated at 313 nm for 24 hours at merry-go round apparatus. All the solutions were combined and solvent was removed under reduced pressure. Two products were separated by silica gel chromatography column with hexane / benzene as eluent. One product was identified as 4,4'-dithiodibenzophenone by compare the retention time with the sample above on HPLC and GC. Another product was identified by its spectroscopic data as p-mercaptobenzophenone.

p-Mercaptobenzophenone (p-HSBP)

MS (EI) m/e 214, 137, 105, 99, 77

IR (CCl_4) 3030, 2570 (S=O), 1650 (C=O), 1590, 1490 cm-1

^1H NMR (300 MHz, $CDCl_3$) δ 3.6 (s, 1H), 7.3 (d, J = 7.6 Hz, 2H), 7.5 (d, J = 7.6 Hz, 2H), 7.6 (t, J = 7.2 Hz, 1H), 7.7 (d, J = 7.2 Hz, 2H), 7.8 (d, J = 7.6 Hz, 2H)

Product from p-(t-Butylthio)benzophenone

0.02 M solution of p-(t-butylthio)benzophenone in benzene was irradiated. Nitrogen gas was bubbled through the solution for all the time during the irradiation. A 450-watt medium-pressure lamp around by a pyrex filter was used. The irradiation was stopped after 90% starting ketone disappearance. One product was identified as 4,4'-dithiodibenzophenone by comparing its retention time with authentic sample on HPLC.

Product from p-(sec-Butylthio)benzophenone

0.02 M solution of p-(sec-butylthio)benzophenone in benzene was irradiated. Nitrogen gas was bubbled through the solution all the time during the irradiation. A 450-watt medium-pressure lamp around by a pyrex filter was used. The irradiation was stopped after 90% starting ketone disappearance. One product was identified as 4,4'-dithiodibenzophenone by comparing its retention time with authentic sample on HPLC.

Products from p-(Benzylthio)acetophenone

4-(Benzylthio)acetophenone (1g) and HSPh (1g) were dissolved in benzene (40 ml) in a test tube. The test tube was sealed with a rubber stopper and oxygen was removed by bubbling argon through the solution for 10 minutes. The reaction mixture was irradiated for 24 hours. A 450-watt medium-pressure lamp around by a pyrex filter was used. Toluene and bibenzyl were identified by comparing the retention time with authentic samples on GC. The solvent was removed from the reaction mixture under reduced pressure. A yellow solid was separated by silica gel column chromatography. The product was identified by its spectroscopy data as 4,4'-dithiodiacetophenone.

4,4'-dithiodiacetophenone ((p-APS)2)

^{1}H NMR (300 MHz, CDCl3) δ 2.55 (s, 3H), 7.54 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H)

^{13}C NMR (75 MHz, CDCl3) δ 26.34, 126.25, 129.27, 135.95, 142.52, 197.41

MS 302(M+), 287, 270, 255, 184, 136, 123, 108, 43(base)

IR (CCl_4) ν 3075, 3062, 3031, 2957, 2925, 2857, 1689, 1587, 1560, 1356, 1259, 1012, 954

Product from p-Bromomethylacetophenone

The solution of p-bromomethylacetophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylacetophenone was identified by comparing the retention time with authentic sample.

Product from p-(Phenylthio)methylacetophenone

The solution of p-(phenylthio)methylacetophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylacetophenone was identified by comparing the retention time with authentic sample.

Product from m-(Phenylthio)methylbenzophenone

The solution of m-(phenylthio)methylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. m-Methylacetophenone was identified by comparing the retention time with authentic sample.

Product from m-Chloromethylbenzophenone

The solution of m-chloromethylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. m-Methylacetophenone was identified by comparing the retention time with authentic sample.

Product from m-(Phenylthio)methylacetophenone

The solution of m-(phenylthio)methylacetophenone and thiophenol was irradiated at the same condition as the analysis procedure. m-Methylacetophenone was identified by comparing the retention time with authentic sample.

Product from p-Bromomethylbenzophenone

The solution of p-bromomethylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylbenzophenone was identified by comparing the retention time with authentic sample.

Product from p-(Phenylthio)methylbenzophenone

The solution of p-phenylthiomethylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylbenzophenone was identified by comparing the retention time with authentic sample.

Product from p-(t-Butylthio)methylbenzophenone

The solution of p-(t-butylthio)methylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylbenzophenone was identified by comparing the retention time with authentic sample.

Product from p-(sec-Butylthio)methylbenzophenone

The solution of p-(sec-butylthio)methylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylbenzophenone was identified by comparing the retention time with authentic sample.

Product from p-Chloromethylbenzophenone

The solution of p-chloromethylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylbenzophenone was identified by comparing the retention time with authentic sample.

Product from p-(Phenylsulfinyl)methylbenzophenone.

The solution of p-(phenylsufinyl)methylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-

Methylbenzophenone was identified by comparing the retention time with authentic sample.

Product from p-(Phenylsulfonyl)methylbenzophenone.

The solution of p-(phenylsufonyl)methylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylbenzophenone was identified by comparing the retention time with authentic sample.

Product from p-(n-Butylthio)methylbenzophenone.

The solution of p-(n-butylthio)methylbenzophenone and thiophenol was irradiated at the same condition as the analysis procedure. p-Methylbenzophenone was identified by comparing the retention time with authentic sample.

Products from o-Benzoyl-N,N-dibenzylaniline hydrochloride

0.2g o-Benzoyl-N,N-dibenzylaniline hydrochloride was dissolved in 10 ml CH_3CN in a 25 x 200 test tube with a rubber stopper on it. Argon gas was bubbled through the solution to remove the oxygen for 10 minutes. The sample was irradiated by using a 450-watt medium-pressure lamp around by a pyrex filter and monitored by HPLC for 24 hours. 2 products were detected and

separated by silica gel column chromatography with CH_2Cl_2/hexane as eluent. One product with less retention time was identified as 1-benzyl,2,3-diphenylindole by its spectroscopic data.

1-Benzyl,2,3-diphenylindole ($BzPh_2$-indole) mp 155-157 ^oC.

IR (CCl_4) ν 3089, 3065, 3034,2917, 2863, 1604, 1496, 1462, 1363, 1215,1030;

MS (FAB) 359 (100), 268, 91

^1H NMR (500 MHz, CD_3CN) δ 5.3 (s,2H), 6.9(d, J = 7.33 Hz, 2H), 7.2-7.4 (m,16H), 7.7(dt, J = 7.54 and J < 1.0 Hz,1H)

^{13}C NMR (75 MHz, CDCl3) δ 47.48, 110.63, 111.55, 115.80, 119.87, 120.57, 122.52, 125.75, 126.30, 127.34, 127.55, 128.34, 128.57, 128.85, 130.10, 131.27, 131.98, 135.32, 137.19, 138.10, 138.33

Spectroscopic data for X-ray structure is given in table 72 in Appendix part.

Product from o-Benzoyltrimethylanilinium tetrafluoroborate

0.1 g o-benzoyltrimethylanilinium tetrafluoroborate was placed in a test tube. 10 ml CH3CN was added. Argon was bubbled through the solution to remove the oxygen for 10 min. The reaction mixture was irradiated for 2 hours until 95% conversion of starting ketone. The solvent was removed under reduced pressure. White crystals were recrystallized from methanol. The product was identified by its spectroscopic data as 1,1-dimethyl,3-hydroxy,3-phenyldihydroindolium tetrafluoroborate.

1,1-dimethyl,3-hydroxy,3-phenyldihydroindolium tetrafluoroborate (Me_2Ph-Indole) mp 194-195 ^oC.

IR (KBr) ν 3483 (OH, strong), 1477, 1466, 1076.

^1H NMR (500 MHz, CD_3CN) δ 7.8(d(broad), J = 8.19 Hz, 1H), 7.7 (td, J = 8.19 and J = 1.29 Hz, 1H), 7.6 (td, J = 7.54 and J = 1.08 Hz, 1H), 7.5-7.4(m, 5H), 7.3

(dd, J = 1.08 and J = 7.76 Hz, 1H), 4.77 (d, J = 1.29 Hz, OH), 4.38 (d, J = 12.50 Hz, 1H, CH_2), 4.11 (d(broad), J = 12.71 Hz, 1H, CH_2), 3.7 (s, CH_3), 3.6 (s, CH_3). Decoupling experiment shows that 4.11 is coupled with 4.38 and 4.77, addition of D_2O to the sample causes disappearance of 4.8 and sharping 4.1
^{13}C NMR (125 MHz, CD_3CN): δ 148.7, 141.2, 139.6, 133.1, 132.9, 129.8, 129.7, 127.5, 127.3, 118.7, 81.5 (CH_2), 81.3 (COH), 59.7 (CH_3), 55.8 (CH_3)
MS (FAB, MF) 240 (positive).

Product from p-bromobenzophenone.

The solution of 0.02M p-bromobenzophenone and 0.05 M thiophenol was irradiated at 313 nm. Benzophenone was identified by comparing the GC retention time with authentic sample.

Product from 3-bromo-4-methoxyacetophenone.

The solution of 0.02M 3-bromo-4-methoxyacetophenone and 0.05 M thiophenol was irradiated at 313 nm. p-methoyxacetophenone was identified by comparing the HPLC retention time with authentic sample.

D Molecular Mechanics Calculations

The calculations were performed on an Macintosh II computer. PCMODEL version 2 was used for molecular mechanics calculations. This program uses MMX force field with the pi VESCF calculations.

MMX is an advanced version of MM2 force field by N. L. Allinger and pi VESCF which is developed from MMP1(QCPE-318) also by N. L. Allinger. These modifications were completed by J. J. Gajewski and K. E. Gilbert. This program was distributed by Serena Software, Box 3076, Bloomigton, IN 47402-3076.

One of the two available dihedral angles was used to obtain the minimized conformations. The dihedral drive was performed by calculating each dihedral angle rotating around a certain bond. The calculation was done in the following process. The structures needed to calculated were made with PCMODEL input mode. All the aromatic carbons, carbonyl carbonIn and carbonyl oxygen were selected as pi atoms. Sulfur atom was not selected as pi atom. In the input mode, the bond and angles for rotation are chosen by select D-DRV. Calculations were done in the minim mode. Parameters were entered by choosing the following choices.

