THESIS

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Michael Anthony Meador

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CONFORMATIONAL EFFECTS IN PHOTOCHEMICAL δ-HYDROGEN ABSTRACTION

By

Michael Anthony Meador

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ABSTRACT

CONFORMATIONAL EFFECTS IN PHOTOCHEMICAL δ-HYDROGEN ABSTRACTION

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Michael Anthony Meador

The photocyclization of various o-alkoxyphenyl ketones was investigated. This proceeds via the intramolecular abstraction of an alkoxy hydrogen by the excited carbonyl oxygen to give rise to a 1,5-biradical which cyclizes to a substituted 3-hydroxy-2,3-dihydrobenzofuran. Comparisons of the hydrogen abstraction rate constants, k_H, for these ketones with those of appropriate 2,6-diacylalkoxybenzenes reveals an excited state equilibrium between a reactive and an unreactive triplet conformer, involving rotation of the alkoxy group about the phenyl-oxygen bond.

The considerably lower photocyclization quantum yield for o-benzyloxyacetophenone (o-BzOAP) relative to that for o-benzyloxybenzophenone reflects the conformational requirements for biradical cyclization. The biradical is initially formed in a conformation favoring disproportionation. The C-OH fragment of the biradical must undergo a 90° rotation prior to cyclization. This rotation is

restricted in the o-BzOAP biradical due to the demands of delocalization. The low quantum yield results from this restriction.

The photocyclization of a series of α-(o-alkylphenyl)-acetophenones was studied. This involves formation of a 1,5-biradical by intramolecular abstraction of an o-alkyl hydrogen by the excited carbonyl oxygen, which cyclizes to the corresponding 2-phenyl-2-hydroxyindane. In all cases, the photocyclization of these ketones is efficient and chemical yields are in excess of 95%. Comparison of the k_H values for α-(o-tolyl)acetophenone and α-mesitylacetophenone reveals an excited state equilibrium between a reactive and an unreactive triplet conformer, arising from rotation of the α-phenyl ring.

The unusually low maximum photocyclization quantum yield for α-mesitylacetophenone suggests a second mode of disproportionation, 1,4-hydrogen transfer, which is unaffected by the addition of pyridine.

To My Wife

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INTRODUCTION

Ketone photochemistry has occupied the mainstream of organic photochemistry from its infancy, just as carbonyl chemistry has been in the forefront of organic chemistry. A great deal of knowledge concerning the behavior of excited state carbonyl compounds has been compiled over the years. The study of the photochemistry of carbonyl compounds has helped in the understanding of very fundamental questions in photochemistry, but a great many questions remain unanswered. In that sense, ketone photochemistry, and photochemistry itself, is still somewhat in its pioneering stage.

A prerequisite to any discussion of photochemistry involves mention of the photophysics and the nature of the excited states of the system under study. The photophysics of an excited state molecule is best described with the aid of a Jablonski[1] diagram.

Initial absorption of light promotes an electron from the ground state, S_0, to an upper excited singlet. For most organic molecules, electronic spins are paired in the ground state. Hence, it is a singlet, having a net electronic spin of zero. The upper excited singlets usually decay rapidly ($k_{ic} = 10^{11}$-$10^{14} s^{-1}$)[2] via internal conversion to the lowest excited singlet. From here, the excited

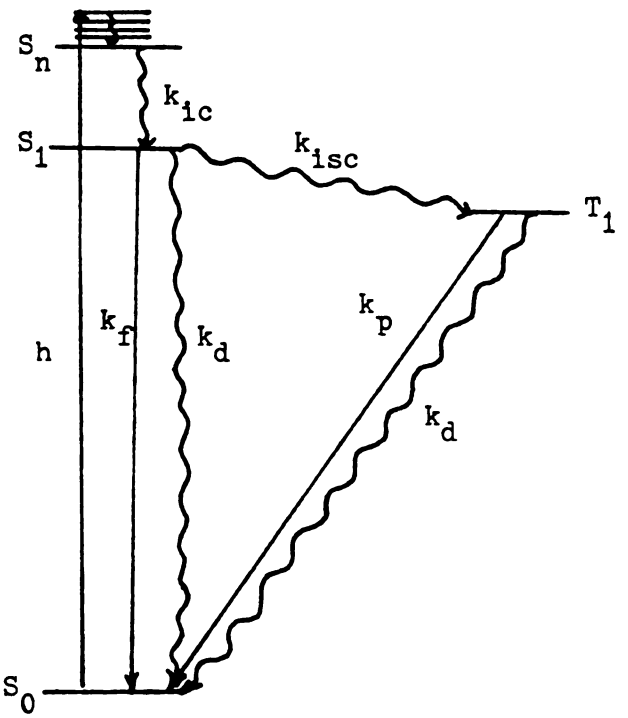


Figure 1a. A Jablonski diagram depicting the photophysics of an excited state molecule.

molecule has a number of options open to it. It can decay to the ground state, emitting a photon of light (fluorescence). This process usually has a rate constant, k_f, on the order of 10^6 to $10^9 s^{-1}$.[2] Decay from the excited singlet to the ground state is also possible via radiationless decay, with a rate constant k_d of from 10^5 to $10^8 s^{-1}$.[2] Chemical reactions can also occur from the excited singlet,

giving rise to products. Finally, the excited singlet can undergo intersystem crossing to an excited triplet state. This proceeds with spin inversion of an electron, resulting in parallel electronic spins of the two unpaired electrons. The triplet state has a net spin of one, and an overall spin multiplicity of three. Typical rate constants for intersystem crossing, k_{isc}, are on the order of 10^7 to 10^{10}-s^{-1}.[2] Direct population of the triplet state from the ground state, by absorption of light, is forbidden by spin selection rules. Hence, the intensity of such a transition is extremely low,[3] but can be maximized with a laser.

As is the case with the excited singlet, the excited triplet has a number of decay modes available to it. Radiative decay (phosphorescence) typically proceeds with a rate constant, k_p, from 10^{-1} to $10^4 s^{-1}$.[2] Quenching of the triplet state by energy transfer or electron transfer (charge transfer) can occur with a rate constant as high as the rate of diffusion in a given solvent ($\leq 10^{10} M^{-1} s^{-1}$).[4] Triplet-triplet annihilation can occur if the triplets are formed in high enough concentrations, with a bimolecular rate constant close to diffusion.[5] This is of particular concern in laser photochemistry. Finally, the triplet state can undergo chemical reactions which give rise to products.

In ketones, phenyl ketones in particular, intersystem crossing is both rapid and efficient. The quantum yield for intersystem crossing in phenyl ketones is close to

unity.[6] The rate constant for intersystem crossing in phenyl ketones is on the order of 10^{10} to $10^{11} s^{-1}$,[7] considerably faster than any other process that normally occurs from the excited singlet. Therefore, irradiation of a phenyl ketone results in an indirect population of the first excited triplet state. Almost all photochemical reactions that occur from these compounds, then, arise from the triplet state.

Phenyl ketones have two different low lying triplets: a π,π^* triplet and an n,π^* triplet. Common valence bond representations of these triplets are depicted in Figure 1b.

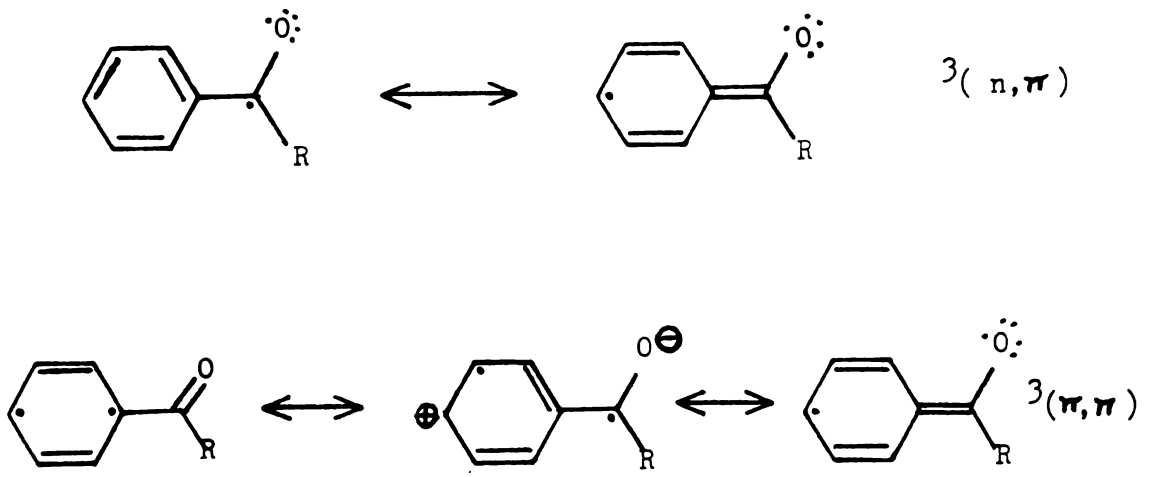


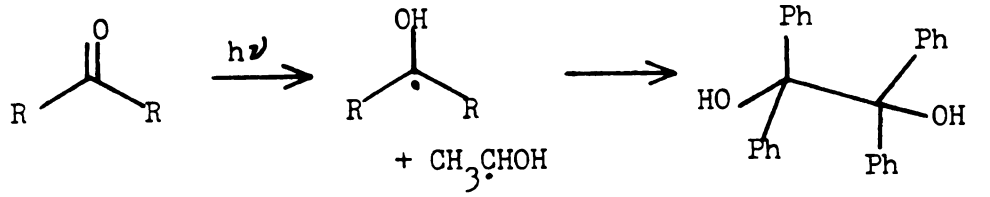
Figure 1b. Valence bond representations of the π,π^* and n,π^* ketone triplets.

The (n,π*) triplet arises by promotion of an electron from a non-bonding orbital on the carbonyl oxygen to a π*-antibonding orbital of the aromatic system. The net effect is a slightly electron-deficient oxygen. This deficiency gives the n,π* triplet chemical behavior similar to that of an alkoxy radical.[6,8] Reactions arising from the n,π* triplet, then, are those expected of an alkoxy radical, with hydrogen abstraction being the most predominant.

The π,π* triplet, on the other hand, arises from promotion of an electron from a π-bonding orbital to a π*-antibonding orbital. This can result in a shift of electron density from the aromatic π-system to the carbonyl oxygen, creating an electron rich oxygen. This shift can be seen in the middle resonance form for the $^3(\pi,\pi^*)$ in Figure 2. The π,π* triplet is less susceptible to nucleophilic attack and radical reactions at the carbonyl oxygen than is the n,π* triplet. However, thermal equilibration[6] and quantum mechanical mixing of the two triplets can occur if they are close enough in energy. As a result, ketones with a π,π* lowest triplet do undergo hydrogen abstraction to some extent, but not with the same efficiency as n,π* triplets.[6,9]

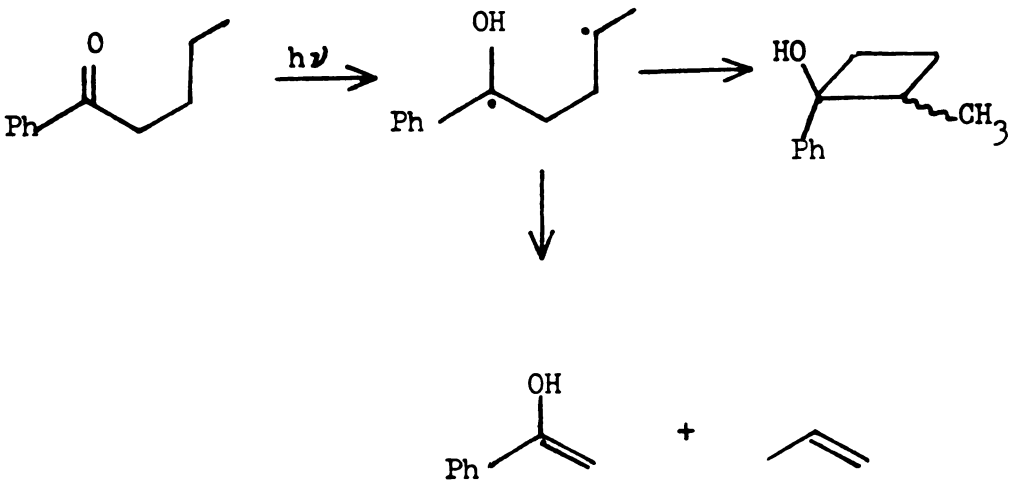
Ketones with an n,π* lowest triplet readily abstract hydrogen atoms from compounds having reactive hydrogens, e.g., alcohols, ethers, and some alkanes. This reaction was first observed by Ciamician and Silber[10] in the photolysis

of benzophenone in ethanol. One of the products observed was benzpinacol, formed by coupling of benzophenone ketyl radicals (Reaction 1).



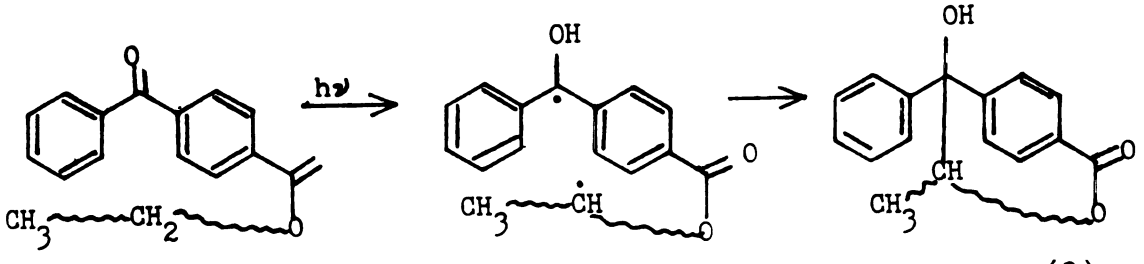
(1)

Intramolecular hydrogen abstraction is also possible. Perhaps the best known example of this is the Norrish Type II[11] reaction (Reaction 2). This reaction involves formation of a 1,4-biradical[12] 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 a cyclobutanol.[11-13]



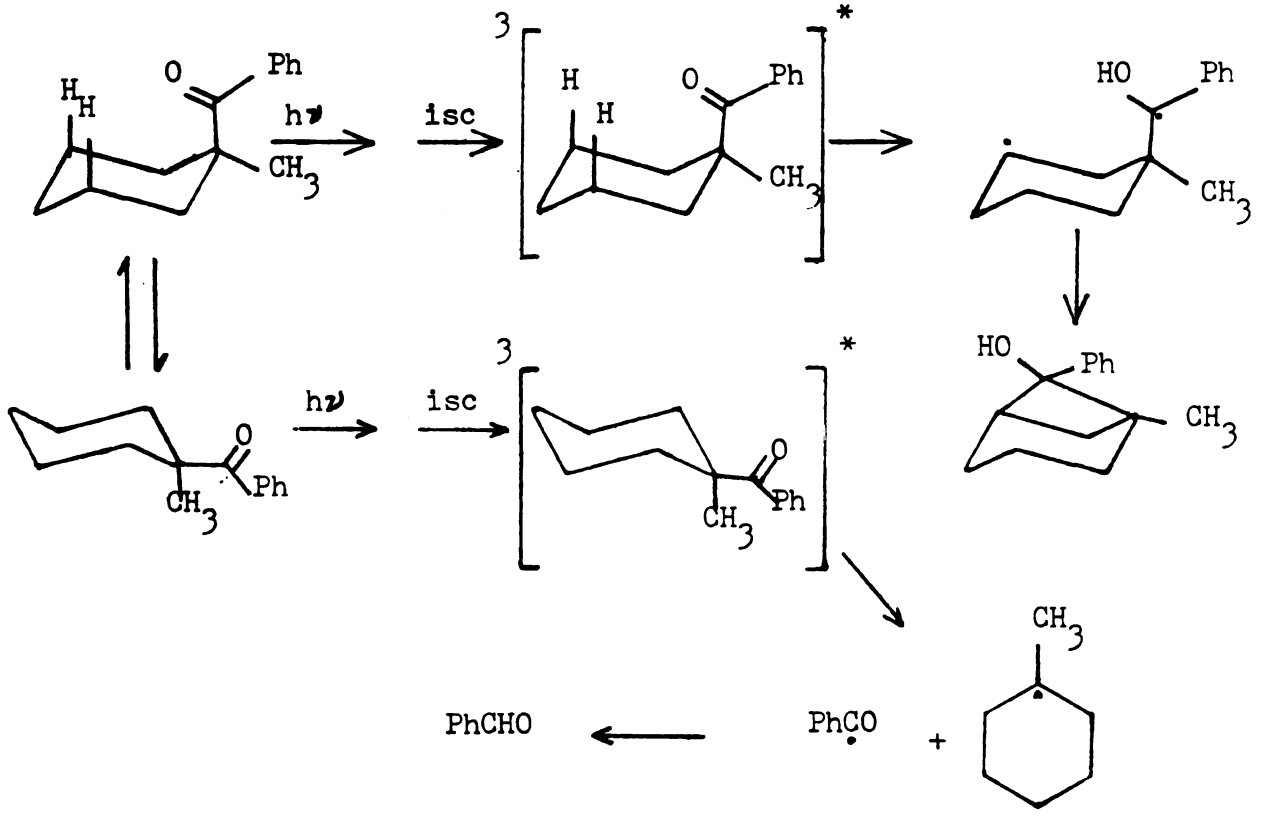
(2)

Intramolecular hydrogen abstraction carries with it certain geometric constraints. The most obvious is that the hydrogen being abstracted must be physically accessible to the carbonyl oxygen. A good example of this requirement is seen in work reported by Breslow and Winnik.[14] This report describes the intramolecular photochemical hydrogen abstraction in a series of p-benzoylbenzoate esters of long chain alcohols (Reaction 3). For this system, there exists a direct correlation between the statistically predicted number of sites of attack on the alkyl chain and the experimentally determined rate constants.[14,15]



(3)

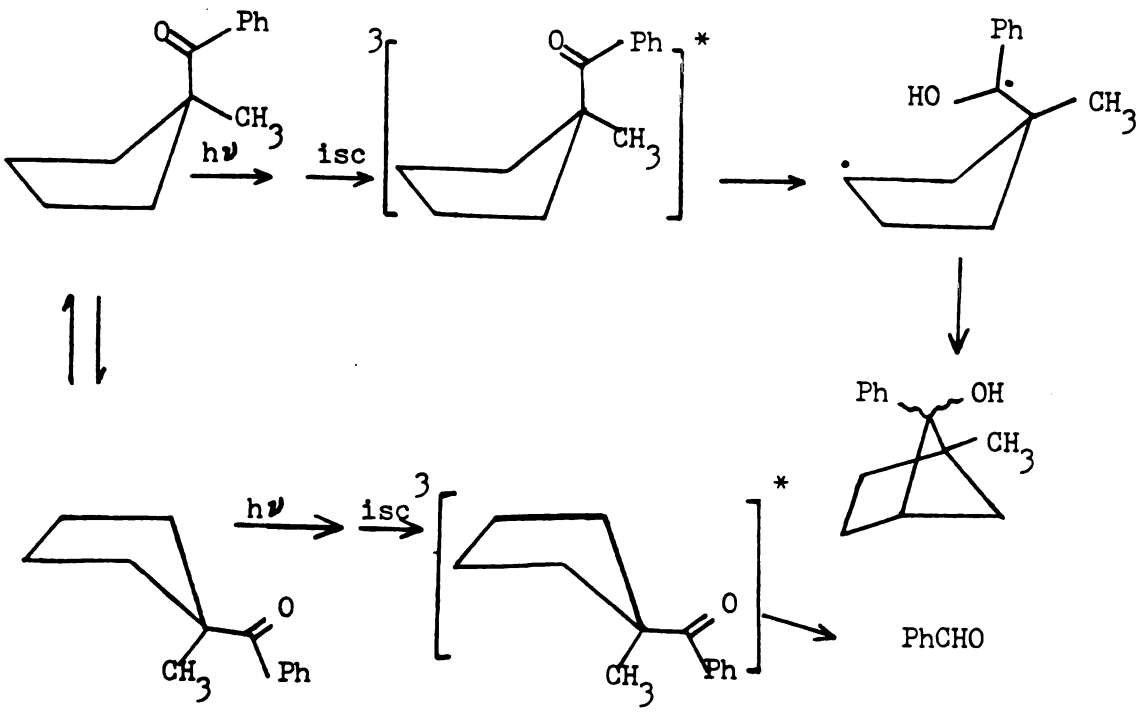
There are a number of examples of conformational effects in ketone photochemistry. Lewis[16] has investigated conformational effects in the photochemistry of 1-methylcyclohexyl phenyl ketone and a number of substituted analogues. Lewis reports that for 1-methylcyclohexyl phenyl ketones, there exist two different ketone triplets each leading to different photoproducts (Scheme 1). The ketone conformer with



Scheme 1

the benzoyl group in an axial position undergoes γ-hydrogen abstraction followed by cyclization to the corresponding 6-hydroxy-1-methyl-6-phenylbicyclo-[3.1.1]-heptane. The ketone conformer having the benzoyl group in an equatorial position cannot undergo hydrogen abstraction since the carbonyl group is oriented away from those hydrogens. Instead, it undergoes acyl cleavage giving rise to benzaldehyde as well as other products expected from the benzoyl and 1-methylcyclohexyl radicals. Lewis had found that the ratio of products produced from the two pathways is entirely dependent upon the ground state population of each ketone conformer.

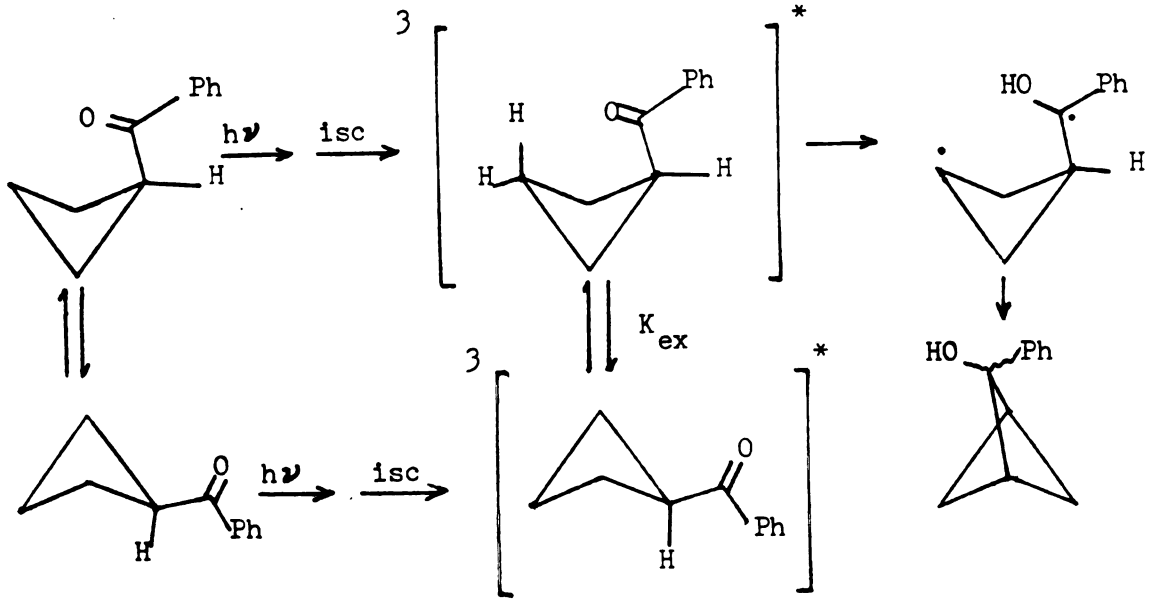
There are two different ketone conformers for 1-methylcyclopentyl phenyl ketone, which lead to either γ-hydrogen abstraction or acyl cleavage (Scheme 2). However, Lewis[16] found that product ratios are not controlled by ground state populations of the respective conformers, but rather by the relative rate constants for γ-hydrogen abstraction and acyl cleavage.



Scheme 2

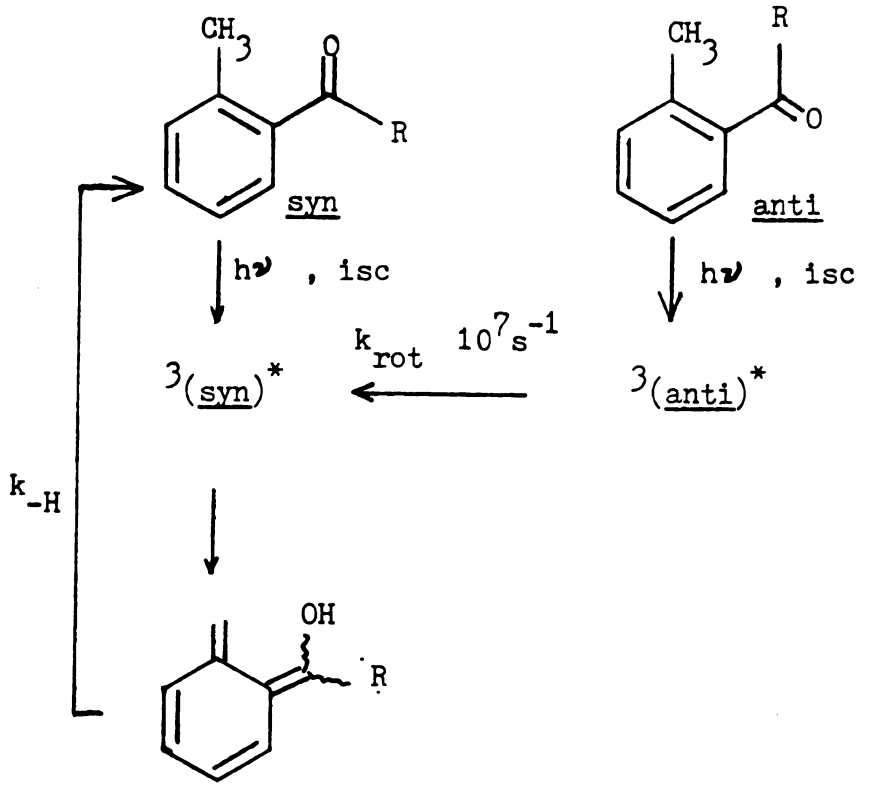
Alexander[17] has reported that an excited state equilibrium between the two triplet ketone conformers is an important

factor in the photochemistry of cyclobutyl phenyl ketone (Scheme 3).



Scheme 3

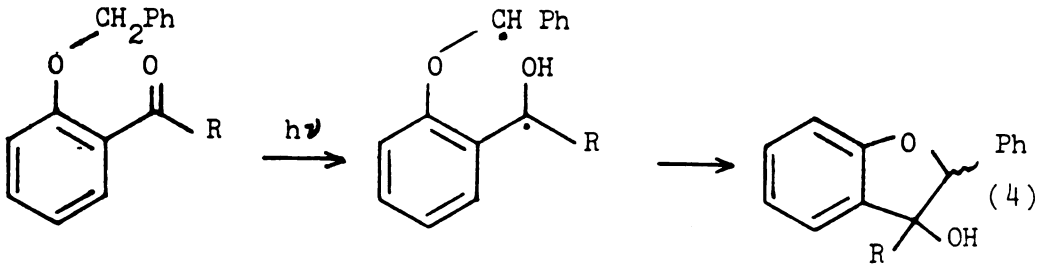
Another type of conformational effect, rotational control, is found in the photoenolization of o-alkylphenyl ketones. Wagner and Chen[18] have proposed a mechanism involving two kinetically distinct ketone rotamers, designated syn and anti (Scheme 4). The short-lived syn triplet can enolize directly upon photolysis ($k_H = 10^9 s^{-1}$). The anti triplet must first rotate ($k_{rot} = 10^7 s^{-1}$) into the syn



Scheme 4

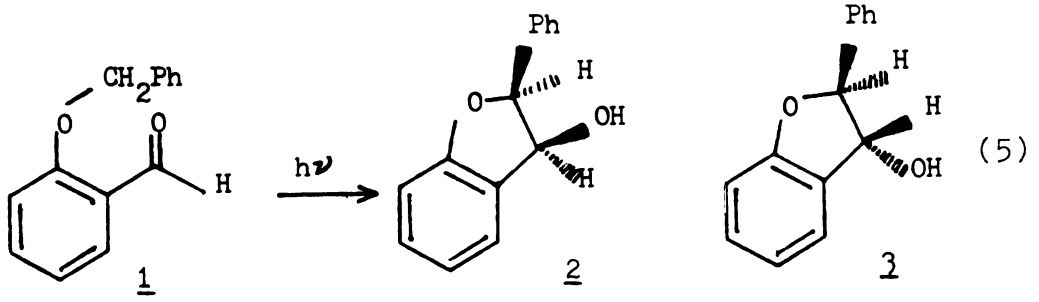
conformer before enolization can occur. Flash spectroscopy on this system by Wirz[19] and Scaiano[20] supports this mechanism.

We envisioned that the photochemistry of o-alkoxyphenyl ketones might present another example of this type of rotational control. The photochemistry of o-benzyloxyphenyl carbonyl compounds had been investigated by Pappas,[21-25] and by Lappin and Zannucci,[26] but neither group reported observing such conformational effects. These compounds provide an example of photochemical δ-hydrogen abstraction (Reaction 4).



(4)

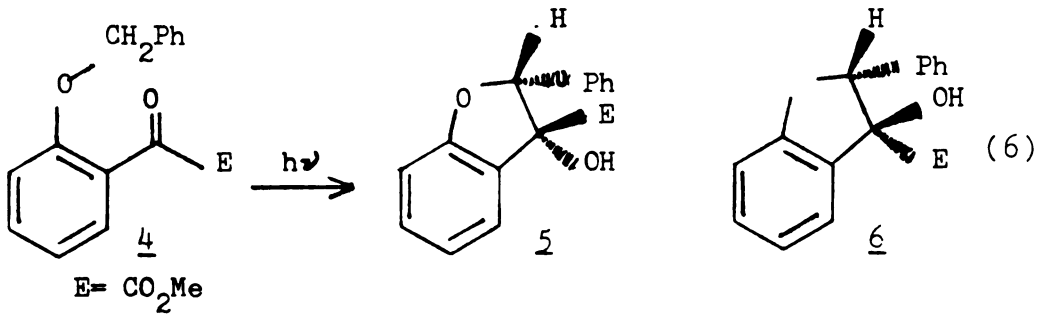
This reaction was first observed by Pappas and Blackwell[21] for o-benzyloxybenzaldehyde, 1. Irradiation of 1 in acetonitrile gave rise to two photoproducts, which readily dehydrated upon treatment with hydrochloric acid to give 2-phenylbenzofuran. Spectroscopic data revealed the structures of the two photoproducts as Z and E - 2-phenyl-3-hydroxy-2,3-dihydrobenzofuran (2 and 3 respectively),[21,22] (Reaction 5).



1 2 3 (5)

A more extensive investigation of this reaction, undertaken by Pappas,[23-25] concerns the photochemistry of a series

of methyl o-aryloxyphenyl glyoxylates, 4, (Reaction 6) Again, two isomeric 3-hydroxy-2,3-dihydrobenzofurans, 5 and 6, result from the photolysis of 4.

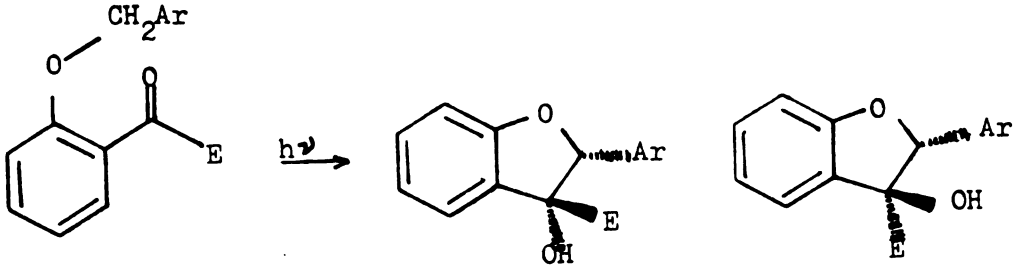


(6)

The stereoselectivity of this reaction is influenced by temperature. For example, in acetonitrile the ratio of 5 to 6 decreases slightly when the reaction temperature is raised from -35°C to 80°C (5:6 = 2.5:1 at -35°C, 5:6 = 1.5:1 at 80°C). A more dramatic example of this was found in heptane when the relative yields of 5 and 6 were measured at 0°C and 100°C. The ratio of 5:6 decreased from 20:1 to 3:1 over this temperature range. This indicates that isomer 5, in which the phenyl and carbomethoxy groups are trans, is the kinetically preferred product. This isomer would also be the thermodynamically preferred product since the two bulkiest groups, phenyl and carbomethoxy, are trans to each other.

The stereoselectivity of this reaction also depends on the polarity of the reaction medium (Table 1). The relative

Table 1. Photokinetic Data for a Series of Methyl o-Aryloxyphenyl Glyoxylates.[24]



4a Ar = Ph
4b Ar = p-CH_3Ph
4c Ar = p-ClPh

5 6

Compound	Solvent	5/6	ϕ_{5+6}	τ^{-1}, $10^7 s^{-1}$
4a	t-BuOH	1.0 (35°C)	0.47	1.3
	CH_3CN	2.2 (35°C)	0.56	3.7
	C_6H_6	6.7 (35°C)	0.89	4.3
	C_6H_6	14.6 (0°C)	----	---
4b	C_6H_6	16.0 (0°C)	0.69	3.5
4c	C_6H_6	21.2 (0°C)	0.78	2.1
4a-d_1	CH_3CN	2.1 (35°C)	0.52	---
	C_6H_6	7.2 (35°C)	0.86	---
4a-d_2	CH_3CN	1.9 (35°C)	0.41	---
	C_6H_6	7.4 (35°C)	0.81	---

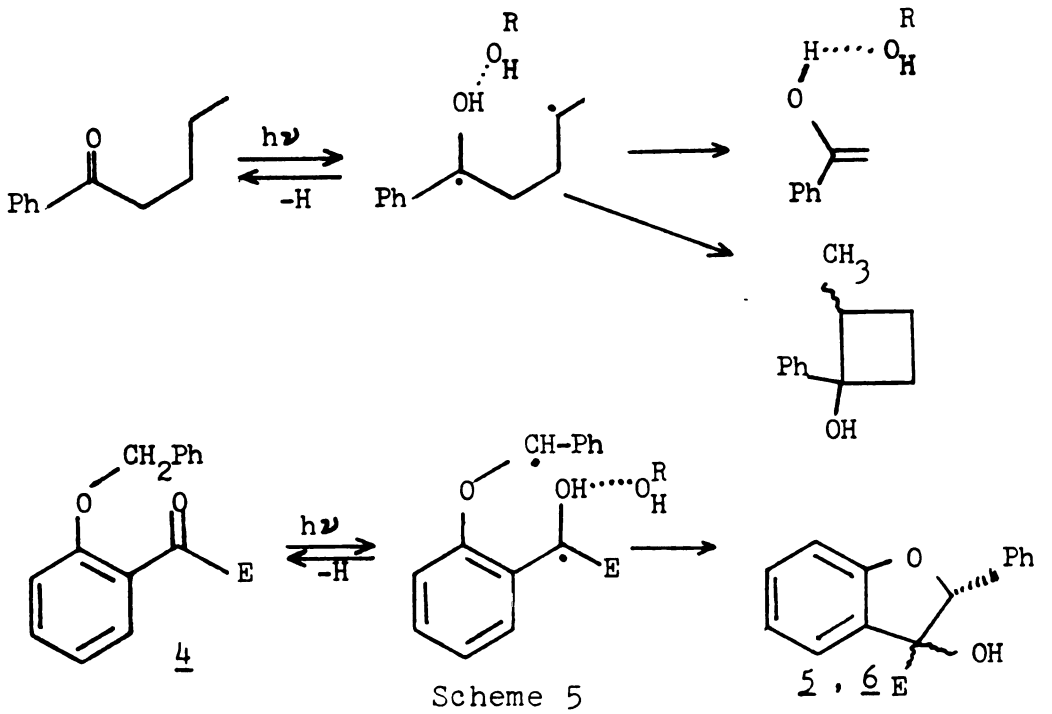
yields of 5 and 6 in benzene are 6.7:1 while they are 1:1 in acetonitrile.

Quenching of greater than 80% of the reaction by the addition of 1,3-pentadiene, a known triplet quencher, does not alter the relative yields of 5 and 6. This demonstrates that both photoproducts are formed from the same triplet.

Pappas also observed a slight sensitivity of the reciprocal triplet lifetime to the nature of the aryloxy substituent, e.g., 4b and 4c.

Decreases in the photoproduct quantum yield and in the reciprocal triplet lifetime of glyoxylate 4a were observed in polar solvents, such as t-butyl alcohol, versus nonpolar solvents. Pappas suggests two possible explanations for such behavior. The first is that t-butyl alcohol solvates the hydroxyl group of the biradical and presents a steric barrier to cyclization (Scheme 5). This steric barrier is reflected in the decreased photoproduct quantum yield for 4a.

The same type of behavior has been observed for valerophenone. Wagner[27] reports that added t-butyl alcohol increases the quantum yield for acetophenone formation in the photolysis of valerophenone, 7. However, the quantum yield of cyclobutanol products, 9, is decreased in the presence of t-butyl alcohol. Solvation of the biradical, 8, suppresses reverse hydrogen abstraction in the biradical to reform starting ketone. At the same time, this solvation increases



Scheme 5

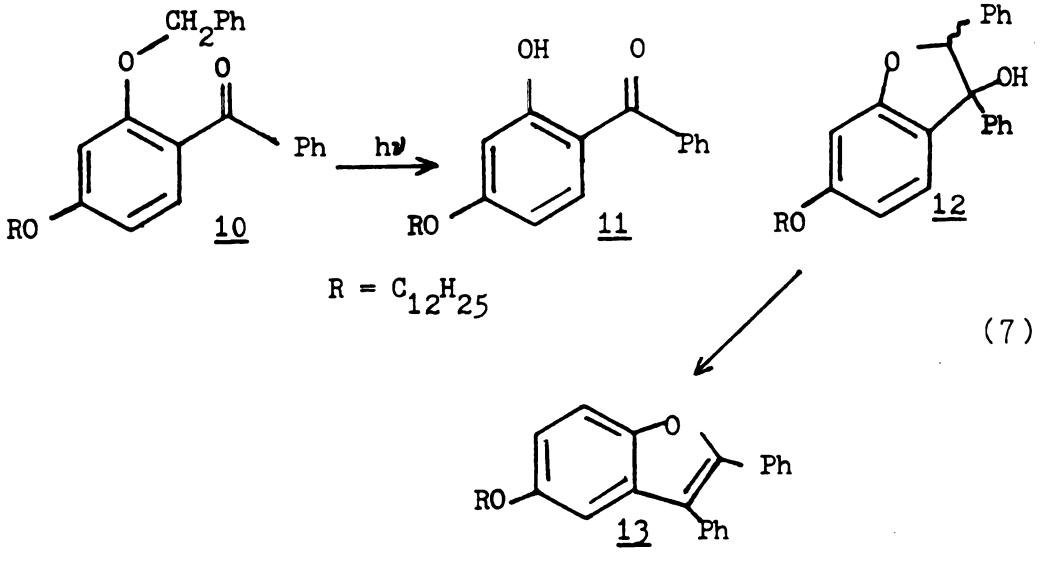
the steric barrier to cyclization, thereby lowering the yield of cyclobutanols (Scheme 5).

This observation, however, does not explain the decreased reciprocal triplet lifetime in t-butyl alcohol. It is possible that the energies of the n,π* and π,π* triplets of the glyoxylate are inverted in polar solvents. Pappas reports[25] a shift in the triplet energy of 4a from 62 to 67 kcal/mole in isopentane and EPA glasses, respectively. This shift, he suggests, is indicative of compounds with an n,π* lowest triplet.[28] Wagner[29] has observed that the triplet lifetimes of p-methoxyvalerophenone and p-methylvalerophenone are longer in polar solvents, indicative of a stabilization of the less reactive π,π* triplet. Pappas suggests that the same type of stabilization may occur for

glyoxylate 4a in t-butyl alcohol thereby lowering the reciprocal triplet lifetime of this compound.

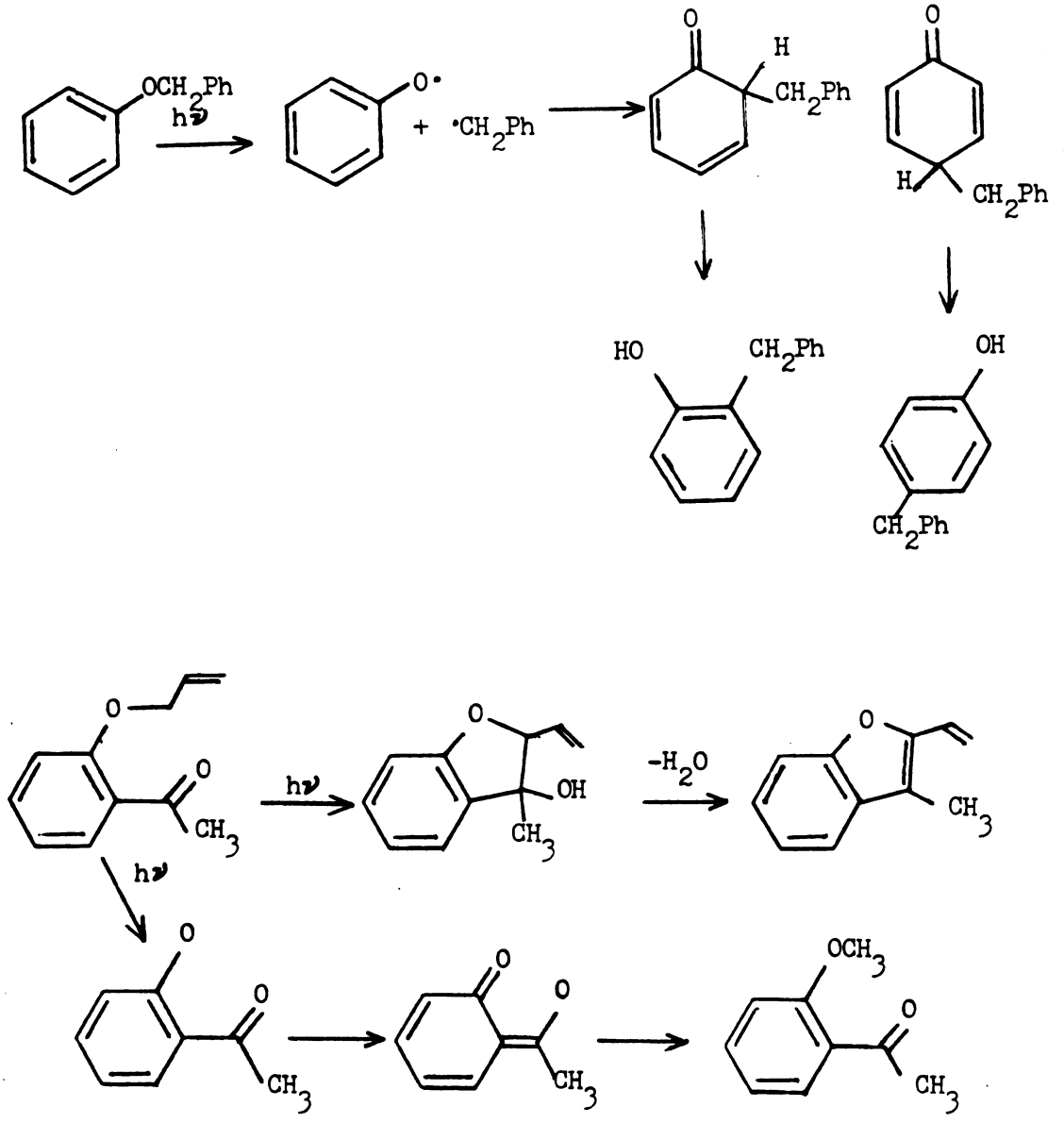
Pappas reports that there is essentially no isotope effect on the photocyclization of glyoxylate 4a. Wagner[30] has reported an isotope effect, k_H/k_D of 4.8 for γ-hydrogen abstraction by nonanophenone in benzene. Therefore, the lack of an isotope effect for δ-hydrogen abstraction in glyoxylate 4a suggests that hydrogen abstraction is not the rate determining step in the overall mechanism for the photocyclization of this compound.

Lappin and Zannucci[26] have investigated the photochemistry of 2-benzyloxy-4-dodecyloxybenzophenone, 10, and report the formation of 2-hydroxy-4-dodecycloxybenzophenone, 11, in addition to the expected photocyclization products, 12 (Reaction 7).



(7)

This hydroxybenzophenone probably arises from a photo-Fries rearrangement involving cleavage of the benzyloxy C-O bond. Similar behavior has been observed for a number of alkoxybenzenes (Scheme 6). For example, benzyl phenyl

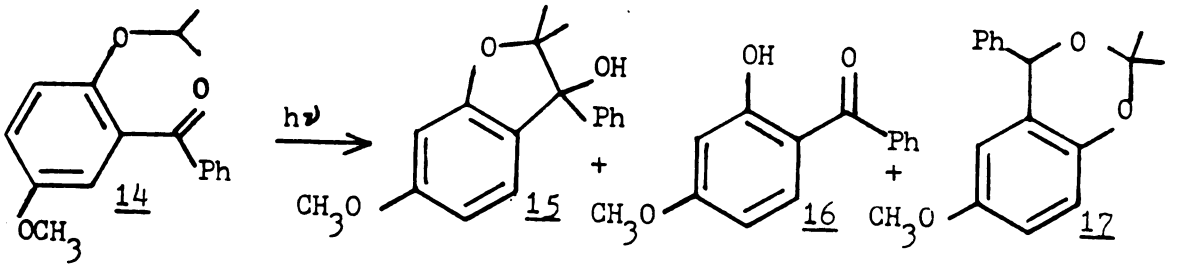


Scheme 6

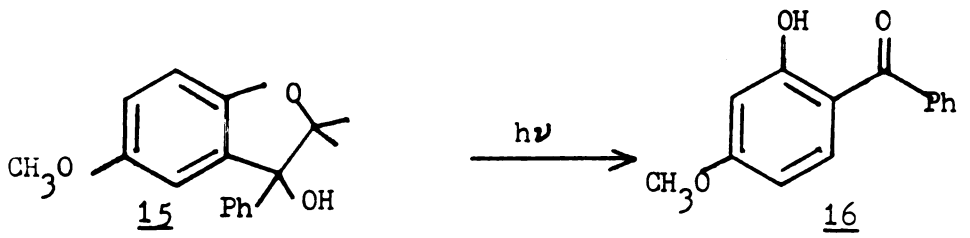
ether photochemically rearranges to both 2- and 4-benzylphenol *via* initial cleavage of the benzyloxy C-O bond followed by recombination of the resulting benzyl and phenoxy radicals. Leary and Oliver[31c] have reported that the same cleavage occurs for both 2,5-dimethoxybenzophenone and 2,4,6-trimethoxybenzophenone in carbon tetrachloride to produce the corresponding 2-hydroxybenzophenones. The same photocleavage is also observed for *o*-methoxybenzophenone both in carbon tetrachloride solutions and in the solid state.[31c] Jones and Sullivan[31d] report that irradiation of 2-allyloxyacetophenone in methanol gives rise to 2-methoxyacetophenone in 12% yield, as well as the expected 3-methyl-2-vinylbenzofuran (1% yield). Cleavage of the allyloxy C-O bond, followed by interception of the resulting phenoxy radical by methanol would give rise to 2-methoxyacetophenone (Scheme 6).

Prolonged irradiation of 2-benzyloxy-4-dodecycloxybenzophenone also produced 2,3-diphenylbenzofuran, 13, (presumably as a secondary photoproduct arising from the photochemical dehydration of 3-hydroxy-2,3-dihydrobenzofuran, 12) in 64% yield[26] (Reaction 7).

Photolysis of 2-isopropoxy-4-methoxybenzophenone,[26] 14, produced the expected benzofuranols, 15, 2-hydroxy-4-methoxybenzofuran, 16, and 2,2-dimethyl-4-phenyl-8-methoxy-1,3-benzodioxane, 17 (Reaction 8).



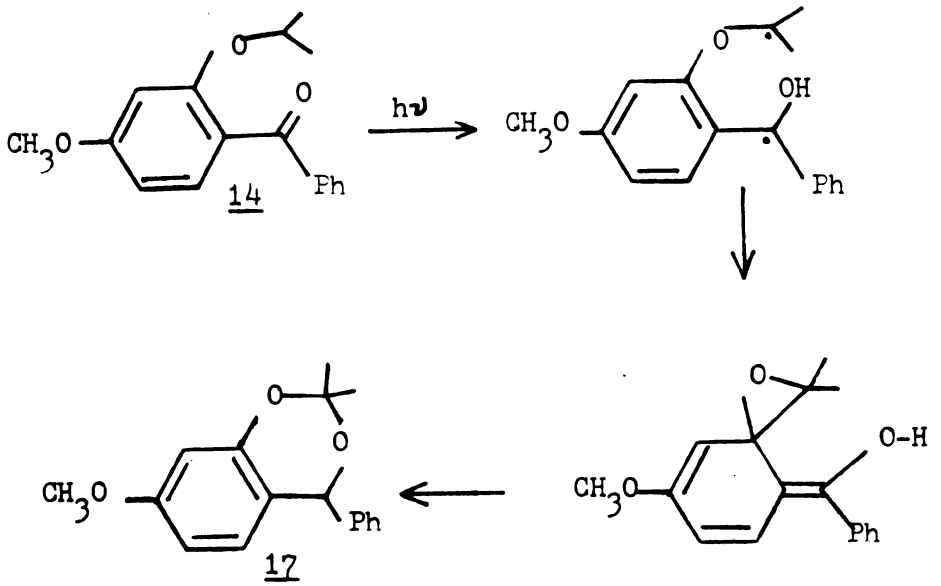
Solvent	Φ_{15}	Φ_{17}
Cyclohexane	0.26	0.15
Acetonitrile	0.023	0.005



Irradiation of 2,3-dimethyl-3-hydroxy-3-phenyl-2,3-dihydrobenzofuran, 15, produced 2-hydroxy-4-methoxybenzophenone, 16, indicating that 16 is formed as a secondary photoproduct from 15.

The benzodioxane, 17, is not formed as a secondary photoproduct. Lappin is unable to provide a definite mechanism for its formation, but suggests that it may be formed as the product of a bimolecular reaction between ketone 14 and its

biradical. Another plausible mechanism involves cyclization of the biradical to a spiro epoxide which rearranges to the observed benzodioxane, 17 (Scheme 7).

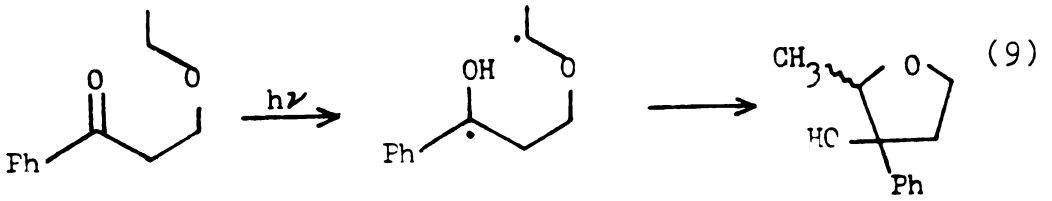


Scheme 7

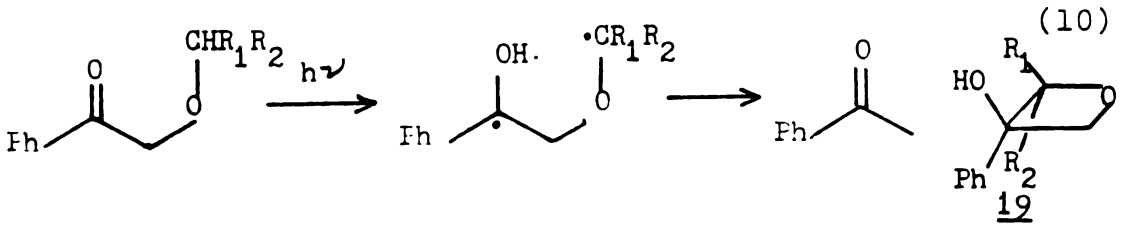
Both Lappin and Pappas report rate constants for hydrogen abstraction in o-benzyloxyphenyl carbonyl compounds on the order of $10^7 s^{-1}$.

Wagner[32] has reported a rate constant of 1-2 x $10^7 s^{-1}$ for photochemical hydrogen abstraction in β-ethoxypropiophenone (Reaction 9).

Turro and Lewis[33] report rate constants for γ-hydrogen abstraction in a series of α-alkoxyacetophenones in benzene on the order of $10^9 s^{-1}$ (Reaction 10).



(9)



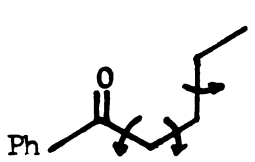
(10)

19

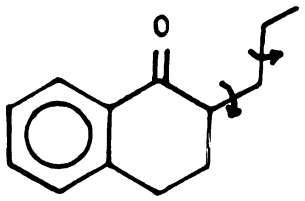
Ketone	R_1	R_2	ϕ_{19}	k_r, $10^9 s^{-1}$
18 a	H	H	0.42	3.2
18 b	H	CH_3	0.59	8.4
18 c	CH_3	CH_3	0.40	8.2

Intramolecular photochemical γ-hydrogen abstraction has been found to be much faster in cyclic ketones than in acyclic ones.[34] This is due to an immobilization of the possible rotations involved in the formation of the six-center transition required for γ-hydrogen abstraction.[35] 2-Benzoylnorborane[34] requires about the same activation energy for hydrogen abstraction as valerophenone (3.6 ± 0.2 kcal/mole). However, the activation entropy for hydrogen abstraction in 2-benzoylnorborane is approximately 8 eu

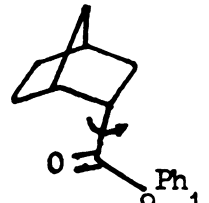
more than for valerophenone (Scheme 8). Therefore, the rate enhancement observed for γ-hydrogen abstraction in 2-benzoylnorborane is purely the result of easing the entropic requirements necessary for transition state formation. As can be seen in Scheme 8, an approximate ten fold increase in the rate of hydrogen abstraction accompanies an immobilization of each carbon-carbon bond.[34,35]



k_H $1.2 \times 10^8 s^{-1}$



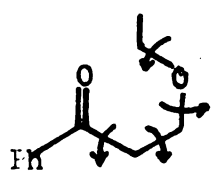
$6.0 \times 10^8 s^{-1}$



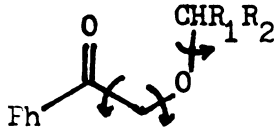
$7 \times 10^9 s^{-1}$

Scheme 8[35]

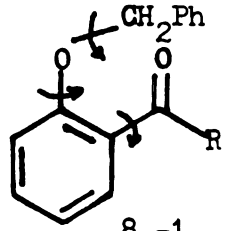
In light of the results above, a comparison of β-ethoxypropiophenone and α-alkoxyacetophenones with o-benzyloxyphenyl ketones provides an estimated rate constant of at least $10^8 s^{-1}$, ten times greater than what is reported!



k_H $10^7 s^{-1}$

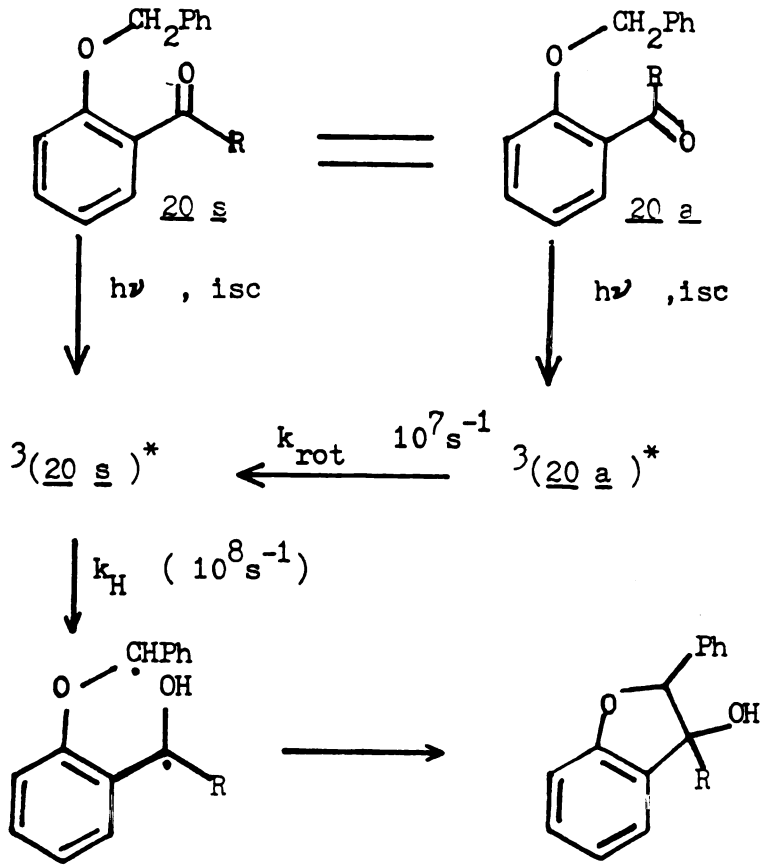


$10^9 s^{-1}$



$10^8 s^{-1}$ (predicted)
$10^7 s^{-1}$ (observed)

One possible explanation for this discrepancy is summarized in Scheme 9.



Scheme 9

The scheme shown is similar to that suggested by Wagner and Chen for o-alkylphenyl ketones.[18] Hence, it is possible that there are two different triplet rotamers for o-benzyloxyphenyl ketones - a syn triplet, ^{3}(20s)*, and an

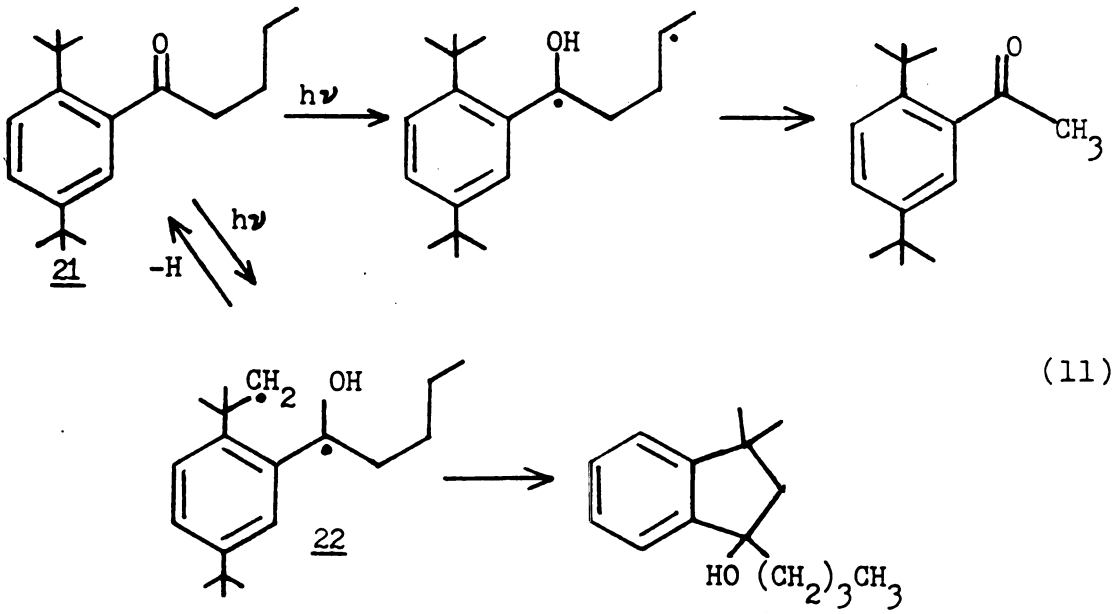
anti triplet, ^{3}(20a)*, δ-hydrogen abstraction can occur directly only from the syn triplet. However, the anti triplet can give rise to hydrogen abstraction by first rotating to the syn triplet. The rate constant for such a rotation has been measured by Wagner[18] as $10^7 s^{-1}$ for o-alkylphenyl ketones. This is approximately the same value reported by both Pappas[21-25] and Lappin[26] for the rate constant for δ-hydrogen abstraction in o-benzyloxyphenyl carbonyls!

The object of the first portion of this thesis deals with the reexamination of the photochemistry of o-alkoxyphenyl ketones with particular emphasis on elucidating any special conformational effects.

Although it is not as common as γ-hydrogen abstraction, photochemical δ-hydrogen abstraction has been observed in a number of systems besides o-alkoxyphenyl carbonyl compounds. Bergmark[36] reports that photolysis of 2,5-di-tert-butylacetophenone, 21, did not give rise to any detectable amounts of 2,5-di-tert-butylacetophenone, the expected photoproduct of γ-hydrogen abstraction (Reaction 11). Bergmark suggests that a highly competitive δ-hydrogen abstraction occurs to produce biradical 22. This biradical does not cyclize, presumably for steric reasons, but rapidly disproportionates to starting material.

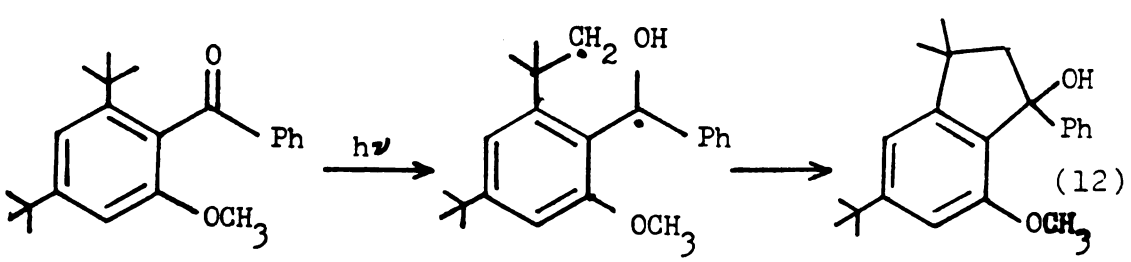
Bergmark cites the observation by Porter[37] that the quantum yield for the photoreduction of 2-tert-butylbenzophenone in isopropanol is only half that of benzophenone.

He suggests that the same highly reversible δ-hydrogen abstraction is responsible for this decreased quantum yield.



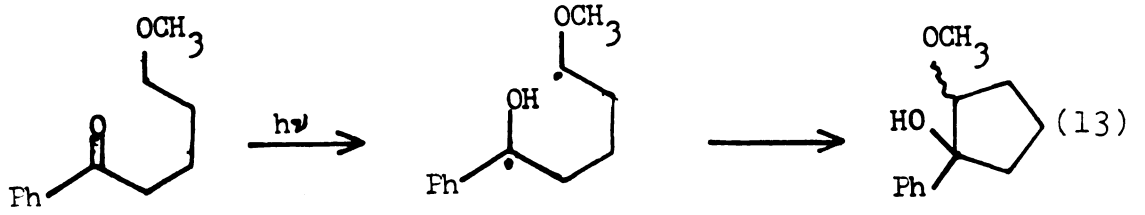
(11)

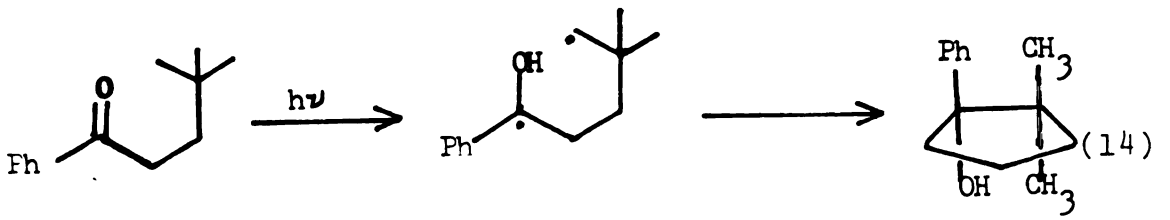
In fact, O'Connell[38] has reported such a δ-hydrogen abstraction for 2,4-di-tert-butyl-6-methoxybenzophenone followed by cyclization to 1,1-dimethyl-2-hydroxy-4-methoxy-2-phenyl-6-tert-butylindane (Reaction 12).



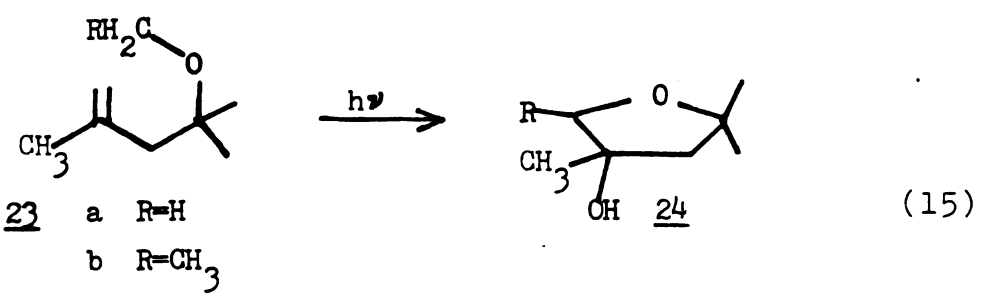
(12)

Wagner[32] has reported that both γ-methoxyvalerophenone and γ,γ-dimethylvalerophenone readily undergo photochemical δ-hydrogen abstraction (Reactions 13, 14).



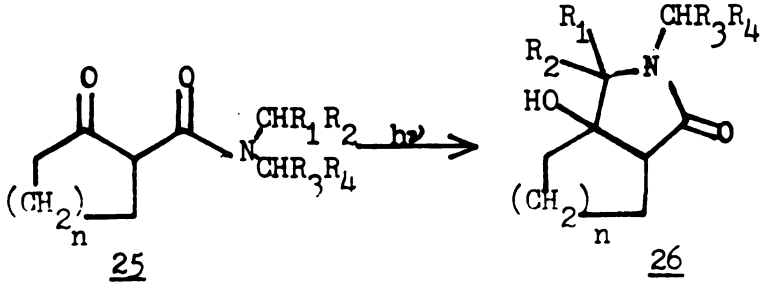


A few years prior to Wagner's work on β-ethoxypropiophenone, Stephenson and Parlett[39] reported that both 4-methyl-4-methoxy-2-pentanone, 23a, and 4-methyl-4-ethoxy-2-pentanone, 23b, undergo facile photochemical δ-hydrogen abstraction to produce the corresponding 5-substituted-2,2,4-trimethyl-4-hydroxytetrahydrofuran, 24 (Reaction 15).



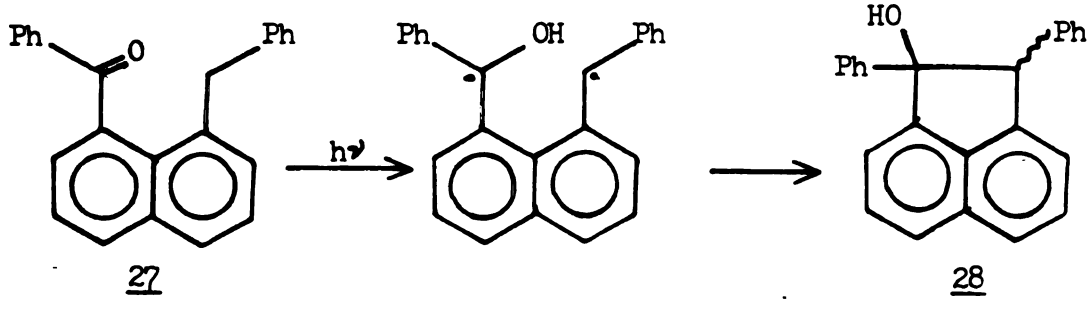
23 a R=H
b R=CH3

Aoyama and co-workers[40] have reported photochemical δ-hydrogen abstraction in a series of N,N-dialkyl-2-oxacycloalkylcarboxamides, 25, giving rise to the corresponding lactams, 26 (Reaction 16).



(16)

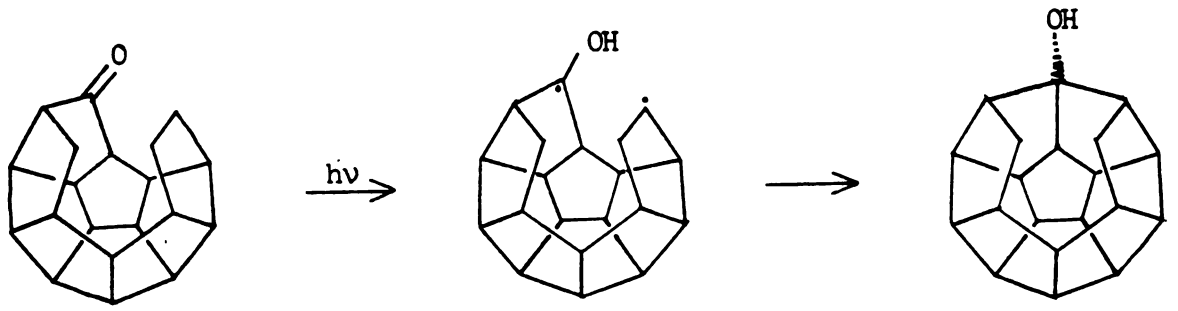
Schlessinger and co-workers[41] have reported that 1-benzoyl-8-benzylnaphthalene, 27, undergoes δ-hydrogen abstraction followed by cyclization to the corresponding alcohol, 28, in 91% yield (Reaction 17).



(17)

Perhaps the most elegant application of photochemical δ-hydrogen abstraction was reported by Paquette[42] in the total synthesis of dodecahedrane (Reaction 18).

The second portion of this thesis will deal with a new example of photochemical δ-hydrogen abstraction found for



a series of α-(o-alkylphenyl)-acetophenones. Particular emphasis will be placed on the conformational effects that manifest themselves in this reaction.

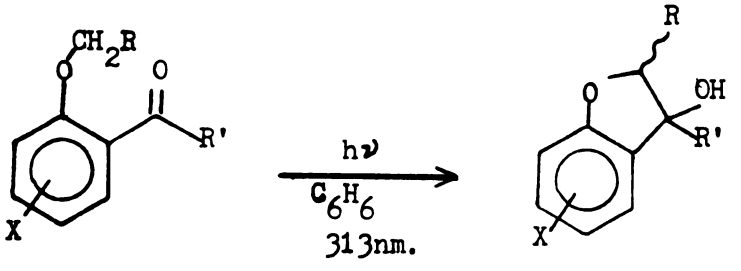
Although a great deal has been published concerning the behavior of 1,4-biradicals, very little is known about 1,5-biradical behavior. This topic will be addressed in this thesis, in particular the behavior of 1,5-biradicals produced from o-alkoxyphenyl ketones.

RESULTS

A. o-Alkoxyphenyl Ketones

1. Identification of Photoproducts

Irradiation of degassed 0.02 to 0.04 M benzene solutions of various o-alkoxyphenyl ketones at 313 nm produced the corresponding 2,3-disubstituted 3-hydroxy-2,3-dihydrobenzofurans (both E and Z isomers) as the major photoproducts (Reaction 19). E and Z refer to the positions of the 2-substituent and the hydroxyl group.

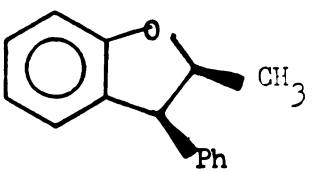


(19)

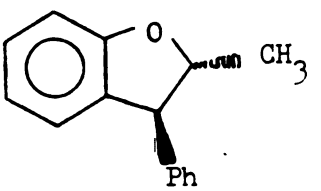
Structural assignments were based upon spectral data obtained for these compounds (^{1}H and ^{13}C nmr, i.r., and mass spectrum). ^{1}H nmr proved particularly useful in assigning the stereochemistries of the diastereomeric benzofuranol photoproducts. Pappas[22] has reported that the diastereomer of 2-methyl-3-phenyl-2,3-dihydrobenzofuran in which the phenyl and methyl substituents are cis has a

methyl signal at 0.74 ppm. The methyl group in the <u>trans</u> isomer appears at 1.37 ppm (Scheme 10).

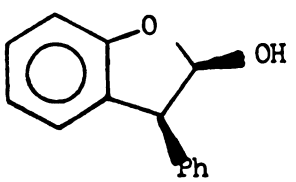
Pappas



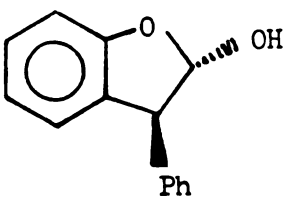
δ_{CH_3} 0.74 ppm.



1.37 ppm.

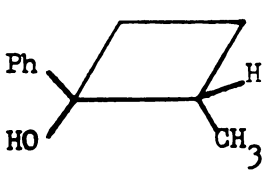


δ_{OH} 1.40 ppm.

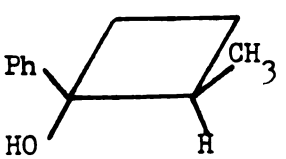


2.5 ppm.

Lewis



δ_{CH_3} 1.10 ppm.



o.60 ppm

Scheme 10

Lewis and Hilliard[43] observed the same effect for the two diastereomers of 2-methyl-1-phenylcyclobutanols (Scheme 10). The same is also true for the hydroxyl proton in the two diastereomers of 2-phenyl-3-hydroxy-2,3-dihydrobenzofurans (Scheme 10). Pappas[22] has found that the hydroxyl proton in the cis isomer is shielded and appears upfield of the hydroxyl proton of the trans isomer.

The stereochemical assignments of the dihydrobenzofuranol photoproducts were based upon these considerations. Thus, the methyl group of E-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran (phenyl and hydroxyl are trans; phenyl and methyl are cis) appears upfield of the methyl group of the Z isomer, because it is in the shielding cone of the benzene ring (Scheme 11). Similarly, the hydroxyl proton of the Z isomer is shielded and appears upfield of the hydroxyl proton of the E isomer. Both the hydroxyl proton and C-2 proton of Z-2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran are shielded by adjacent benzene rings and appear upfield of their respective signals for the E isomer (Scheme 11).

In some cases, the benzofuran photoproducts were produced in quantitative yields. In such instances, it was possible to monitor the progress of the photoreaction by ^{1}H nmr spectroscopy. An example of this is seen in Figure 2. In this experiment, a solution of o-benzyloxybenzophenone

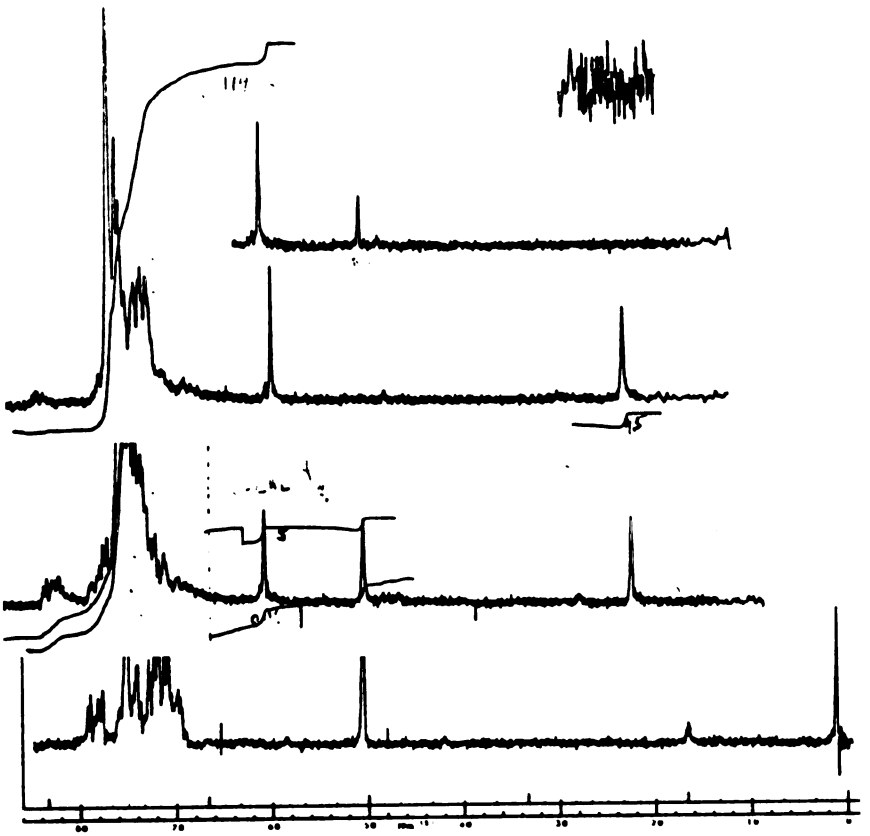
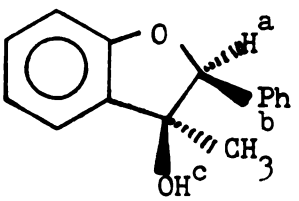
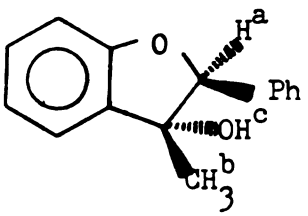
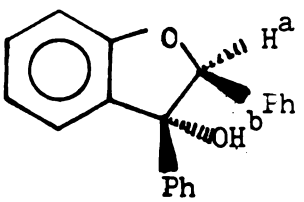


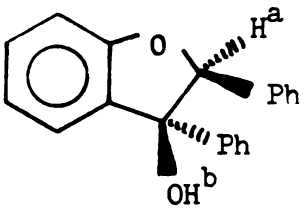
Figure 2. Monitoring the photocyclization of o-benzyloxybenzophenone in d_6-benzene by ^{1}H-nmr.





δ_a	5.52	5.30
δ_b	1.11	1.70
δ_c	2.48	1.45





δ_a	5.77	5.66
δ_b	2.62	1.95

Scheme 11

in d_6-benzene was placed in a 5 mm nmr tube, degassed with a steady stream of nitrogen, and irradiated at 313 nm. As the reaction progressed, the methylene peak at 4.5 ppm was lost and replaced by the methine proton resonance of the photoproduct (5.5 ppm). The upper spectrum in Figure 12 corresponds to the reaction mixture at 100% ketone conversion. Treatment of this sample with deuterium oxide resulted in the disappearance of the singlet at 1.9 ppm,

confirming the presence of the hydroxyl group in the photoproduct.

A number of these 3-hydroxy-2,3-dihydrobenzofuran photoproducts readily fragment in the mass spectrometer, with loss of water, as would be expected.[44] An example of this can be seen in Figure 3, the mass spectrum of 2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran (produced by the photolysis of o-benzyloxybenzophenone). The base peak (M/e = 270) corresponds to the molecular weight of 2,3-diphenylbenzofuran.

The 3-hydroxy-2,3-dihydrobenzofuran photoproducts readily dehydrate upon treatment with hydrochloric acid. The same behavior was observed by Pappas.[21] Thus, treatment of a sample of 2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran with hydrochloric acid gave rise to a compound whose mass spectrum correlates well with that of an authentic sample of 2,3-diphenylbenzofuran (Figures 4 and 5).