1. Electrostatic interaction (ndc = 4 mmx88 only).
2. Set dielectric constant 1.5.
3. Are there any constants to be read in? n
4. Dihedral angle is endocyclic? n
5.Set for planar pi-system? n
6.singlet rhf calc.
7. Start geometry optimization after full SCF.

After calculation, enter 0 to save all the structures calculated and minimized energies in a named file.

APPENDIX

This section contains the raw experimental data, such as quantum yield measurements and Stern-volmer quenching studies. Analysis conditions, concentrations of the materials used are provides.

Table 19. Values of the Response Factors in GC Analysis.

Std / Compound	Column /Condition	R.F.
C_{16} / actophenone	DB-wax / 120°C	2.23
C_{16} / dibenzyl	DB-1 / 150°C	1.28
C_7H14 / toluene	DB-1 / RT	1.09
C_{20} / o-BzSAP	DB-1[a]	1.997
C_{20} / o-HSAP	DB-1[a]	3.398
C13Ph / o-HSBP	DB-1 /180°C	2.60
C24 / o-BzSBP	DB-1 /230°C	1.65
C_{26} / p-MeBP	DB-210[b]	1.336
C_{26} / p-BuSCH2BP	DB-210[b]	1.64

[a] int T130° C,final T 155°C, rate 12°C / min. [b] init T 80°C, init col hold time 2.00 min, final T #1: 170°C, rate:50°C / min.,hold time 4.00min. Final temp #2: 230°C, rate: 50°C / min., hold time: 21 min.

Table 22. Values of the Response Factors in HPLC Analysis.

Std / Compound	Column	R. F.
MeBz / p-BzSBP	Microsorb Si[a]	0.154
MeBz / $(p\text{-BPS})_2$	Microsorb Si[a]	0.0364
MeBz / p-BzSAP	Microsorb Si[b]	0.192
MeBz / $(p\text{-APS})_2$	Microsorb Si[b]	0.0461
Cl_2CNPh / $PhSO_2CH_2BP$	Microsorb Si[c]	0.0367
Cl_2CNPh / p-MeBP	Microsorb Si[d]	0.0337
Cl_2CNPh / $PhSOCH_2BP$	Microsorb Si[f]	0.025
$C_{10}Bz$ / o-BzNBP:HCl	Reverse phase CN HPLC[e]	0.0142
$C_{10}Bz$ / 1-Bz,2,3-Ph_2indole	Reverse phase CN HPLC[e]	0.066
C_8Bz/AP	Microsorb Si HPLC[d]	1.09
MeBz/p-MeAP	Microsorb Si HPLC[d]	0.77
MeBz/p-MeBP	Microsorb Si HPLC[d]	0.0719
MeBz/m-MeAP	Microsorb Si HPLC[d]	1.35
MeBz/m-MeBP	Microsorb Si HPLC[g]	0.175
MeBz/p-$BrCH_2AP$	Microsorb Si HPLC[d]	0.156
MeBz/p-$PhSCH_2AP$	Microsorb Si HPLC[d]	0.13
MeBz / p-$PhSCH_2BP$	Microsorb Si HPLC[d]	0.043
MeBz/p-t-$BuSCH_2BP$	Microsorb Si HPLC[d]	0.0575
MeBz/p-sec-BuSCH2BP	Microsorb Si HPLC[d]	0.0687
MeBz/m-$PhSCH_2AP$	Microsorb Si HPLC[d]	0.181
MeBz/m-$ClCH_2BP$	Microsorb Si HPLC[g]	0.188
MeBz/m-$PhSCH_2BP$	Microsorb Si HPLC[d]	0.144
MeBz/p-$ClCH_2BP$	Microsorb Si HPLC[d]	0.0854

Table 20 (Cont'd.).

MeBz/p-$BrCH_2BP$	Microsorb Si HPLC[d]	0.0462
Mebz/p-t-BuSBP	Microsorb Si HPLC[a]	0.0567
MeBz/$(p\text{-SBP})_2$	Microsorb Si HPLC[a]	0.0359
MeBz/$(p\text{-SBP})_2$	Microsorb Si HPLC[d]	0.0366
MeBz/p-sec-BuSBP	Microsorb Si HPLC[d]	0.176
MeBz/o-BzSAP	Microsorb Si HPLC[b]	0.113
MeBz/$(o\text{-APS})_2$	Microsorb Si HPLC[b]	0.074

[a] Hexane /ethyl acetate (95 / 5), Rate: 1.5ml / min. @ 270nm. [b] Hexane /ethyl acetate (90 / 10), Rate: 1.5ml / min., @ 270nm.

[c]

Time	Flow Rate	Hexane%	Duration Tme
0	1.0	100	0.5
6	1.5	85	0.5
16	1.5	100	0.5
30	1.0	100	0.5
end		@270 nm	

[d] Hexane/AcOEt (95/5) 1.0 ml/min. @270 nm. [e] H_2O / CH_3OH (5 / 95), 1.0 ml / min., @270 nm.

[f]

Time	Flow Rate	Hexane%	Duration Tme
0	1.0	98	0.5
8	1.0	50	0.5
25	1.0	98	0.5
31	end	@270 nm	

[g] Hexane/AcOEt (97/3) 1.0 ml/min. @270 nm.

Table 21. Quenching of 4,4'-Dithiodibenzophenone Formation upon Irradiation of p-(Benzylthio)benzophenone.

$Kq\tau = 125$

HPLC analysis: Ultrasphere Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Sample	[Naphethalene] x 10^3	[(p-SBP)$_2$ / MeBz]$_A$	Φ_0 / Φ
#1	0	1.172	1.0
#2	4.009	0.773	1.516
#3	8.019	0.597	1.963
#4	12.03	0.477	2.457
#5	16.04	0.386	3.036

[p-BzSBP] = 0.01989M, [MeBz] = 0.07051M, 2 hours, 366nm.

Table 22. Quantum Yields for Irradiation of p-(Benzylthio)benzophenone.

Compound	(Compound / Std)$_A$	Concentration	Φ
Dibenzyl	0.495	0.00109	0.15
p-BzSBP	2.821	0.01686	0.40
(p-BPS)$_2$	0.855	0.00121	0.17

[p-BzSBP] = 0.01973 M. [MeBz] = 0.03881 M. [C_{16}] = 0.001722 M. 3 hours, 313 nm. RF: MeBz/p-BzSBP 0.154; C_{16}/Dibenzyl 1.28; MeBz/(p-BPS)$_2$ 0.0364. VP actinometer: [VP] = 0.1004 M. [C_8Bz] = 0.00604 M. (AP/C_8Bz)$_A$ = 0.358. [AP] = 0.00236 M. Io = 0.00714 ein l^{-1}.

Table 23. Quantum Yields for Irradiation of p-(t-Butylthio)benzophenone.[a]

HPLC analysis: Microsorb-Si

Hexane / Ethyl acetate 95: 5 @270 nm

Flow Rate 1.5 ml / min.

Compound	(Compound / MeBz)$_A$	Concentration	Φ
p-t-BuSBP	6.553	0.01803	0.37
(p-SBP)$_2$	0.732	0.00128	0.18

[a][p-t-BuSBP] = 0.02061 M, [C_8Bz] = 0.04854 M, 3 hours, 313 nm.

RF: MeBz/p-t-BuSBP 0.0567; MeBz/ (p-SBP)$_2$ 0.0359.

VP actinometer: [VP] = 0.09766 M. [C_8Bz] = 0.00797 M.

(AP / C_8Bz)$_A$ =0.263 M. [AP] = 0.00228 M Io = 0.00692 ein l^{-1}.

Table 24. Quenching of 4,4'-Dithiodibenzophenone Formation upon Irradiation of p-(t-Butylthio)benzophenone

HPLC analysis: Microsorb-Si

Hexane / ethyl acetate,@ 270nm, Program

	Time	Flow Rate	Hexane%	Duration time
$kq\tau = 683$	0	1.3	99	0.5
	1	1.3	98	0.5
	6	1.3	85	0.5
	13	1.3	100	0.5
	20	end		

Sample	[Naphethalene]	$[(p\text{-SBP})_2/MeBz]_A$	Φ_0/Φ
#1	0	1.921	1.0
#2	0.0125	1.090	1.76
#3	0.00094	1.265	1.52
#4	0.00218	0.748	2.57
#5	0.00359	0.597	3.22
#6	0.00531	0.398	4.83
#7	0.00624	0.348	5.52
#8	0.00874	0.287	6.69

[p-t-BuSBP] = 0.01058 M, [MeBz] = 0.00979M, 1 hour, 366 nm

Table 25. Quenching of 4,4'-Dithiodibenzophenone Formation upon Irradiation of p-(sec-Butylthio)benzophenone.

$K_q\tau = 7669$

HPLC analysis: Microsorb Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Sample	[Naphethalene] x 10^3	[(p-SBP)$_2$ / MeBz]$_A$	Φ_0 / Φ
#1	0	0.248	1.0
#2	0.0349	0.208	1.19
#3	0.0698	0.157	1.58
#4	0.116	0.134	1.85
#5	0.233	0.0895	2.77
#6	0.466	0.0613	4.05
#7	0.698	0.0478	5.19
#8	0.931	0.0346	6.82
#9	1.16	0.0343	7.22
#10	1.40	0.0329	7.54

[p-sec-BuSBP] = 0.01003 M, [MeBz] = 0.00992 M, 24 hours, 366nm

Table 26. Quantum Yield for Irradiation of p-(sec-Butylthio)benzophenone[a]

Compound	(Compound / Std)$_A$	Concentration	Φ
p-sec-BuSBP	5.678	0.00917	0.019[b]
$(p\text{-BPS})_2$	0.209	0.0000702	0.0052[c]

[a][p-sec-BuSBP] = 0.00979 M. [MeBz] = 0.00918 M.

RF: MeBz/ p-sec-BuSBP 0.176; MeBz/ $(p\text{-BPS})_2$ 0.0366.

VP actinometer: [valerophenone] = 0.1009 M. [C_8Bz] = 0.00626 M.

[b]30 hours, 313 nm, $(AP/C_8Bz)_A$ = 1.552, $[AP]_{total}$ = 0.01059 M.

Io = 0.0321 ein l^{-1}.

[c]10 hours, 313 nm, $(AP/C_8Bz)_A$ = 0.0658, [AP]= 0.00449 M. Io = 0.0136 ein l^{-1}.