Irradiation of degassed samples of 2,6-diacylalkoxybenzenes produced photoproducts which underwent secondary photoreactions. This is not surprising since these photoproducts are themselves o-alkoxyphenyl ketones and would absorb strongly at 313 nm (Reaction 20). In cases where photoproduct quantum yields and triplet lifetimes were measured, ketone conversions were kept at 5 - 10% to minimize the possibility of such secondary reactions. The structures of these secondary photoproducts were not

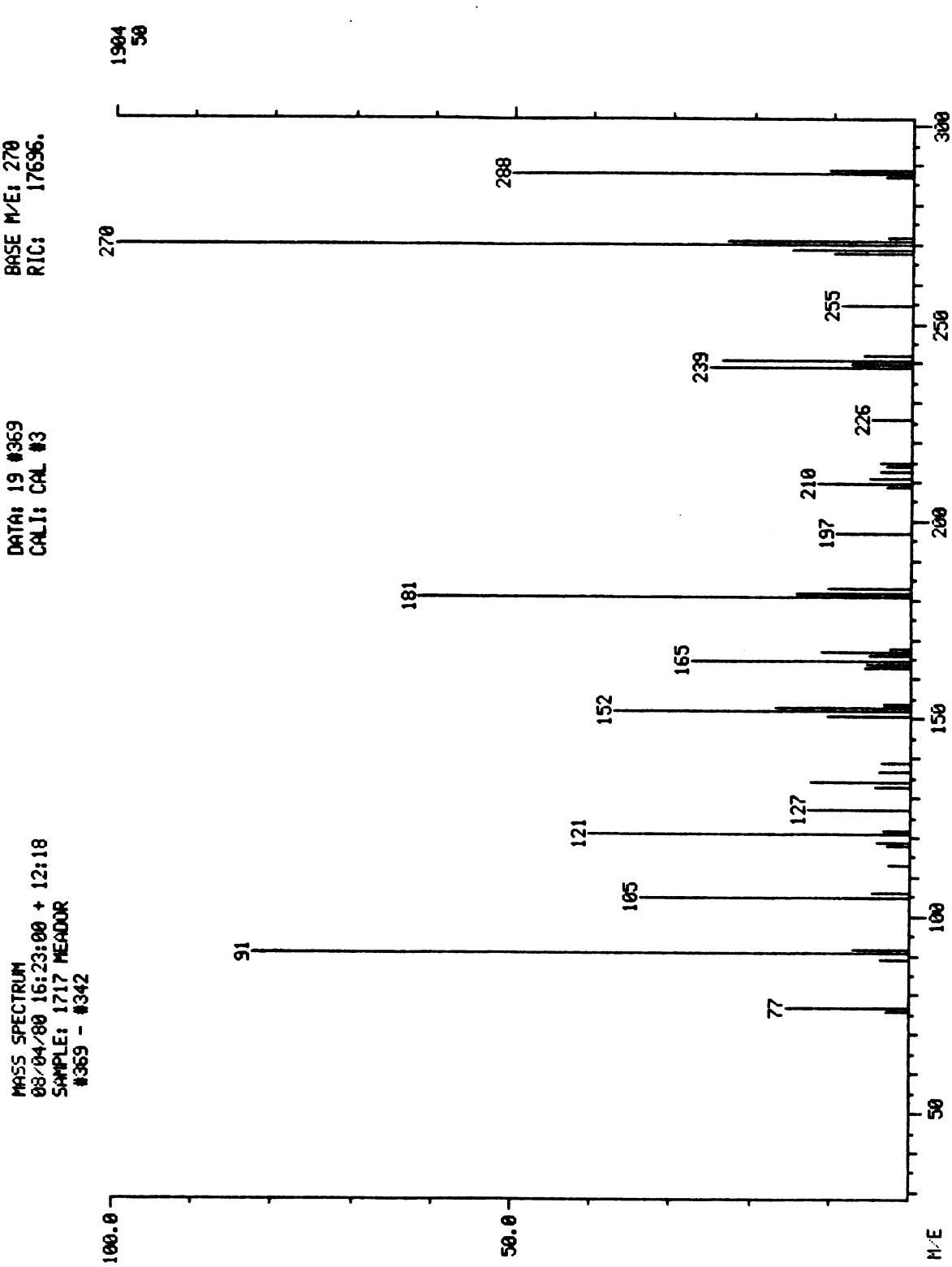
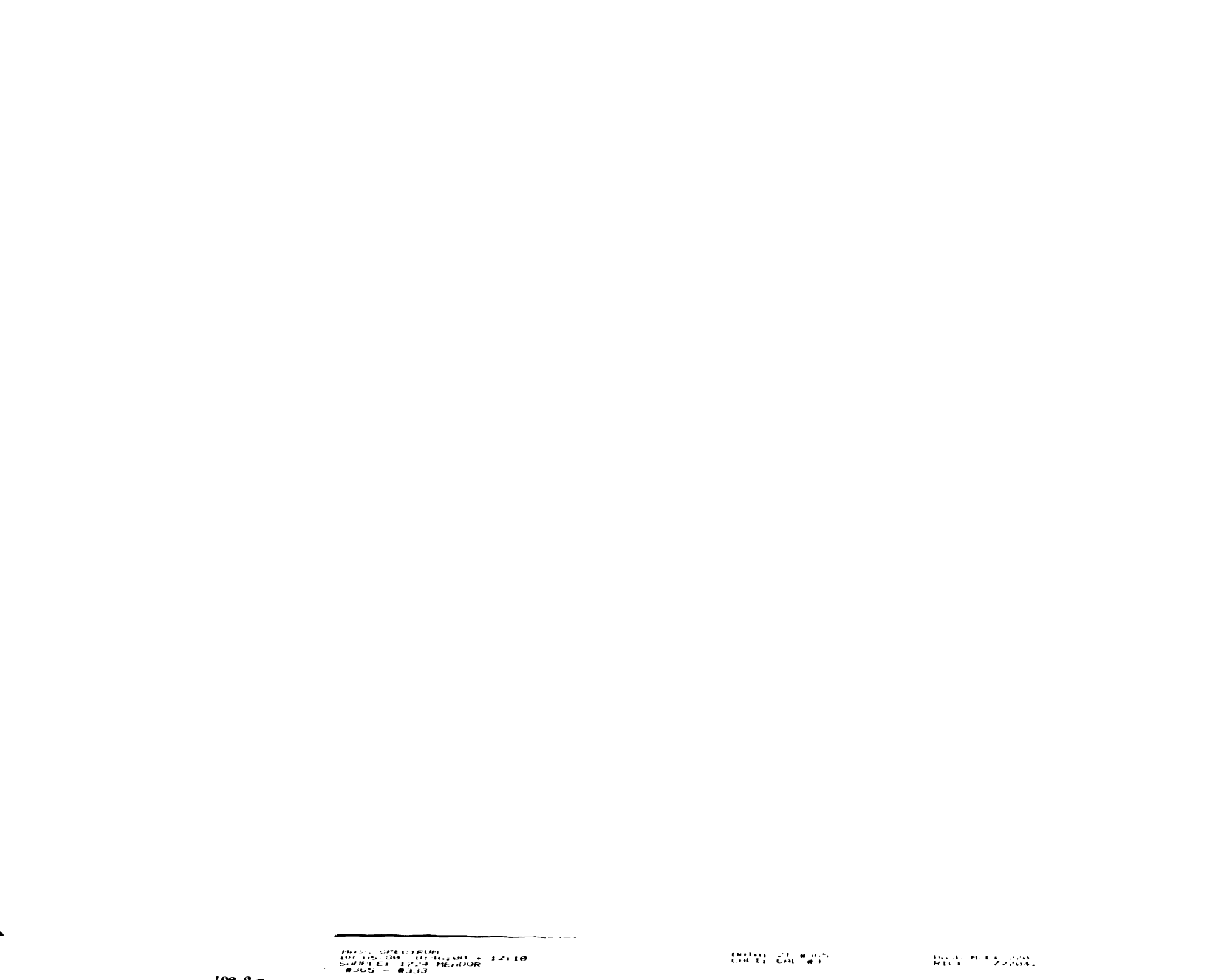


Figure 3. The mass spectrum of 2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran.


SPECTRUM
SWITCH 1724 MENDOR
#365 - #333
Delay 21 #365
CH1: CH #1
RT1 22504.

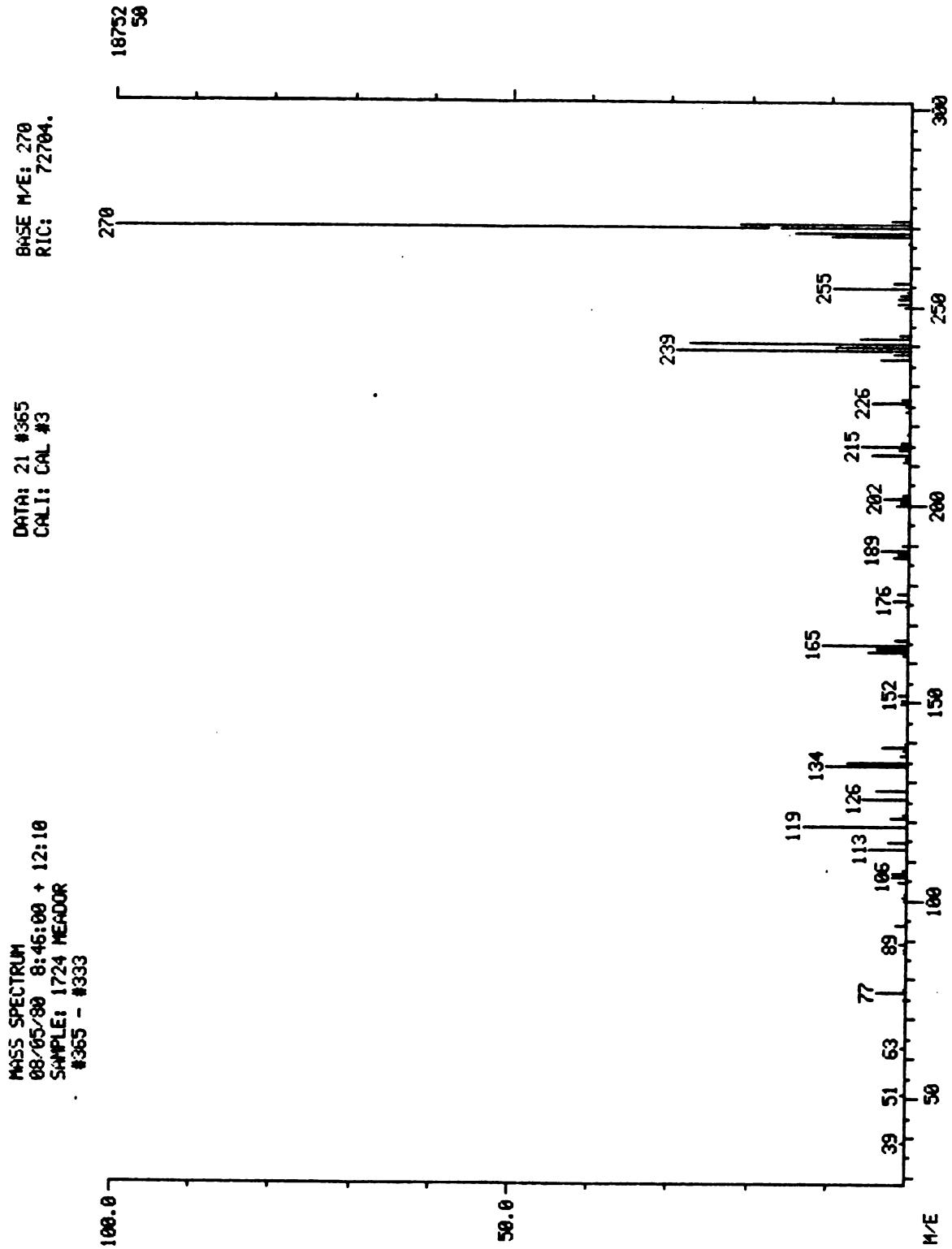


Figure 4. Mass spectrum of the product arising from the treatment of the crude photolysate from o-benzyloxybenzophenone with hydrochloric acid.

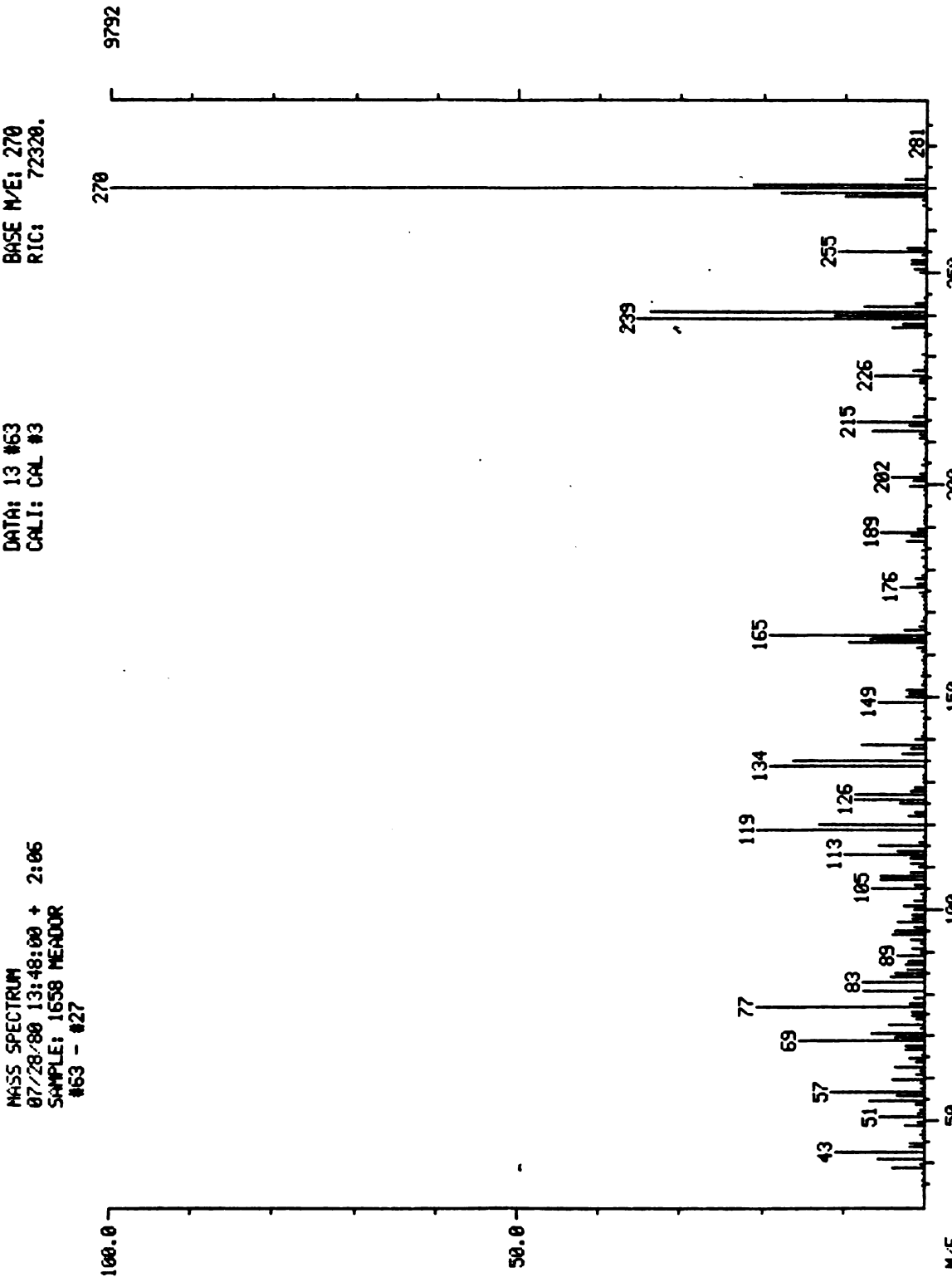
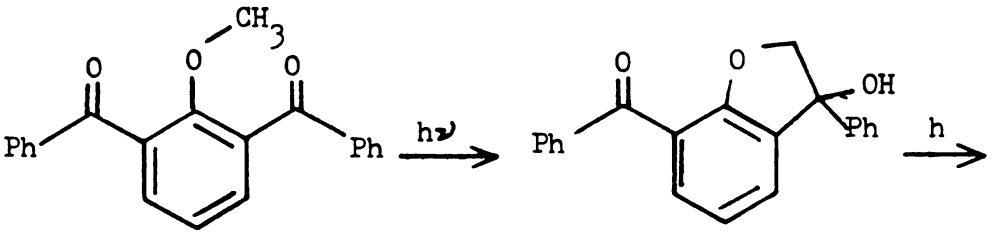


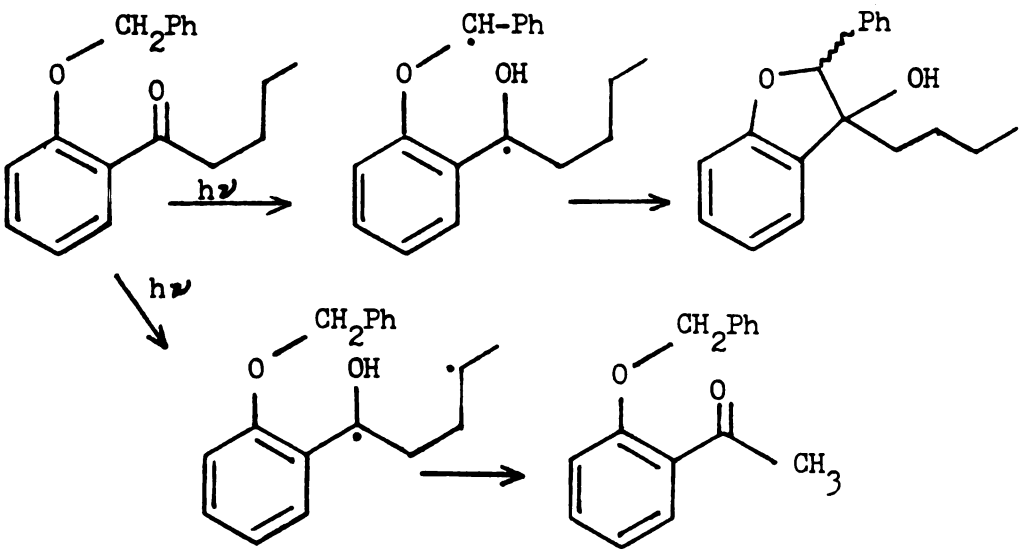
Figure 5. Mass spectrum of "authentic" 2,3-diphenylbenzofuran.

determined since knowledge of their structure had no direct bearing upon this project.



(20)

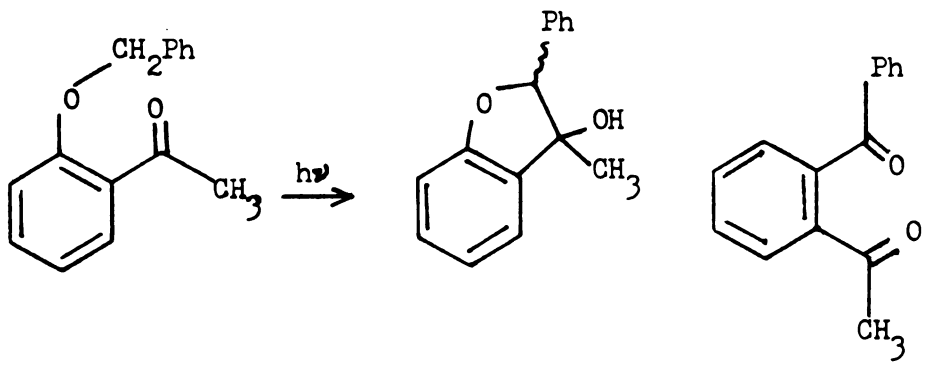
No photoproducts attributable to δ-hydrogen abstraction were detected from the irradiation of o-benzyloxyvalerophenone, 29. Instead, o-benzyloxyacetophenone, 30 arising from γ-hydrogen abstraction, was the only photoproduct observed (Reaction 21).



(21)

2-Acetylbenzophenone was produced as the major photoproduct from o-benzyloxyacetophenone, in addition to

Z-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran and a trace amount of the E isomer (Reaction 22).

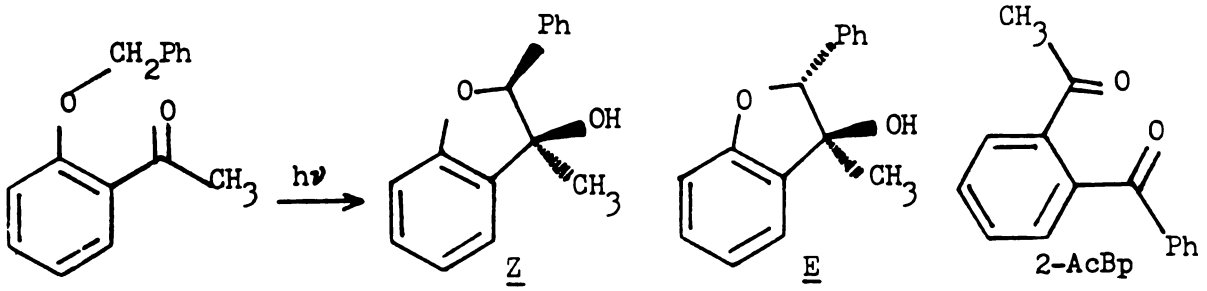


(22)

Photolysis of o-benzyloxyacetophenone in benzene containing varying amounts of pyridine resulted in a dramatic increase in the amounts of Z and E-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofurans. The quantum yield of 2-acetylbenzophenone was essentially unaffected. The stereoselectivity of the photocyclization was also affected by added pyridine. In the absence of pyridine, the photocyclization strongly favored formation of the less hindered Z isomer. However, the quantum yields of Z and E isomers are nearly equal in benzene containing 2.2 M pyridine (Table 2).

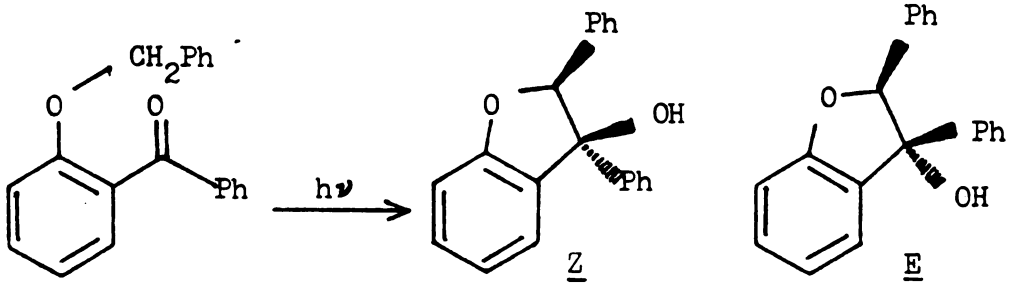
Added pyridine also affected the stereoselectivity of the photocyclization of o-benzyloxybenzophenone. There is almost no stereoselectivity in benzene containing 2.2 M pyridine. The overall quantum yields for photocyclization are reduced (Table 3). This reduction is also observed for o-methoxybenzophenone in the presence of added

Table 2. The Effects of Pyridine on the Quantum Yields for Photoproduct Formation from o-Benzyloxyacetophenone in Benzene at 25°C.



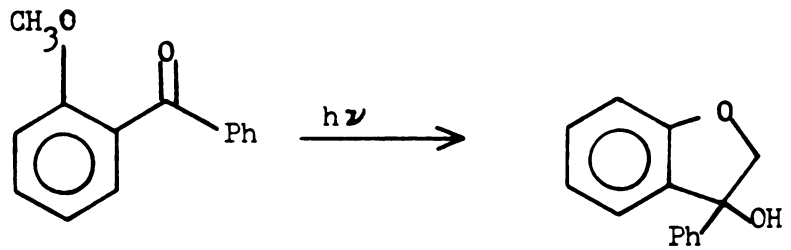
[Pyridine], M	ϕ_{Z}	ϕ_{E}	$\phi_{2\text{-AcBP}}$	ϕ_{total}
0.0	0.0226	0.00	0.0589	0.0815
0.544	0.0598	0.0301	0.0670	0.157
1.09	0.0872	0.0528	0.0579	0.198
1.63	0.101	0.0666	0.0517	0.219
2.18	0.118	0.0811	0.0456	0.245

Table 3. The Effects of Pyridine on the Quantum Yields for Z and E Photoproducts from o-Benzyloxybenzophenone in Benzene at 25°C.



[Pyridine], M	ϕ_Z	ϕ_E	ϕ_{total}
0.00	0.831	0.108	0.939
1.24	0.358	0.290	0.648
2.47	0.323	0.293	0.616

Table 4. The Effect of Pyridine on the Photocyclization Quantum Yield of o-Methoxybenzophenone in Benzene at 25°C.



[Pyridine], M	ϕ_{cyc}
0.00	0.299
1.24	0.157
2.47	0.151

pyridine (Table 4).

2. Kinetic Results

Stern-Volmer quenching[45] was used to measure the triplet lifetime of a number of o-alkoxyphenyl ketones. In these experiments, a conjugated diene, e.g., 2,5-dimethyl-2,4-hexadiene, is used to quench the triplet ketone by energy transfer. A mathematical relationship holds between the ratio of photoproduct in the absence and presence of quencher and the concentration of quencher used. This relationship is given in Equation 1.

$$\frac{\phi^{o}}{\phi} = 1 + k_q \tau_T [Q] \qquad \text{Equation 1}$$

where ϕ^{o} = quantum yield in the absence of quencher

ϕ = quantum yield in the presence of quencher

τ_T = ketone triplet lifetime

$[Q]$ = concentration of quencher

k_q = rate constant for energy transfer quenching by the diene

Thus, a plot of ϕ^{o}/ϕ versus $[Q]$ should give a straight line with an intercept of 1.0 and a slope of $k_q\tau_T$. In most cases, energy transfer quenching by dienes is close to the rate of diffusion in a given solvent.[46] For example, k_q is known to equal 5-6 x $10^{9}M^{-1}s^{-1}$ in benzene at

25°C.[47] Therefore, the triplet lifetime can be calculated from the slope of the Stern-Volmer plot.

The photoproduct quantum yields and triplet lifetimes of a number of o-alkoxyphenyl ketones are given in Table 5.

Intersystem crossing quantum yields were measured for o-benzyloxybenzophenone and o-benzyloxyacetophenone and each was found to be 1.0. These measurements were made using the ketone to sensitize the isomerization of either trans-stilbene or cis-piperylene.[48]

A number of o-alkoxyphenyl ketones were studied by nanosecond laser flash spectroscopy using a Molectron nitrogen laser as the excitation source (λ_{exc} = 337.1 nm, E_{exc} = 3 to 10 mJ). This technique involves monitoring the absorbance of a traisient species, e.g., a ketone triplet, at a fixed wavelength as a function of time. The result is a simple first-order decay curve, where

$$\ell n \frac{A}{A_\infty - A_t} = k_{exp}\, t \qquad \text{Equation 2}$$

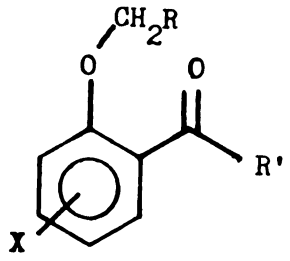
where A_∞ = infinite (baseline) absorbance of the transient

A_t = absorbance of the transient at time, t

k_{exp} = transient decay rate constant

Thus, the triplet lifetimes can be measured directly from

Table 5. Results of Stern-Volmer Quenching of Various o-Alkoxyphenyl Ketones with 2,5-Dimethyl-2,4-hexadiene in Benzene at 25°C.



Ketone	R	R'	X	ϕ_{pdt}	$k_q \tau_T$, $M^{-1 \cdot k}$
o-BzOBP[a]	Ph	Ph	H	0.83 ±0.02[b] 0.108 ±0.002[c]	101.0±1.7
o-BzOBP[d]	Ph	Ph	H	0.46	51.5
o-BzOBP[a,e]	Ph	Ph	H	----	0.5596±0.016
o-MeOBP[a]	H	Ph	H	0.30 ±0.05	2580.0±230.0
o-BzOAP[a]	Ph	CH_3	H	0.0226±0.004	1720.0±30.0
o-BzOAP[f]	Ph	CH_3	H	----	2200.0
o-BzO-5-MeBP[a]	Ph	Ph	5-CH_3	0.55 ±0.03	163.0±6.0
2,2'-DiBzOBP[a]	Ph	2-($PhCH_2O$)Ph	H	0.46 ±0.001	68.8±2.9
o-BzOVP[a]	Ph	$(CH_2)_3CH_3$	H	0.30 ±0.04 (0.53)[g]	300.0±60.0

Table 5.—Continued.

Table 5. Continued.

Ketone	R	R'	X	ϕ_{pdt}	$k_q \tau_T$, M^{-1}
2,6-DBB	Ph	Ph	6-COPh	0.88 ±0.04[i]	12.0±1.5
				0.29 ±0.02[j]	11.5±1.4
2,6-DAB[h]	Ph	CH_3	6-$COCH_3$	0.169 ±0.006	72.8±3.3
2,6-DBA	H	Ph	6-COPh	0.77 ±0.007	266.0±20.0

[a] 313 nm irradiation of degassed 0.04 M solutions of ketone in benzene.

[b] Quantum yield for the formation of the cis isomer.

[c] Quantum yield for the formation of the trans isomer.

[d] 313 nm irradiation of degassed 0.04 M solutions of ketone in 1,4-dioxane, $k_q = 5.4 \times 10^9 M^{-1}s^{-1}$ at 25°C.

[e] n-Octyl mercaptan used as quencher, $k_q = 1.4 \times 10^7 M^{-1}s^{-1}$ in benzene at 25°C.

[f] 313 nm irradiation of degassed 0.04 M solutions of ketone in benzene containing 1.0 M pyridine.

[g] Quantum yield for the formation of o-benzyloxyacetophenone. Value in parentheses represents the maximized quantum yield obtained in benzene containing 1.0 M pyridine.

[h] 313 nm irradiation of degassed 0.02 M solutions of ketone in benzene at 25°C.

[i] Quantum yield for formation of the cis isomer. [j] Quantum yield for the formation of the trans isomer.

[k] 2,5-Dimethyl hexadiene used as quencher unless otherwise noted.

the decay curve. In addition, Stern-Volmer quenching can be used to not only measure the triplet lifetime, but also the rate constant for energy transfer quenching, k_q. For this experiment, k_{exp} is plotted as a function of quencher concentration. The following relationship holds -

$$k_{exp} = \tau_T^{-1} + k_q [Q] \quad . \qquad \text{Equation 3}$$

The slope of the line is k_q, and the intercept is τ_T^{-1}.

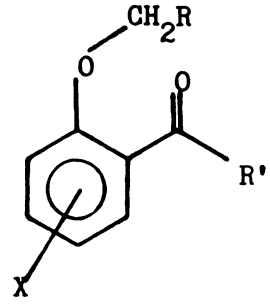
The results of nanosecond laser spectroscopy of a number of o-alkoxyphenyl ketones[49] in benzene and methanol are presented in Tables 6 and 7. Note that the value of k_q for many of these ketones is approximately one-half that of the accepted value for ketones, $5.0 \times 10^9 M^{-1}s^{-1}$.

Rate constants lower than 'normal' values were also observed for the energy transfer quenching of triplet 2-keto-[2,2]-paracyclophane, 2-KPCP, by a number of triplet quenchers in both benzene and methanol. These values are summarized in Table 8.

In an attempt to better understand the quenching process for this ketone, Arrhenius parameters were determined for the quenching of triplet 2-KPCP by 2,5-dimethyl-2,4-hexadiene and 1,3-cyclooctadiene in methanol. These values are presented in Table 9.

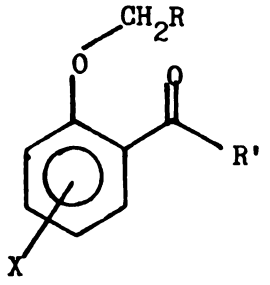
Arrhenius parameters were also determined for the triplet

Table 6. Kinetic Data Measured for Some o-Alkoxyphenyl Ketones in Benzene by Laser Flash Spectroscopy.



Ketone	R	R'	X	τ_T, nsec	$k_q \tau_T$, M^{-1}	k_q, $10^9 M^{-1} s^{-1}$
o-MeOBP	H	Ph	H	1080.0	5160.0	6.77
o-BzOBP	Ph	Ph	H	53.0±4.0	112.0	1.94
o-BzOAP	Ph	CH_3	H	455.0±15.0	1360.0	2.90
2,6-DiMeOBP	H	Ph	6-OCH_3	1910.0±8.0	4330.0±300	2.83±0.57
2,2'-DiBzOBP	Ph	2-($PhCH_2O$)Ph	H	70.0±3.0	62.0±2.0	0.84±0.02
o-BzO-5-MeBP	Ph	Ph	5-CH_3	47.0	136.0	2.97
o-BzOVP	Ph	$(CH_2)_3CH_3$	H	83.0±3.0	195.0	2.94

Table 7. Kinetic Data Measured for Some o-Alkoxyphenyl Ketones in Methanol by Laser Flash Spectroscopy.



Ketone	R	R'	X	τ_T, nsec	$k_q \tau_T$	k_q, $10^9 M^{-1}s^{-1}$
o-MeOBP	H	Ph	H	121.0	1120.0	9.2
o-BzOBP	Ph	Ph	H	50.0	264.0	5.78
o-BzOAP	Ph	CH_3	H	590.0	5750.0	9.38
2,6-DiMeOBP	H	Ph	6-OCH_3	157.0±3.0	827.0	5.37
2,2'-DiBzOBP	Ph	2-($PhCH_2O$)Ph	H	128.0	777.0	5.73
o-BzO-5-MeBP	Ph	Ph	5-CH_3	243.0	1510.0	6.64
o-BzOVP	Ph	$(CH_2)_3CH_3$	H	246.0	1290.0	5.32

Table 8. Rate Constants for the Energy Transfer Quenching of Some Phenyl Ketone Triplets by Various Dienes in Benzene and Methanol at 27°C.

Ketone	Quencher	Solvent	k_q, $10^9 M^{-1}s^{-1}$
2-Keto-[2,2]-Paracyclophane	2,5-Dimethyl-2,4-hexadiene	Benzene	1.72
2-Keto-[2,2]-Paracyclophane	1-Methylnaphthalene	Benzene	1.40
2-Keto-[2,2]-Paracyclophane	1,3-Cyclooctadiene	Benzene	0.147
2-Keto-[2,2]-Paracyclophane	2,5-Dimethyl-2,4-hexadiene	Methanol	2.30
2-Keto-[2,2]-Paracyclophane	1,3-Cyclooctadiene	Methanol	0.187
o-Benzyloxybenzophenone	2,5-Dimethyl-2,4-hexadiene	Benzene	1.94
o-Benzyloxybenzophenone	2,5-Dimethyl-2,4-hexadiene	Methanol	5.78
p-Methoxyacetophenone	2,5-Dimethyl-2,4-hexadiene	Benzene	5.88[a]
p-Methoxyacetophenone	2,5-Dimethyl-2,4-hexadiene	Methanol	8.31[a]

[a] J. C. Scaiano, unpublished results, measured at 27.

Table 9. Arrhenius Parameters for the Energy Transfer Quenching of 2-Keto-2,2-Paracyclophane and p-Methoxyacetophenone with Various Quenchers in Methanol.

Ketone	Quencher	Log A	E_a, kcal/mole
2-Keto-[2,2]-Paracyclophane	2,5-Dimethyl-2,4-hexadiene	10.69±0.25	1.82±0.28
2-Keto-[2,2]-Paracyclophane	1,3-Cyclooctadiene	9.14±0.09	1.19±0.099
p-Methoxyacetophenone[a]	2,5-Dimethyl-2,4-hexadiene	11.74	2.49

[a] J. C. Scaiano, unpublished results.

decay of a number of o-alkoxyphenyl ketones in chlorobenzene and methanol. These values are summarized in Table 10.

3. Spectroscopy

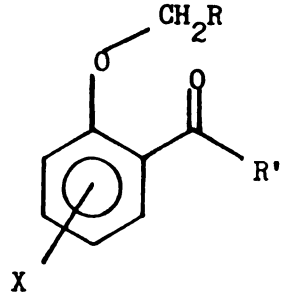
a. Phosphorescence Spectra - Representative phosphorescence spectra of some o-alkoxyphenyl ketones are shown in Figures 6-9.

Phosphorescence spectra of all o-alkoxyphenyl ketones studied in this thesis were recorded in two different solvent glasses at 77°K - EPA and 2-methyltetrahydrofuran. The triplet energies for these ketones were calculated from the highest energy (0,0) band are are reported in Table 11.

b. Ultraviolet-visible Absorption Spectra - Ultraviolet-visible absorption spectra were recorded for all o-alkoxyphenyl ketones studied in this thesis in n-heptane. The wavelengths of the absorption maxima and their corresponding extinction coefficients are reported in Table 12.

c. Triplet-Triplet Absorption Spectra - Triplet-triplet absorption spectra of all ketones studied by laser flash spectroscopy were recorded in both benzene and methanol. Representative spectra are shown in Figures 10 and 11.

Table 10. Arrhenius Parameters for Triplet Decay of Various o-Alkoxyphenyl Ketones in Chlorobenzene and Methanol.



				Chlorobenzene		Methanol	
Ketone	R	R'	X	E_a, kcal/mole	Log A	E_a, kcal/mole	Log A
o-BzO-5-MeBP	Ph	Ph	5-CH_3	4.50±0.45	10.3±0.36	3.83±0.23	9.32±0.20
o-BzOAP	Ph	CH_3	H	3.66±0.60	9.03±0.47	3.73±0.70	8.98±0.54
o-MeOBP	H	Ph	H	4.17±0.65	9.21±0.51	3.05±0.15	9.06±0.13
2,2'-DiBzOBP	Ph	2-($PhCH_2O$)Ph	H	3.07±0.50	9.29±0.39	-----	-----
o-BzOVP	Ph	$(CH_2)_3CH_3$	H	4.77±0.44	10.44±0.34	4.73±0.11	9.96±0.08

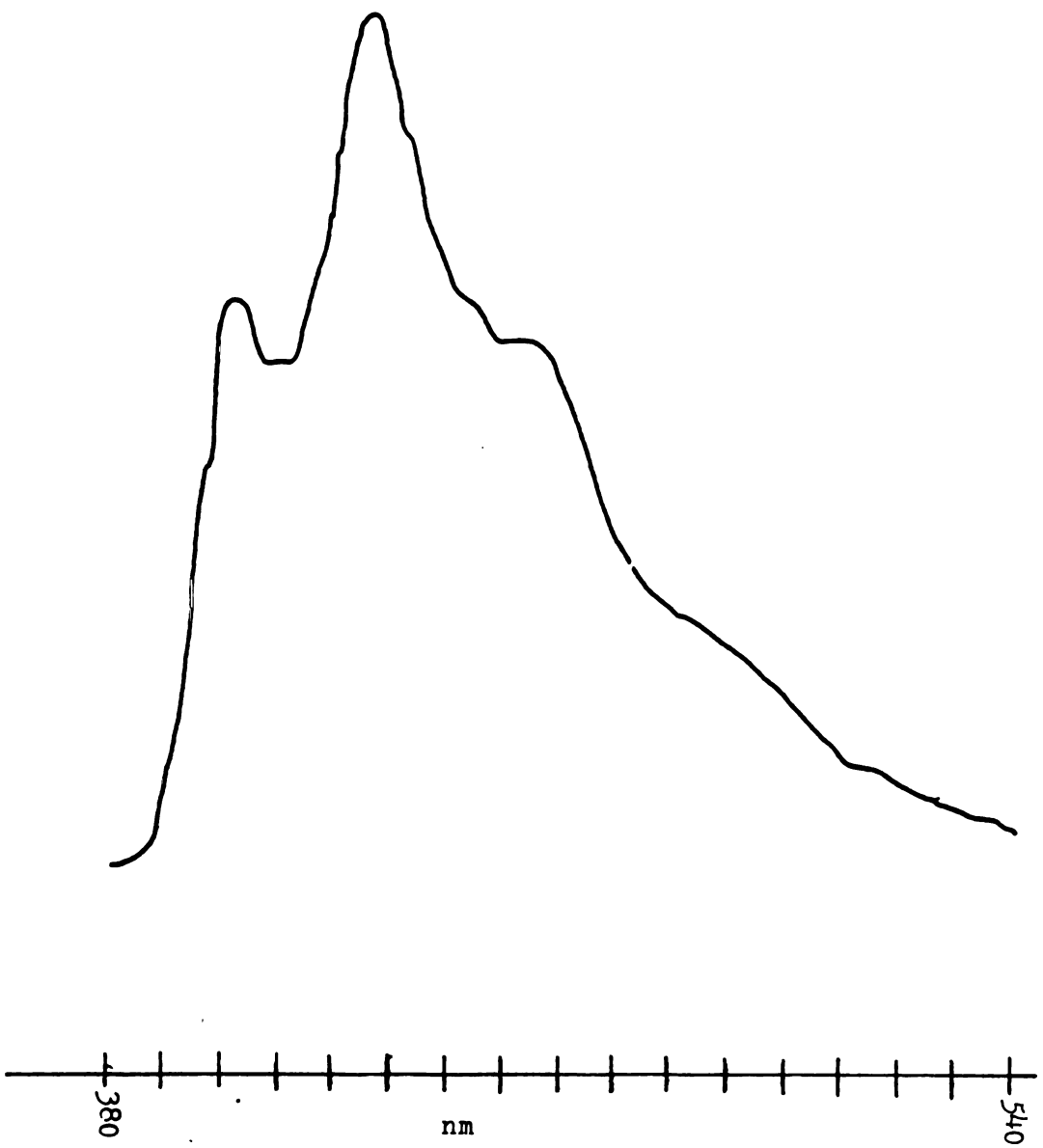


Figure 6. The phosphorescence spectrum of o-benzyloxyacetophenone in 2-methyltetrahydrofuran at 77°K.

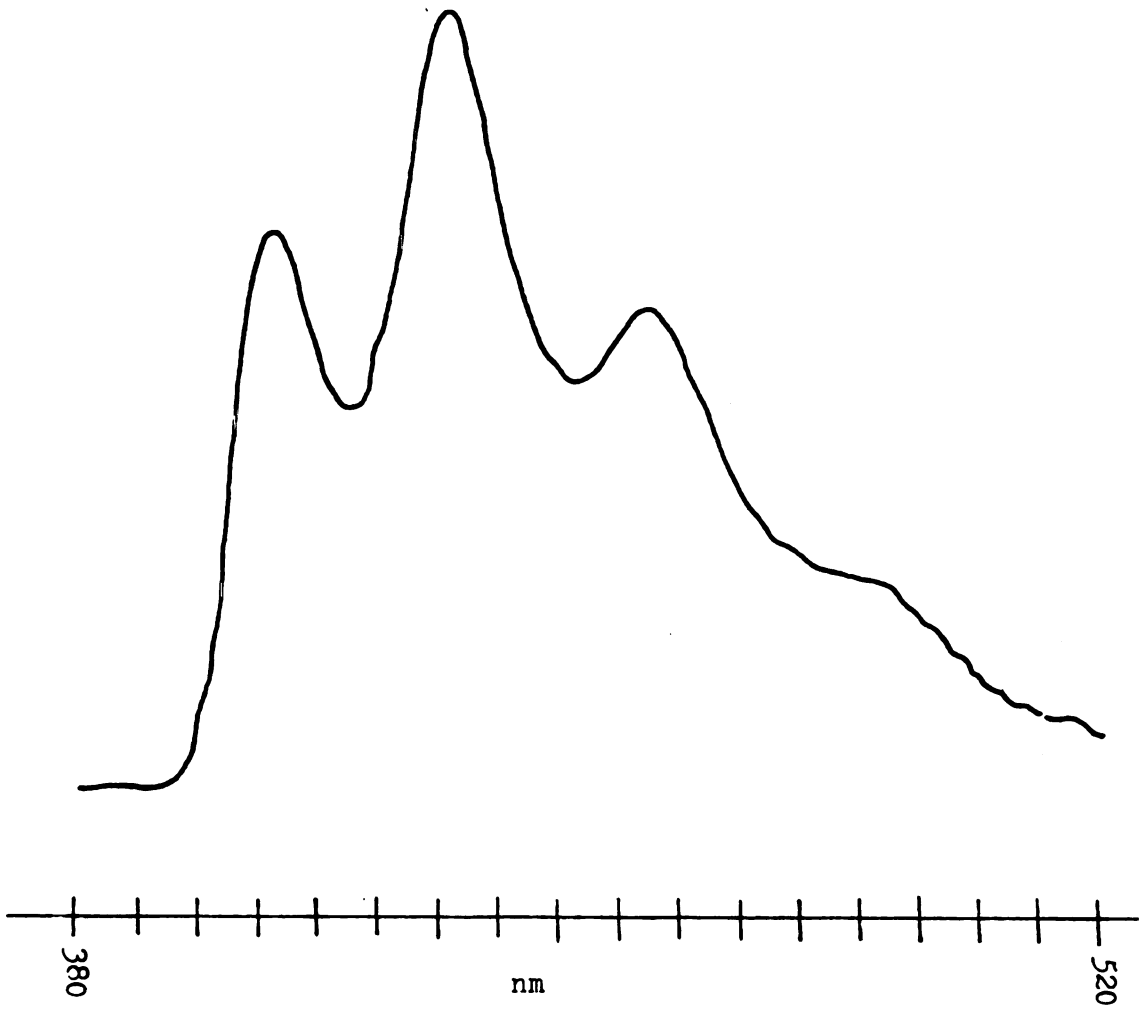


Figure 7. The phosphorescence spectrum of o-benzyloxybenzophenone in 2-methyltetrahydrofuran at 77°K.

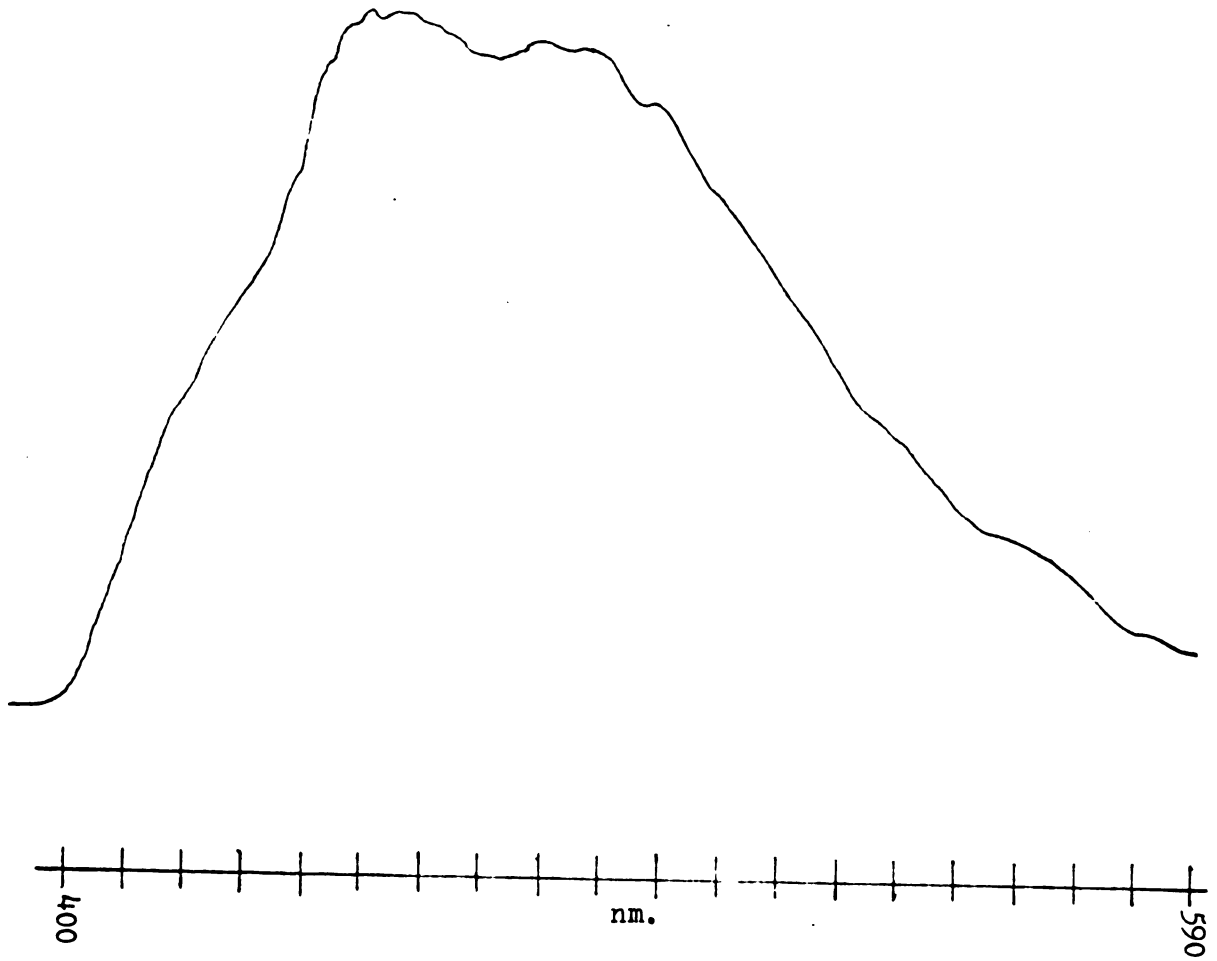


Figure 8. The phosphorescence spectrum of 2,6-dimethoxybenzophenone in 2-methyltetrahydrofuran at 77°K.

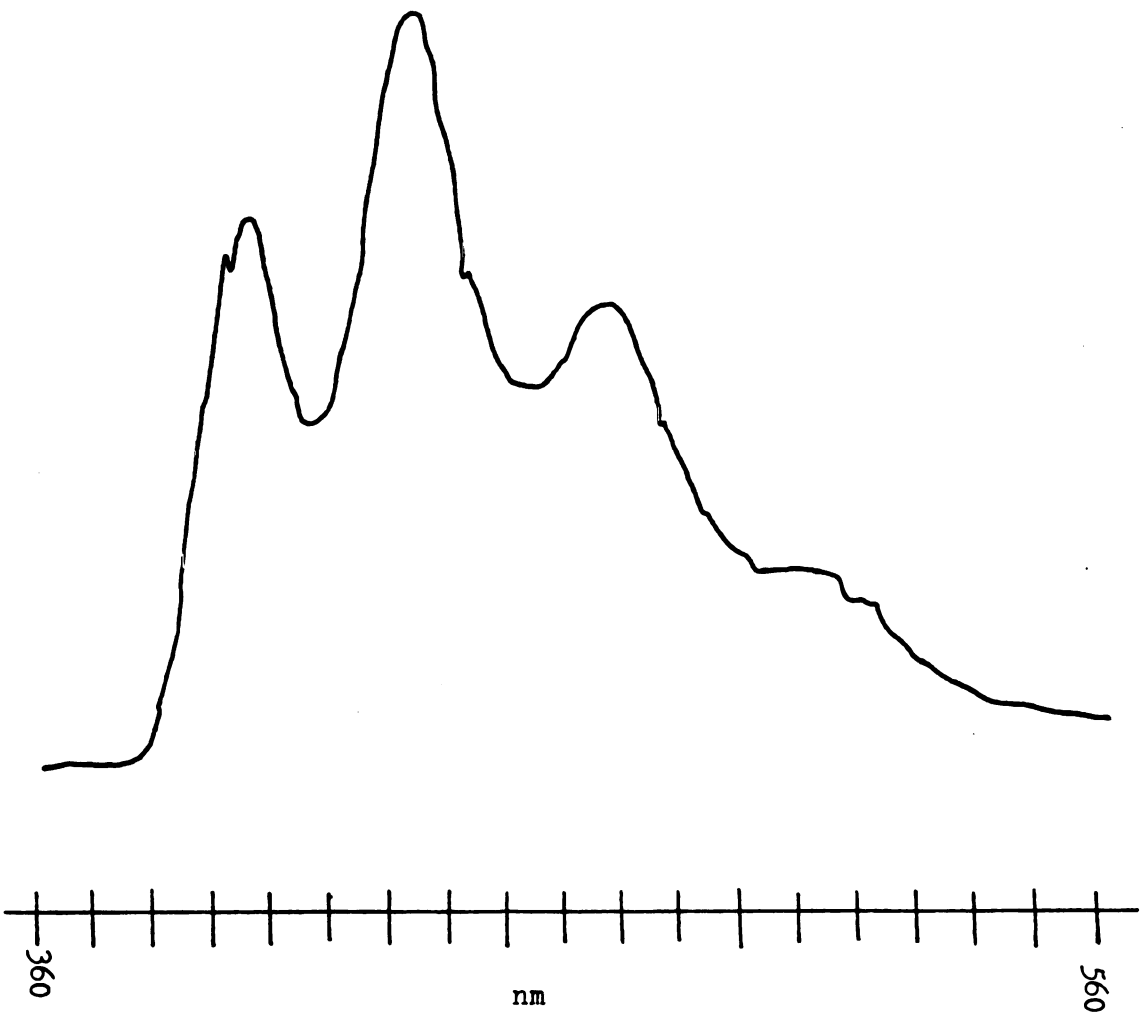
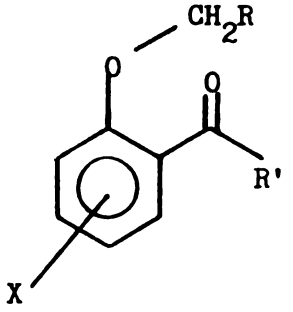


Figure 9. The phosphorescence spectrum of 2,6-dibenzoylanisole in 2-methyltetrahydrofuran at 77°K.

Table 11. Triplet Energies of Various o-Alkoxyphenyl Ketones in EPA and 2-Methyltetrahydrofuran at 77°K.



Ketone	R	R'	X	EPA $\lambda_{0,0}$ nm	EPA $E_{0,0}$ kcal/mole	2-Methyl THF $\lambda_{0,0}$ nm	2-Methyl THF $E_{0,0}$ kcal/mole
o-BzOAP	Ph	CH_3	H	400	71.5	403	71.0
o-BzOBP	Ph	Ph	H	415	68.9	414	69.1
o-MeOBP	H	Ph	H	415	68.9	416	68.8
o-BzO-5-MeBP	Ph	Ph	5-CH_3	423	67.6	421	67.9
2-2'-DiBzOBP	Ph	2-($PhCH_2O$)Ph	H	416	68.8	418	68.4
o-BzOVP	Ph	$(CH_2)_3CH_3$	H	400	71.5	403	71.0
2,6-DiMeOBP	H	Ph	6-OCH_3	415 (sh)	68.9	425 (sh)	67.3
2,6-DBA	H	Ph	6-COPh	415	68.9	415	68.9
2,6-DAB	Ph	CH_3	6-$COCH_3$	400	71.5	404	70.8
2,6-DBB	Ph	Ph	6-COPh	418	68.4	417	68.6

Table 11. Continued.

Ketone	R	R'	X	EPA $\lambda_{0,0}$ nm	EPA $E_{0,0}$ kcal/mole	2-Methyl THF $\lambda_{0,0}$ nm	2-Methyl THF $E_{0,0}$ kcal/mole
Benzophenone[a]				413	69.2	417	68.6
Acetophenone[a]				386	74.1	388	73.7

[a]S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973, pp. 31, 33.

Table 12. Ultraviolet-Visible Absorbtion Maxima[a] for a Series of o-Alkoxyphenyl Ketones in Heptane.

Ketone	L_a	Other Absorbtion Maxima
o-Benzyloxybenzophenone	243 (9440)	288 (1260) 300 sh (1025)
o-Benzyloxyacetophenone	230 (5200)	288 (2200)
o-Methoxybenzophenone	239 sh (12,700)	243 (14,400), 248 (15,400), 254 (12,700) 282 (2576), 286 sh (2538)
2,6-Dimethoxybenzophenone	241 (15,600)	271 sh (3370), 277 sh (3260), 287 sh (1890), 329 sh (94.74), 343 sh (84.21), 359 sh (52.60)
o-Benzyloxyvalerophenone	240 (11,830)	296 (4866)
2,2'-Dibenzyloxybenzophenone	253 (7020)	301 (4335)
o-Benzyloxy-5-methyl-benzophenone	243 (11,890)	288 (2028), 305 sh (1934)
2,6-Dibenzoylbenzyloxybenzene	248 (15,904)	281 sh (2397)
2,6-Dibenzoylanisole	247 (15,027)	280 sh (2198)
2,6-Diacetylbenzyloxybenzene	218 (28,316)	292 (1518)

[a]Values in parentheses are molar extinction coefficients.

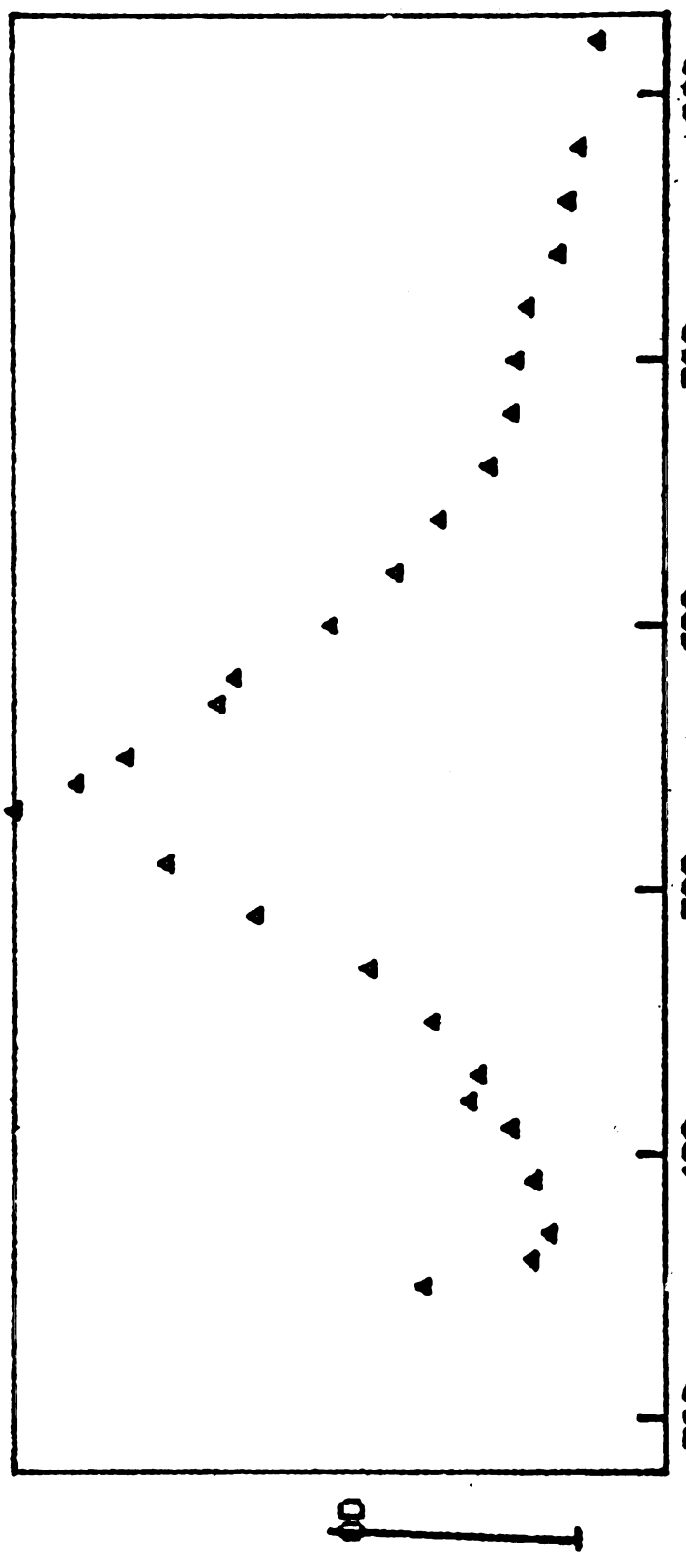


Figure 10. Triplet-triplet absorption spectrum of 2-methoxybenzophenone in benzene.

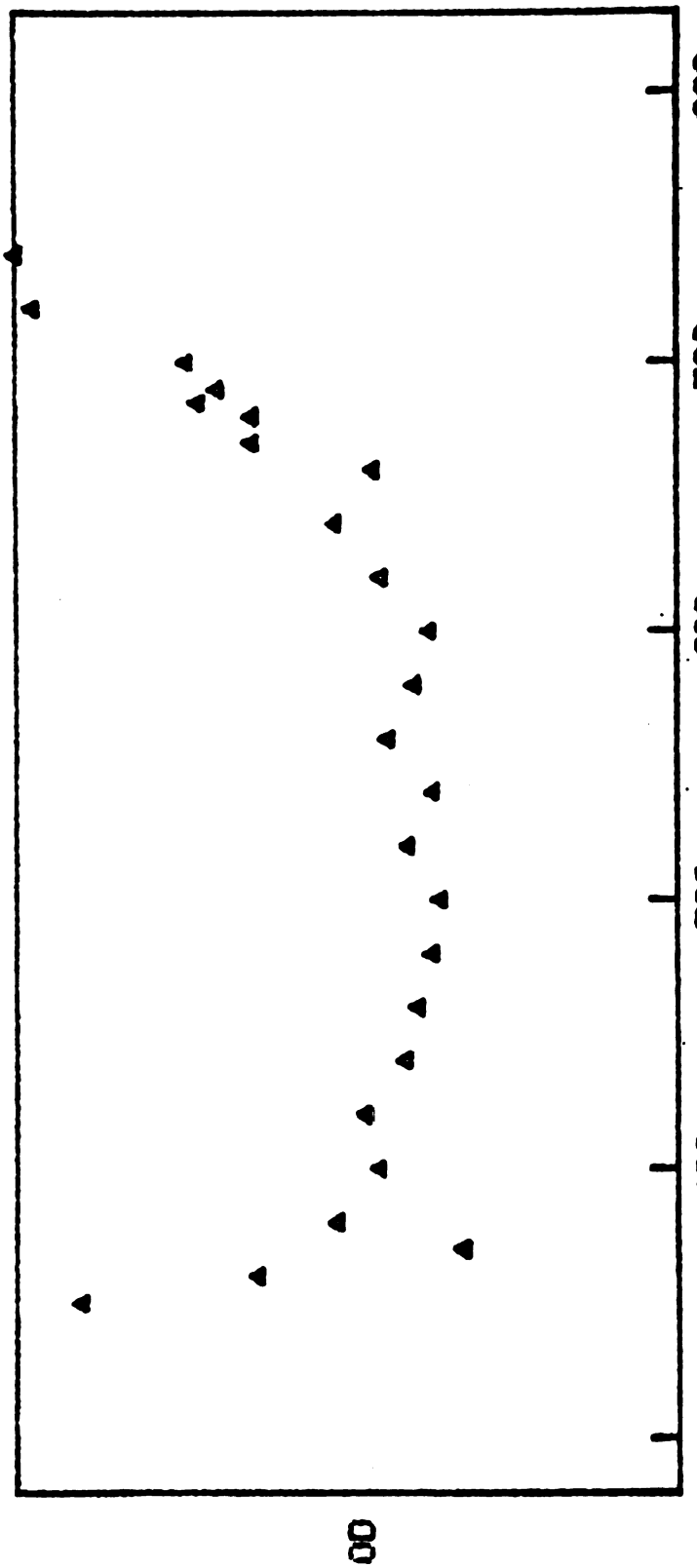


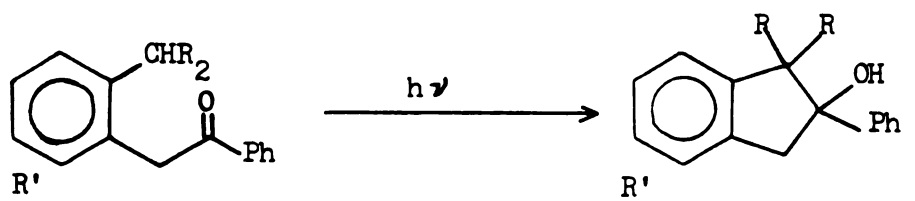
Figure 11. The triplet-triplet absorption spectrum of 2,6-dimethoxybenzophenone in benzene.

d. ^{13}C - nmr Spectra - ^{13}C - nmr spectra (250 MHz) were recorded for a number of o-alkoxyphenyl ketones in k_1-chloroform. In general, it was found that the chemical shift of the alkoxy carbon of 2,6-diacyclalkoxybenzenes were 6-10 ppm downfield of the alkoxy carbons of their monoacyl counterparts. These chemical shifts, as well as those of the carbonyl carbons are presented in Table 13.

B. α-(o-Alkylphenyl)acetophenones

1. Identification of Photoproducts

Irradiation of 0.10 M cyclohexane solutions of a number of α-(o-alkylphenyl)acetophenones under an argon atmosphere with a medium pressure mercury lamp filtered through Pyrex afforded the corresponding 2-phenyl-2-hydroxyindane in quantitative yield (Reaction 23). No purification of the photolysate was required.

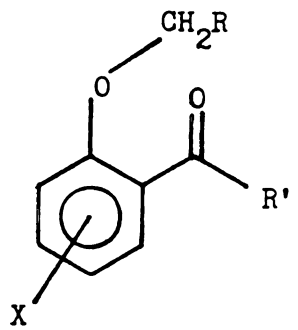


(23)

Structural assignments of all photoproducts were based upon spectral data (^1H and ^{13}C nmr, i.r., and mass spectrum).

A ^1H nmr spectrum (250 MHz, $CDCl_3$) of 2-phenyl-2-hydroxyindane, formed by the photolysis of α-(o-tolyl)acetophenone

Table 13. ^{13}C Chemical Shifts for the Alkoxy Carbon and Carbonyl Carbon in Various o-Alkoxyphenyl Ketones.[a]

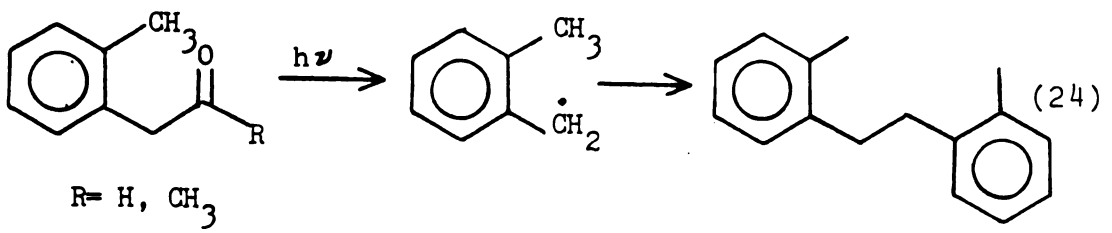


Ketone	R	R'	X	δ_{OCH_2-R}	$\delta_{C=O}$
o-BzOBP	Ph	Ph	H	68.65	192.3
o-BzO5-MeBP	Ph	Ph	5-CH_3	69.32	196.8
2,2'-DiBzOBP	Ph	2-($PhCH_2O$)Ph	H	70.00	195.5
o-BzOAP	Ph	CH_3	H	70.6	199.8
o-BzOVP	Ph	$(CH_2)_3CH_3$	H	70.66	203.7
2,6-DBB	Ph	Ph	6-COPh	77.12	195.5
2,6-DAB	Ph	CH_3	6-$COCH_3$	79.4	200.0
2,6-Dicyanobenzyloxybenzene				76.90	-----
o-MeOBP	H	Ph	H	55.33	196.2
2,6-DiMeOBP	H	Ph	6-OCH_3	55.70	195.2
2,6-DBA	H	Ph	6-COPh	61.6	195.5
Anisole				54.0[74]	

[a]Spectra recorded in $CDCl_3$/TMS at 250 MHz. Chemical shifts are reported from TMS (δ = 0.0).

in cyclohexane is shown in Figure 12. A common feature of the ^1H nmr spectra of these 2-phenyl-2-hydroxyindanes is an AB quartet occurring from 3.0 to 4.0 ppm and corresponding to the methylene protons of the indane ring.

Such a photocyclization does not occur for either α-(o-tolyl)acetone or α-(o-tolyl)acetaldehyde. 1,2-Di-(o-tolyl)ethane, formed by acyl cleavage is the only photoproduct isolated (Reaction 24).



R= H, CH_3 (24)

Spectral data for all 2-phenyl-2-hydroxyindane photoproducts is presented in detail in the Experimental Section.

2. Kinetic Data

Triplet lifetimes of some α-(o-alkylphenyl)acetophenones were measured by Stern-Volmer quenching in benzene at 25°C. These lifetimes and the corresponding photoproduct quantum yields are presented in Table 14.

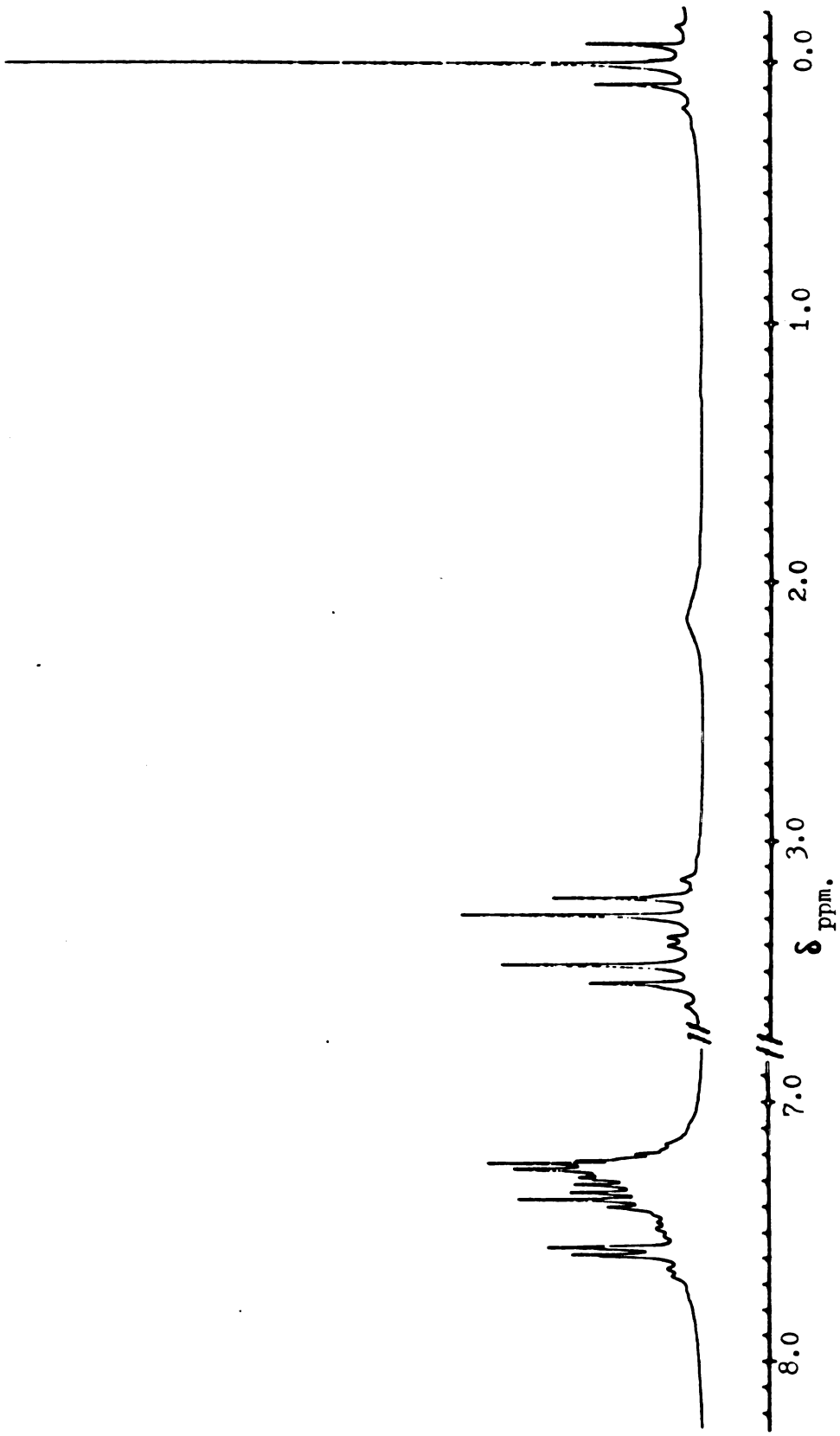
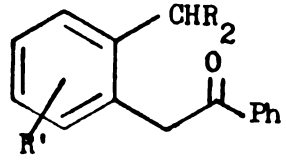


Figure 12. 250 MHz ^{1}H-nmr spectrum of 2-phenyl-2-hydroxyindane in $CDCl_3$.

Table 14. Kinetic Data for Various α-(o-Alkylphenyl)acetophenones in Benzene at 25°C.[a]



Ketone	R	R'	ϕ_{pdt}	$k_q \tau_T$, M^{-1}	τ_T, nsec[b]	$1/\tau_T, 10^8 s^{-1}$
α-TAP	H	H	1.00±0.05	30.6 ±1.3	6.14	1.63
α-(DMP)AP	H	5-CH_3	0.62±0.04	19.2 ±0.40	3.80	2.63
α-MAP	H	4,6-$(CH_3)_2$	0.44±0.02	4.59±0.14	0.930	10.8
α-(DIP)AP	CH_3	5-$CH(CH_3)_2$	0.42±0.07	3.36±0.09	0.672	14.9
α-(TIP)AP	CH_3	4,6-$(CH(CH_3)_2)_2$	0.041±0.003	3.25±0.27[d]	0.650	15.4

[a]313 nm irradiation of degassed 0.025 M ketone solutions in benzene at 25°C.

[b]Calculated from $k_q \tau_T$ assuming $k_q = 5.0 \times 10^9 M^{-1} s^{-1}$ in benzene at 25°C.

[c]Value in parenthesis represents the maximized photoproduct quantum yield obtained in benzene containing ca. 1 M pyridine.

[d]1,3-Cyclohexadiene used as quencher. For all other ketones 2,5-dimethyl-2,4-hexadiene was used.

3. Spectroscopy

a. Phosphorescence Spectra - Phosphorescence spectra were recorded for all α-(o-alkylphenyl)acetophenones in both EPA and 2-methyltetrahydrofuran glasses at 77°K. Representative phosphorescence spectra are shown in Figures 13 and 14. Triplet energies calculated from the wavelength of the 0,0 band are reported in Table 15.

b. Ultraviolet-Visible Absorption Spectra - Ultraviolet visible spectra were recorded for all α-(o-alkylphenyl)acetophenones studied. The wavelengths of the absorption maxima and their corresponding extinction coefficients are reported in Table 16.

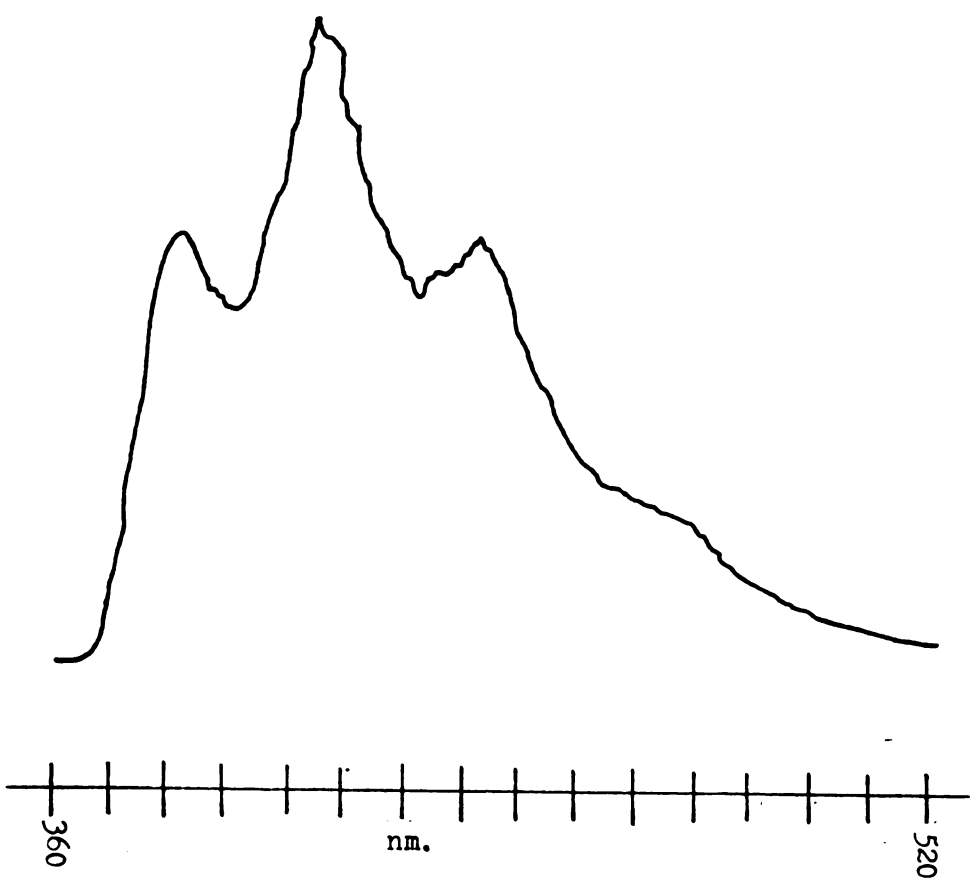


Figure 13. The phosphorescence spectrum of α-(o-tolyl) acetophenone in 2-methyltetrahydrofuran at 77°K.

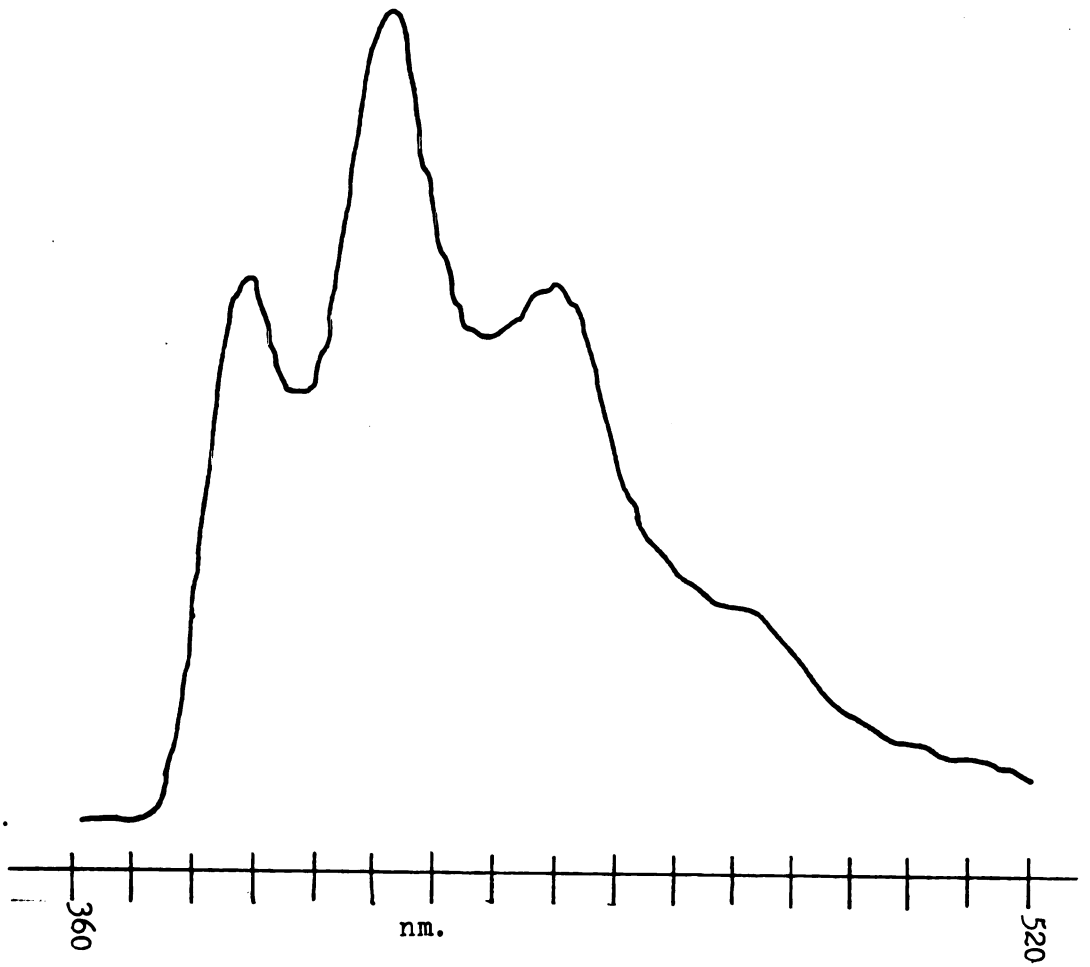
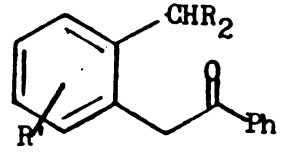


Figure 14. The phosphorescence spectrum of α-mesitylacetophenone in 2-methyltetrahydrofuran at 77°K.

Table 15. Triplet Energies of Various α-(o-Alkylphenyl)acetophenones in EPA and 2-Methyltetrahydrofuran at 77°K.



Ketone	R	R'	EPA		2-Methyltetrahydrofuran	
			$E_{0,0}$, kcal/mole	$\lambda_{0,0}$, nm	$E_{0,0}$, kcal/mole	$\lambda_{0,0}$, nm
α-TAP	H	H	73.5	389	73.2	391
α-MAP	H	4,6-$(CH_3)_2$	73.7	388	73.5	389
α-(DIP)AP	CH_3	5-$CH(CH_3)_2$	73.9	387	73.7	388
α-(TIP)AP	CH_3	4,6-$(CH(CH_3)_2)_2$	73.7	388	73.7	388
Deoxybenzoin[a]					72.0	
Valerophenone[b]					74.3	

[a] In 2-methylpentane, H. G. Heine, et al., J. Org. Chem., 39, 691 (1974).

[b] In methylcyclohexane, P. J. Wagner, A. E. Kemppainen, H. N. Schott, J. Amer. Chem. Soc. 95, 5604 (1971).

Table 16. Ultraviolet-Visible Absorbtion Maxima[a] for Various α-(o-Alkylphenyl)acetophenones in Heptane.