Table 27. Quenching of 4,4'-dithiodiacetophenone Formation upon Irradiation of p-(Benzylthio)acetophenone

$K_q\tau = 69.9$

HPLC analysis: Ultrasphere Si
Hexane / ethyl acetate (90 : 10)
1.5 ml / min, @ 270nm

Sample	[1-methylnaphethalene]	$((p\text{-APS})_2 / MeBz)_A$	Φ_0 / Φ
#1	0	1.328	1.0
#2	0.004501	1.055	1.26
#3	0.01252	0.707	1.88
#4	0.01660	0.618	2.15
#5	0.02672	0.467	2.84

[p-BzSAP] = 0.008629 M, [methyl benzoate] = 0.008144, 3 hours, 366nm

Table 28. Quantum Yield for Irradiation of p-(Benzylthio)acetophenone in Benzene[a]

Compound	$(Compound / Std)_A$	[Compound]	Φ
dibenzyl	0.434	0.000927	0.16
p-BzSAP	2.166	0.01668	0.47
$(p\text{-APS})_2$	0.740	0.00137	0.24

[a][p-BzSAP] = 0.01944 M. $[C_{16}]$ = 0.001669 M, [MeBz] = 0.0401 M, 3 hours, 313 nm. RF: C_{16}/dibenzyl 1.28; MeBz/p-BzSAP 0.192; MeBz/$(p\text{-APS})_2$ 0.0461. VP actinometer: [valerophenone] = 0.1004 M. $[C_8Bz]$ = 0.00604 M. $(AP/C_8Bz)_A$ = 0.287. [AP] = 0.00189 M. Io = 0.00573 ein l^{-1}.

Table 29. Quenching of Toluene Formation upon Irradiation of o-(Benzylthio)benzophenone.

$K_q\tau = 2.07 \pm 0.1$ GC analysis: 1400 varien Gas Chromatography DB-1 magbor column, Room temperature

$[Q]^a$	(Toluene / C_7)A	Φ_0 / Φ	$[Q]^b$	(Toluene / C_7)A	Φ_0 / Φ
0	0.480	1.0	0	0.244	1.0
0.0646	0.422	1.14	0.1986	0.176	1.386
0.1835	0.349	1.37	0.441	0.124	1.968
0.2792	0.321	1.50	0.516	0.115	2.122
0.3136	0.301	1.59	0.672	0.0966	2.526
0.3946	0.268	1.79	0.790	0.0924	2.641
0.4837	0.244	1.97			

[a]Run 1: [o-BzSBP] = 0.01995 M, [C_{7H7}] = 0.001738 M, [HSPh] = 0.09876M, 43 hours, 366nm

[b]Run 1: [o-BzSBP] = 0.01922 M, [C_{7H7}] = 0.001703 M, [HSPh] = 0.04797 M, 6 x 24 hours, 366nm

Table 30. Quantum Yields for Irradiation of o-(Benzylthio)benzophenone in Benzene[a]

Compound	(Compound / Std)$_A$	[Compound]	Φ
toluene	0.480	0.000909	0.0041
o-BzSBP	2.22	0.01905	0.0041
o-HSBP	0.164	0.000567	0.0026

[a][o-BzSAP] = 0.01995 M. [C_7] = 0.001738 M, [C_{24}] = 0.005386 M, [C_{13}Ph] = 0.001351 M, [HSPh] = 0.09876 M, 43 hours, 366 nm.

RF: C_7/toluene 1.09; C_{24}/o-BzSBP 1.65; C_{13}Ph/o-HSBP 2.60.

VP actinometer: [valerophenone] = 0.0902 M. [C_{16}] = 0.00662 M.

(AP/C_{16})$_A$ = 2.703. [AP] = 0.0399 M, Io = 0.22.

Table 31. Quenching of Dibenzyl Formation upon Irradiation of o-(Benzylthio)acetophenone at 366nm

$K_q\tau = 11.6$

GC analysis: 3400 varien Gas Chromatography

DB-210 magbor column

Program:

Initial column temp.: 80° C

Initial col. hold time: 5 min.

Final col. temp. 200° C

Rate: 8.0°C / min

Sample	[1-Methylnaphethalene]	(Dibenzyl / C_{20})$_A$	Φ_0/Φ
#1	0	0.311	1.0
#2	0.02127	0.241	1.29
#3	0.04106	0.186	1.67
#4	0.06007	0.175	1.78
#5	0.08373	0.154	2.02
#6	0.1077	0.137	2.27

[o-BzSAP] = 0.02079M, [C_{20}] = 0.001227M, 366 nm.

Table 32. Quantum Yield for Irradiation of o-(Benzythio)acetophenone[a]

Compound	(Compound / Std)$_A$	Concentration	Φ
Dibenzyl	0.3046	0.000703	0.018
o-BzSAP	2.5644	0.008650	0.036
(o-APS)$_2$	0.344	0.000760	0.019

[a][o-BzSAP] = 0.01007 M. [MeBz] = 0.02985 M, [C_{16}] = 0.001802 M.18 hours at 313 nm. RF: C_{16}/Dibenzyl 1.28; MeBz/(o-APS)$_2$ 0.074; MeBz/o-BzSAP 0.113. [Valerophenone] = 0.09766 M. [C_8Bz] = 0.00797 M. (AP/C_8Bz)$_A$ = 1.515. [AP] = 0.01316 M, Io = 0.0399 ein l^{-1}.

Table 33. Quantum Yield for Irradiation of o-(Benzythio)acetophenone[a]

Compound	(Compound / Std)$_A$	Concentration	Φ
o-BzSAP	8.130	0.017696	0.081
o-APSH	0.9364	0.00347	0.064
Toluene	2.265	0.00437	0.081

[a][o-BzSAP] = 0.02208 M. [C_7] = 0.001772 M. [C_{20}] = 0.001090 M
[HSPh] = 0.04927 M, 17 hours at 313 nm
RF: C_7/toluene 1.09; C_{20}/o-APSH 3.390; C_{20}/o-BzSAP 1.997.
[Valerophenone] = 0.0997M. [C_{16}] = 0.00926M. (AP/C_{16})$_A$ = 0.867.
[AP] = 0.0179 M. Io = 0.0543 ein l^{-1}.

Table 34. Quenching of formation of p-Methylbenzophenone from Irradiation of p-(Phenylthio)methylbenzophenone[a]

$K_q\tau = 0.74$

GC analysis: 3400 varien Gas Chromatography

DB-210 magbor column

Initial column temp.: 80° C, Initial col. hold time: 2 min.

Final col. temp. #1: 170° C, Rate: 50.0°C/min, hold time: 4 min.

Final col. temp. #2: 220° C, Rate: 50.0°C/min, hold time: 21 min.

Sample	[Naphethalene]	(p-MeBP / C_{26})$_{area}$	Φ_0/Φ
#1	0	0.480	1.0
#2	0.260	0.407	1.18
#3	0.641	0.332	1.45
#4	0.809	0.290	1.66
#5	0.989	0.267	1.80
#6	1.183	0.240	2.00
#7	1.420	0.233	2.06
#8	1.566	0.221	2.17
#9	1.841	0.209	2.30

[a][p-PhSCH$_2$BP] = 0.005775M, [C_{26}] = 0.001774M, [HSPh] = 0.01454M, 1 hour at 366nm

Table 35. Quantum Yields for Irradiation of p-(Phenylthio)methybenzophenone[a]

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Compound	$(p\text{-}PhSCH_2BP / MeBz)_A$	Concentration	Φ
$p\text{-}PhSCH_2BP$	21.02	0.00869	0.27

[a][$p\text{-}PhSCH_2BP$] = 0.00982 M, [MeBz] = 0.00961 M, [HSPh] = 0.0514 M, 2.5 hours at 313 nm. RF: MeBz/$p\text{-}PhSCH_2BP$ 0.043.
VP actinometer: [VP] = 0.1003 M. $[C_8Bz]$ = 0.00700 M. $(AP/C_8Bz)_A$ = 0.1836.
[AP] = 0.00140 M, Io = 0.00425 ein l^{-1}.

Table 36. Quantum Yield for Irradiation of p-(Phenylthio)methylbenzophenone[a]

GC analysis: 3400 varien Gas Chromatography
DB-210 magbor column
Initial column temp.: 80° C, Initial col. hold time: 2 min.
Final col. temp. #1: 170° C, Rate: 50.0°C/min, hold time: 4 min
Final col. temp. #2: 230° C, Rate: 50.0°C/min, hold time: 21 min

Compound	$(Compound / C_{26})_A$	[Compound]	Φ
PhSSPh	0.6062	0.001296	0.16
$p\text{-}PhSCH_2BP$	1.1057	0.00317	0.27
p-MeBP	0.6559	0.00161	0.19

[a][$p\text{-}PhSCH_2BP$] = 0.005413M, $[C_{26}]$ = 0.001836M, [HSPh] = 0.009073M.
RF: C_{26}/ $p\text{-}PhSCH_2BP$ 1.56; C_{26}/p-MeBP 1.34; C_{26}/PhSSPh1.164; 10 min., 366nm:

Table 37. Effect of Thiophenol Concentration on Quantum Yield for Irradiation of p-(Phenylthio)methybenzophenone[a]

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Sample	[HSPh]	(p-MeBP/MeBz)$_A$	[p-MeBP]	Φ
#1	0	0.024	0.0000166	0.0091
#2	0.000379	0.276	0.000191	0.105
#3	0.000759	0.397	0.000274	0.136
#4	0.00152	0.606	0.000419	0.230
#5	0.00340	0.483	0.000334	0.184
#6	0.0514	0.672	0.000464	0.255
#7	0.1029	0.687	0.000475	0.261
#8	0.5170	0.564	0.000390	0.215

[a][p-PhSCH$_2$BP] = 0.00982 M, [MeBz] = 0.00961 M, 1 hours, 313 nm, actinometer: [VP] = 0.1003 M. [C$_8$Bz] = 0.00700 M. [AP] = 0.000600 M

Table 38. Quantum Yields for Irradiation of p-(t-Butylthio)methylbenzophenone[a]

HPLC annalysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)$_A$	Concentration	Φ
p-t-BuSCH$_2$BP	18.26	0.009880	0.35
p-MeBP	0.806	0.000545	0.18

[a][p-t-BuSCH$_2$BP] = 0.01095 M, [MeBz] = 0.00941M, [HSPh] = 0.0681 M, 2 hours, 313 nm. RF: MeBz/p-MeBP 0.0.0719; MeBz/p-t-BuSCH$_2$BP 0.0575. VP actinometer: [VP] = 0.1003 M. [C$_8$Bz] = 0.00700 M. (AP/C$_8$Bz)$_A$ = 0.134. [AP] = 0.00102 M. Io = 0.00310 ein l^{-1}.

Table 39. Quenching of p-Methylbenzophenone Formation upon Irradiation of p-(t-Butylthio)methylbenzophenone.

$K_q\tau = 27.6$

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Sample	[Naphethalene]	(p-MeBP/MeBz)$_A$	Φ_0/Φ
#1	0	0.749	1.0
#2	0.0146	0.531	1.41
#3	0.0315	0.412	1.82
#4	0.0453	0.347	2.16
#5	0.0663	0.276	2.71
#6	0.0810	0.228	3.29

[p-t-BuSCH$_2$BP] = 0.00879 M, [MeBz] = 0.00985M, [HSPh] = 0.00492 M, 1 hour, 366 nm

Table 40. Quantum Yields for Irradiation of p-(sec-Butylthio)methylbenzophenone[a]

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)$_A$	Concentration	Φ
p-sec-BuSCH$_2$BP	8.441	0.005582	0.38
p-MeBP	1.214	0.000843	0.21

[a][p-2-BuSCH$_2$BP] = 0.007114 M, [MeBz] = 0.00966 M, [HSPh] = 0.0732 M, 2.5 hours, 313 nm. RF: MeBz/p-sec-BuSCH$_2$BP 0.0687; MeBz/p-MeBP 0.0719. VP actinometer: [VP] = 0.1003 M. [C$_8$Bz] = 0.00700 M. (AP/C$_8$Bz)$_A$ = 0.1728. [AP] = 0.00132 M, Io = 0.00400 ein l^{-1}.

Table 41. Quenching of p-Methylbenzophenone Formation upon Irradiation of p-(sec-Butylthio)methylbenzophenone

$K_q\tau = 16.9$

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Sample	[Naphethalene]	(p-MeBP/MeBz)$_A$	Φ_0/Φ
#1	0	1.063	1.0
#2	0.0694	0.474	2.24
#3	0.1075	0.379	2.80
#4	0.1501	0.305	3.49
#5	0.1726	0.268	3.97

[p-2-BuSCH$_2$BP] = 0.0105 M, [MeBz] = 0.00931 M, [HSPh] = 0.0747 M, 2 hour, 366 nm

Table 42. Quenching of p-Methylbenzophenone Formation upon rradiation of p-(n-Butylthio)methylbenzophenone

$Kq\tau = 16.5$

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Sample	[Naphethalene]	(p-MeBP/MeBz)$_A$	Φ_0/Φ
#1	0	1.931	1.0
#2	0.0585	0.981	1.97
#3	0.0888	0.797	2.42
#4	0.1186	0.646	2.99
#5	0.1503	0.553	3.49
#6	0.1947	0.458	4.22

[p-BuSCH$_2$BP] = 0.0150 M, [MeBz] = 0.00879 M, [HSPh] = 0.0740 M, 2 hour, 366 nm

Table 43. Quantum Yield of Irradiation of p-(n-Butylthio)-methylbenzophenone

Compound	(Compound / C_{26})$_A$	Concentration	Φ
p-BuSCH$_2$BP	0.936	0.00464	0.36
p-MeBP	0.350	0.00141	0.20

[p-BuSCH$_2$BP] = 0.00716 M, [C_{26}] = 0.00302M, [HSPh] = 0.0133M, 2 hours, 366nm. RF: C_{26}/p-MeBP 1.336; C_{26}/p-BuSCH$_2$BP 1.64.

VP actinometer: [VP] = 0.09978 M. [C_{16}] = 0.006352 M. (AP/C_{16})$_A$ = 0.1391.

[AP] = 0.00197 M

Table 44 . Quantum Yield of Irradiation of p-Bromomethylbenzophenone

HPLC analysis: Microsorb-Si

Hexane / Ethyl acetate (95 : 5)

1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)$_A$	Concentration	Φ
p-BrCH$_2$BP	33.50	0.0159	0.45
p-MeBP	2.78	0.00206	0.30

[p-BrCH$_2$BP] = 0.0190 M, [MeBz] = 0.0103 M, [HSPh] = 0.0960 M.

2 hours, 313 nm. RF: MeBz/p-BrCH$_2$BP 0.0462; MeBz/p-MeBP 0.0719.

VP actinometer: [VP] = 0.1005 M. [C_{16}] = 0.0075 M. (AP/C_{16})$_A$ = 0.1344.

[AP] = 0.00224 M, Io = 0.00681 ein l^{-1}.

Table 45. Quenching of p-MethylbenzophenoneFormation upon Irradiation of p-Chloromethylbenzophenone.

$k_q\tau = 11$

GC annalysis: 3400 varien Gas Chromatography

DB-210 magbor column

Initial column temp.: 80° C, Initial col. hold time: 2 min.

Final col. temp. #1: 160° C, Rate: 40.0°C/min, hold time: 3.5min.

Final col. temp. #2: 1800° C, Rate: 40.0°C/min, hold time: 10 min.

Sample	[Naphethalene]	(PhSSPh / C_{26})$_A$	Φ_0/Φ
#1	0	0.889	1.0
#2	0.037	0.577	1.54
#3	0.088	0..364	2.44
#4	0.161	0..275	3.23
#5	0.378	0..160	5.56
#6	0.524	0.128	6.95
#7	0.650	0.109	8.16
#8	0.733	0.0906	9.81

[p-$ClCH_2BP$] = 0.00746M, [C_{24}] = 0.001796M, [HSPh] = 0.0171M. 50 min, 366nm

Table 46. Quantum Yield of Irradiation of p-Chloromethylbenzophenone

HPLC analysis: Microsorb-Si

Hexane / ethyl acetate (95 : 5)

1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)$_A$	Concentration	Φ
p-ClCH$_2$BP	13.73	0.0220	0.48
p-MeBP	0.670	0.000906	0.48

[p-ClCH$_2$BP] = 0.0229 M, [MeBz] = 0.0188M, [HSPh] = 0.0519 M,

1 hour, 313 nm, RF: MeBz/p-ClCH$_2$BP 0.0854; MeBz/p-MeBP 0.0719.

VP actinometer: [VP] = 0.1016 M. [C$_8$Bz] = 0.01978 M. (AP/C$_8$Bz)$_A$ = 0.0288.

[AP] = 0.000622 M, Io = 0.00188 ein l^{-1}.

Table 47. Quantum Yield of Irradiation of p-Phenylsulfinylmethylbenzophenone

HPLC analysis: Microsorb Si.

For p-MeBp: Hexane : EtOAc 95:5, 1.0 ml / min,@270 nm

For p-PhSCH$_2$BP: @270 nm Program

Time	Duration time	Flowrate	Hexane	:	EtOAc
0	0.5	1.0	98	:	2
8	2	1.0	50	:	50
25	1	1.0	98	:	2
31	end				

Compound	(Compound / $Cl_2CNPh)_A$	Concentration	Φ
p-PhSOCH$_2$BP	4.199	0.00271	0.33
p-MeBP	5.358	0.00466	0.35

[p-PhSOCH$_2$BP] = 0.00725 M, [Cl_2CNPh] = 0.0258M, [HSPh] = 0.0909M.

4 hours, 366nm. RF: Cl_2CNPh/p-PhSOCH$_2$BP 0.025;Cl_2CNPh/p-MeBP 0.0337.

VP actinometer: [VP] = 0.09978 M. [C_{16}] = 0.006352 M. $(AP/C_{16})_A$ = 0.02127.

[AP] = 0.00301 M.

Table 48. Quenching of p-Methylbenzophenone Formation upon Irradiation of p-Phenylsulfonylmethylbenzophenone.

HPLC analysis: Microsorb-Si

$K_q\tau = 515$ Hexane / ethyl acetate (95 : 5)

$\Phi_{p\text{-MeBP}} = 0.29$ 1.0 ml / min, @ 270nm

Sample	[Naphethalene]	(p-MeBP / $Cl_2CNPh)_{area}$	Φ_0/Φ
#1	0	2.541	1.0
#2	0.000922	1.605	1.58
#3	0.00184	1.292	1.97
#4	0.00277	1.034	2.46
#5	0.00369	0.895	2.84
#6	0.00461	0.739	3.44
#7	0.00553	0.653	3.89
#8	0.00646	0.532	4.77
#9	0.00738	0.560	4.54

[p-$PhSO_2CH_2BP$] = 0.00498M, [Cl_2CNPh] = 0.0153M, [HSPh] = 0.0140M. 1.5 hours, 366nm.

Table 49. Quantum Yield of Irradiation of p-Phenylsulfonylmethyl-benzophenone

HPLC analysis: Microsorb Si 270@ Program

Time	Duration time	Flowrate	Hexane	:	i-propanol
0	0.5	1.0	100	:	0
6	0.5	1.5	85	:	15
16	0.5	1.5	100	:	0
30	0.5	1.0	100	:	0

Compound	(Compound / Cl_2CNPh)A	Concentration	Φ
p-$PhSO_2CH_2BP$	5.621	0.004983	0.35
p-MeBP	2.541	0.00149	0.29

[p-$PhSO_2CH_2BP$] = 0.00498M, [Cl_2CNPh] = 0.0153M, [HSPh] = 0.0140M. 1.5 hours, 366nm.

RF: Cl_2CNPh/p-$PhSO_2CH_2BP$ 0.0367; Cl_2CNPh/p-MeBP0.0337.

VP actinometer: [VP] = 0.09978 M, [C_{16}] = 0.006352 M, $(AP/C_{16})_A$ = 0.1047

[AP] = 0.00148 M. Io = 0.00449 ein l^{-1}.

Table 50. Effect of Thiophenol concentration on Quantum Yield for Irradiation of p-(Phenylthio)methyacetophenone.