Ketone	L_a	Other Absorbtion Maxima
α-(o-Tolyl)acetophenone	238 (8066)	271 (651.9), 279 (508.3), 286 (364.6), 325 (45.30)
α-Mesitylacetophenone	237 (12,023)	268 (761.9), 287 (425.4), 320 (23.81)
α-(2,5-Dimethylphenyl)-acetophenone	238 (8768)	267 (914.0), 277 (944.0), 286 (417.9) 325 (79.3)
α-(2,5-diisopropylphenyl)-acetophenone	232 (20,909)	265 (2314), 275 (2061), 286 (942.0), 326 (124)
α-(2,4,6-triisopropylphenyl)-acetophenone	237 (16,690)	268 (1255), 287 (781.6), 325 (45.98)

[a]Molar extinction coefficients are in parentheses.

DISCUSSION

A. o-Alkoxyphenyl Ketones

1. Determination of Meaningful Hydrogen Abstraction Rate Constants

a. Steric Effects on Energy Transfer Quenching - The importance of determining accurate values of energy transfer rate constants, k_q's, is obvious. Without reliable k_q values, it is not possible to determine accurate excited state (singlet or triplet) lifetimes by Stern-Volmer quenching. Thus, a great deal of activity has dealt with the careful determination of k_q values for a number of excited state molecules and appropriate quenchers.[4,50-56]

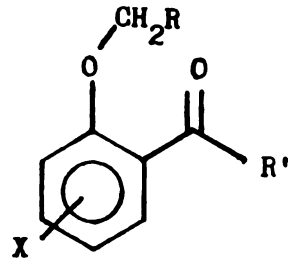
It is widely accepted that the rate constant for the quenching of triplets by energy transfer in benzene at 25°C is 5.0 - 6.0 x $10^9 M^{-1}s^{-1}$.[57,58] Scaiano[51] has undertaken a rather extensive study of the energy transfer quenching of various triplet organic molecules with a number of triplet quenchers and has found this value to be accurate. Turro[59] has examined the quenching of acetone phosphorescence by a number of acyclic 1,3-dienes and found k_q values ranging from 3.0 - 6.0 x $10^9 M^{-1}s^{-1}$. The quenching rate constants

of these dienes are slightly dependent upon the electronic nature of the diene.

Wagner[50] has shown that the rate constants for the quenching of the Norrish Type II reaction of α,α-dimethylvalerophenone and valerophenone with 2,5-dimethyl-2,4-hexadiene vary similarly with viscosity in a number of different hydrocarbon and primary alcohol solvents. Wagner and Chen[58] have found the same trend for the quenching of the Norrish Type II reaction of o-methyl-γ-methylvalerophenone and valerophenone with 2,5-dimethyl-2,4-hexadiene in a number of primary alcohol solvents of varying viscosities. Hence, energy transfer is not strongly sensitive to either α-dimethyl or o-methyl substitution.

In order to further test the steric sensitivity of energy transfer, k_q values were measured by nanosecond laser flash spectroscopy for a number of o-alkoxyphenyl ketones, having o-alkoxy substituents of various sizes. 2,5-Dimethyl-2,4-hexadiene was used as the triplet quencher. These results, presented in Table 17, demonstrate that energy transfer is sensitive to the degree of steric congestion ortho to the carbonyl. Only the least congested ketone, o-methoxybenzophenone, has a 'normal' k_q value in benzene. The most sterically crowded ketone, 2,2'-dibenzyloxybenzophenone, has the smallest k_q value in benzene, $8.4 \times 10^8 M^{-1}s^{-1}$. All other ketones have k_q values on the order of $2.9 \times 10^9 M^{-1}s^{-1}$, nearly one-half the normal value of $5\text{-}6 \times 10^9 M^{-1}s^{-1}$! Hence, steric bulk ortho to the carbonyl does

Table 17. Kinetic Data Measured for Some o-Alkoxyphenyl Ketones in Benzene by Laser Flash Spectroscopy.



Ketone	R	R'	X	τ_T, nsec	$k_q \tau_T$, M^{-1}	k_q, $10^9 M^{-1}s^{-1}$
o-MeOBP	H	Ph	H	1080.0	5160.0	6.77
o-BzOBP	Ph	Ph	H	52.0 4.0	112.0	1.94
o-BzOAP	Ph	CH_3	H	455.0±15.0	1360.0	2.90
2,6-DiMeOBP	H	Ph	6-OCH_3	1910.0±8.0	4330.0±300	2.83±0.57
2,2'-DiBzOBP	Ph	2-($PhCH_2O$)Ph	H	70.0±3.0	62.0±2.0	0.84±0.02
o-BzO-5-MeBP	Ph	Ph	5-CH_3	47.0	135.0	2.97
o-BzOVP	Ph	$(CH_2)_3CH_3$	H	83.0±3.2	195.0	2.94

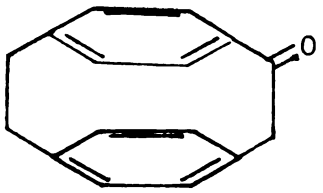
reduce the rate constant for energy transfer from these ketone triplets to 2,5-dimethyl-2,4-hexadiene.

Literature examples of energy transfer rate constants less than 5.0-6.0 x $10^9 M^{-1}s^{-1}$ in benzene are rare. Turro[60] has found that the quenching of acetone phosphorescence by cis,cis-1,3-cyclooctadiene has a rate constant of 1.1 x $10^9 M^{-1}s^{-1}$ in benzene. This measurement confirms an earlier report by Sakurai and co-workers[61] that 1,3-cyclooctadiene is a poor alkanone triplet quencher. Both Turro[60] and Sakurai[61] ascribe the low quenching rate constant for 1,3-cyclooctadiene to the lack of co-planarity of the two olefin moeities in this molecule.

Energy transfer quenching of the triplet lifetime of 2-keto-2,2-paracyclophane is also slower than 'normal',[62] (Table 18). Nanosecond laser flash spectroscopy reveals k_q values for this ketone with various triplet quenchers in benzene are at least one-third of the normal values.

Arrhenius parameters were determined for the quenching of the triplet lifetime of 2-KPCP and acetophenone by 2,5-dimethyl-2,4-hexadiene and 1,3-cyclooctadiene in chlorobenzene and methanol over similar temperature ranges. A comparison of the Arrhenius parameters (Table 19) for the quenching of these two ketones reveals nearly identical activation energies (ca. 1.5 kcal/mole) but quite different pre-exponential (A) factors. In all cases, A factors for the quenching of triplet 2-KPCP are nearly an order of

Table 18. Rate Constants for the Energy Transfer Quenching of the Triplet Lifetime of 2-Keto[2,2]-paracyclophane with Various Triplet Quenchers in Benzene and Methanol at 27°C.



2-KPCP, E_T = 69.3 kcal/mole in 2-Methyltetrahydrofuran

Solvent	Quencher	k_q, $10^9 M^{-1}s^{-1}$
Benzene	2,5-Dimethyl-2,4-hexadiene	1.72
Benzene	1-Methylnaphthalene	1.40
Benzene	1,3-Cyclooctadiene	0.147
Methanol	2,5-Dimethyl-2,4-hexadiene	2.30
Methanol	1,3-Cyclooctadiene	0.187

Table 19. Arrhenius Parameters for the Energy Transfer Quenching of Triplet 2-Keto-[2,2]-Paracyclophane and Acetophenone by Various Triplet Quenchers in Chlorobenzene and Methanol.

Ketone	Quencher	Solvent	Log A	E_a, kcal/mole
Acetophenone[a]	2,5-DMHD[b]	Chlorobenzene	10.98±0.28	1.75±0.35
Acetophenone[a]	1,3-COD[c]	Chlorobenzene	9.55±0.69	0.58±0.84
2-KPCP[a]	2,5-DMHD	Chlorobenzene	10.04±0.93	1.5±1.20
2-KPCP[a]	1,3-COD	Chlorobenzene	9.00±0.38	1.52±0.48
2-KPCP[d]	2,5-DMHD	Methanol	10.69±0.25	1.82±0.28
2-KPCP[d]	1,3-COD	Methanol	9.14±0.09	1.19±0.10

[a] J. C. Scaiano, private communication.

[b] 2,5-Dimethyl-2,4-hexadiene.

[c] cis,cis-1,3-cyclooctadiene.

[d] This author.

magnitude less than those for the quenching of triplet acetophenone. These lower A factors indicate a greater entropic requirement for energy transfer from triplet 2-KPCP than from triplet acetophenone.

Efficient energy transfer from triplet to quencher requires maximum overlap of the orbitals of both ketone and quencher.[50] Cram[63] has found that the carbonyl and benzene rings of 2-KPCP are orthogonal in the ground state of this ketone. Since the molecule is quite rigid, the excited state geometry must also have some lack of co-planarity between the carbonyl and aromatic π-system. Hence, the low A factors for the energy transfer quenching of triplet 2-KPCP probably reflect the inability of the quencher orbitals to completely overlap with both the carbonyl and aromatic π-orbitals of the ketone.

The steric bulk of the o-alkoxy substituents of o-alkoxyphenyl ketones also prevent complete overlap of the π-orbitals of ketone and quencher. The result is a lower than normal k_q value for these ketones.

b. Contribution of Triplet Decay to the Overall Triplet Lifetime

Reciprocal triplet lifetimes were calculated from the slopes of Stern-Volmer quenching plots ($k_q\tau_T$) assuming that $k_q = 2.9 \times 10^9 M^{-1}s^{-1}$ for all ketones except o-methoxybenzophenone and 2,6-dibenzoylanisole (2,6-DBA). Although k_q

values were not measured for diketones 2,6-DBB, 2,6-DBA, and 2,6-DAB, it was assumed that they were nearly equal to thoseof their monoketone analogues. These reciprocal triplet lifetimes are presented in Table 20.

The reciprocal triplet lifetime, τ_T^{-1}, is a sum of the rate constants for hydrogen abstraction, k_H, and triplet decay, k_d. That is -

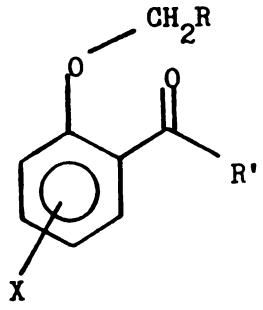
$$\tau_T^{-1} = k_H + k_d \ .$$

Hence, the contribution of triplet decay to the overall triplet lifetime must be determined and k_d subtracted from τ_T^{-1} in order to obtain an accurate appraisal of k_H.

Typical values for k_d in phenyl ketones are on the order of 10^5 to $10^6 s^{-1}$.[65] Wagner[29a] has found k_d values for p-methoxyphenyl alkyl ketones on the order of $1.6 \times 10^6 s^{-1}$. Turro and Lewis[66] have reported that k_d for p-methoxybutyrophenone measures $6.0 \times 10^5 s^{-1}$ in benzene. Favaro[67] has measured k_d values for 4-methoxybenzophenone and 4,4'-dimethoxybenzophenone in benzene of $1.7 \times 10^5 s^{-1}$ and $6.25 \times 10^4 s^{-1}$, respectively.

It is unlikely that the k_d values for o- and p-alkoxyphenyl ketones differ greatly from each other. There is no known reason why k_d values should be sensitive to the nature of the alkoxy substituent, i.e., k_d's for o-methoxyphenyl ketones and o-benzyloxyphenyl ketones should be equal.

Table 20. Kinetic Results of Laser Flash Spectroscopy on a Series of o-Alkoxyphenyl Ketones in Benzene at 25°C.



Ketone	R	R'	X	$k_q\tau^a$, M^{-1}	$k_q\tau^b$, M^{-1}	τ, nsec	k_q, $10^9 M^{-1}s^{-1}$
o-BzOBP	Ph	Ph	H	101.0	112.0	52.5	1.94
o-MeOBP	H	Ph	H	2580.0	5160.0	1075.0	6.77
o-BzO-5-MeBP	Ph	Ph	5-CH_3	163.0	135.0	46.7	2.97
2,6-DiMeOBP	H	Ph	6-OCH_3	-----	4330.0	1909.0	2.83
2,2'-DiBzOBP	Ph	2-($PhCH_2O$)Ph	H	68.8	62.0	69.9	0.84
o-BzOAP	Ph	CH_3	H	1720.0	1360.0	455.0	2.90
o-BzOVP	Ph	$(CH_2)_3CH_3$	H	300.0	195.0	82.9	2.94

[a]Value obtained by Stern Volmer quenching of product formation.

[b]Value obtained by Stern-Volmer quenching of triplet lifetime (laser flash spectroscopy).

Wagner[29a] has shown that k_d values for p-methoxyphenyl alkyl ketones do not change with different alkyl groups. Therefore, k_d values for o-alkoxyphenyl ketones can be approximated by those for their p-methoxy analogues. That is, k_d for o-benzyloxybenzophenone can be approximated by k_d for p-methoxybenzophenone. δ-Hydrogen abstraction rate constants calculated from reciprocal triplet lifetimes and assumed k_d values are presented in Table 21.

The quantum yield for photoproduct formation from these ketones can be represented by -

$$\phi_{pdt} = \phi_{isc}\, k_H \tau_T \alpha \quad .$$

where ϕ_{isc} = intersystem crossing quantum yield for the ketone

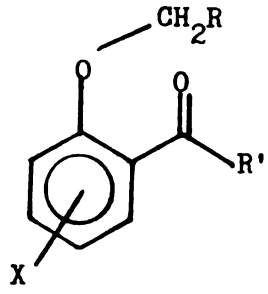
k_H = rate constant for δ-hydrogen abstraction

τ_T = ketone triplet lifetime

α = efficiency with which the intermediate (biradical) converts to product

Intersystem crossing quantum yields for o-benzyloxybenzophenone and o-benzyloxyacetophenone are both 1.0. There is no reason why ϕ_{isc} should not equal 1.0 for all the o-alkoxyphenyl ketones studied. If α is 1.0, then $\phi_{pdt}\tau_T^{-1}$ equals k_H. If α is less than unity, this product represents a lower limit for k_H. For the sake of comparison, values

Table 21. Calculated k_H Values for Some o-Alkoxyphenyl Ketones in Benzene at 25°C.



Ketone	R	R'	X	ϕ_{pdt}	τ_T^{-1} 10^7 s^{-1}	k_H^a $10^7 s^{-1}$	k_H^b $10^7 s^{-1}$
o-BzOBP	Ph	Ph	H	0.94[c]	2.87	2.85	2.70
o-MeOBP	H	Ph	H	0.30	0.194	0.177	0.0582
o-BzO-5-MeBP	Ph	Ph	5-CH_3	0.52	1.78	1.76	0.926
2,2'-DiBzOBP	Ph	2-($PhCH_2O$)Ph	H	0.46	4.22	4.21	1.94
o-BzOAP	Ph	CH_3	H	0.0226(0.32)[d]	0.169	0.009	0.0532
o-BzOVP	Ph	$(CH_2)_3CH_3$	H	0.30(0.53)[d]	0.967	0.807	0.510
2,6-DBB	Ph	Ph	6-COPh	1.00[c]	24.7	24.7	24.7
2,6-DBA	H	Ph	6-COPh	0.77	2.21	2.19	1.70
2,6-DAB	Ph	CH_3	6-$COCH_3$	0.169	3.98	3.82	0.673

Table 21. Continued. Notes.

[a]Calculated from $1/\tau$, assuming $k_d = 1.6 \times 10^6 s^{-1}$ for o-BzOAP, o-BzOVP, and 2,6-DAB[29a]

$k_d = 1.7 \times 10^5 s^{-1}$ for all o-alkoxybenzophenones, 2,6-DBB, and 2,6-DBA.[67]

$k_d = 6.25 \times 10^4 s^{-1}$ for 2,2'-DiBzOBP.[67]

[b]Product of ϕ_{max} (when available) and $1/\tau$.

[c]Total quantum yield for both isomeric benzofuranol photoproducts.

[d]Values in parentheses represent maximized quantum yields obtained by the addition of pyridine to the reaction mixture prior to photolysis.

calculated from both assumptions are presented in Table 21.

Discrepancies between the two calculated k_H values can arise from a number of sources. The assumed triplet decay rate constants may not be correct for o-alkoxyphenyl ketones. This is probably the case for o-benzyloxyacetophenone since the calculated k_H value is much less than its lower limit. The other source of discrepancies comes when α is less than one. Biradical inefficiencies are well known in ketone photochemistry, and will be addressed later in this thesis.

2. Structure - Reactivity Relationships

o-Benzyloxybenzophenone is approximately fifty times more reactive than o-benzyloxyacetophenone. This difference in reactivity is directly attributable to the nature of the lowest excited triplet of each ketone. o-Benzyloxybenzophenone, like 2-benzyloxy-4-dodecycloxybenzophenone,[26] has a n,π^* lowest triplet. o-Benzyloxyacetophenone, like o-methoxyvalerophenone,[29a] has a π,π^* lowest triplet. Since n,π^* triplets are inherently more reactive than π,π^* triplets in hydrogen abstraction reactions,[6] it is not surprising to find that o-benzyloxybenzophenone is more reactive than o-benzyloxyacetophenone.

δ-Hydrogen abstraction rate constants for o-alkoxyphenyl ketones are sensitive to the reactivity of the alkoxy hydrogens. o-Benzyloxybenzophenone is thirty times

more reactive than o-methoxybenzophenone, reflecting the greater reactivity of a benzylic hydrogen in comparison with a methyl or primary hydrogen. Walling[68] has reported an eighty-fold difference in the reactivity of a methyl hydrogen and a benzyl hydrogen in the photoreduction of benzophenone. Wagner[69] reported a fifty-fold difference in the rate constants for γ-hydrogen abstraction in γ-phenylbutyrophenone and butyrophenone.

3. Conformational Effects

Hydrogen abstraction rate constants for o-benzyloxybenzophenone, o-methoxybenzophenone, and o-benzyloxyacetophenone are in the same range (10^6 - $10^7 s^{-1}$) as that reported by Pappas[25] for methyl o-benzyloxyphenyl glyoxylates and by Lappin[26] for 2-benzyloxy-4-dodecycloxybenzophenone. Stern-Volmer quenching plots for these ketones (cf. Figures 15-17) are linear, and, hence, do not reveal the presence of more than one triplet,[44b] contrary to what was anticipated. However, as mentioned previously, these k_H values are at least an order of magnitude lower than what is predicted for these ketones. It is tempting to assume that this decreased reactivity is the result of the presence of two rapidly interconverting triplets, one reactive and the other unreactive. If this conformational interconversion is faster than hydrogen abstraction, the observed reciprocal triplet lifetime is actually the linear sum of the products

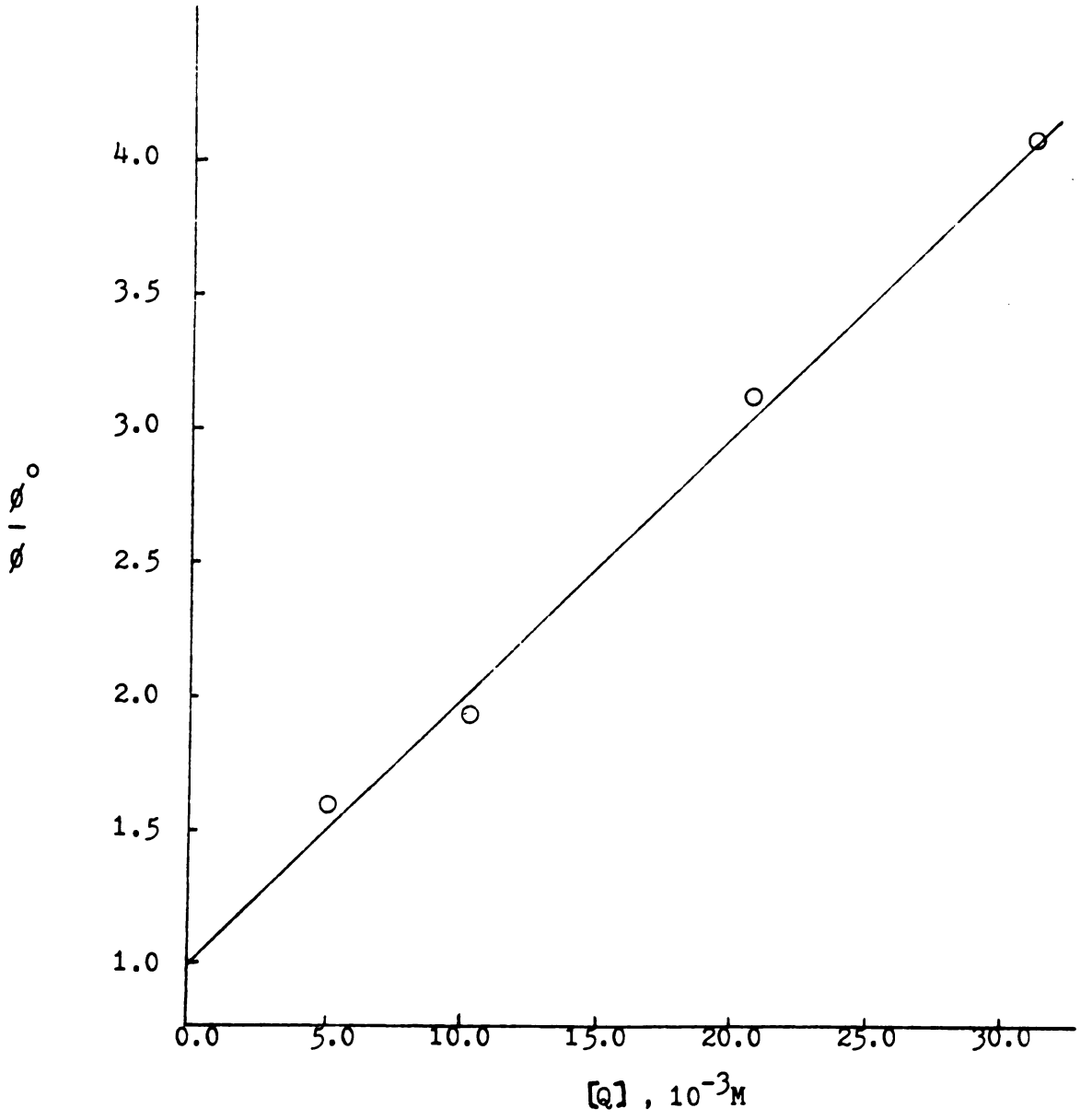


Figure 15. Stern-Volmer plot for the quenching of o-benzyloxybenzophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.

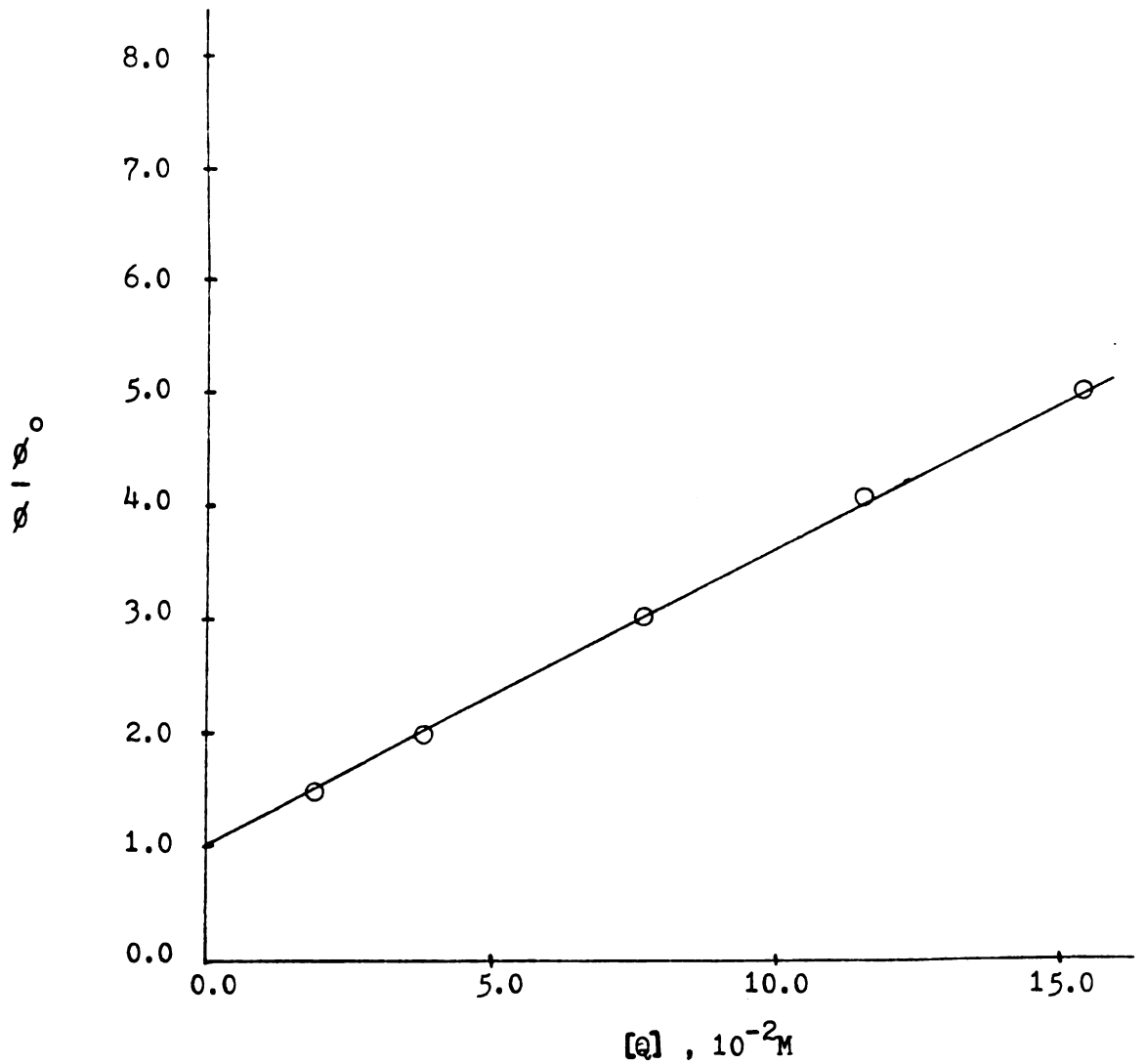


Figure 16. Stern-Volmer plot for the quenching of o-methoxybenzophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.

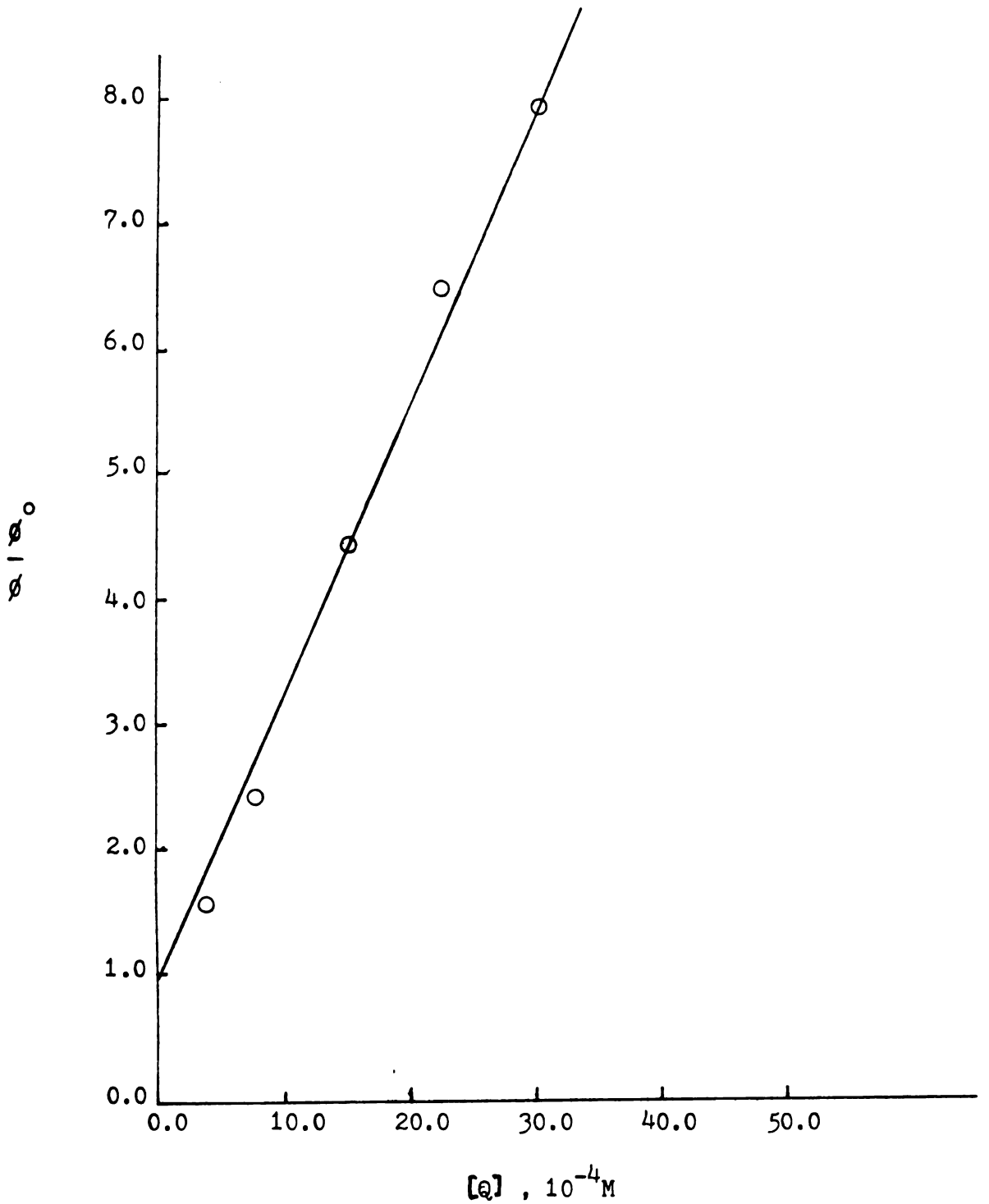


Figure 17. Stern-Volmer plot for the quenching of o-benzyloxyacetophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.

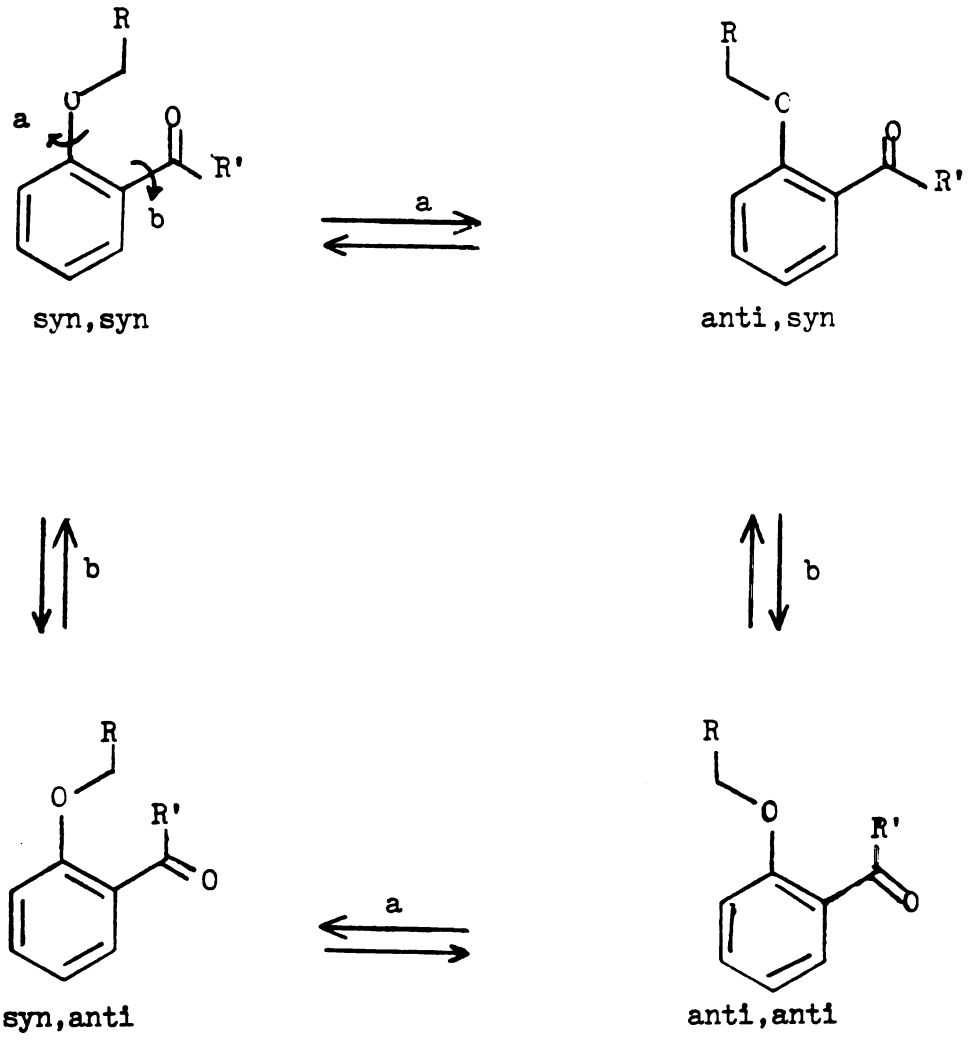
of the reciprocal triplet lifetimes, τ_i^{-1}, and fractional populations of each triplet conformer, χ_i.[70] That is -

$$\tau_{obsd}^{-1} = \sum_i \chi_i \cdot \tau_i^{-1} \quad .$$

In such cases, only one triplet lifetime would be observed by Stern-Volmer quenching.[70] The existence of two triplet conformers for these ketones, therefore, could go undetected. (Note that if such a conformational change is occurring in o-alkoxyphenyl ketones, it must be faster than hydrogen abstraction since k_H's for these ketones are sensitive to the reactivity of the o-alkoxy hydrogens.)

Two important internal rotations are available to o-alkoxyphenyl ketones. Each rotation produces two different conformers. Therefore, if both rotations occur freely, four different rotational isomers are produced. Of these four rotamers, only one, the (syn,syn) conformer, is reactive.

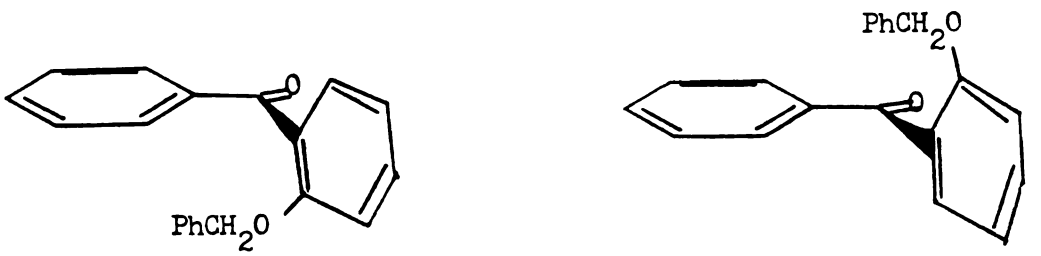
Because both the alkoxy oxygen and the carbonyl conjugate with the benzene ring, rotations of these substituents are somewhat restricted in the ground state. Since this conjugation is even more important in the excited state,[71] these rotations are more restricted. It was not possible to predict the relative importance of each of these rotations on the overall mechanism for δ-hydrogen abstraction in these ketones. Therefore, model compounds were



synthesized and studied in order to test the effects of each rotation on the efficiency of hydrogen abstraction in these ketones.

o-Alkoxybenzophenones have a special conformational problem. Hoffmann[71] has shown that in the excited state of benzophenone, only one benzene ring is coplanar with the carbonyl. Montaudo and co-workers[72] suggest that ^{1}H

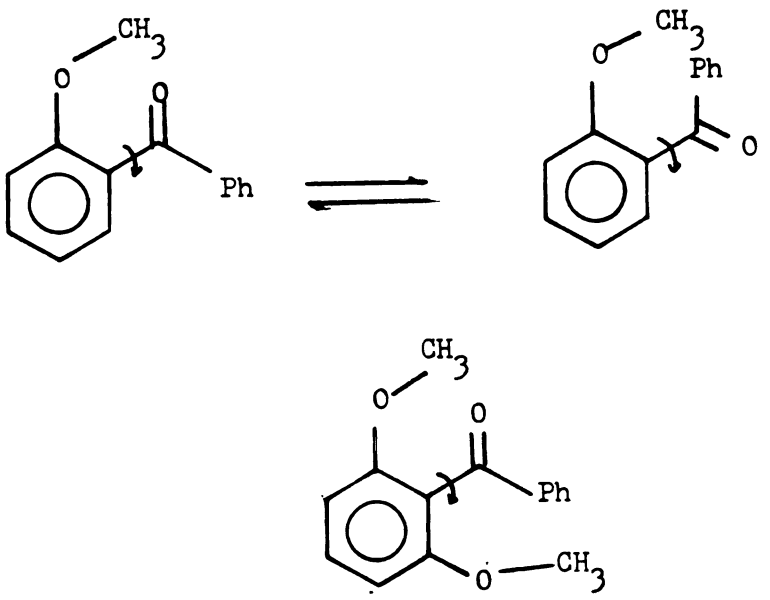
nmr and dipole moment measurements reinforce earlier notions[73] that in solution the ground state conformation of benzophenone is 'propellor-like' with each benzene ring tilted approximately 20° out of the plane of the carbonyl. However, ortho substitution increases the dihedral angle between the carbonyl and the substituted ring to as much as 45°,[72] depending upon the size of the ortho substituent. Based upon this ground state preference, it is unlikely that the alkoxy substituted ring is coplanar with the carbonyl. It is possible, then, that the alkoxy hydrogens may not be as available to the carbonyl oxygen in this arrangement as they would be if the alkoxy substituted ring was coplanar with the carbonyl (Scheme 12). Hence, δ-hydrogen abstraction may not be very efficient from this conformation. Ortho benzyloxy substitution of both benzene rings, as in 2,2'-dibenzyloxybenzophenone, would ensure that one benzyloxy substituted ring remains nearly coplanar with the carbonyl at all times. Hence, the efficiency of hydrogen abstraction and k_H would be increased. However, k_H for 2,2'-dibenzyloxybenzophenone is only 1.5 times larger than k_H for o-benzyloxybenzophenone. The smallest increase possible would be due to the increased statistical favorability of two benzyloxy groups, i.e., a factor of two. The observed increase is less than that and would suggest that the efficiency of δ-hydrogen abstraction in o-alkoxybenzophenones is not severely affected by this type of excited state conformational preference.



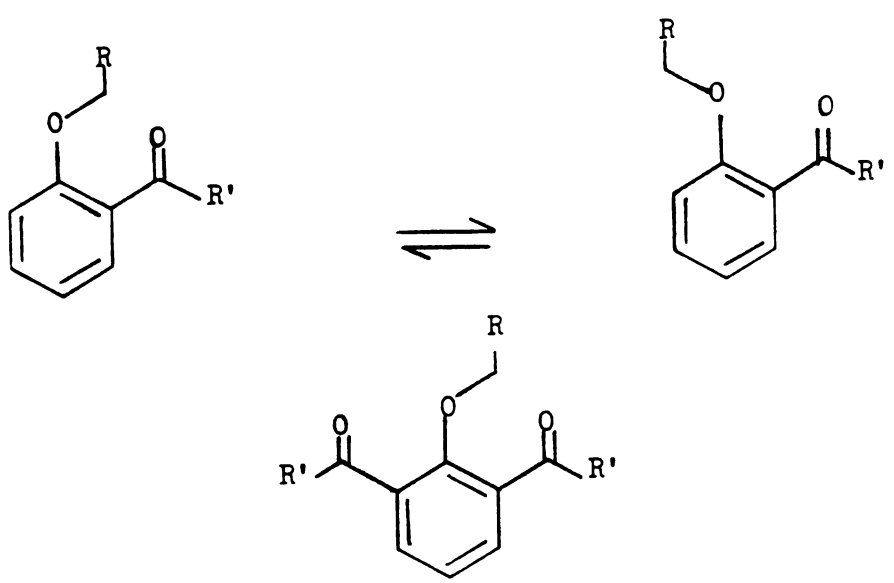
Scheme 12

Rotation about the acyl-phenyl bond has been found to be an important conformational factor in the photochemistry of o-alkylphenyl ketones.[18] It was envisioned that if such a rotation is important to hydrogen abstraction in o-alkoxyphenyl ketones, 2,6-dialkoxyphenyl ketones might be more reactive than o-alkoxyphenyl ketones. For example, 2,6-dimethoxybenzophenone should have a shorter lifetime than o-methoxybenzophenone (Scheme 13). The triplet lifetime of 2,6-dimethoxybenzophenone (determined by laser flash spectroscopy) is more than twice that of o-methoxybenzophenone, determined by the same technique! Rotation about the acyl-phenyl bond, therefore, does not have a significant effect on the rate of hydrogen abstraction in o-alkoxyphenyl ketones.