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Sample	[HSPh]	(p-MeAP/MeBz)$_A$	[p-MeAP]	Φ
#1	0	0.0112	0.0000811	0.038
#2	0.00381	0.0890	0.000644	0.30
#3	0.0245	0.1040	0.000753	0.35
#4	0.0496	0.1053	0.000762	0.35
#5	0.0904	0.0829	0.000600	0.28
#6	0.505	0.0899	0.000651	0.30

[p-PhSCH$_2$AP] = 0.00841 M, [MeBz] = 0.00940 M, 1 hours, 313 nm.

RF: MeBz/p-MeAP 0.77. VP actinometer: [VP] = 0.1003 M. [C$_8$Bz] = 0.00700 M.

(AP/C$_8$Bz)$_A$ = 0.09363. [AP] = 0.0007144 M. Io = 0.00216.

Table 51. Quenching of p-Methylacetophenone Formation upon Irradiation of p-(Phenylthio)methylacetophenone.

HPLC analysis: Normal phase Si

$Kq\tau = 0.24$ Hexane / ethyl acetate (95:5)

1.0ml / min, @ 270nm

Sample	[Naphethalene]	(p-MeAP/MeBz)$_A$	Φ_0/Φ
#1	0	0.110	1.0
#2	0.558	0.0943	1.136
#3	1.078	0.0871	1.263
#4	1.678	0.0788	1.383
#5	2.051	0.0722	1.151

[p-PhSCH$_2$AP] = 0.007638M, [MeBz] = 0.01784M, [HSPh] = 0.04112M. 4 hours, 366nm

Table 52. Quantum Yield for Irradiation of p-(Phenylthio)methyl-acetophenone

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)A	Concentration	Φ
p-PhSCH$_2$AP	2.976	0.00913	0.31
p-MeAP	0.0589	0.001078	0.35

[p-PhSCH$_2$AP] = 0.01018 M, [HSPh] = 0.05482 M. [MeBz] = 0.02378 M, 2 hours, 366 nm. RF: MeBz/ p-MeAP 0.77; MeBz/p-PhSCH$_2$AP 0.13.

Table 53. Quenching of p-Methylacetophenone Formation upon Irradiation of p-Bromomethylacetophenone

$Kq\tau < 0.1$

HPLC analysis: Normal phase Si
Hexane / ethyl acetate (95:5)
1.0ml / min, @ 270nm

Sample	[Naphethalene]	(p-MeAP/MeBz)$_A$	Φ_O/Φ
#1	0	9.45	1.0
#2	0.1248	10.15	0.93
#3	0.08676	9.42	1.00
#4	0.4497	9.97	0.95
#5	1.1959	9.61	0.98

[p-$BrCH_2AP$] = 0.0183 M, [MeBz] = 0.01173 M, [HSPh] = 0.1137 M. 6 hours, 366nm

Table 54. Quantum Yield of Irradiation of p-Bromomethylacetophenone

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)$_A$	Concentration	Φ
p-BrCH$_2$AP	9.12	0.0166	0.22
p-MeAP	0.218	0.00197	0.25

[p-BrCH$_2$AP] = 0.0183 M, [MeBz] = 0.01173 M, [HSPh] = 0.1137 M, 6 hour, 366 nm. RF: MeBz/p-BrCH$_2$AP 0.156; MeBz/p-MeAP 0.77.

VP actinometer: [VP] = 0.1006 M. [C_{16}] = 0.00750 M. (AP/C_{16}) = 0.290.

[AP] = 0.00485 M.

Table 55. Quantum Yields of Irradiation of m-(Phenylthio)methylbenzophenone

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)$_A$	Concentration	Φ
m-PhSCH$_2$BP	6.278	0.00863	0.47
m-MeBP	0.854	0.00143	0.39

[m-PhSCH$_2$BP] = 0.01036 M, [MeBz] = 0.00955M, [HSPh] = 0.0556 M, 2 hours, 313 nm. RF: MeBz/m-PhSCH$_2$BP 0.144; MeBz/m-MeBP 0.175.

VP actinometer: [VP] = 0.1016 M. [C$_8$Bz] = 0.01978 M. (AP/C$_8$Bz)$_A$ = 0.0557. [AP] = 0.00120 M, Io = 0.00364.

Table 56. Quenching of m-Methylbenzophenone Formation upon Irradiation of m-(Phenylthio)methylbenzophenone.

$K_q\tau = 40$

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (97 : 3)
1.0 ml / min, @ 270nm

Sample	[Naphethalene]	(m-MeBP/MeBz)$_A$	Φ_0/Φ
#1	0	1.085	1.0
#2	0.0249	0.503	2.157
#3	0.0505	0.340	3.191
#4	0.0741	0.270	4.019
#5	0.0991	0.215	5.047
#6	0.1229	0.199	5.453

[m-PhSCH$_2$BP] = 0.01016 M, [MeBz] = 0.00925M, [HSPh] = 0.00532 M, 1 hour, 366 nm

Table 57. Quantum Yields of Irradiation of m-Chloroxymethylbenzophenone

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)$_A$	Concentration	Φ
m-ClCH$_2$BP	17.21	0.0306	0.038
m-MeBP	0.292	0.000483	0.036

[m-ClH$_2$BP] = 0.0311 M, [MeBz] = 0.009448 M, [HSPh] = 0.0546 M, 15 hours, 313 nm. RF: MeBz/m-ClCH$_2$BP 0.188; MeBz/m-MeBP 0.175

VP actinometer: [VP] = 0.1003 M. [C$_8$Bz] = 0.00700 M. (AP/C$_8$Bz)$_A$ =0.574. [AP] = 0.00438 M, Io = 0.0133.

Table 58. Quenching of m-Methylbenzophenone Formation upon Irradiation of m-Chloromethylbenzophenone.

$Kq\tau = 312$

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (97 : 3)
1.0 ml / min, @ 270nm

Sample	[Naphethalene]	(m-MeAP/MeBz)$_A$	Φ_0/Φ
#1	0	0.266	1.0
#2	0.00359	0.124	2.15
#3	0.00453	0.107	2.49
#4	0.00640	0.0899	2.96
#5	0.00952	0.0625	4.25
#6	0.01077	0.0574	4.64
#7	0.01420	0.0509	5.22

[m-$ClCH_2$BP] = 0.01114 M, [MeBz] = 0.01105 M, [HSPh] = 0.0546 M, 4 hours, 366 nm

Table 59. Quantum yields of Irradiation of m-(Phenylthio)methyl-acetophenone

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (95 : 5)
1.0 ml / min, @ 270nm

Compound	(Compound / MeBz)$_A$	Concentration	Φ
m-PhSCH$_2$AP	4.684	0.008088	0.36
m-MeAP	0.136	0.00175	0.32

[m-PhSCH$_2$AP] = 0.01004 M, [MeBz] = 0.00954M, [HSPh] = 0.0555 M, 3 hours, 313 nm. RF: MeBz/m-PhSCH$_2$AP 0.181; MeBz/m-MeAP 1.35.

VP actinometer: [VP] = 0.1003 M. [C$_8$Bz] = 0.00700 M. (AP/C$_8$Bz)$_A$ = 0.235. [AP] = 0.00179 M, Io = 0.00543 ein l^{-1}.

Table 60. Quenching of m-Methylacetophenone Formation upon Irradiation of m-Phenylthiomethylacetophenone.

$K_q\tau = 1.88$

HPLC analysis: Microsorb-Si
Hexane / ethyl acetate (98 : 2)
1.0 ml / min, @ 270nm

Sample	[Naphethalene]	(m-MeAP/MeBz)$_A$	Φ_0/Φ
#1	0	0.114	1.0
#2	0.1278	0.0896	1.272
#3	0.3396	0.0689	1.655
#4	0.4577	0.0619	1.840
#5	0.5960	0.0529	2.154
#6	0.7441	0.0474	2.405

[m-PhSCH$_2$AP] = 0.01079 M, [MeBz] = 0.00931M, [HSPh] = 0.0487 M, 6 hours, 366 nm

Table 61. Quantum yield of Irradiation of o-Benzoyl-N,N-dibenzylaniline Hydrochloride in acetonitrile.

Compound	(Compound / Std)$_A$	[Compound]	Φ
Bz_2NBP:HCl[a]	7.397	0.01724 M	0.0145
$BzPh_2$-indole[b]	1.640	0.0008148 M	0.0067

[a][BzNBP:HCl] =0.0198 M, [std] = [C_{10}Bz] = 0.1644 M, VP actinometry: [VP] = 0.09960 M, [C_{16}] = 0.006695 M, [AP] = 0.03344 M. Irradiation: 366nm, 27 hours

b[BzNBP:HCl] =0.01967 M, [std] = [C_{10}Bz] = 0.07528 M, VP actinometry: [VP] = 0.1010 M, [C_{16}] = 0.006924 M, [AP] = 0.0234 M. Irradiation: 366nm, 24 hours

Table 62. Effct of Water on Quantum Yield of Irradiation of o-Benzoyl-N,N-dibenzylaniline Hydrochloride

H_2O(%)	Δ(Bz_2NBP:HCl / Std)$_A$	Φ	($BzPh_2$-indole /Std)$_A$	Φ
0	1.17	0.0145	1.12	0.0067
2	0.90	0.0112	0.55	0.0033
4	0.37	0.0046	0.49	0.0029
6	0.08	0.00099	0.29	0.0017
8	0.08	0.00099	0.15	0.00090
10			0.098	0.00059

[BzNBP:HCl] =0.02078 M, [std] = [C_{10}Bz] = 0.009933 M, 366nm, 24 hours, in acetonitrile.

Table 63. Quenching of N-Benzyl-2,3-diphenylindole Formation upon Irradiation of o-Benzoyl-N,N-dibenzylaniline Hydrochloride.[b]

HPLC analysis: Reverse phase column

CH_3OH/H_2O (95 / 5)

$k_q\tau = 2.44$ Rate: 1.0 ml/min. @ 270nm

Sample	[Ethyl Sorbate]	($BzPh_2$-indole / $C_{10}Bz)_A$	Φ_0/Φ
#1	0	0.8175	1.0
#2	0.2123	0.5471	1.494
#3	0.3972	0.4117	1.986
#4	0.5931	0.3296	2.480
#5	0.8059	0.2806	2.914
#6	1.0154	0.2344	3.488

[a][Bz_2NBP:HCl] =0.0198 M, [std] = [$C_{10}Bz$] = 0.1644 M, 366nm, 27 hours, in acetonitrile.

Table 64. Quenching of N-Benzyl-2,3-diphenylindole Formation upon Irradiation of o-Benzoyl-N,N-dibenzylaniline Hydrochloride in 8% Aqueous Acetonitrile Solution.

$k_q\tau = 219.8$

HPLC analysis: Reverse phase column

CH_3OH/H_2O (95/5)

Rate: 1.0 ml/min. @ 270nm

Sample	[Sodium Sorbate]	($BzPh_2$-indole / $C_{10}Bz)_A$	Φ_0/Φ
#1	0	0.3379	1.0
#2	0.0007457	0.2933	1.152
#3	0.002088	0.2145	1.575
#4	0.002833	0.2033	1.662
#5	0.004325	0.1737	1.946
#6	0.005220	0.1565	2.158

[Bz_2NBP:HCl] =0.008353 M,[std] = [$C_{10}Bz$] = 0.004921 M, Irradiation: 366 nm, 48 hours

Table 65. Quenching of N-Benzyl-2,3-diphenylindole Formation upon Irradiation of o-Benzoyl-N,N-dibenzylaniline Hydrochloride in 4% Aqueous Acetonitrile Solution with Sodium Sobate.

$k_q\tau = 347.0$

HPLC analysis: Reverse phase column

CH_3OH / H_2O (95/5)

Rate: 1.0 ml/min. @ 270nm

Sample	[Sodium Sorbate]	($BzPh_2$-indole / $C_{10}Bz)_A$	Φ_0/Φ
#1	0	0.858	1.0
#2	0.000895	0.753	1.14
#3	0.00209	0.548	1.57
#4	0.00313	0.411	2.09
#5	0.00403	0.375	2.29
#6	0.00537	0.300	2.86

[Bz_2NBP:HCl] =0.007834 M,[std] = [$C_{10}Bz$] = 0.005305 M, Irradiation: 365nm, 36 hours

Table 66. Quenching of N-Benzyl-2,3-diphenylindole Formation upon Irradiation of o-Benzoyl-N,N-dibenzylaniline hydrochloride in 8% Aqueous Acetonitrile Solution with Ethyl Sobate.

HPLC analysis: Reverse phase column

CH_3OH/H_2O (95/5)

Rate: 1.0 ml/min. @ 270nm

Sample	[Ethyl Sobate]	($BzPh_2$-indole / $C_{10}Bz)_A$	Φ_0/Φ
#1	0	1.080	1.0
#2	0.05792	0.982	1.099
#3	0.1187	0.950	1.137
#4	0.1783	0.775	1.395
#5	0.2558	0.402	2.684
#6	0.3089	0.357	3.030
#7	0.3519	0.349	3.098

[Bz_2NBP:HCl] =0.007337 M,[std] = [$C_{10}Bz$] = 0.005177 M, Irradiation: 366 nm, 36 hours

Table 67. Quenching of N-Benzyl-2,3-diphenylindole Formation upon Irradiation of o-Benzoyl-N,N-dibenzylaniline Hydrochloride in 8% Aqueous Acetonitrile Solution.

HPLC annalysis: Reverse phase column

CH_3OH/H_2O (95/5)

Rate: 1.0 ml/min. @ 270nm

Sample	[Quencher] [b]	($BzPh_2$-indole / $C_{10}Bz)_A$	Φ_0/Φ
#1	0	0.397	1.0
#2	0.000867	0.436	0.911
#3	0.00318	---	----
#4	0.0114	0.496	0.800
#5	0.0239	0.503	0.789
#6	0.0509	0.438	0.906

[Bz_2NBP:HCl] =0.007530 M,[std] = [$C_{10}Bz$] = 0.004930 M, Irradiation: 366 nm, 48 hours. [b]1-naphethylethylamine hydrochloride

Table 68. Stern-volmer Analysis of o-Benzoyltrimethylanilinium tetrafluroborate in CH_3CN

$\Phi = 0.56$ UV analysis: @340 nm

$kq\tau = 86$

Sample	[Et Sorbate]	ΔA_{340}	Φ_0/Φ
#1	0	0.260	1.0
#2	0.00564	0.162	1.60
#3	0.0142	0.119	2.18
#4	0.0218	0.094	2.77
#5	0.0272	0.077	3.38
#6	0.0347	0.064	4.06

[TMeNBP:BF_4] =0.0186 M, Irradiation: 366 nm, 2.5 hours. VP actinometer: [VP] = 0.10067 M, [C16] = 0.007834 M, [AP] = 0.00245,

[TMeNBP:BF_4] = 0.0127 x A_{340} - 0.0013

Table 69. Stern-volmer Analysis of o-Benzoyltrimethylanilinium tetrafluroborate in CH_3CN

$\Phi = 0.34$ IR analysis: @1674.5-1664.5 cm^{-1}.

$kq\tau = 146$

Sample	[2,4-Hexadiene]	$\Delta Area_{1674.5-1664.5}$	Φ_o/Φ
#1	0	1.6724	1.0
#2	0.00186	1.2308	1.359
#3	0.00372	1.0683	1.565
#4	0.00558	0.9426	1.774
#5	0.00744	0.7473	2.238
#6	0.00930	0.7844	2.132
#7	0.01116	0.6934	2.412
#8	0.01303	0.5343	3.130
#9	0.01674	0.4786	3.494

[TMeNBP:BF_4] =0.04027 M, Irradiation: 313 nm, 14 hours.

VP actinometer: [VP] = 0.09978 M, [C_{16}] = 0.006352 M, [AP] = 0.0121 M.

[Me_3NBP:BF_4] = 0.00916 x $A_{1674.5-1664.5}$ - 0.00286

Table 70. Torsion Angles for N-Benzyl-2,3-diphenylindole

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
C9	N1	C2	C3	-0.38	(0.37)
C9	N1	C2	C21	-177.50	(0.30)
C10	N1	C2	C3	176.69	(0.31)
C10	N1	C2	C21	-0.43	(0.50)
C2	N1	C9	C4	0.16	(0.36)
C2	N1	C9	C8	-178.13	(0.35)
C10	N1	C9	C4	-176.99	(0.30)
C10	N1	C9	C8	4.72	(0.56)
C2	N1	C10	C11	105.64	(0.38)
C9	N1	C10	C11	-77.75	(0.42)
N1	C2	C3	C4	0.44	(0.37)
N1	C2	C3	C31	177.75	(0.30)
C21	C2	C3	C4	177.25	(0.33)
C21	C2	C3	C31	-5.44	(0.58)
N1	C2	C21	C22	-66.02	(0.48)
N1	C2	C21	C26	110.91	(0.39)
C3	C2	C21	C22	117.49	(0.45)
C3	C2	C21	C26	-65.58	(0.51)
C2	C3	C4	C5	176.60	(0.38)
C2	C3	C4	C9	-0.34	(0.37)
C31	C3	C4	C5	-0.74	(0.62)
C31	C3	C4	C9	-177.68	(0.31)
C2	C3	C31	C32	139.14	(0.38)
C2	C3	C31	C36	-41.81	(0.51)
C4	C3	C31	C32	-44.03	(0.50)
C4	C3	C31	C36	135.01	(0.38)
C3	C4	C5	C6	-178.21	(0.37)
C9	C4	C5	C6	-1.56	(0.52)
C3	C4	C9	N1	0.11	(0.38)
C3	C4	C9	C8	178.53	(0.32)
C5	C4	C9	N1	-177.41	(0.30)
C5	C4	C9	C8	1.01	(0.51)
C4	C5	C6	C7	0.55	(0.57)
C5	C6	C7	C8	1.12	(0.61)
C6	C7	C8	C9	-1.65	(0.57)
C7	C8	C9	N1	178.66	(0.35)
C7	C8	C9	C4	0.59	(0.53)
N1	C10	C11	C12	-10.53	(0.52)
N1	C10	C11	C16	171.16	(0.33)
C10	C11	C12	C13	-179.55	(0.39)
C16	C11	C12	C13	-1.23	(0.60)
C10	C11	C16	C15	179.88	(0.38)
C12	C11	C16	C15	1.48	(0.59)
C11	C12	C13	C14	1.13	(0.68)
C12	C13	C14	C15	-1.23	(0.69)
C13	C14	C15	C16	1.48	(0.68)
C14	C15	C16	C11	-1.64	(0.66)
C2	C21	C22	C23	-179.25	(0.40)

Table 70. (Cont'd).

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C26	C21	C22	C23	3.71 (0.62)
C2	C21	C26	C25	179.13 (0.34)
C22	C21	C26	C25	-3.79 (0.56)
C21	C22	C23	C24	-0.26 (0.73)
C22	C23	C24	C25	-3.30 (0.73)
C23	C24	C25	C26	3.29 (0.65)
C24	C25	C26	C21	0.32 (0.59)
C3	C31	C32	C33	178.36 (0.35)
C36	C31	C32	C33	-0.71 (0.55)
C3	C31	C36	C35	-179.48 (0.36)
C32	C31	C36	C35	-0.40 (0.56)
C31	C32	C33	C34	0.82 (0.62)
C32	C33	C34	C35	0.20 (0.65)
C33	C34	C35	C36	-1.31 (0.69)
C34	C35	C36	C31	1.42 (0.66)

Table 71. Bond Angles for N-benzyl-2,3-diphenylindole

Atom1	Atom2	Atom3	Angle
C2	N1	C9	108.4(3)
C2	N1	C10	126.9(3)
C9	N1	C10	124.6(3)
N1	C2	C3	109.4(3)
N1	C2	C21	121.1(3)
C3	C2	C21	129.4(3)
C2	C3	C4	107.1(3)
C2	C3	C31	126.8(3)
C4	C3	C31	126.1(3)
C3	C4	C5	134.7(3)
C3	C4	C9	106.5(3)
C5	C4	C9	118.7(3)
C4	C5	C6	119.2(4)
C5	C6	C7	120.6(4)
C6	C7	C8	121.9(4)
C7	C8	C9	117.2(4)
N1	C9	C4	108.6(3)
N1	C9	C8	129.0(3)
C4	C9	C8	122.4(3)
N1	C10	C11	113.3(3)
C10	C11	C12	123.8(3)
C10	C11	C16	118.8(3)
C12	C11	C16	117.3(3)
C11	C12	C13	121.4(4)
C12	C13	C14	120.7(4)
C13	C14	C15	119.2(4)
C14	C15	C16	120.5(4)
C11	C16	C15	120.8(4)
C2	C21	C22	122.0(3)
C2	C21	C26	120.7(3)
C22	C21	C26	117.2(3)
C21	C22	C23	120.1(4)
C22	C23	C24	120.7(4)
C23	C24	C25	119.3(4)
C24	C25	C26	120.3(4)
C21	C26	C25	122.1(4)
C3	C31	C32	121.2(3)
C3	C31	C36	120.8(3)
C32	C31	C36	118.0(3)
C31	C32	C33	121.4(4)
C32	C33	C34	120.0(4)
C33	C34	C35	119.6(4)
C34	C35	C36	120.8(4)
C31	C36	C35	120.3(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 71 (Cont'd).