2,6-Diacyl substitution about the alkoxy group can help determine the importance of alkoxy group rotations to δ-hydrogen abstraction in o-alkoxyphenyl ketones (Scheme 14).



Scheme 13



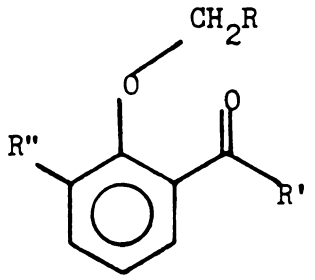
Scheme 14

2,6-Diacylalkoxybenzenes, then, are models for the (syn,syn) conformer. If alkoxy rotations are of any significance in the mechanism of δ-hydrogen abstraction, k_H values for 2,6-diacylalkoxybenzenes should be much larger than those of their monoacyl counterparts. In all cases, this rate enhancement is observed for 2,6-diacylalkoxybenzenes (Table 22)! Wagner and Siebert[29b] have shown that meta-acyl substitution has no effect on the rate constant for γ-hydrogen abstraction in valerophenones. Hence, the larger k_H values for 2,6-diacylalkoxybenzenes are a true indication of the effect that rotation of the alkoxy group has on the efficiency of δ-hydrogen abstraction in o-alkoxyphenyl ketones.

Although the large k_H values for 2,6-diacylalkoxybenzenes indicate that alkoxy group rotation is important to the overall hydrogen abstraction mechanism, the exact mechanism of the interconversion of the two conformers resulting from such a rotation has yet to be established. Three basic mechanisms have been proposed for such interconversions - ground state equilibrium,[16] rate determining excited state rotation,[18] or excited state equilibrium.[17]

Proton nmr[74] indicates, not surprisingly, that the preferred ground state conformation of o-substituted anisoles is one in which the methoxy group is rotated a full 180° away from the ortho substituent. The same ground state preference should also be true for all

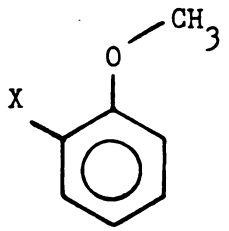
Table 22. Hydrogen Abstraction Rate Constants for 2,6-Diacylalkoxybenzenes and Corresponding o-Alkoxyphenyl Ketones in Benzene at 25°C.



R"	R	R'	ϕ_{pdt}	k_H, $10^7 s^{-1}$
H	Ph	Ph	0.94[a]	2.70
COPh	Ph	Ph	1.00[a]	24.70
H	H	Ph	0.30	0.177
COPh	H	Ph	0.77	2.19
H	Ph	CH_3	0.0226	0.0532
$COCH_3$	Ph	CH_3	0.119	3.82

[a]Total quantum yield for the formation of both 3-hydroxy-2,3-dihydrobenzofuran isomers.

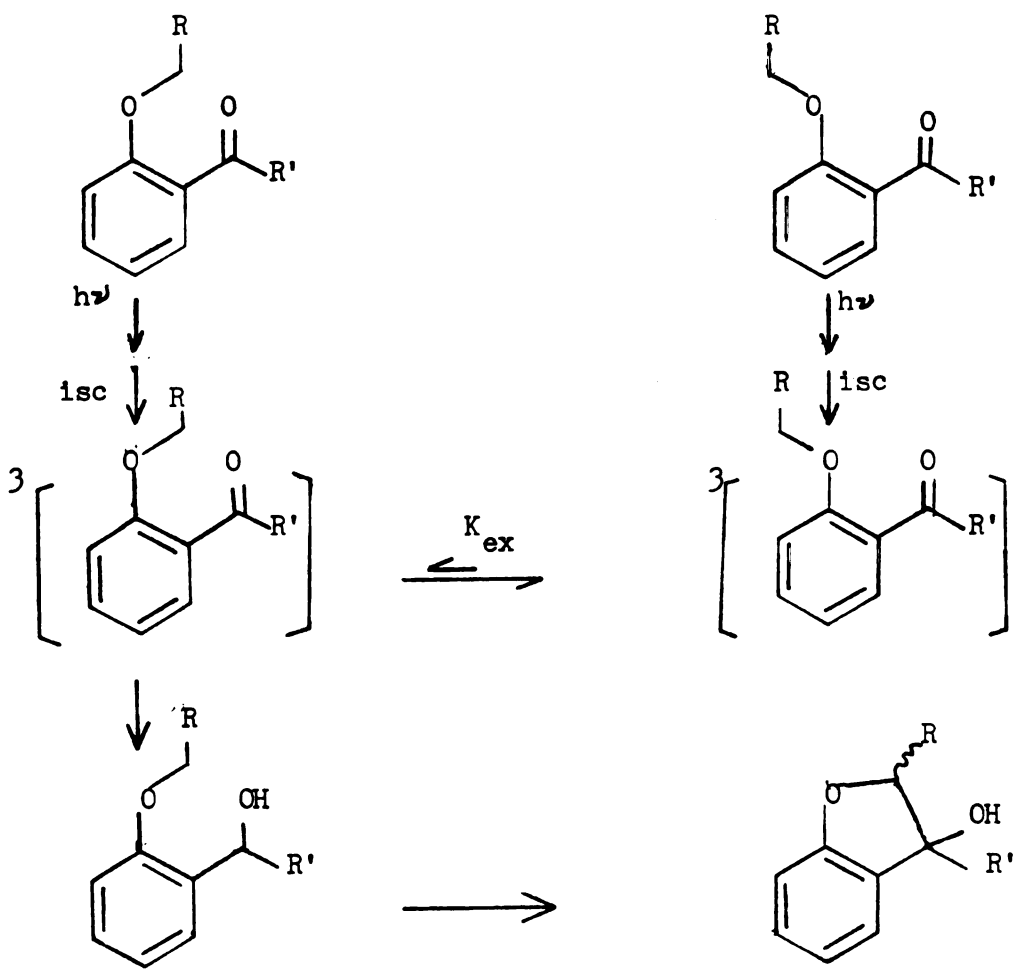
o-alkoxyphenyl ketones, since steric repulsions between the alkoxy group and carbonyl should be equal to if not greater than those felt in the anisoles described above. Therefore, if ground state equilibrium populations of the two ketone conformers limited the efficiency of hydrogen abstraction, quantum yields for photoproduct formation could not be more than 0.5 and could be much smaller. However, the photoproduct quantum yield for o-benzyloxybenzophenone is 1.0. Hence, a ground state equilibrium between these two conformers does not have a significant effect on the efficiency of hydrogen abstraction in these ketones.



Rate determining rotation of the alkoxy group would make k_H values for these ketones insensitive to the C-H

bond strength of the alkoxy hydrogens. As pointed out earlier, k_H values for o-alkoxyphenyl ketones are sensitive to the reactivity of the alkoxy hydrogens. Therefore, alkoxy group rotation is not the rate determining step in the mechanism for δ-hydrogen abstraction.

This leaves an excited state equilibrium between the two triplet conformers as the only mechanistic alternative. A mechanism based upon this excited state equilibrium is summarized in Scheme 15.



Scheme 15

The ^{13}C nmr chemical shifts of the alkoxy carbons in 2,6-diacyalkoxybenzenes are a full 7 to 10 ppm downfield relative to those of their monoacyl counterparts (Table 23). Similar chemical shift differences have been observed by Strothers[74] for a series of 2,6-dialkylanisoles (Table 23). In this system, increasingly bulky alkyl substituents force the methoxy group out of the plane of the benzene ring, thereby disrupting conjugation of the methoxy oxygen with the aromatic system. This loss of conjugation is manifested by the higher chemical shift values of the methoxy carbons of these compounds. These results are substantiated by other ^{13}C nmr studies[75] and by electronic absorption spectroscopy.[76] Since the chemical shift differences in 2,6-diacylalkoxybenzenes are of the same magnitude and direction as those reported by Stothers for 2,6-dialkylanisoles,[74] it is reasonable to assume that the same conformation is preferred in these compounds as well. That is, the alkoxy group of 2,6-diacylalkoxybenzenes is actually orthogonal to the plane of the central benzene ring, just as it is in 2,6-di-t-butylanisole.[74]

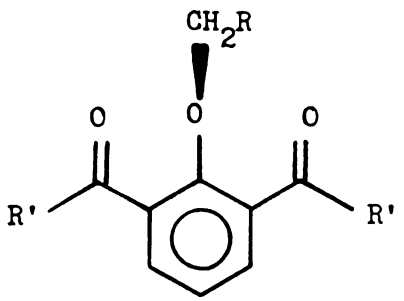
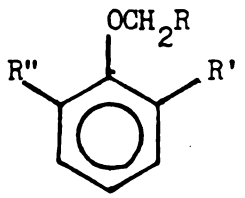


Table 23. ^{13}C Chemical Shifts of the Alkoxy Carbons of Substituted Anisoles.



R	R'	R"	$\delta_{O-CH_2-R'}$ ppm
H	COPh	H	55.33
Ph	COPh	H	68.65
Ph	$COCH_3$	H	70.60
Ph	CN	CN	76.90
Ph	COPh	COPh	77.12
Ph	$COCH_3$	$COCH_3$	79.40
H	COPh	COPh	61.60
H	H	H	54.0[a]
H	CH_3	CH_3	57.9[a]
H	$CH(CH_3)_2$	$CH(CH_3)_2$	61.2[a]
H	$C(CH_3)_3$	$C(CH_3)_3$	63.7[a]

[a]Reference 74.

Furthermore, the exact geometry of the (syn,syn) conformer is most likely one in which the alkoxy group is not totally coplanar with the aromatic system, but approaches co-planarity as far as steric repulsions from the carbonyl will allow it. This conformation is still reactive since the alkoxy hydrogens are still quite accessible to the carbonyl oxygen.

Excited state equilibrium constants can be calculated from the ratio of k_H for an o-alkoxyphenyl ketone to that of its 2,6-diacylalkoxybenzene analogue. This calculation assumes that the 2,6-diacylalkoxybenzenes provide an accurate measure of k_H for the (syn,syn) conformer of the corresponding o-alkoxyphenyl ketones. That is, k_H for 2,6-diacylalkoxybenzenes represent the intrinsic k_H values for their corresponding o-alkoxyphenyl ketone analogues. The calculation of these excited state equilibrium constants invokes the Winstein-Holness relationship.[77] This relationship, which holds only for systems in which conformational changes are faster than reaction, states that -

$$k_H^{obs} = K_{ex}\, k_H^{int}$$

where k_H^{obs} = observed rate constant for hydrogen abstraction (k_H for an o-alkoxyphenyl ketone

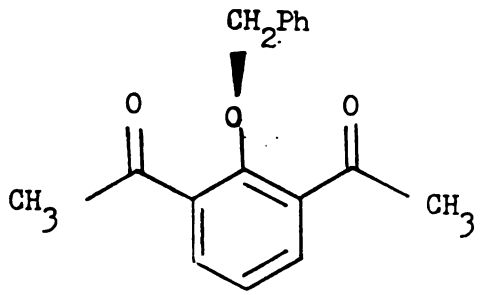
K_{ex} = excited state fractional equilibrium population of the reactive conformer

k_H^{int} = intrinsic hydrogen abstraction rate constant (k_H for the appropriate 2,6-diacylalkoxybenzene).

These excited state equilibrium constants are summarized in Table 24.

The K_{ex} values for both o-benzyloxybenzophenone and o-methoxybenzophenone are surprisingly similar. This would seem to indicate that the magnitude of K_{ex} is not strongly influenced by the size of the alkoxy substituent.

Excited state equilibrium favors the unreactive conformer in o-benzyloxyacetophenone by nearly 99:1! This is almost an order of magnitude larger than the excited state preference for the unreactive conformer of o-benzyloxybenzophenone. The larger K_{ex} value for o-benzyloxybenzophenone may reflect the fact that the benzyloxy substituted ring is probably not coplanar with the carbonyl groups, as it must be in o-benzyloxyacetophenone. Hence, the steric repulsions due to the carbonyl group are not as strong in the benzophenone as they are in the acetophenone.



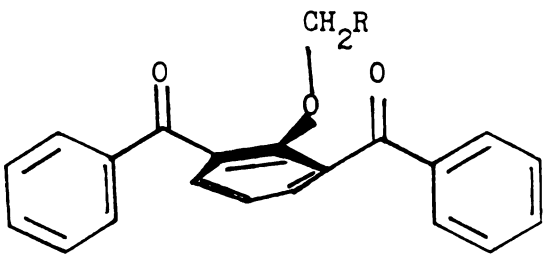
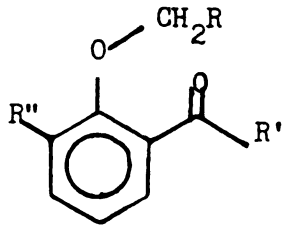


Table 24. Excited State Equilibrium Constants for o-Alkoxyphenyl Ketones in Benzene at 25°C.



R	R'	R"	k_H, $10^7 s^{-1}$	K_{ex}
Ph	Ph	H	2.70	0.109
Ph	Ph	COPh	24.70*	
Ph	CH_3	H	0.0532	0.0139
Ph	CH_3	$COCH_3$	3.82*	
H	Ph	H	0.177	0.0808
H	Ph	COPh	2.19*	

*Note that these values are assumed to be the intrinsic k_H values for the corresponding o-alkoxyphenyl ketones.

The intrinsic rate constant for δ-hydrogen abstraction in o-benzyloxybenzophenone is in good agreement with the predicted value of $10^8 s^{-1}$. Correction of the intrinsic k_H for o-methoxybenzophenone for the reduced reactivity of an o-methoxy group, also brings it within the predicted range. The intrinsic k_H for o-benzyloxyacetophenone is also somewhat lower than the predicted k_H. It has been established that the excited state reactivities of both o-methoxyvalerophenone[29a] and o-benzyloxyvalerophenone are approximately one-eighth that of valerophenone. An o-alkoxy substituent stabilizes the π,π* triplet relative to the n,π* triplet of these ketones by resonance.[29a] Since the π,π* triplet is lowered in energy there is more π,π* character in the triplet of these ketones and the excited state reactivity is reduced.[29a] Assuming that the same is true for o-benzyloxyacetophenone, correction of the intrinsic k_H for this reactivity decrease puts it in good agreement with the predicted value.

Evidence for a 1,5-Biradical Intermediate

n-Alkyl mercaptans are known to trap biradicals with rate constants on the order of $1 \times 10^7 M^{-1} s^{-1}$.[78] Attempts to trap the presumed biradical formed from o-benzyloxybenzophenone with n-octylmercaptan, a known biradical trapping agent,[78c] were unsuccessful. Instead, the lifetime value obtained indicates that the ketone triplet was quenched.

Mercaptans are known to quench ketone triplets, as well, with similar rate constants.[74] Therefore, if the ketone triplet is substantially longer lived than the biradical, it will be quenched preferentially. This is the case here, indicating that the biradical lifetime is much shorter than the ketone triplet lifetime.

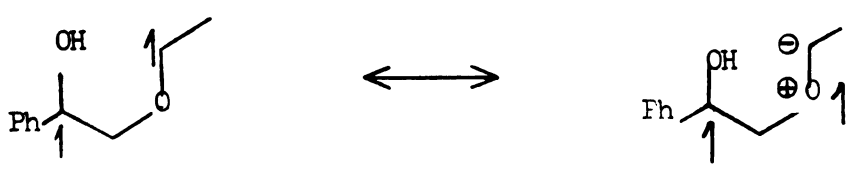
For the same reason, it was not possible to observe the biradical directly by nanosecond laser flash spectroscopy. Absorptions from the longer lived ketone triplet masked those of the biradical. In such cases, it is possible to "fine-tune" the system.[80] This is accomplished by adding sufficient amounts of a diene quencher to shorten the triplet lifetime enough to make it shorter lived than the biradical, thereby making the biradical spectrum visible. Attempts to observe the biradical by this technique in benzene solution were unsuccessful. However, addition of 1.0 M pyridine did make the biradical formed from o-benzyloxybenzophenone visible (τ_{BR} = 13 nsec).[81] Hence, in the absence of pyridine this biradical is too short-lived to be observed on the nanosecond time scale of the laser apparatus. The effects of pyridine on the lifetime of this biradical will be discussed later.

It has been shown that 1,4-biradicals which have an oxygen atom incorporated in their backbone have dramatically shorter lifetimes than their pure hydrocarbon analogs. Caldwell[82] has found that the Norrish Type II biradicals

formed from benzyl phenacyl ethers have lifetimes two orders of magnitude less than their hydrocarbon counterparts (Scheme 16). Caldwell[82] has also found that preoxetane biradicals (Scheme 16), formed from the Paterno-Büchi reaction of benzophenone with various olefins, have similarly short lifetimes, on the order of 1.5 to 4.0 nsec depending upon the olefin and experimental conditions. Peters[83] reported similar lifetimes for the Paterno-Büchi biradical formed from benzophenone and dioxene.

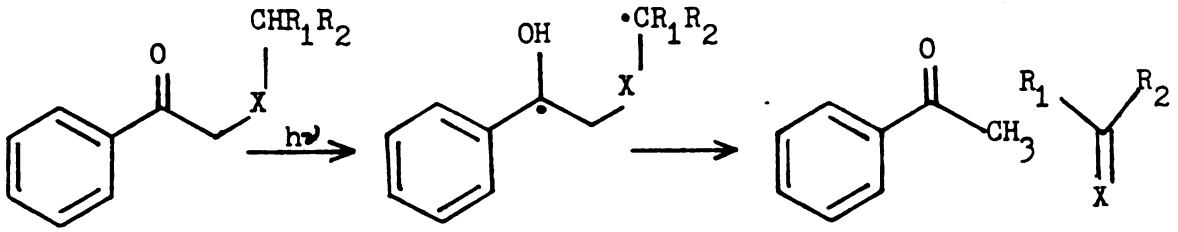
This effect has only been observed in circumstances where the biradical backbone contains an oxygen atom, and is not observed if there is an alkoxy substituent on the biradical. The lifetime of the Norrish Type II biradical formed from γ-methoxyvalerophenone (30 ± 6 nsec)[82] is close to the 38 nsec lifetime of the biradical produced from valerophenone by the same process.

Two explanations have been put forth[82,83] to account for the shorter lifetime of these biradicals. One is that resonance with the oxygen decreases the average distance between the two radical centers and thereby destabilizes the biradical (Scheme 17).

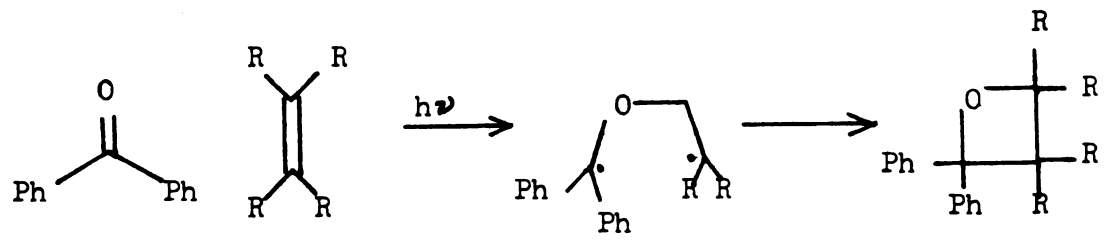


Scheme 17

Table 25. Lifetimes of Some Norrish Type II Biradicals.



R_1	R_2	X	Methanol τ_{BR}, nsec	Heptane τ_{BR}, nsec
Ph	Ph	O	4.9±1.5	6.4±1.6
Ph	H	O	1.3	1.7
Ph	Ph	CH_2	222.±18.	113.±13.
Ph	H	CH_2	146.±18.	55.± 8.
OCH_3	H	CH_2	70.± 5.	30.± 6.

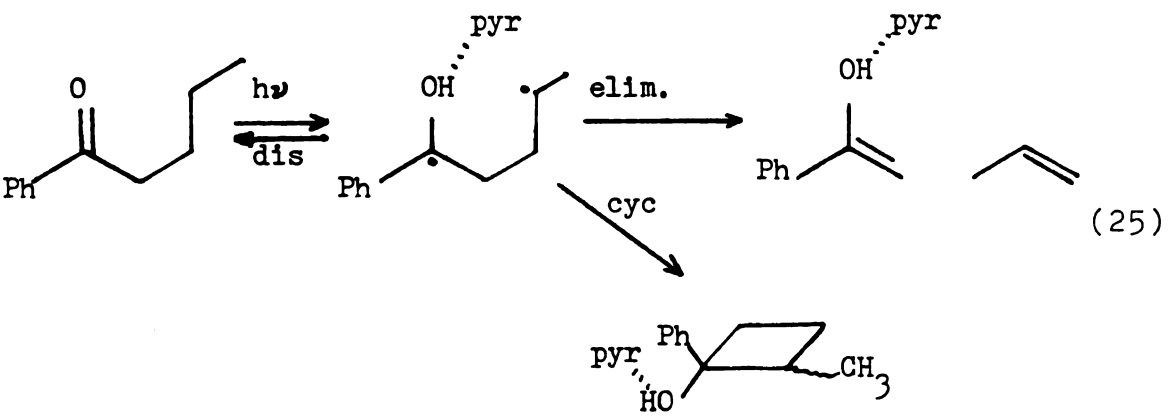


Alternatively, some biradical conformations have an angle of 90° between a 2p oxygen orbital and the half-filled orbital of the adjacent radical center. Spin-orbit coupling from these conformations is enhanced thereby enhancing the

rate of intersystem crossing (believed to be the rate determining step in biradical decay[84]) and reducing the triplet lifetime. However, these conformations should also exist in the biradical formed from γ-methoxyvalerophenone. Since this biradical has a 'normal' lifetime, it is unlikely that the latter explanation is a correct one.

Since the biradical formed from o-benzyloxybenzophenone contains an oxygen atom in its backbone, it is not surprising that it is extremely short-lived in the absence of pyridine.

Wagner[85] has demonstrated that pyridine and other weak Lewis bases, such as t-butyl alcohol, solvate Norrish Type II biradicals and suppress disproportionation of the biradical to starting ketone (Reaction 25). The quantum

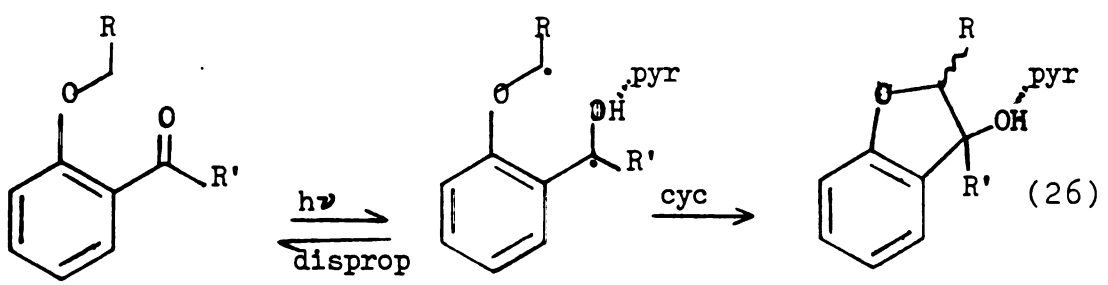


(25)

yields of elimination products are enhanced, while those of cyclization products are diminished slightly, for

steric reasons.

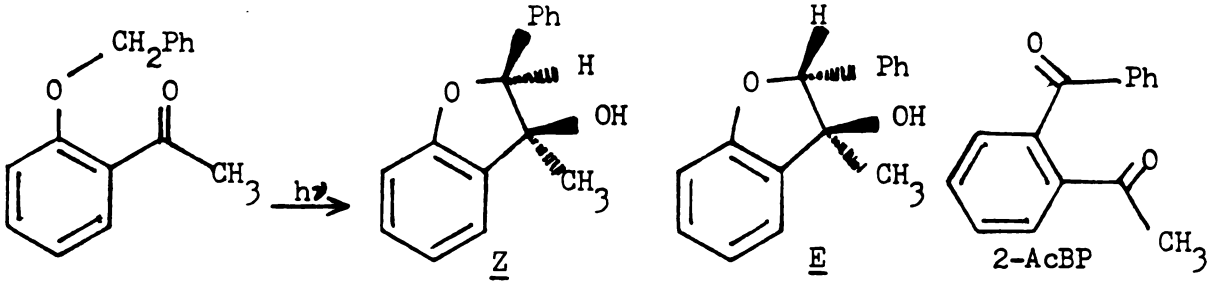
In the case of o-alkoxyphenyl ketones, there are only two competitive reactions possible from the biradical - cyclization and disproportionation (Reaction 26). Addition of pyridine should totally suppress disproportionation while offering a slight steric barrier to cyclization. The net result should be an overall enhancement of the photocyclization quantum yield. Although the photocyclization quantum yield for o-benzyloxybenzophenone in the absence of pyridine is already close to 1.0, addition of pyridine (ca. 2 M) increases the photocyclization quantum yield for o-benzyloxyacetophenone nearly ten-fold (Table 26)!



(26)

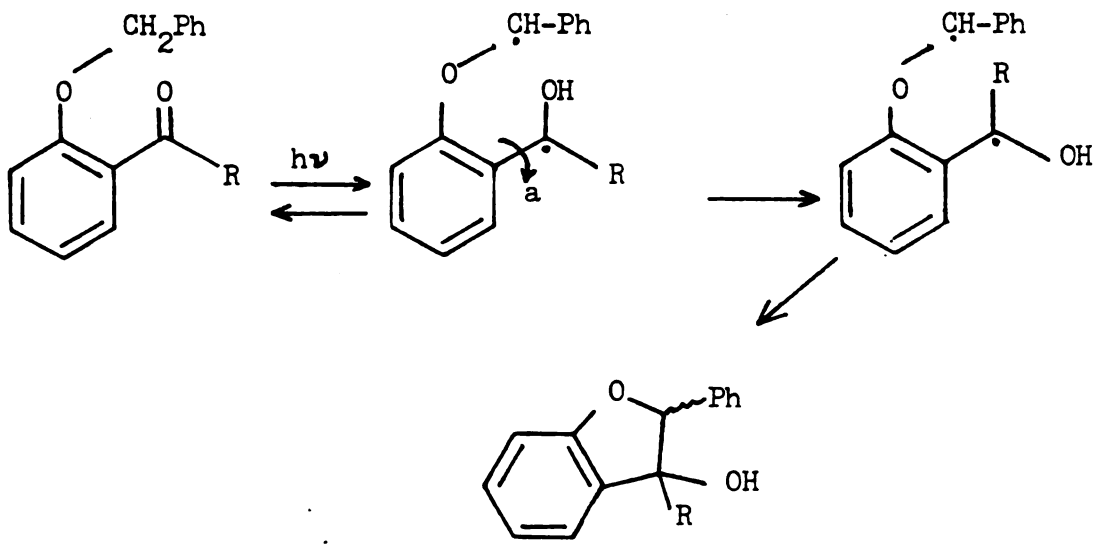
The effect of added pyridine on the photocyclization quantum yield for o-benzyloxyacetophenone is rather dramatic compared to its effect on the Norrish Type II reaction. For example, pyridine increases the quantum yield for the formation of o-benzyloxyacetophenone from o-benzyloxyvalerophenone by a factor of only 1.8.

Table 26. Effects of Pyridine on Photoproduct Quantum Yields from o-Benzyloxyacetophenone in Benzene at 25°C.



[Pyridine], M	ϕ_{Z}	ϕ_{E}	$\phi_{2\text{-AcBP}}$
0.00	0.0226	Trace	0.0589
0.544	0.0598	0.0301	0.0670
1.63	0.101	0.0666	0.0517
2.18	0.118	0.0811	0.0456

The biradical derived from o-benzyloxyacetophenone is initially formed in a conformation which favors disproportionation (Scheme 17) over cyclization. To avoid disproportionation, the biradical must undergo rotation about bond a. Conradi and co-workers[86] have measured the line broadening of the epr spectrum of benzaldehyde ketyl radical. They deduce a rate constant for bond rotation on the order of $10^{3}s^{-1}$ at 25°C. This is somewhat lower than what would be expected for such a rotation. Molecular orbital



Scheme 17

calculations[87] predict a barrier to rotation in this system of approximately 8 kcal/mole. Based upon this value, one would expect a rate constant for rotation on the order of $10^7 s^{-1}$. Coincidentally, this is the same value found for rotation in the electronically similar triplet ketone.[18]

Regardless of whether or not the experimentally determined value is correct, it is clear that the requirement that the C-OH fragment remain coplanar with the benzene ring, in order to maximize delocalization of the odd

electron, demands that rotation about bond a is highly restricted. Therefore, the biradical formed from o-benzyloxyacetophenone initially exists in a conformation favoring disproportionation and would not be able to undergo rotation fast enough to make cyclization competitive with disproportionation.

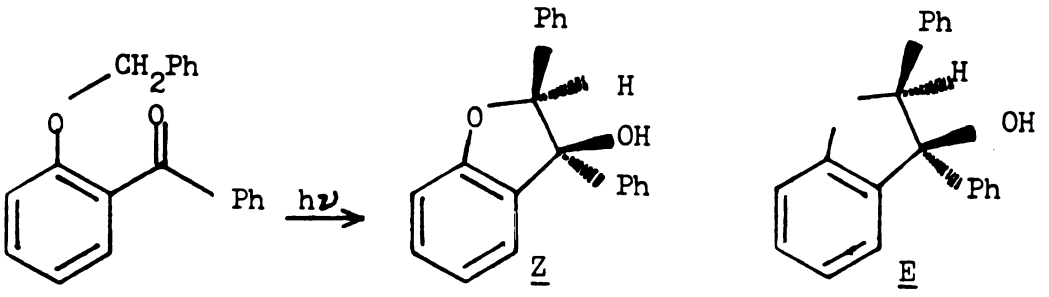
However, pyridine solvates the ketyl portion of the biradical and prevents disproportionation from this conformation, giving the biradical more time to undergo rotation and subsequent cyclization. This solvation would also increase the steric bulk at the ketyl radical center and may force rotation about bond a, i.e., increase the rate of rotation.

Pyridine solvation of the biradical also results in a loss of stereoselectivity for biradical cyclization. In the absence of pyridine, cyclization of biradicals derived from o-benzyloxyacetophenone and o-benzyloxybenzophenone clearly favors formation of the kinetically preferred product. That is, cyclization of these biradicals in the absence of pyridine favors the isomer in which the less bulky hydroxyl group is cis to the C-2 phenyl (Z isomer). Addition of pyridine increases the steric bulk of the hydroxyl group, since the pyridine is now hydrogen bonded to the hydroxyl proton. Since the hydroxyl group is now comparable in size to a methyl (in the o-benzyloxyacetophenone derived biradical) or a phenyl (in o-benzyloxybenzophenone

derived biradical), cyclization proceeds with no stereochemical preference.

The photocyclization quantum yields for both o-benzyloxybenzophenone and o-methoxybenzophenone are reduced by the addition of pyridine. At the same time, however, addition of pyridine to both of these ketones results in the formation of a new photoproduct, whose structure is presently undetermined (Tables 27 and 28). Laser flash spectroscopy

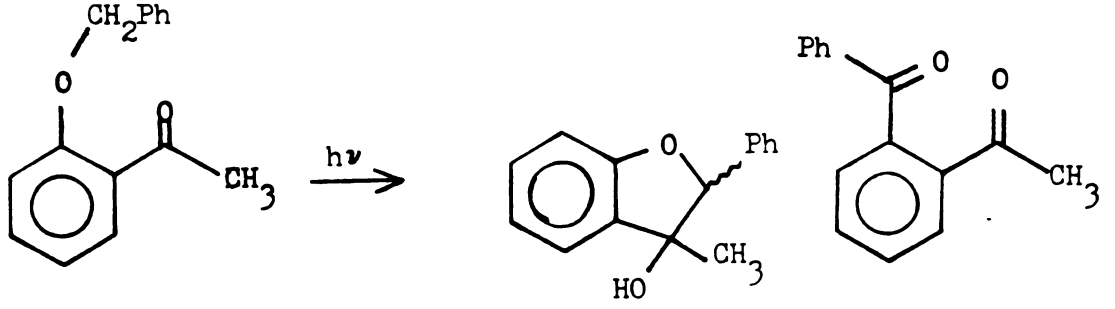
Table 27. Effects of Pyridine on the Photocyclization Quantum Yields for o-Benzyloxybenzophenone in Benzene at 25°C.



[Pyridine], M	Z	E	a unknown	total
0.0	0.831	0.108	0.00	0.939
1.24	0.358	0.290	0.280	0.928
2.47	0.323	0.293	0.310	0.926

[a]Estimated

Table 28. Effects of Pyridine on the Photocyclization Quantum Yield for o-Methoxybenzophenone in Benzene at 25°C.



[Pyridine], M	ϕ_{cyc}	$\phi_{unknown}$	ϕ_{total}
0.0	0.299	0.0242	0.323
1.24	0.157	0.110	0.267
2.47	0.151	0.135	0.286

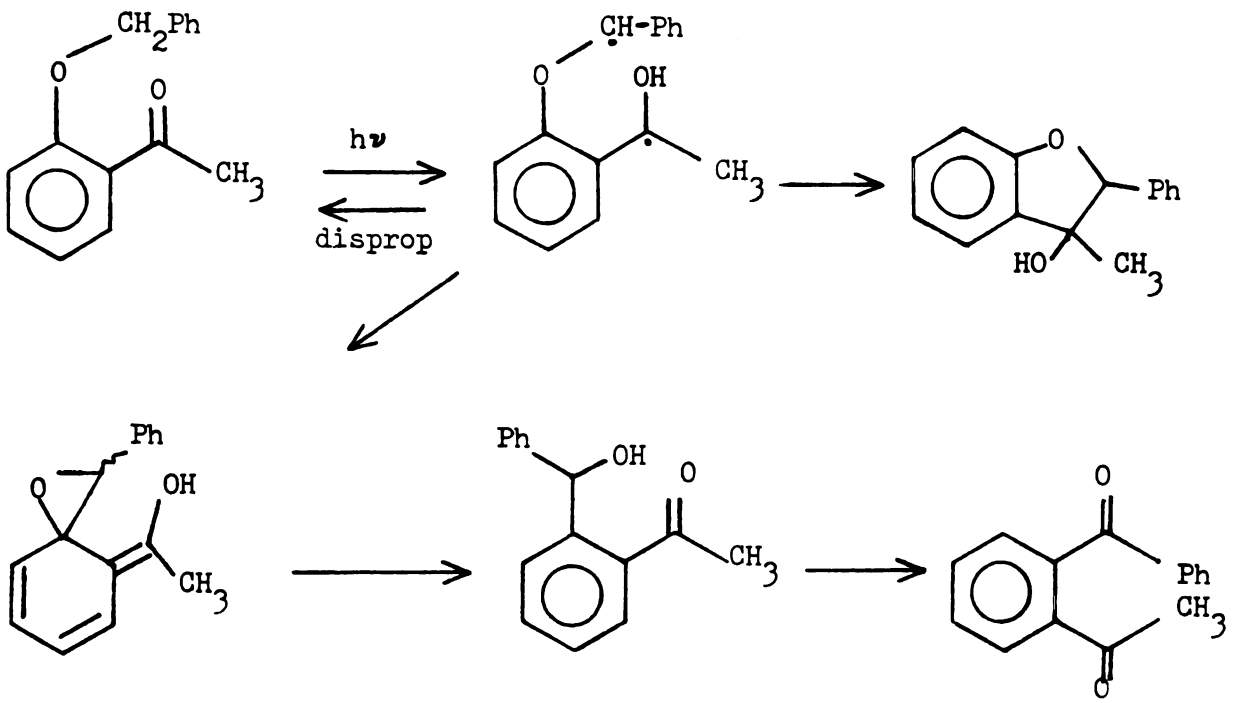
reveals that the triplet lifetime of o-benzyloxybenzophenone is only slightly affected by the addition of pyridine (τ_{BR} = 58 nsec in benzene, 75 nsec in benzene containing 1M pyridine).[81] Hence the lower photocyclization quantum yield for o-benzyloxybenzophenone is not due to quenching of the ketone triplet. Therefore, the lower photocyclization quantum yield for o-benzyloxybenzophenone must be due to some interaction of pyridine with the biradical. The lifetime of the o-benzyloxybenzophenone derived biradical is an order of magnitude larger in benzene containing 1M pyridine (13 nsec)[81] than it is in the absence of pyridine

(less than 4 nsec).[81] It may be possible that solvation of the biradical reduces the rate constant for cyclization enough to make some other biradical process competitive. It is this process which gives rise to the new photoproduct. Unfortunately, this product was too unstable to be isolated by flash chromatography.[88] Hence, any discussion of its origin is purely speculative.

Spectral analysis of the photoproduct formed from o-methoxybenzophenone in the presence of pyridine reveals it is probably o-methoxybenzhydrol. It is likely that this product arises from photoreduction of o-methoxybenzophenone.

The quantum yield for the formation of 2-acetylbenzophenone, 33, from o-benzyloxyacetophenone, 30, is not affected by the addition of pyridine (see Table 26). This suggests that 2-acetylbenzophenone may be formed from the biradical via a pathway which is not affected by the presence of pyridine. Such a pathway is outlined in Scheme 18. According to this mechanism, the biradical has two competitive cyclization reactions available to it - one leads to formation of the usual benzofuranol photoproducts, the other leads to formation of the quinoid structure, 31. Addition of pyridine would not affect the rate with which the biradical cyclizes to 31, since such a cyclization does not involve the hydroxyl proton. Rearrangement of 31 to 2-acetylbenzhydrol, 32, should be fast since it involves a rearomatization of the benzene ring. Hence, the overall rate constant for the formation of 2-acetylbenzhydrol

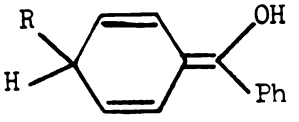
from the o-benzyloxyacetophenone biradical should be unaffected by the addition of pyridine. It is not clear whether the oxidation of 2-acetylbenzyhydrol to 2-acetylbenzophenone proceeds photochemically or thermally.



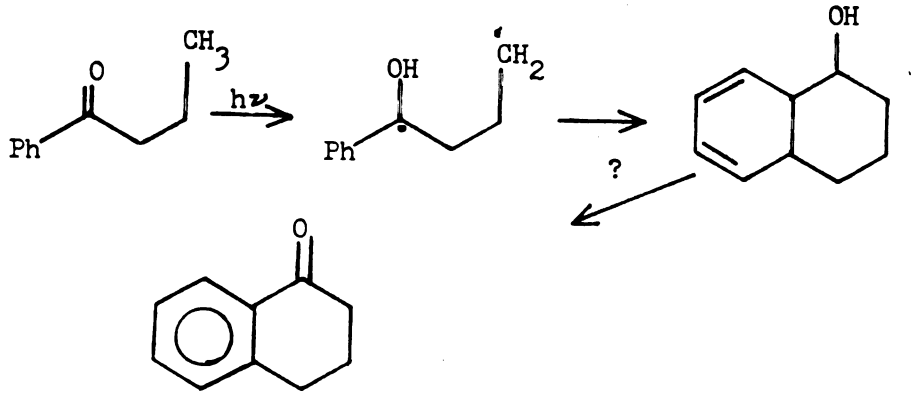
Scheme 18

Both radicals and biradicals are known to undergo ring coupling reactions which give rise to compounds with structures similar to 31. Benzyl radicals couple to form 1-alkyliden-2,5-cyclohexadienes.[89] The same coupling reaction has been found to occur with the semi-benzpinacol radicals formed from the photoreduction of benzophenone.[90] Steel has shown that these ring coupled products are formed in yields on the order of a few percent from the

photoreduction of benzophenone.[91]



Pitts and co-workers[92] have reported that photolysis of butyrophenone produces a trace amount of material whic they believe may be α-tetralone (as well as the usual Type II products). They postulate that it is formed from the cyclization of the Norrish Type II biradical.



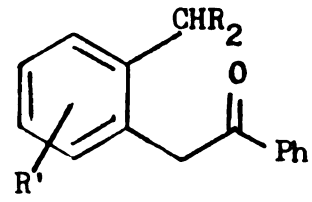
Hence, the mechanism described in Scheme 18 provides a plausible and rather attractive explanation for the formation of 2-acetylbenzophenone <u>via</u> the photolysis of <u>o</u>-benzyloxybenzophenone.