Atom1	Atom2	Atom3	Angle
C4	C5	H5	121.(2)
C6	C5	H5	120.(2)
C5	C6	H6	119.(2)
C7	C6	H6	121.(2)
C6	C7	H7	120.(2)
C8	C7	H7	118.(2)
C7	C8	H8	120.(2)
C9	C8	H8	123.(2)
N1	C10	H10a	106.(2)
N1	C10	H10b	107.(2)
C11	C10	H10a	112.(2)
C11	C10	H10b	107.(2)
H10a	C10	H10b	111.(3)
C11	C12	H12	117.(2)
C13	C12	H12	122.(2)
C12	C13	H13	119.(3)
C14	C13	H13	120.(3)
C13	C14	H14	122.(2)
C15	C14	H14	119.(2)
C14	C15	H15	123.(3)
C16	C15	H15	117.(3)
C11	C16	H16	115.(2)
C15	C16	H16	124.(2)
C21	C22	H22	120.(2)
C23	C22	H22	120.(2)
C22	C23	H23	119.(3)
C24	C23	H23	120.(3)
C23	C24	H24	124.(2)
C25	C24	H24	117.(2)
C24	C25	H25	118.(2)
C26	C25	H25	122.(2)
C21	C26	H26	119.(2)
C25	C26	H26	119.(2)
C31	C32	H32	119.(2)
C33	C32	H32	119.(2)
C32	C33	H33	117.(3)
C34	C33	H33	123.(3)
C33	C34	H34	121.(3)
C35	C34	H34	119.(3)
C34	C35	H35	117.(3)
C36	C35	H35	122.(3)
C31	C36	H36	116.(2)
C35	C36	H36	123.(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 72. Bond Distances for N-benzyl-2,3-diphenylindole

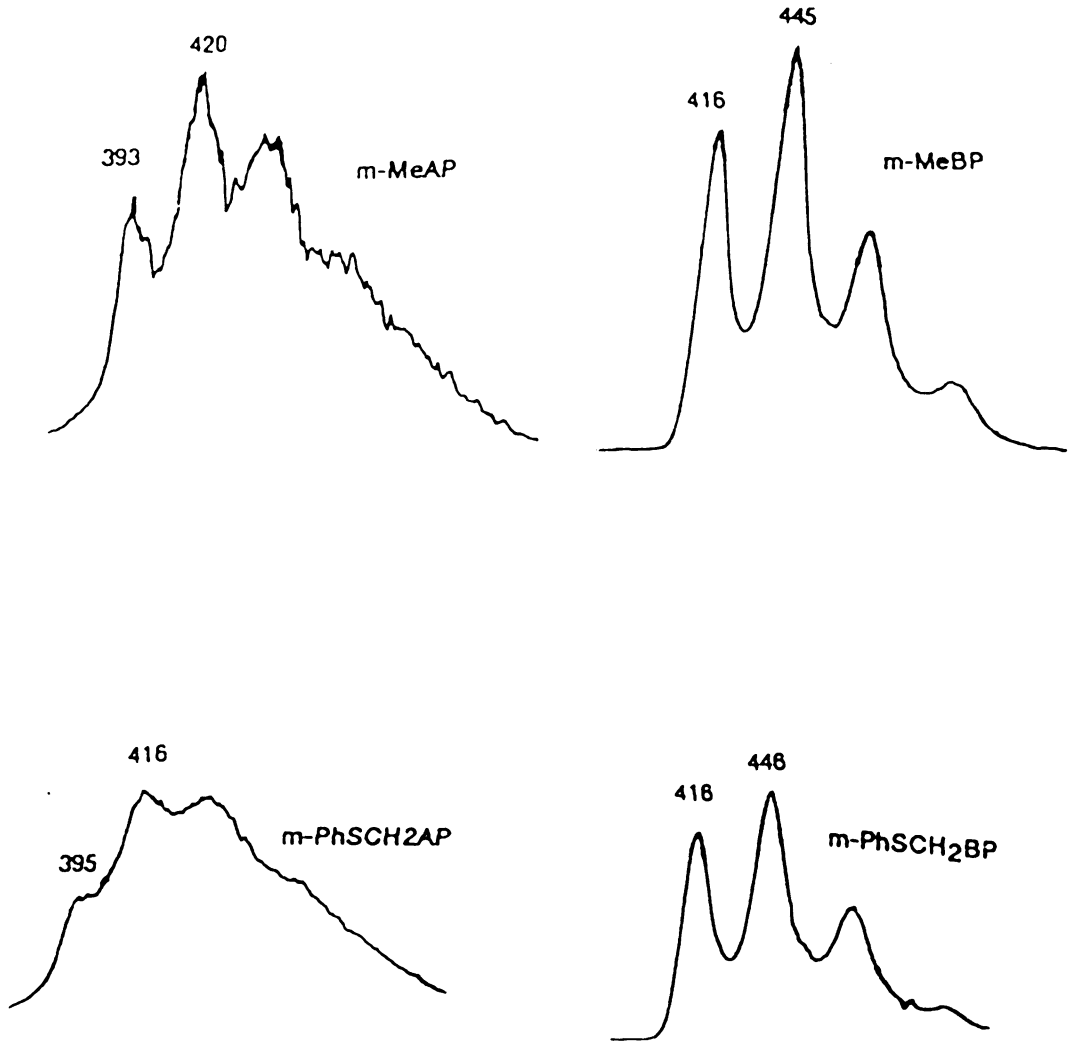
Atom1	Atom2	Distance
N1	C2	1.391(4)
N1	C9	1.377(5)
N1	C10	1.459(5)
C2	C3	1.371(5)
C2	C21	1.475(5)
C3	C4	1.442(5)
C3	C31	1.480(5)
C4	C5	1.400(5)
C4	C9	1.405(5)
C5	C6	1.386(6)
C6	C7	1.395(6)
C7	C8	1.374(6)
C8	C9	1.397(5)
C10	C11	1.513(5)
C11	C12	1.370(5)
C11	C16	1.381(5)
C12	C13	1.378(6)
C13	C14	1.353(7)
C14	C15	1.359(6)
C15	C16	1.383(6)
C21	C22	1.384(6)
C21	C26	1.372(5)
C22	C23	1.399(6)
C23	C24	1.362(6)
C24	C25	1.352(6)
C25	C26	1.378(6)
C31	C32	1.389(5)
C31	C36	1.389(5)
C32	C33	1.386(6)
C33	C34	1.370(7)
C34	C35	1.378(7)
C35	C36	1.387(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

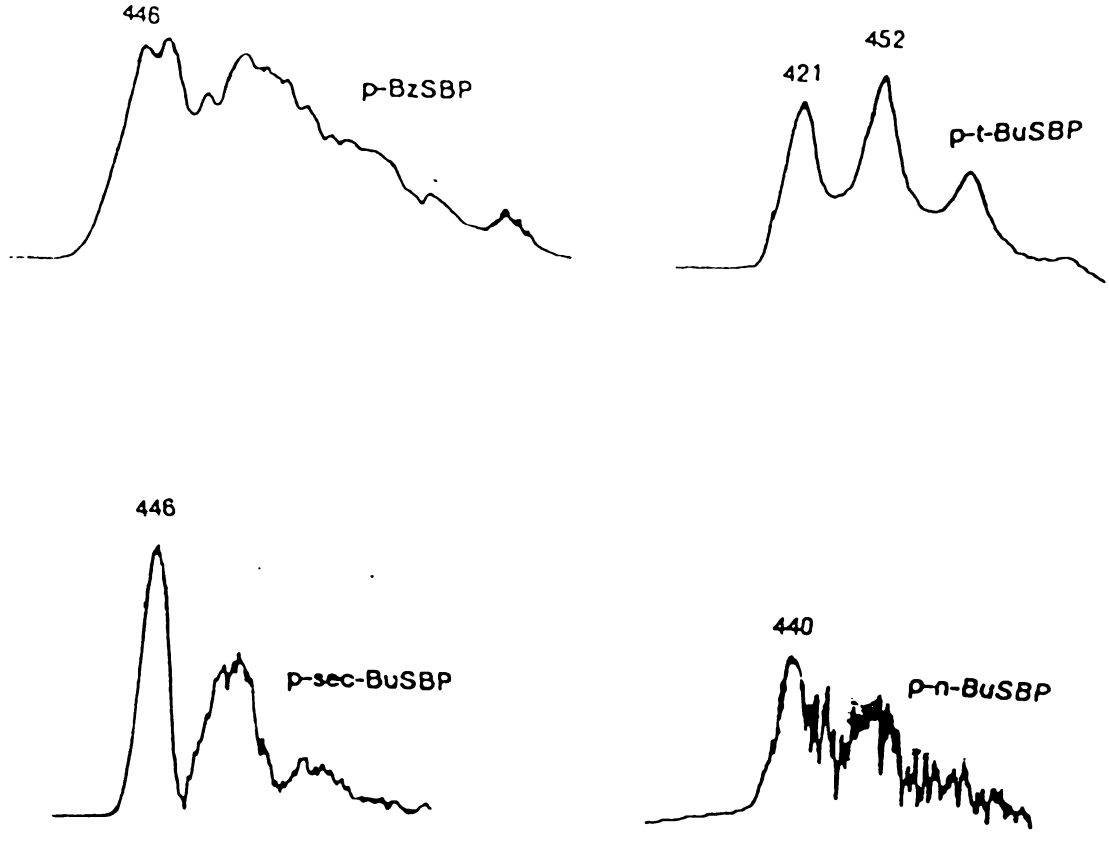
Table 72 (Cont'd).

Atom1	Atom2	Distance
C5	H5	0.98(4)
C6	H6	1.03(4)
C7	H7	0.96(4)
C8	H8	1.02(4)
C10	H10a	0.97(3)
C10	H10b	1.01(3)
C12	H12	0.97(4)
C13	H13	1.00(4)
C14	H14	0.97(4)
C15	H15	0.93(4)
C16	H16	0.96(3)
C22	H22	1.10(4)
C23	H23	1.08(5)
C24	H24	1.03(4)
C25	H25	1.00(3)
C26	H26	0.97(4)
C32	H32	0.97(3)
C32	H33	1.99(4)
C33	H33	0.93(4)
C34	H34	1.00(4)
C35	H35	1.04(5)
C36	H36	1.08(4)

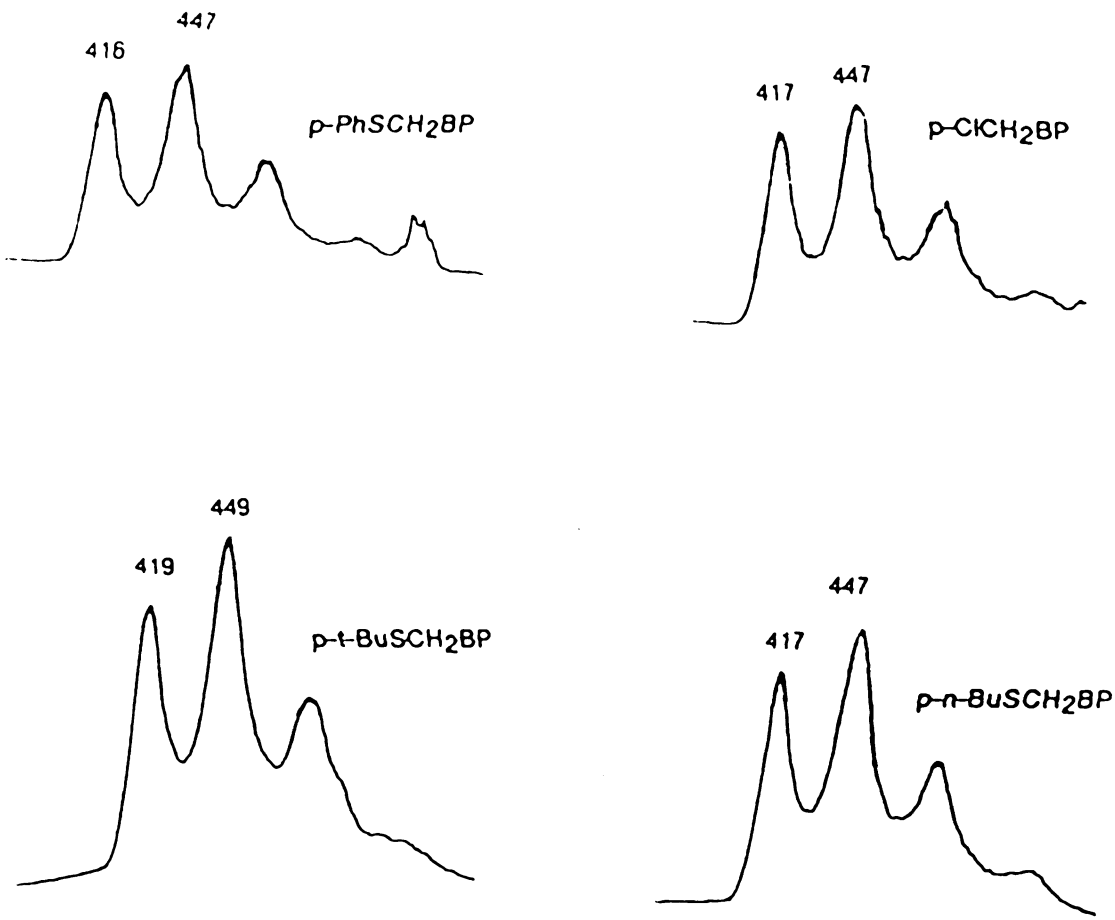
Numbers in parentheses are estimated standard deviations in the least significant digits.



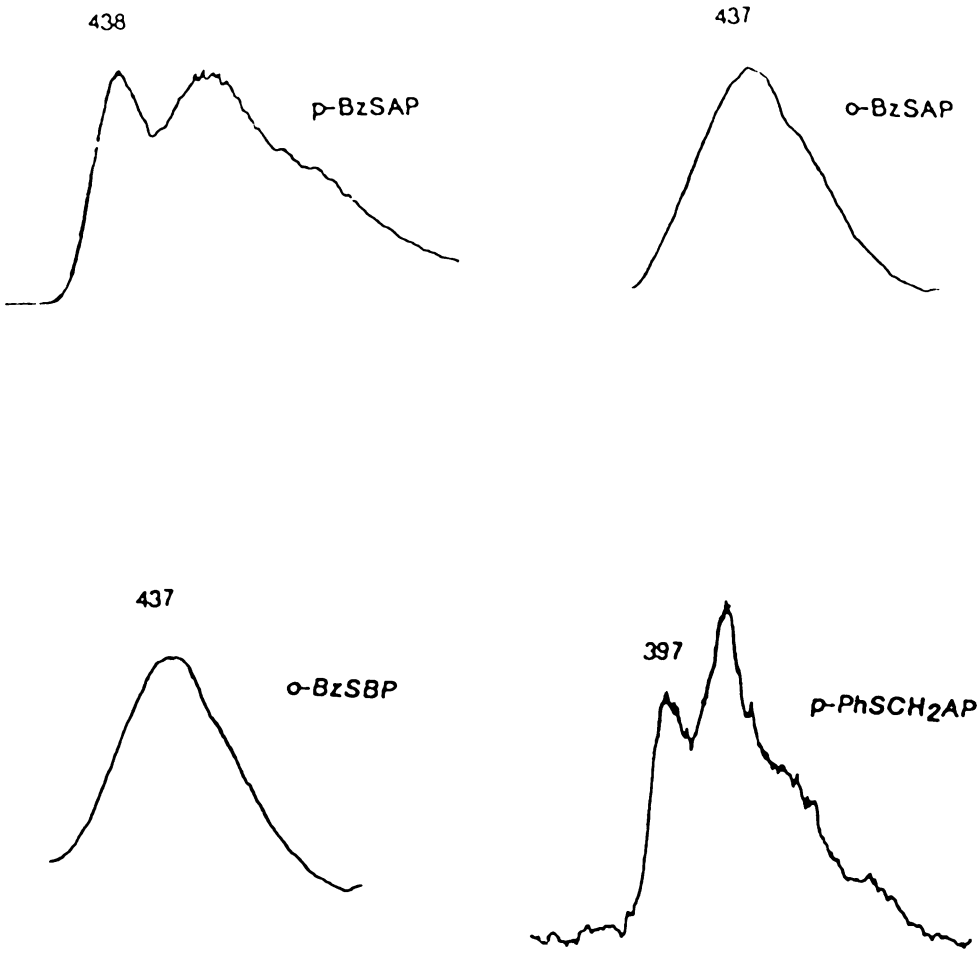
Scheme 5. Phosphoresence Spectra for m-MeAP, m-MeBP, m-PhSCH$_2$AP and m-PhSCH$_2$BP in 2-Methyltetrahydrofuran.



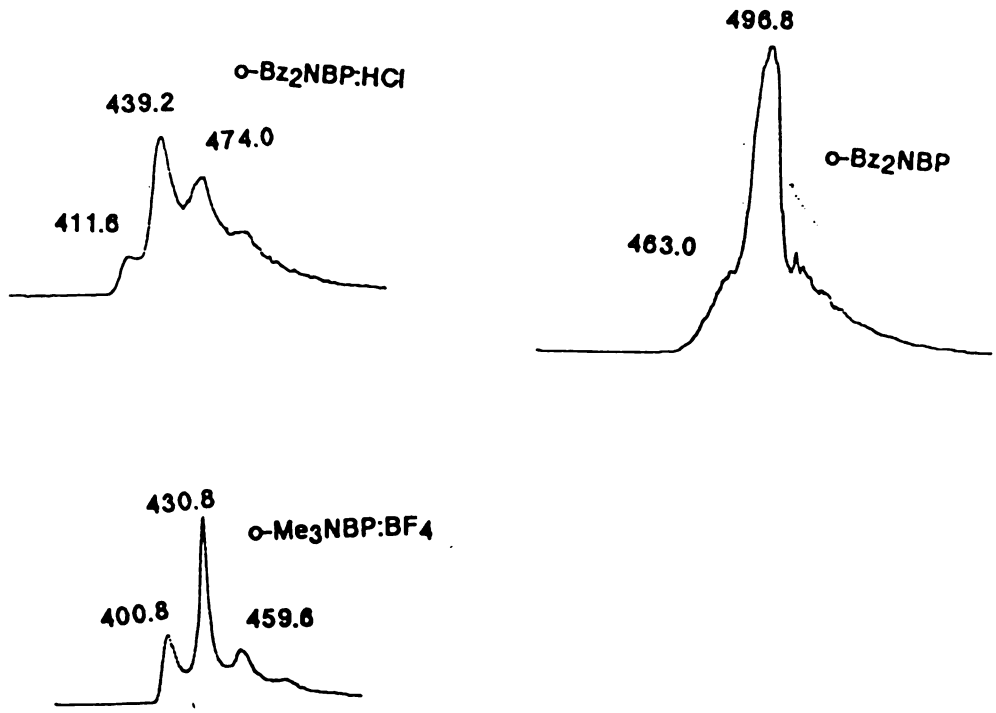
Scheme 6 Phosphoresence Spectra for p-BzSBP, p-t-BuSBP, p-sec-BuSBP and p-n-BuSBP in 2-Methyltetrahydrofuran.



Scheme 7 Phosphoresence Spectra for p-PhSCH2BP, p-ClCH2BP, p-t-BuSCH2BP and p-n-BuSCH2BP in 2-Methyltetrahydrofuran.



Scheme 8. Phosphoresence Spectra for p-BzSAP, o-BzSAP, o-BzSBP and p-PhSCH$_2$AP in 2-Methyltetrahydrofuran.



Scheme 9. Phosphoresence Spectra for o-Bz_2BP:HCl, o-Bz_2BP and o-Me_3BP:BF_4 in MeOH / EtOH.

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