B. α-(o-Alkylphenyl)acetophenones

1. Hydrogen Abstraction Rate Constants

The rather short triplet lifetimes for α-(o-alkylphenyl)acetophenones suggest that hydrogen abstraction is the predominant process from the triplet. Acyl cleavage is not competitive with hydrogen abstraction since rate constants for such a process in α-phenylacetophenones are on the order of $10^6 s^{-1}$. Lewis[93] reports that k_α for α-(4-methylphenyl)acetophenone is $3.6 \times 10^6 s^{-1}$ in benzene. Furthermore, hydrogen abstraction is much faster than triplet decay in this system. The photocyclization quantum yield for α-(o-tolyl)acetophenone (Table 29) is noteworthy, since such a value is possible only if k_H is much larger than both k_d and k_α. Lewis[93] has reported a k_d value on the order of $10^6 s^{-1}$ for α-(4-methylphenyl)acetophenone in benzene. Assuming that the k_d values for α-(4-methylphenyl)-acetophenone and α-(o-methylphenyl)acetophenone are similar, non-reactive decay accounts for less than 1% of the overall triplet lifetimes of these ketones. Hence, the reciprocal triplet lifetimes of these ketones are in accurate measure of the rate constant for hydrogen abstraction, k_H. These values are presented in Table 29.

Table 29. Photokinetic Parameters for a Series of α-(o-Alkylphenyl)acetophenones in Benzene at 25°C.



Ketone	R	R'	ϕ_{pdt}	$k_q\tau_T$, M^{-1}	τ_T^a, nsec	$1/\tau_T=k_H$, $10^9 s^{-1}$
α-TAP	H	H	1.00	30.7	6.14	0.163
α-(DMP)AP	H	5-CH_3	0.62	19.0	3.80	0.263
α-MAP	H	4,6-CH_3	0.44(0.54)[b]	4.65	0.93	1.08
α-(DIP)AP	CH_3	5-$CH(CH_3)_2$	0.42	3.36	0.672	1.49
α-(TIP)AP	CH_3	4,6-$CH(CH_3)_2$	0.041	3.25	0.65	1.54

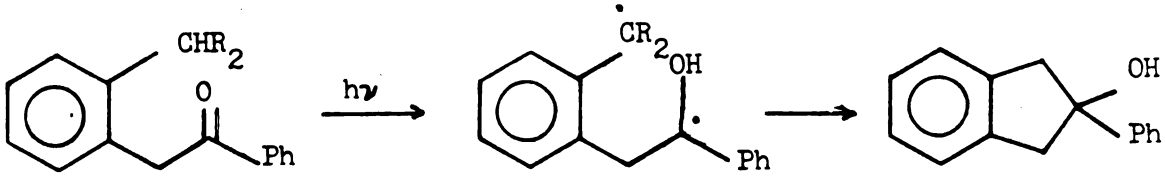
[a]Calculated from $k_q\tau_T$, assuming $k_q=5\times10^9 M^{-1}s^{-1}$ in benzene at 25°C. [b]Maximized photocyclization quantum yield, obtained in benzene containing 1M pyridine.

2. Glimpses of a 1,5-Biradical Intermediate

The quantum yield for the formation of 2-phenyl-2-hydroxyindanes from α-(o-alkylphenyl)acetophenones can be represented by -

$$\phi_{pdt} = \phi_{isc}\ \tau_T\ k_H \quad .$$

It has been established that k_H and $1/\tau$ are essentially equal. The photocyclization quantum yield of 1.0 for α-(o-tolyl)acetophenone indicates that ϕ_{isc} must be 1.0, as we well. Varying the alkyl substituent on the α-phenyl ring should not affect the value of the intersystem crossing yield. Lewis[93,94] has measured intersystem crossing quantum yields for a number of α-phenylacetophenones and found them all to be 1.0. Therefore, photocyclization quantum yields less than one are attributable to some inefficiency in cyclization of the presumed 1,5-biradical (Reaction 27).



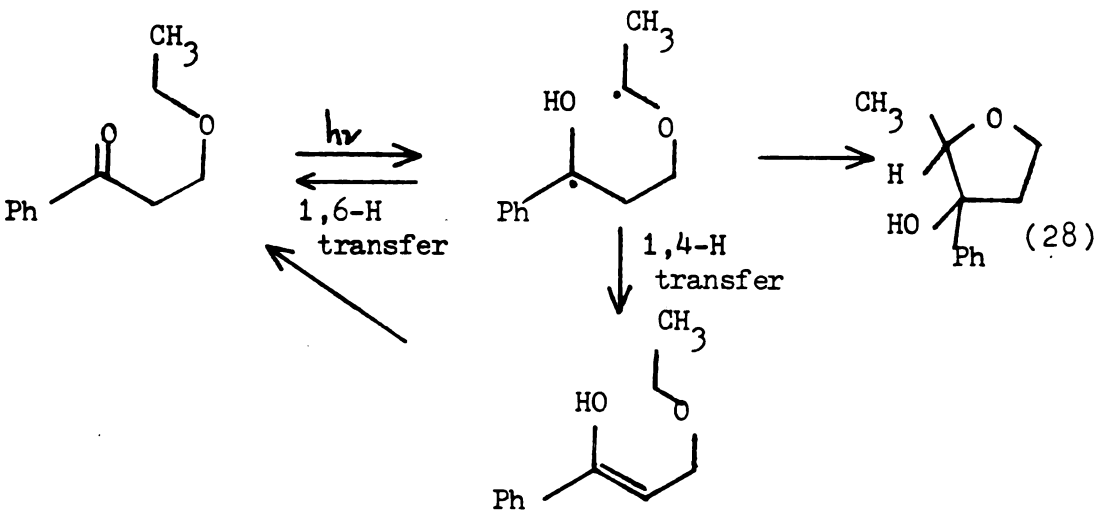
(27)

There is no direct evidence for the intermediacy of this biradical. Attempts to trap the biradical with n-dodecylmercaptan[78] were unsuccessful, presumably due to the

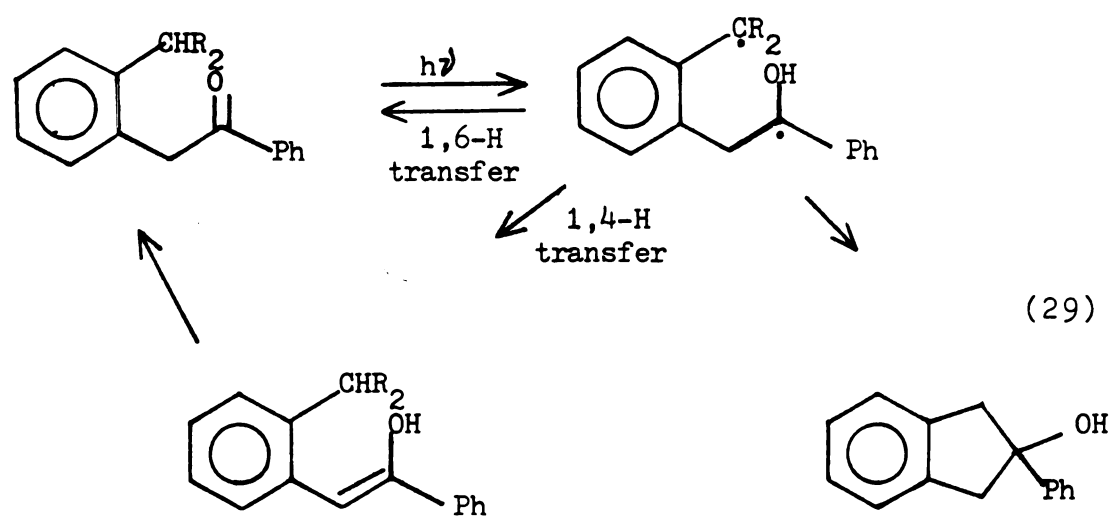
unreactive nature of a benzyl radical towards radical scavengers. There is, however, some rather convincing indirect evidence for its existence.

Recall that pyridine increases the photocyclization of o-benzyloxyacetophenone by suppressing disproportionation of the biradical to starting material. Added pyridine also increases the photocyclization quantum yield of α-mesitylacetophenone, albeit to a much lesser extent (from 0.44 to a maximum of 0.54). This result is reminiscent of typical biradical behavior and points toward the existence of a 1,5-biradical in this reaction.

It is interesting that the maximum photocyclization quantum yield for α-mesitylacetophenone is only 0.54, especially since that for α-(o-tolyl)acetophenone is 1.0. This would suggest that there may be another mode for biradical disproportionation, which is unaffected by the presence of pyridine. Wagner and Chiu[32b] have found that the 1,5-biradical formed by the photolysis of β-ethoxypropiophenone undergoes two different modes of disproportionation - 1,6-hydrogen transfer (the expected mode) and 1,4-hydrogen transfer (Reaction 28). 1,4-Hydrogen transfer (enolization), does not involve the hydroxyl proton, and hence is unaffected by addition of pyridine. Enolization is also the major disproportionation reaction from this biradical.



The same disproportionation pathway is available to 1,5-biradicals produced from (o-alkylphenyl)acetophenones (Reaction 29).



This added mode of disproportionation would also account for the unusually low photocyclization quantum yield for

α-(2,4,6-triisopropylphenyl)acetophenone, as well as explaining why ϕ_{max} for α-mesitylacetophenone is less than 1.0. The biradical essentially has two options available - disproportionation (via both 1,4- and 1,6-H transfer) and cyclization. Although cyclization is much faster than disproportionation in α-(o-tolyl)acetophenone, added substitution of both the α-phenyl ring and the o-methyl carbon reduces the rate of cyclization. Disproportionation is also affected, but to a much lesser extent. Therefore, ketones with bulky R or R' substituents should have photocyclization quantum yields less than unity, as is observed in the extreme for α-(2,4,6-triisopropylphenyl)acetophenone.

3. Substituent Effects on the Photoreactivity of α-(o-Alkylphenyl)acetophenones

The photocyclization of α-(o-alkylphenyl)acetophenones is quite sensitive to the reactivities of the o-methyl hydrogens (Table 29). This sensitivity manifests itself in two different effects.

First of all, alkyl substitution of the o-methyl group increases the rate of hydrogen abstraction. For example, α-(2,5-diisopropylphenyl)acetophenone is approximately six times more reactive than α-(2,5-dimethylphenyl)acetophenone. Wagner and Leavitt[95] have found that cumene (isopropylbenzene) is approximately 2.5 times more reactive than toluene in the photoreduction of acetophenone, reflecting

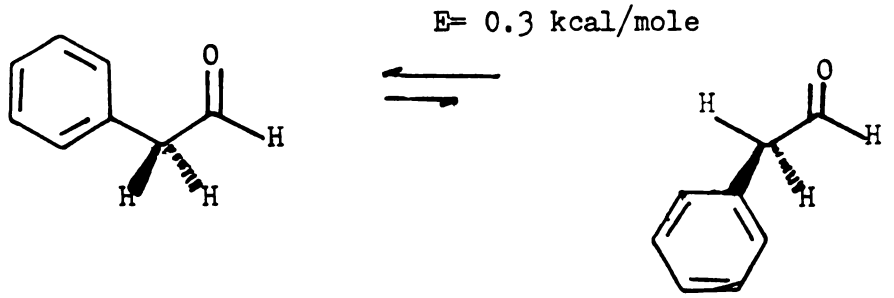
the added reactivity of a tertiary benzylic hydrogen over a primary benzylic one.

Alkyl substituents on the α-phenyl ring also increase the rate of hydrogen abstraction. For example, α-(2,5-dimethylphenyl)acetophenone is twice as reactive as α-(o-tolyl)acetophenone. Similar rate enhancements have been observed in the photoreduction of aromatic ketones with various alkyl substituted toluenes.[95,96] These rate enhancements are, in part, the result of inductive effects on the reactivity of the benzylic hydrogens.

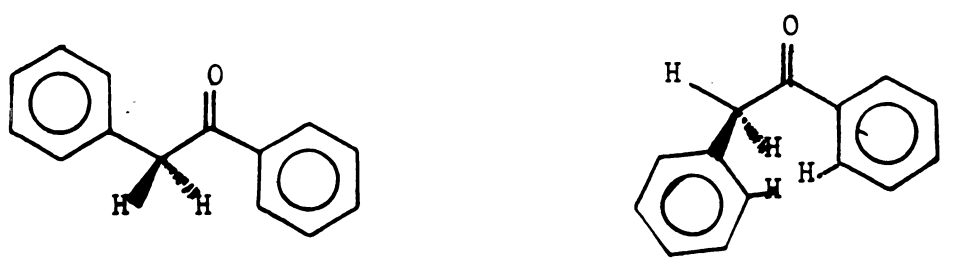
4. Mechanistic Implications

Such inductive effects, however, cannot explain the observation that α-mesitylacetophenone is nearly seven times more reactive than α-(o-tolyl)acetophenone. Several literature reports[97-99] indicate that inductive effects result in only a 1.2 to 1.8 fold greater reactivity for mesitylene relative to toluene in benzylic hydrogen abstraction. Correction of k_H for α-mesitylacetophenone for this inductive increase still leaves a four fold difference in k_H's of α-mesitylacetophenone and α-(o-tolyl)acetophenone. One possible explanation is that hydrogen abstraction in α-(o-tolyl)acetophenone experiences some conformational restrictions which are not present in α-mesitylacetophenone.

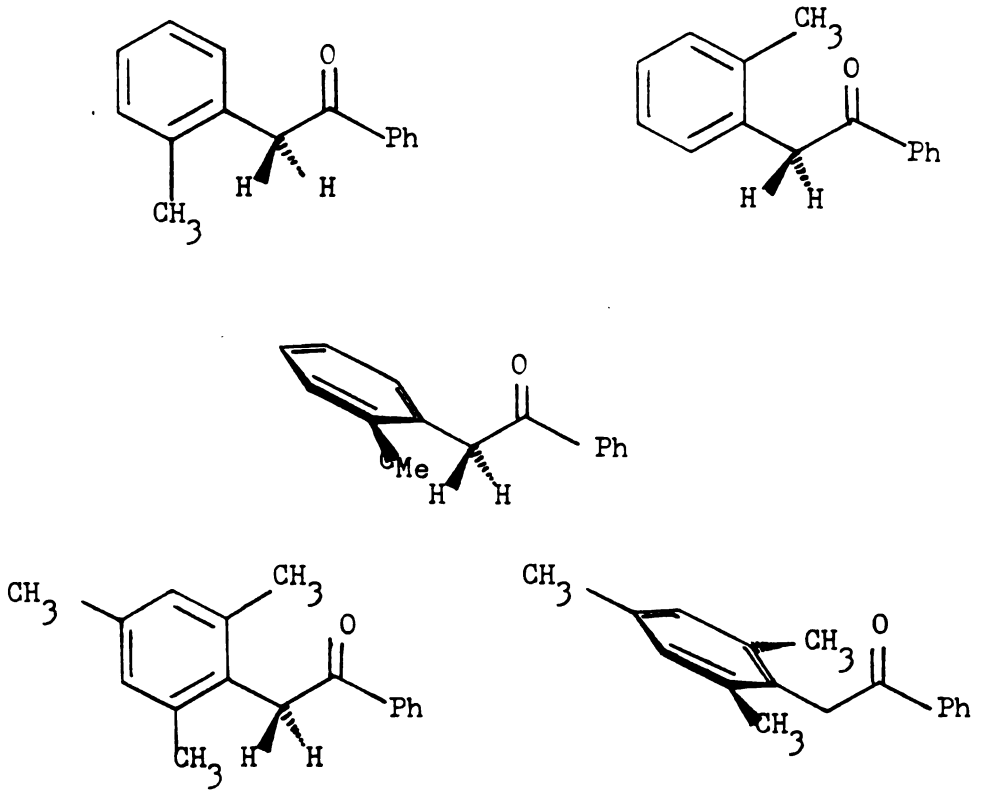
Karabatsos and Fenoglio[100] have shown that the preferred ground state conformation of α-phenylacetaldehyde is one in which the α-phenyl ring eclipses the carbonyl.



This conformation should be even more preferred in the ground state of α-phenylacetophenones since the ortho hydrogens of the two benzene rings interact strongly in the gauche conformation.[101]



Assuming that the α-phenyl ring eclipses the carbonyl in α-(o-alkylphenyl)acetophenones, there are three conformers possible for these ketones.



The preferred conformer would have the α-phenyl ring rotated such that the o-methyl group is a full 180° away from the carbonyl (anti conformer), thereby minimizing steric interactions between the methyl and carbonyl.

δ-Hydrogen abstraction is not possible in this conformer, since the o-methyl hydrogens are not accessible to the carbonyl oxygen. The α-phenyl ring can rotate to give rise to the syn conformer. Examination of Dreiding molecular models reveals that the o-methyl cannot become co-planar with the carbonyl, for steric reasons. Therefore, the syn conformer is one in which the α-phenyl ring rotates far enough to allow hydrogen abstraction to occur,

but not far enough to create serious steric interactions between the o-methyl and the carbonyl.

Symmetric 2,6-dimethyl substitution of the α-phenyl ring, as in α-mesitylacetophenone, would eliminate the possibility of an anti conformer, leaving only the syn and skewed conformers. Hence, the four-fold difference in k_H's for α-mesitylacetophenone and α-(o-tolyl)acetophenone is due to the lack of any unreactive anti conformer for α-mesitylacetophenone. The Winstein-Holness relationship can be applied to this system, since conformational changes are faster than hydrogen abstraction. The four fold difference in k_H's for these two ketones means that the fractional population of the syn conformer is four times greater for α-mesitylacetophenone than it is for α-(o-tolyl)acetophenone.

Given that -

$$S + A + G = 1 = S' + G'$$

where S, A, and G refer to the fractional populations of the syn, anti, and skewed conformers of α-(o-tolyl)acetophenone, and
S' and G' are the fractional populations of the syn and skewed conformers of α-mesitylacetophenone.

Since - $S' = 4S$, then, $S + A + G = 4S + G'$.

Reorganization of the above equation gives -

$$\frac{A + G - G'}{S} = 3 .$$

Wagner and Chen[18] have found an anti/syn ratio of approximately 4 for o-methylacetophenone. The anti/syn ratio for α-(o-tolyl)acetophenone should be similar to that for o-methylacetophenone, since the steric interactions in both systems are nearly the same. Hence, the anti/syn ratio for α-(o-tolyl)acetophenone is approximately 3. This means that (G - G') is negligible. It is unlikely that α-mesitylacetophenone and α-(o-tolyl)acetophenone should have equal populations of skewed conformers. Therefore, the populations of skewed conformers for both these ketones must be minimal, making the (G - G') term unimportant.

Although the nature of the conformational effect has been established for this system, the mechanism of this interconversion has not. The usual three possibilities exist - ground state equilibrium,[16] rate determining rotation,[18] and excited state equilibrium.[17]

Since a ground state equilibrium between syn and anti conformers clearly favors the anti conformers, photocyclization quantum yields would be much less than 0.50 if there were no excited state interconversion. However, ϕ_{pdt} for α-(o-tolyl)acetophenone is 1.0. Hence, ground state equilibrium populations of the syn and anti conformers do not

limit the efficiency of hydrogen abstraction in α-(o-tolyl)-acetophenone.

Rate determining rotational control can be eliminated, since the k_H values for these ketones vary with the reactivity of the o-methyl hydrogens.

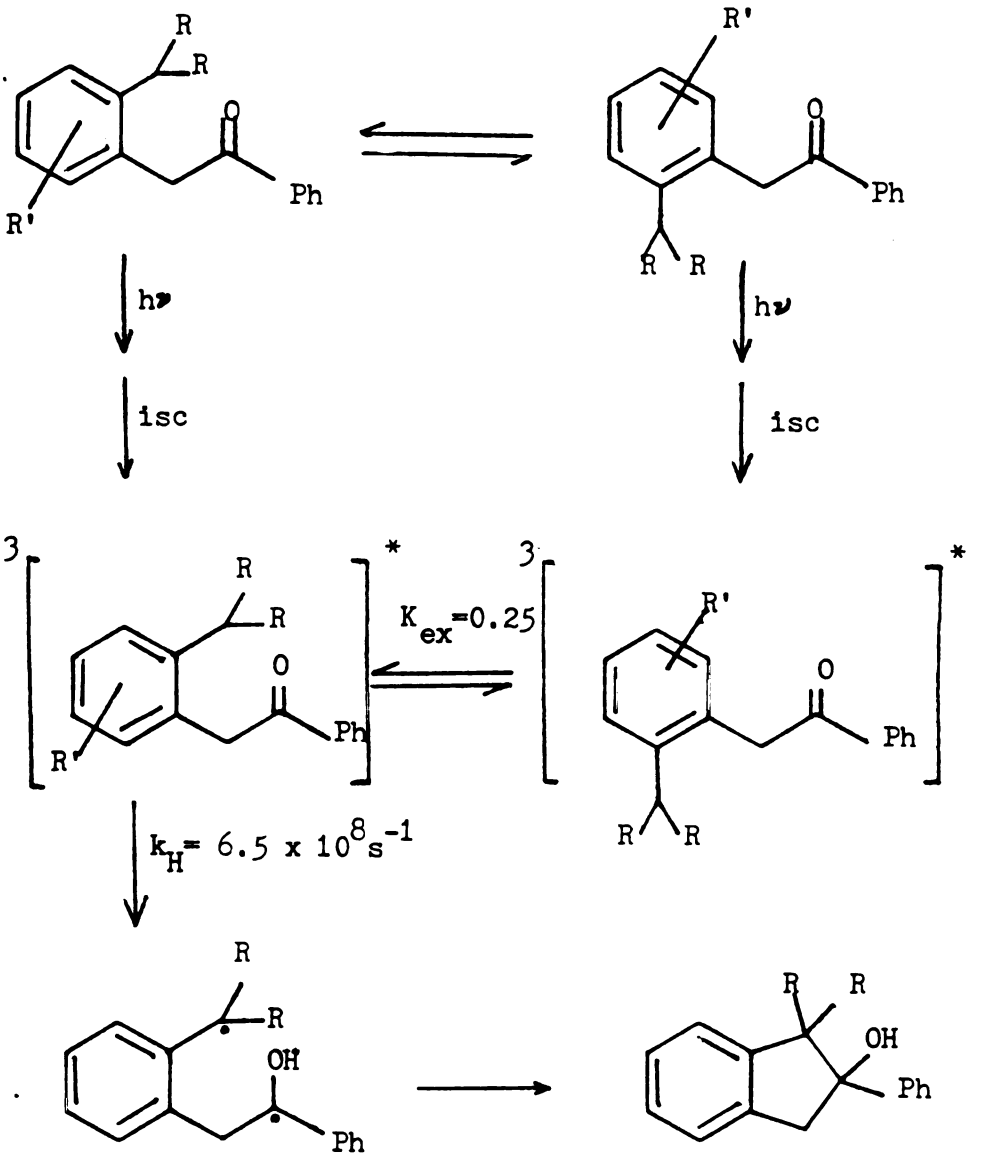
The only mechanistic alternative that remains is an excited state equilibrium between syn and anti conformers. A mechanism based upon this equilibrium is summarized in the scheme on page .

Assuming that excited state equilibrium populations of the skewed conformer are negligible gives an excited state equilibrium constant of 0.25 for the interconversion of anti and syn triplets.

Using this K_{ex} value and invoking the Winstein-Holness relationship, the intrinsic value for the hydrogen abstraction rate constant can be estimated as $6.5 \times 10^8 s^{-1}$.

An apparent contradiction to this mechanism is found when comparing the k_H values of α-(2,5-diisopropylphenyl)-acetophenone and α-(2,4,6-triisopropylphenyl)acetophenone. These rate constants are the same within experimental error! Since the value of k_H would have no effect on the value of K_{ex}, the higher K_{ex} value must be due to something else. The similar k_H values for α-(2,5-diisopropylphenyl)- and α-(2,4,6-triisopropylphenyl)acetophenones suggest that the fractional equilibrium populations of syn conformers are identical for both ketones. This means that -

$$A + G = G' \quad .$$



Hence, the fractional equilibrium population of the skewed conformer of α-(2,4,6-triisopropylphenyl)acetophenone cannot

be negligible. This is not unreasonable since the added steric bulk of an o-isopropyl group may prevent the triplet ketone from attaining the syn or reactive conformation as easily as it does in the case of α-(o-tolyl)acetophenone.

5. Entropic and Enthalpic Differences Between γ- and δ-Hydrogen Abstraction

α-(o-Alkylphenyl)acetophenones are merely one carbon higher homologs of o-alkylacetophenones. It might be useful, at this point, to compare δ-hydrogen abstraction in the former with γ-hydrogen abstraction in the latter.

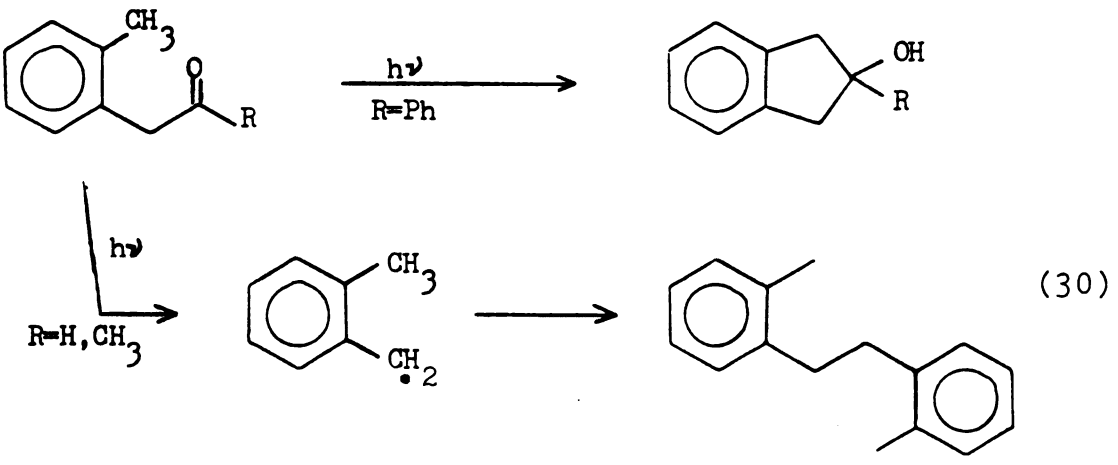
Wagner[18] has measured the rate constant for γ-hydrogen abstraction in o-methylacetophenone as $3 \times 10^9 s^{-1}$. The intrinsic hydrogen abstraction rate constant for α-(o-tolyl)acetophenone is $6.5 \times 10^8 s^{-1}$. It has been determined that α-phenyl substitution[102] affects ketone photoreactivity as much as o-methyl substitution does.[18] Hence, the nearly five-fold difference in rate constants between these two ketones reflects the relative ease of γ- and δ-hydrogen abstraction. Both systems have essentially the same degree of rotational freedom. Therefore, this reactivity difference represents the enthalpic disfavorability of the formation of a seven-center transition state (δ-hydrogen abstraction) relative to formation of a six center transition state (γ-hydrogen abstraction).

Wagner[32] had found a twenty-fold difference in the rates

of γ- and δ- hydrogen abstraction in freely rotating acyclic systems. It was never clear what the relative contributions of entropic and enthalpic factors were to this rate difference. In light of the previous comparison, it appears that entropic and enthalpic factors contribute equally to this twenty-fold rate difference.

6. α-(o-Tolyl)acetone and α-(o-Tolyl)acetaldehyde

A brief mention should be made concerning the photochemistry of α-(o-tolyl)acetone and α-(o-tolyl)acetaldehyde. Irradiation of each of these compounds failed to produce any of the desired photocyclization products. Instead, products arising from acyl cleavage (Norrish Type I reaction[103]) were obtained (Reaction 30). Ogata[104] has also reported



the same results for the photolysis of α-(o-tolyl)acetone. Cleavage rate constants on the order of $10^{10} s^{-1}$ have been reported for dibenzyl ketones.[94] Therefore, since cleavage should be 100 times faster than δ-hydrogen abstraction, no photocyclization products should be formed.

C. Conclusions

1. o-Alkoxyphenyl Ketones

The mechanism of δ-hydrogen abstraction in o-alkoxyphenyl ketones involves an excited state equilibrium prior to hydrogen abstraction. This equilibrium is brought about by rotation of the alkoxy group about the phenyl-oxygen bond, and favors the unreactive (anti,syn) conformer. The (syn,syn) triplet conformer readily undergoes hydrogen abstraction, giving rise to a 1,5-biradical. The (anti,syn) conformer cannot undergo hydrogen abstraction directly, but can equilibrate with the (syn,syn) triplet, thereby leading to hydrogen abstraction. Rotation about the phenyl-acyl bond ($k_{rot} \sim 10^7 s^{-1}$)[18] can occur from the (anti,syn) triplet, but is not rate determining since hydrogen abstraction in these ketones is no faster than such a rotation. There is no evidence that phenyl-acyl bond rotation is taking place in the (anti,syn) triplet, although this rotation may be masked by the kinetics of the excited state equilibrium involving the alkoxy group rotation.

The 1,5-biradical formed from these ketones must undergo rotation about the ketyl radical center in order to avoid rapid disproportionation to starting ketone and in order to cyclize to benzofuranol products. This rotation is severely restricted if $R'=CH_3$, meaning that the yield

of photocyclization products is quite low (ϕ = 0.0226). However, if R' = Ph, this rotation is rapid, cyclization is quite efficient, and the photocyclization quantum yields in such cases approach unity.

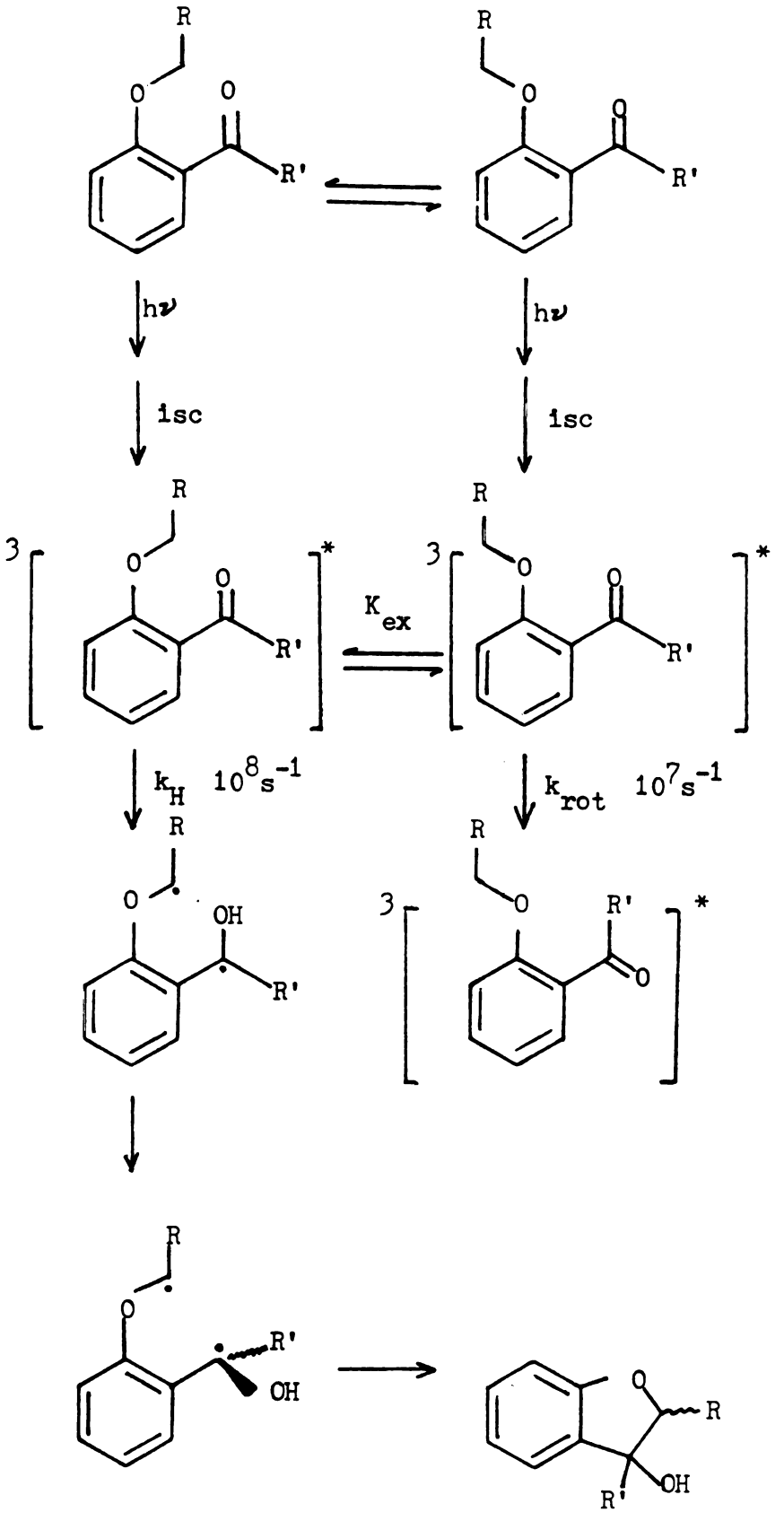
Intrinsic hydrogen abstraction rate constants are in good agreement with the values previously predicted for this system.[105]

2. α-(o-Alkylphenyl)acetophenones

The mechanism for hydrogen abstraction in α-(o-tolyl)-acetophenone also involves an excited state equilibrium between two triplet ketone conformers. Only the syn conformer is reactive, since it is only in this conformation that the o-methyl hydrogens are accessible to the carbonyl oxygen. However, excited state equilibrium for α-(o-tolyl)acetophenone favors the unreactive conformer by by 3:1, due to the steric repulsions between the o-methyl group and the carbonyl. Hydrogen abstraction occurs from the syn triplet with a rate constant of $6.5 \times 10^8 s^{-1}$.

This equilibrium situation breaks down for α-(o-isopropylphenyl)acetophenones, where steric bulk forces the α-phenyl ring to tilt into a skewed conformation. The percentage of skewed conformer in α-(2,4,6-triisopropylphenyl)acetophenone is probably quite substantial and reduces the value of k_H for this ketone.

The photocyclization of α-(o-tolyl)acetophenone proceeds


R
O
O
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3
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K_{ex}
k_H $10^8 s^{-1}$
k_{rot} $10^7 s^{-1}$
OH

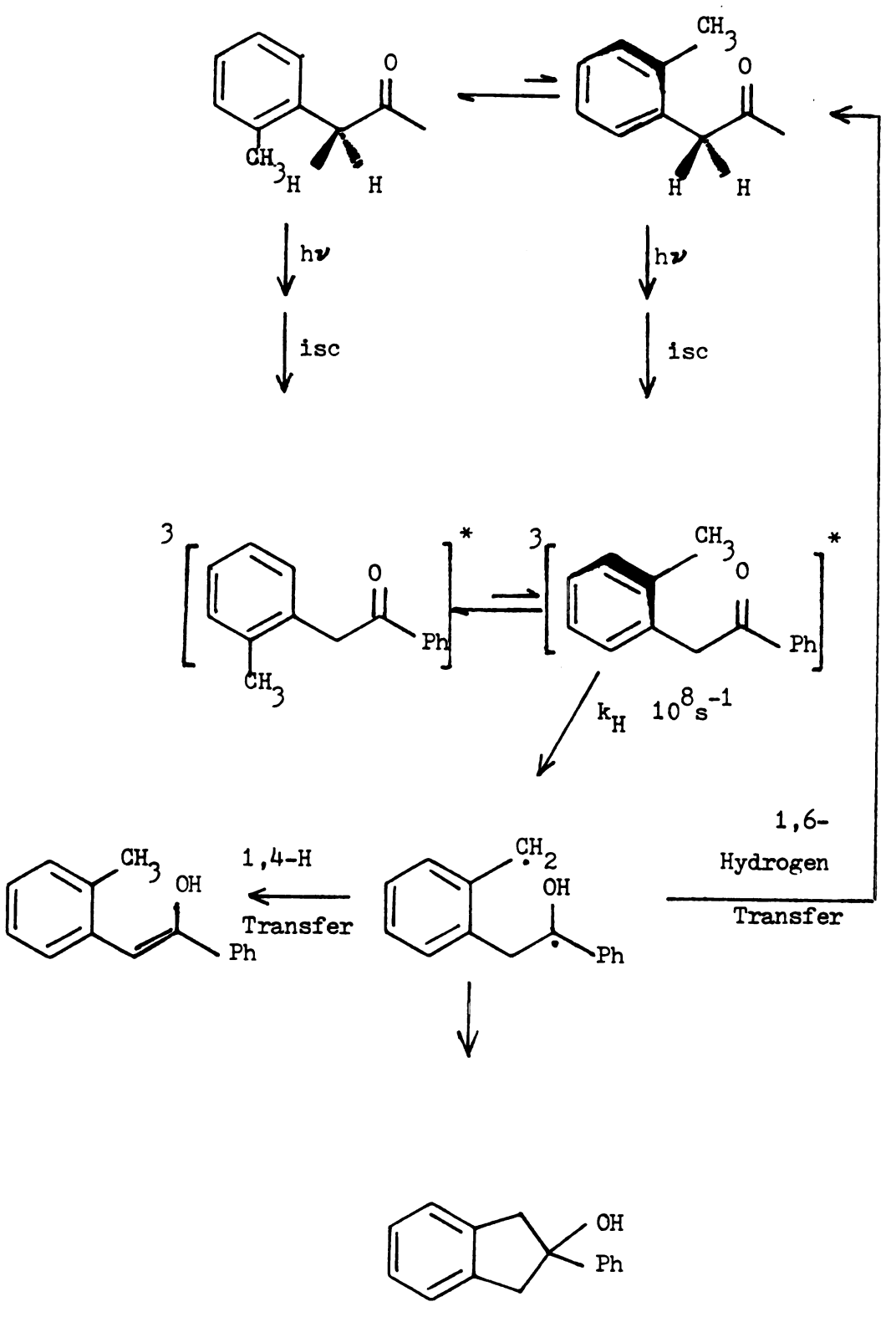
with unit efficiency. However, photocyclization quantum yields of other α-(o-alkylphenyl)acetophenones are less than 1.0. Addition of pyridine increases the photocyclization quantum yield for α-mesitylacetophenone to 0.54. It is unlikely that unreactive triplet decay would account for the extra 46% of the quantum yield. This suggests that there are two modes of biradical disproportionation - 1,4-[32b] and 1,6-hydrogen transfer. 1,6-Hydrogen transfer is suppressed by the presence of pyridine, while 1,4-hydrogen transfer is not.

D. Suggestions for Further Research

1. Laser Detection of 1,5-Biradicals from α-(o-Alkylphenyl)acetophenones

It would be useful to examine α-(o-alkylphenyl)acetophenones by laser flash spectroscopy to determine whether such biradicals are detectable. These biradicals should be longer lived than those produced from o-alkoxyphenyl ketones for reasons discussed previously. Such a study would determine whether heteroatoms in the backbone of 1,5-biradicals shorten their lifetimes as they do in 1,4-biradicals. This study would also provide further information on the mechanism for this effect on biradical lifetimes.

Deuteration of the α-methylene group would help ascertain whether 1,4-hydrogen transfer is an important pathway


CH3
O
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CH2
OH
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Transfer
CH3
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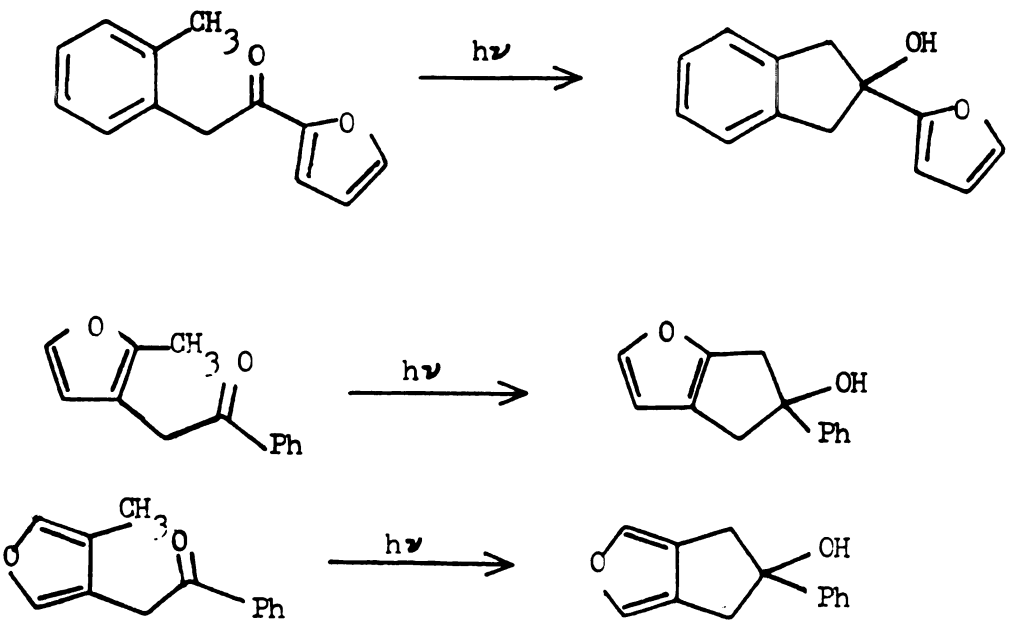
for 1,5-biradical disproportionation in α-(o-alkylphenyl)-acetophenones.

2. Synthetic Applications of δ-Hydrogen Abstraction

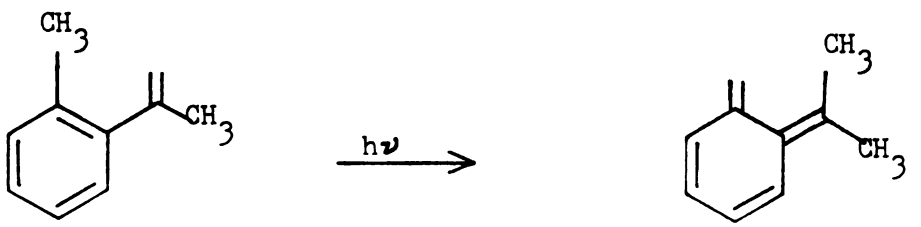
The remarkably high chemical yields for 2-phenyl-2-hydroxyindanes produced from the photocyclization of α-(o-alkylphenyl)acetophenones prompt a more extensive study of the synthetic potential of this photoreaction.

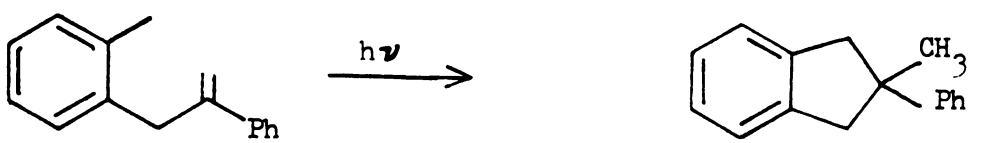
A number of modifications come to mind. It would be especially interesting to replace the phenone ring or the α-phenyl ring with another aromatic system, e.g., furans.



It has been shown that the methylene analogs of o-alkylphenyl ketones undergo efficient γ-hydrogen

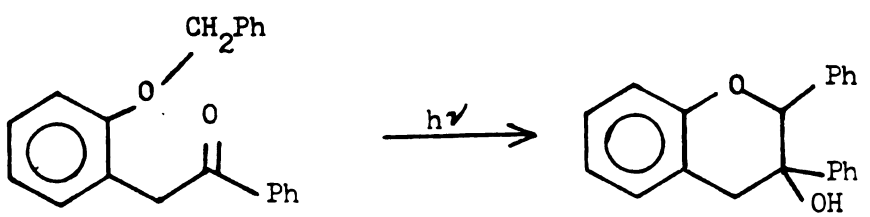
abstraction.[106] The same reaction may be possible for the methylene derivative of α-(o-alkylphenyl)acetophenones and provide a photochemical route to indanes.





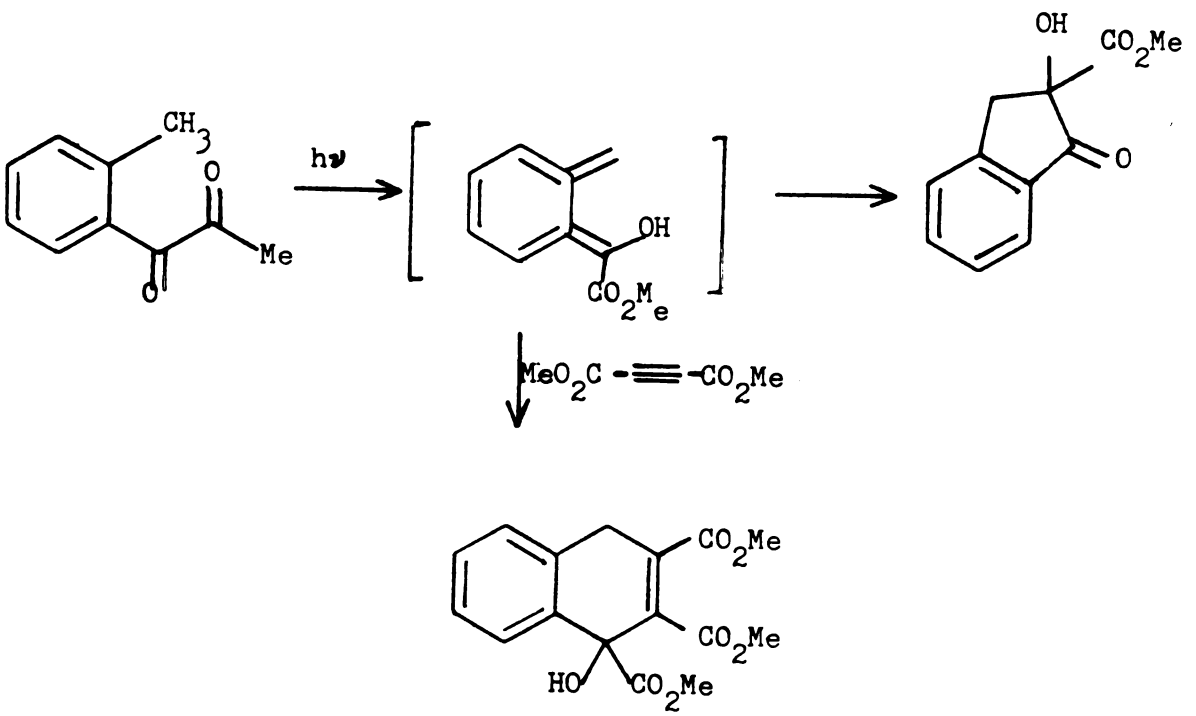
3. ε-Hydrogen Abstraction

Preliminary studies indicate that 2,3-diphenyl-3-hydroxy-3,4-dihydrobenzopyran is formed in approximately 80% yield from the photolysis of α-(o-benzyloxyphenyl) acetophenone. This reaction warrants a more extensive study from both a synthetic and mechanistic standpoint.



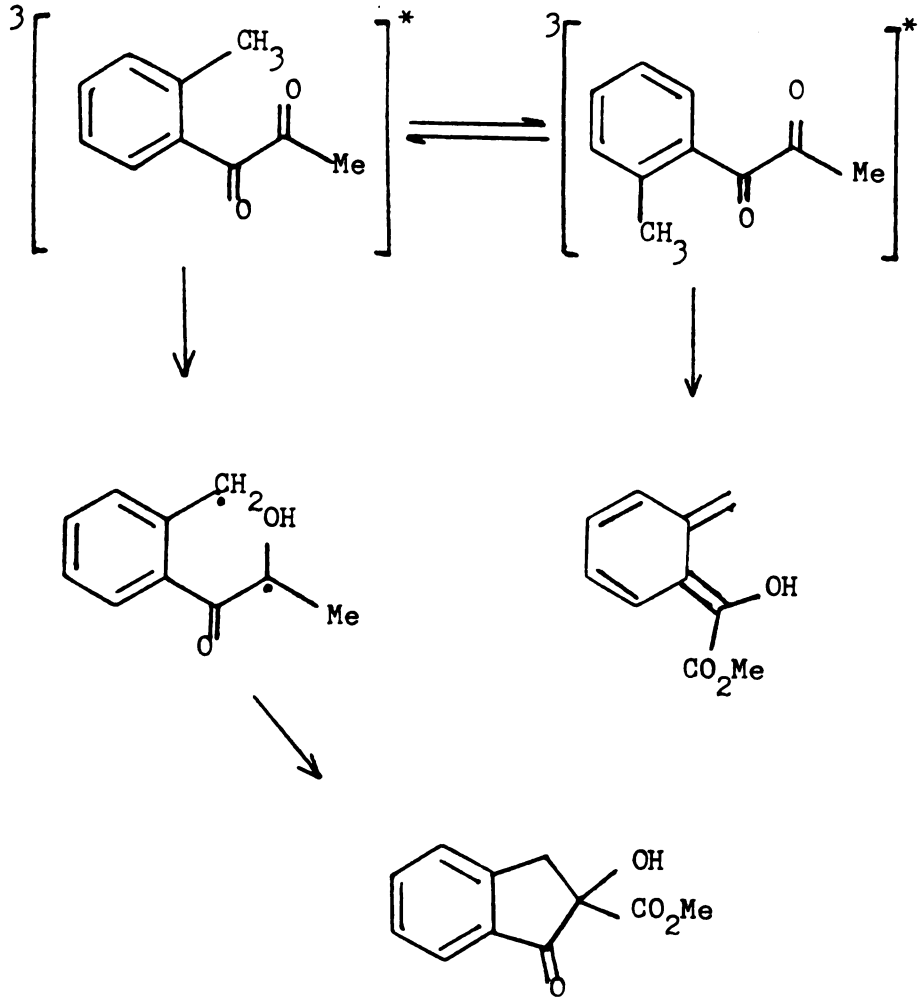
4. Photochemistry of 1-(o-Alkylphenyl)-1,2-Propanediones and Related Compounds

Ogata and Takagi[104] report that the photocyclization of 1-(o-tolyl)-1,2-propanedione proceeds via formation of a photoenol. As a method of proof, they have trapped the enol with dimethyl acetylenedicarboxylate.



Results obtained for α-(o-tolyl)acetophenones suggest an alternative mechanism. It is likely that there are two different ketone triplets for this system. These rotamers, designated a and b, are in equilibrium. Rotamer a leads solely to δ-hydrogen abstraction. Rotamer b leads only to enolization. It would, therefore, be interesting to reexamine this compound and a number of its derivatives

to ascertain which of the above mechanisms is the correct one.



EXPERIMENTAL

A. Preparation and Purification of Chemicals

1. Solvents and Additives

Benzene.[107] - One gallon of thiophene free reagent grade benzene (Mallinkrodt) was repeatedly stirred with 200 ml portions of sulfuric acid for 12-24 hr periods until the sulfuric acid remained water white. The benzene and sulfuric acid were separated and the benzene washed, first with 400 ml distilled water, and then with sufficient amounts of a saturated aqueous sodium bicarbonate solution until the aqueous phase remained basic to pHydrion paper. The benzene was separated from the sodium bicarbonate solution, dried over magnesium sulfate, and filtered into a clean, dry 5.0 ℓ round bottom flask. Phosphorus pentoxide (100 g) was added to this and the solution refluxed overnight. After refluxing, the benzene was distilled through a one meter column packed with stainless steel helices at a rate of 100 ml/hr. The first and last 10% were discarded.

Dioxane.[108] - Scintillation grade 1,4-dioxane was refluxed over calcium hydride for 12 hr and then distilled

through a one meter column packed with glass helices. The first and last 10% were discarded.

Cyclohexane - Spectral grade cyclohexane (Fisher) was used as received.

Heptane - MCB Omni-Solv grade heptane was used as received.

Pyridine[109] - Pyridine (Mallinkrodt) was refluxed over barium oxide for 12 hr and distilled through a one meter column packed with glass helices. The first and last 10% were discarded.

EPA Mixed Solvent - MCB phosphorimetric grade EPA mixed solvent (ethyl ether:isopentane:ethyl alcohol, 5:5:2) was used as received.

2-Methyltetrahydrofuran[110] - 2-Methyltetrahydrofuran (Aldrich) was refluxed over cuprous chloride for 12 hr and distilled. The first and last 10% were discarded. The middle fraction was then distilled from lithium aluminum hydride through a 60 cm Vigreaux column. The initial and final 10% were discarded.

2. Internal Standards

Pentadecane - Pentadecane (Columbia Organics) was washed with sulfuric acid and distilled (10 Torr., b.p. 131°C) by Dr. Peter J. Wagner.

Hexadecane - Hexadecane (Aldrich) was purified by washing with sulfuric acid, followed by distillation, b.p. 105°C (10 Torr) by Dr. Peter J. Wagner.

Nonadecane - Nonadecane (Chemical Samples Company) was purified by recrystallization from ethanol.

Heneicosane - Heneicosane (Chemical Samples Company) was purified by recrystallization from ethanol.

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

Docosane - Docosane (Aldrich) was purified by recrystallization from ethanol.

Tetracosane - Tetracosane (Aldrich) was used as received.

Hexacosane - Hexacosane (Pfaltz and Bauer) was used as received.

3. Quenchers

1,3-Pentadiene - 1,3-Pentadiene (Chemical Samples Company) was used as received.

trans-Stilbene - trans-Stilbene (Fisher Photochemical Grade) was used as received.

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

1,3-Cyclohexadiene - 1,3-Cyclohexadiene (Aldrich) was used as received.

n-Dodecylmercaptan - n-Dodecylmercaptan (Aldrich) was distilled at reduced pressure.

n-Octylmercaptan - n-Octylmercaptan (Aldrich) was distilled at reduced pressure.

4. Ketones

Benzophenone - Benzophenone (Eastman) was purified by Dr. P. J. Wagner, by recrystallization from ethanol.

Acetophenone - Acetophenone (Mallinkrodt) was purified by Dr. A. E. Puchalski by passing the ketone through a short pad of alumina followed by spinning band distillation under reduced pressure (b.p. 105°C, 17 Torr).

Valerophenone[111] - Valerophenone was prepared by Friedel-Crafts acylation of benzene with valeryl chloride in the presence of an aluminum chloride catalyst. Normal work-up procedures afforded the crude product which was vacuum distilled to yield a water white liquid (b.p. 105°C, 2.0 Torr).

ortho-Benzyloxybenzophenone (o-BzOBP) - 2-Hydroxybenzophenone (Aldrich, 10.0 g, 55.5 mmole) was added to a stirred solution of sodium methoxide (Fisher, 3.0 g, 55.6 mmole) in 100 ml methanol. The resulting deep red solution was stirred under nitrogen for 1 hr. Benzyl bromide (Eastman, 6.6 ml, 55.6 mmole) in 25 ml of methanol was added dropwise and the resulting solution refluxed under nitrogen overnight. The methanol was removed on a rotary evaporator and the residue taken up into 150 ml diethyl ether. The ether was washed with saturated sodium bicarbonate (3 x 150 ml). The aqueous layers were combined and washed with ether. The ether extracts were combined, dried ($MgSO_4$), and the solvent removed on a rotary evaporator to afford a yellow oil. This oil was dissolved in hot

chloroform-hexanes and cooled to afford 6.6 g of pure o-BzOBP as white needles (45.4% yield).

m.p. 65-67°C (lit. 62°C[112]).

^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.7-7.8 (m,7H, Ar-H's), 4.9 (s, 2H, O-C$\underline{H}_2$-Ph) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=196.1 (C=O), 138.3, 132.7, 131.9, 129.7, 128.2, 126.5, 120.9, 112.7, 69.97 (O-$\underline{C}H_2$Ph) ppm.

mass spectrum: (m/e) 288 (M+), 197, 105, 91 (Base), 77.

i.r. (CCl_4): 1675 cm^{-1} (C=O), 1250 cm^{-1} (Ar-O-C).

ortho-Methoxybenzophenone (o-MeOBP) - A solution of 2-hydroxybenzophenone (Aldrich, 5.0 g, 25.3 mmole) in 25 ml methanol was added dropwise to a stirred solution of sodium methoxide in methanol (freshly prepared by the addition of 0.6 g of sodium metal to 50 ml methanol under nitrogen). The resulting solution was stirred under nitrogen at room temperature. Dimethyl sulfate (Mallinkrodt, 3.8 g, 30.0 mmole) was added dropwise, and the reaction refluxed overnight. The solvent was removed on a rotary evaporator and the remaining residue taken up into 200 ml diethyl ether. The ether was extracted with aqueous 10% potassium hydroxide (3 x 100 ml). The ether layer was dried (Na_2SO_4) and the solvent removed on a rotary evaporator to afford a pale yellow oil. This oil was dissolved in hot ethanol and cooled to afford 3.2 g (60% yield) of pure o-MeOBP as white needles.

m.p. 36-38°C (lit. 39°C).[113]

^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.7-7.8 (m, 3H, Ar-H's), 3.6 (s, 1H, OCH_3) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=196.2 (C=O), 157.1, 137.6, 132.7, 131.7, 129.5, 129.3, 128.6, 120.3, 111.2, 55.33 (OCH_3) ppm.

mass spectrum: (m/e) 212 (M+), 195, 135 (Base), 105, 92, 77.

i.r. (CCl_4): 1680 cm^{-1} (C=O), 1260 cm^{-1} (Ar-O-C).

Ortho-Benzyloxyacetophenone (o-BzOAP) - 2-Hydroxyacetophenone (Aldrich, 4.0 g, 29.4 mmole) was added to a stirred solution of potassium hydroxide (Fisher, 2.5 g, 44.6 mmole) in 100 ml of methanol under a nitrogen atmosphere. The solution was stirred at room temperature for 1 hr, after which benzyl chloride (Fisher, 5.0 ml, 44.6 mmole) was added dropwise and the solution refluxed overnight. The solvent was removed on a rotary evaporator and the residue taken up into 200 ml ether. The ether was washed with 10% aqueous potassium hydroxide (3 x 150 ml) and dried (Na_2SO_4). The ether was removed on a rotary evaporator to provide a pale yellow oil. This oil was dissolved in hot chloroform-hexane and cooled to afford pure o-BzOAP as white crystals (5.6 g, 83% yield).

m.p. 39-41°C.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.9-7.7 (m, 9H, Ar-H's), 5.15 (s, 2H, O-CH_2Ph), 2.50 (s, 3H, CH_3) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=199.8 (C=O), 158.0, 136.1, 133.5, 130.4, 128.2, 127.5, 120.8, 112.7, 70.6, 70.55 (O-$\underline{C}H_2$Ph) ppm.
mass spectrum: (m/e) 226 (M+), 208, 183, 121, 107, 91 (base), 77.
i.r. (CCl_4): 1680 cm^{-1} (C=O), 1260 cm^{-1} (Ar-O-C).

2-Hydroxyvalerophenone[114] - Phenyl valerate (16.5 g, 92.7 mmole, prepared from valeryl chloride and phenol) in 100 ml petroleum ether (b.p. 60-110°C) was added to a stirred suspension of aluminum chloride (Fisher, 24.7 g, 0.105 mole) in 100 ml petroleum ether under a nitrogen atmosphere. The resulting mixture was refluxed with stirring under nitrogen for 3 hr. The reaction was then cooled to room temperature and the mixture poured over crushed ice. After the ice had melted, the aqueous solution was extracted with ether (3 x 200 ml). The ether was dried (Na_2SO_4) and the solvent removed on a rotary evaporator. The resulting liquid was vacuum distilled (1.0 Torr, b.p. 60-90°C) to afford 6.0 g (36% yield) of 2-hydroxyvalerophenone. Spectral data were consistent with those in the literature.[114]
^{1}H-nmr (60 MHz, $CDCl_3$): 12.2 (s, 1H, OH), 6.5-7.5 (m, 4H, Ar-H's), 2.9 (t, 2H, $C\underline{H}_2CO$), 2.0-0.9 (m, 7H, $C\underline{H}_2C\underline{H}_2C\underline{H}_2$) ppm.
mass spectrum: (m/e) 178 (M+), 149, 136, 121 (Base), 93, 65.

ortho-Benzyloxyvalerophenone (o-BzOVP) - 2-Hydroxyvalerophenone (10.0 g, 56.2 mmole) was added to a stirred solution of potassium hydroxide (Fisher, 3.2 g, 57.0 mmole) in 20 ml of methanol under a nitrogen atmosphere. This solution was stirred at room temperature for 1 hr, after which benzyl chloride (Eastman, 6.7 ml, 56.4 mmole) was added dropwise. The resulting solution was refluxed under nitrogen for 2 hr, cooled to room temperature, and the solvent removed on a rotary evaporator. The resulting residue was taken up into 200 ml of ether, and the ether washed with 200 ml distilled water. The ether layer was dried (Na_2SO_4) and the solvent removed on a rotary evaporator. The crude product was vacuum distilled to afford 8.0 g (53.1% yield). This oil was crystallized from hot hexanes to afford 6.7 g of o-BzOVP as white platelets.

m.p. 26-28°C.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.96-7.68 (m, 9H, Ar-H's), 5.12 (s, 2H, $OC\underline{H}_2Ph$), 2.94 (t, 2H, J=7.32 Hz, $CO-C\underline{H}_2$), 1.60 (m, 2H, $COCH_2C\underline{H}_2$), 1.22 (m, 2H, $C\underline{H}_3$), 0.82 (t, 3H, J=7.32 Hz, $C\underline{H}_3$) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=203.7 (C=O), 157, 136, 133, 130, 129, 128.7, 128.2, 127, 121, 112, 70.7 ($O-\underline{C}H_2Ph$), 43, 26, 22, 14 ppm.

mass spectrum: (m/e) 268 (M+), 211, 121, 91 (Base), 77.

i.r. (CCl_4): 1680 cm^{-1} (C=O), 1270 cm^{-1} (Ar-O-C).

2,2'-Dibenzyloxybenzophenone (2,2'-DiBzOBP) - 2,2'-Dihydroxybenzophenone (Aldrich, 5.0 g., 23.4 mmole) was alkylated with benzyl bromide (Eastman, 5.6 ml, 46.8 mmole) in a solution of potassium hydroxide (Fisher, 2.6 g, 46.8 mmole) in methanol following the procedure described for o-benzyloxyacetophenone. Recrystallization of the residue obtained after work up from hot ethanol afforded 2.6 g (28.2% yield) of 2,2'-DiBzOBP as white needles.

m.p. 98-99.5°C.

^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.6-7.5 (m, 18H, Ar-H's), 4.7 (s, 4H, OCH_2Ph) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=195.5 (C=O), 157.2, 136.3, 132.5, 130.4, 128.1, 127.3, 126.5, 120.8, 112.5, 70.0 ($O-CH_2Ph$) ppm.

mass spectrum: (m/e) 394 (M+), 376, 303, 211, 183, 91 (Base), 77.

i.r. (CCl_4): 1650 cm^{-1} (C=O), 1280 cm^{-1} (Ar-O-C).

2-Benzyloxy-5-methylbenzophenone (o-BzO-5-MeBP) - 2-Hydroxy-5-methylbenzophenone (Aldrich, 5.0 g, 23.6 mmole) was alkylated with benzyl bromide (Eastman, 2.8 ml, 23.6 mmole) in a solution of potassium hydroxide (Fisher, 1.3 g, 23.6 mmole) according to the procedure described for o-benzyloxyacetophenone. The residue obtained after work up was recrystallized from hot methanol to afford pure o-BzO-5-MeBP as white needles (3.0 g, 42% yield).

m.p. 77-78°C.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.89-8.55 (m, 8H, Ar-H's), 4.95 (s, 2H, OCH_2Ph), 2.32 (s, 3H, CH_3) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=196.8 (C=O), 138.3, 136.4, 132.5, 132.2, 130.3, 130.1, 129.5, 129.1, 128.1, 127.4, 126.5, 112.8, 70.1 ((-CH_2Ph), 20.28 ppm.

mass spectrum: (m/e) 302 (M+), 284, 224, 135, 105, 91 (Base), 77.

i.r. (CCl_4): 1675 cm^{-1} (C=O), 1280 cm^{-1} (Ar-O-C).

2,6-Dimethoxybenzophenone (2,6-DiMeOBP) - 2,6-Dimethoxybenzophenone was prepared according to the procedure described by Levine and Sommers.[115] Thus, m-dimethoxybenzene (Aldrich, 13.8 g, 0.100 mole) was added dropwise to a stirred solution of n-butyllithium (Aldrich, 1.6 M, 0.100 mole) in 100 ml anhydrous ether under a nitrogen atmosphere. The resulting solution was refluxed under nitrogen for 2 hr. Methyl benzoate (MCB, 13.6 g, 0.100 mole) in 100 ml anhydrous ether was added dropwise and the solution refluxed for an additional 5 hr. After the solution had cooled to room temperature, it was poured over 200 g crushed ice and 20 ml concentrated hydrochloric acid. The ether layer was separated and the aqueous layer extracted with ether (2 x 200 ml). The ether extracts were combined and neutralized with a saturated aqueous sodium bicarbonate solution. The ether layer was dried (Na_2SO_4) and the solvent removed on a rotary evaporator. Vacuum distillation of the residue

afforded 3.0 g of 2,6-DiMeOBP. The distillate was recrystallized from hot methanol to afford pure 2,6-DiMeOBP as white platelets.

m.p. 98-100°C (lit. 97.5-98°C).[116]

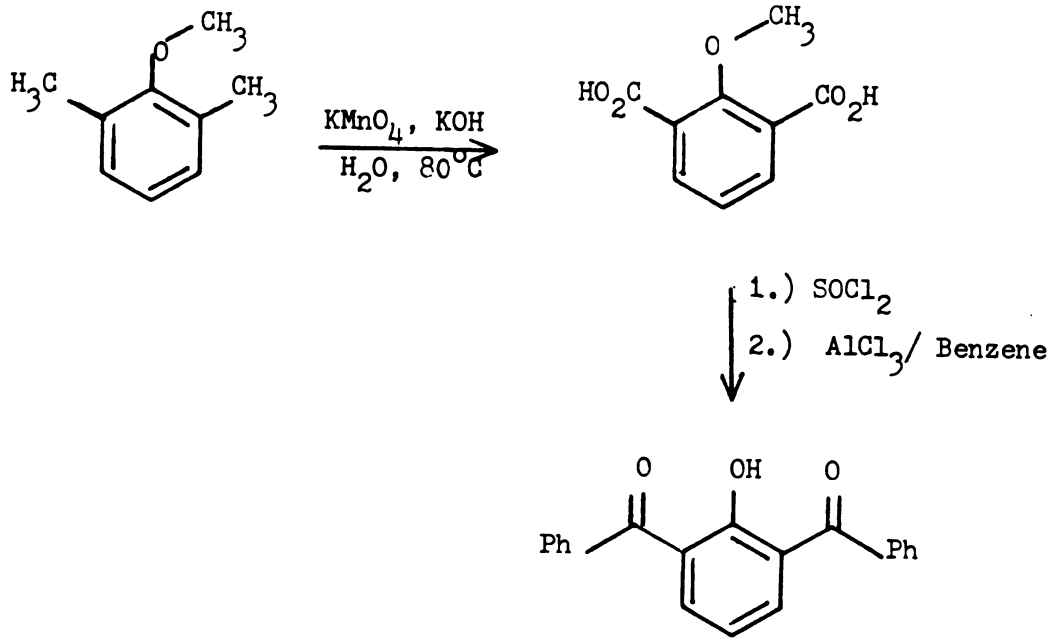
^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.58-7.85 (m, 4H, Ar-H's), 3.65 (s, 3H, OCH_3) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=195.2 (C=O), 157.5, 133.0, 129.2, 128.3, 103.9, 55.7 (OCH_3) ppm.

mass spectrum: (m/e) 242 (M+), 225, 165 (Base), 151, 105, 91, 77.

i.r. (CCl_4): 1675 cm^{-1} (C=O); 1290, 1310 cm^{-1} (Ar-O-C).

2,6-Dibenzoylanisole and 2,6-dibenzoylbenzyloxybenzene were both prepared from 2,6-dibenzoylphenol, which was synthesized by the following route.



Anisole-2,6-Dicarboxylic Acid - 2,6-Dimethylanisole (prepared from the alkylation of 2,6-dimethyl phenol with dimethyl sulfate in a solution of potassium hydroxide in methanol) (20.0 g, 0.147 mole) was added to a vigorously stirred solution of potassium hydroxide (Fisher, 18.3 g, 0.325 mole) and potassium permanganate (Fisher, 103.7 g, 0.657 mole) in 700 ml of distilled water. The reaction mixture was heated to 80°C and maintained at this temperature for 3 hr. The solution was then cooled to room temperature, filtered to remove manganese dioxide, and acidified with concentrated hydrochloric acid. After this solution had cooled, it was filtered and the crystalline product air dried to afford 22.8 g (79% yield) of anisole-2,6-dicarboxylic acid.

m.p. 219-221°C.

mass spectrum: (m/e) 196 (M+), 178, 165, 149, 132, 120, 105, 91, 77.

2,6-Dibenzoylphenol - Anisole-2,6-dicarboxylic acid (15.0 g, 91.5 mmole) was added to 100 ml thionyl chloride (MCB), and the mixture refluxed under nitrogen until all of the acid had dissolved. The excess thionyl chloride was removed under vacuum and the resulting residue vacuum distilled (0.8 Torr, 105-110°C) to afford the desired diacyl chloride (9.5 g, 42% yield).

The diacyl chloride was dissolved in 100 ml of dry

benzene and added to a stirred suspension of aluminum chloride (Fisher, 10.4 g, 78 mmole) in 50 ml dry benzene. The resulting yellow mixture was refluxed under nitrogen for 8 hr. After the solution had cooled to room temperature it was poured into 200 g crushed ice and 20 ml concentrated hydrochloric acid. This was extracted with ether (2 x 200 ml). The ether extracts were combined and washed with aqueous saturated sodium bicarbonate until neutral by pHydrion paper. The ether was dried (Na_2SO_4) and the solvent removed on a rotary evaporator to afford an orange oil. Trituration of this oil with hexanes afforded crysalline 2,6-dibenzoyl phenol (7.2 g, 61% yield).
^{1}H-nmr (60 MHz, $CDCl_3$): δ=13.8 (s, 1H, OH), 6.7-8.0 (m, 13H, Ar-H's) ppm.

2,6-Dibenzoylbenzyloxybenzene (2,6-DBB) - 2,6-Dibenzoylphenol (3.0 g, 9.93 mmole was alkylated with benzyl bromide (Eastman, 1.2 ml, 9.93 mmole) in a solution of potassium hydroxide (Fisher, 0.6 g, 9.93 mmole) in 50 ml methanol following the procedure described for o-benzyloxyacetophenone. Trituration of the residue resulting from work up with hexanes afforded 3.0 g (41% yield) of 2,6-DBB as colorless needles.
m.p. 104-105°C.
^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.63-7.87 (m, 18H, Ar-H's), 4.69 (s, 2H, OCH_2Ph) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=195.5 (C=O), 154.4, 137.0, 135.5, 133.8, 133.4, 131.9, 129.9, 128.3, 127.9, 127.8, 123.5, 77.00 (OCH_2Ph) ppm.

mass spectrum: (m/e) 392 (M+), 315, 286, 181, 105, 91 (Base), 77.

i.r. (CCl_4): 1680 cm^{-1} (C=O), 1250 cm^{-1} (Ar-O-C).

2,6-Dibenzoylanisole (2,6-DBA) - 2,6-Dibenzoylphenol (12.0 g, 39.8 mmole) was alkylated with dimethyl sulfate (Mallinkrodt, 4.0 ml, 43.3 mmole) in a solution of potassium hydroxide (Fisher, 2.4 g, 43.3 mmole) in 200 ml methanol following the procedure described previously. Chromatography of the oil obtained from work up on 200 g alumina using dichloromethane: hexanes (1:9) as the eluent afforded 5.0 g of a water white oil. Crystallization of this oil from carbon tetrachloride afforded 3.0 g (24% yield) of pure 2,6-DBA as a white powder.

m.p. 37-38°C.

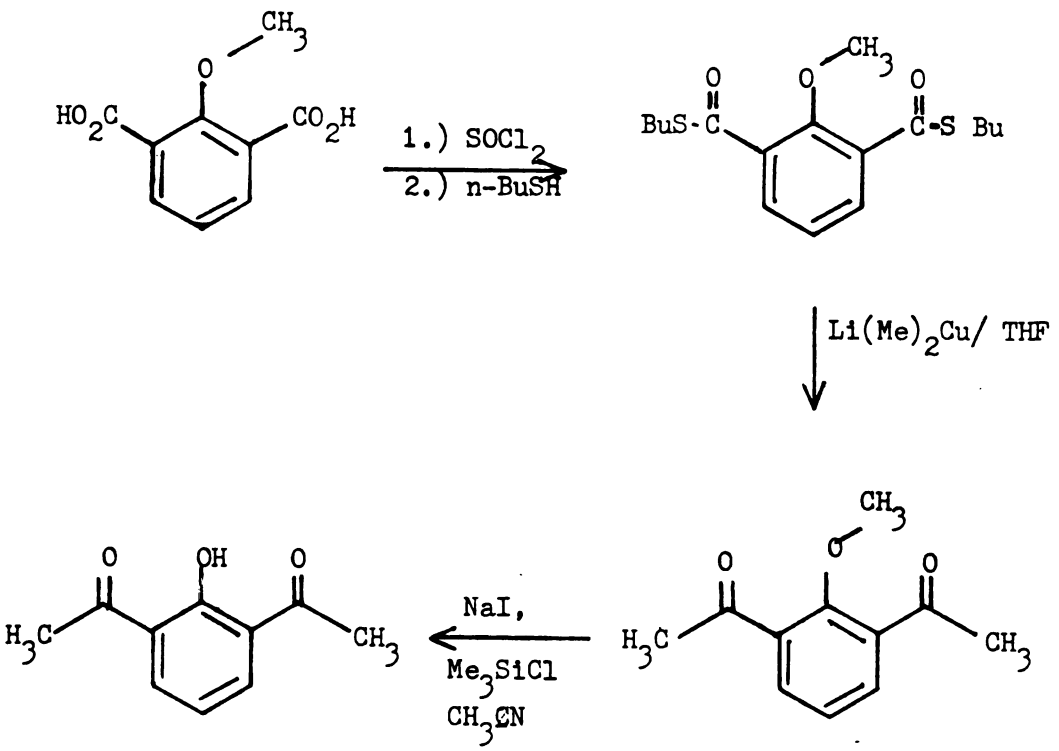
^{1}H-nmr (250 MHz, $CDCl_3$): δ=7.2-8.0 (m, 13H, Ar-H's), 3.43 (s, 3H, OCH_3) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=195.5 (C=O), 136.4, 133.4, 133.0, 131.8, 129.8, 128.5, 123.1, 61.6 (O$\underline{C}H_3$) ppm.

mass spectrum: (m/e) 316 (M+), 299, 285, 239, 225, 211, 181, 147, 105 (Base), 91, 77.

i.r. (CCl_4): 1680 cm^{-1} (C=O), 1250 cm^{-1} (Ar-O-C).

2,6-Diacetylbenzyloxybenzene was prepared according to the following scheme.



2,6-Diacetylanisole - Di-(n-butyl)anisole-2,6-dicarboxylic acid dithioester was prepared by the treatment of the diacyl chloride with two equivalents of n-butyl mercaptan in ether containing two equivalents of pyridine.[118]

Lithium dimethyl cuprate[117] was prepared by the addition of 102 ml methyl lithium (Aldrich, 1.6 M) to a solution of 16.0 g anhydrous cuprous iodide (Fisher) in 50 ml anhydrous THF at 0°C under nitrogen. This solution was

stirred for 15 min, and cooled to -50°C. A solution of the dithioester in 50 ml anhydrous THF was added and the resulting solution stirred at -50°C for 3 hr.[118] After the solution had warmed to room temperature, it was poured into 400 ml of aqueous saturated ammonium bicarbonate solution. This was extracted with ether (3 x 200 ml). The ether extracts were combined and dried (Na_2SO_4). The solvent was removed on a rotary evaporator to afford 9.8 g of a brown liquid. Vacuum distillation of this liquid afforded pure 2,6-diacetylanisole (1.0 Torr, 125-130°C, 6.0 g, 70% yield).

^{1}H-nmr (60 MHz, $CDCl_3$): δ7.1 (t, 1H, p-Ar-H), 7.7 (d, 2H, Ar-H's), 3.8 (s, 3H, O-CH_3), 2.6 (s, 6H, CH_3's) ppm.

2,6-Diacetylphenol - 2,6-Diacetylanisole (5.0 g, 26.0 mmole) was added to a stirred solution of sodium iodide (MCB, 10.0 g, 65.0 mmole) and chlorotrimethylsilane (Aldrich, 8.5 ml, 65.0 mmole) in 70 ml acetonitrile under a nitrogen atmosphere at room temperature.[119] The reaction mixture was refluxed under nitrogen for 20 hr. After the solution had cooled to room temperature, it was poured into 100 ml dilute hydrochloric acid and extracted with ether (3 x 150 ml). The ether extracts were combined and extracted (3 x 150 ml) with a 10% aqueous potassium hydroxide solution. These extracts were combined, acidified with concentrated hydrochloric acid, and extracted with ether

(3 x 150 ml). The ether extracts were combined, dried (Na_2SO_4), and the solvent removed on a rotary evaporator to afford 7.0 g of a brown oil (69.1% yield). This oil, which crystallized upon standing, was recrystallized with hot methanol to afford pure 2,6-diacetylphenol.

^{1}H-nmr (60 MHz, $CDCl_3$): δ=13.1 (s, 1H, OH), 7.8 (d, 2H, m-Ar-H's), 6.8 (t, 1H, p-Ar-H), 2.6 (s, 6H, CH_3's) ppm.

2,6-Diacetylbenzyloxybenzene (2,6-DAB) - 2,6-Diacetylphenol (8.2 g, 46.1 mmole) was alkylated with benzyl bromide (Eastman, 6.0 ml, 50.7 mmole) in a solution of potassium hydroxide (Fisher, 2.8 g, 50.7 mmole) in 100 ml methanol following the previously described procedure. Work up afforded 7.0 g (53% yield) of a brown liquid after removal of the solvent. This liquid was crystallized from hot methanol to afford pure 2,6-DAB as white crystals.

m.p. 69-70°C.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=7.71 (d, 2H, m-Ar-H's), 7.36 (s, 5H, $OCH_2\underline{Ph}$), 7.25 (t, 1H, p-Ar-H), 5.0 (s, 2H, $C\underline{H}_2Ph$), 2.59 (s, 6H, CH_3's) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=(200.0 (C=O), 135.4, 135.1, 132.8, 128.6, 128.3, 124.3, 79.4 (O-$\underline{C}H_2Ph$), 30.66 ppm.

mass spectrum: (m/e) 268 (M+), 253, 235, 225, 147, 91 (Base), 77.

i.r. (CCl_4): 1700 cm^{-1} (C=O), 1240 cm^{-1} (Ar-O-C).

α-(o-Tolyl)acetophenone (α-TAP) - o-Xylyl lithium was prepared by the procedure described by Broaddus[120] from o-xylene (Fisher, 61.0 ml, 0.512 mole), n-butyl lithium (Aldrich, 1.2 M, 110 ml, 0.121 mole) and tetraethylenediamine (Aldrich, 15.2 g, 0.128 mole) in 100 ml anhydrous ether under nitrogen. Benzoic acid (Fisher, 7.8 g, 0.064 mole) in 100 ml anhydrous ether was added dropwise and the solution refluxed under nitrogen for 4 hr. The reaction mixture was cooled and poured into 300 ml dilute hydrochloric acid. This solution was extracted with ether (2 x 200 ml). The ether extracts were combined and washed with aqueous sodium bicarbonate solution (200 ml). The ether layer was dried (Na_2SO_4) and removed on a rotary evaporator to afford a dark liquid. This liquid was vacuum distilled to afford 4.8 g of α-TAP (35.8% yield based upon the amount of benzoic acid). The distillate was recrystallized from hot ethanol to afford white plates.

m.p. 67-68.5°C (lit. 67-68°C)[121].

^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.9-8.1 (m, 9H, Ar-H's), 4.2 (s, 2H, CH_2-Ar), 2.3 (s, 3H, ar-CH_3) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=197.4 (C=O), 136.8, 133.4, 133.1, 130.3, 130.25, 128.6, 128.3, 127.2, 126.1, 43.4, 19.7 ppm.

mass spectrum: (m/e) 210 (M+), 105 (Base), 89, 77.

i.r. (CCl_4): 1690 cm^{-1} (C=O).

α-Mesitylacetophenone was prepared by the reaction of phenyl lithium with α-mesitylacetonitrile, prepared by the procedure described by Fuson and Rabjohn.[122]

α-Mesitylacetonitrile - Mesitylene (Aldrich, 100 g, 0.83 mole) was dissolved in concentrated hydrochloric acid (Mallinkrodt, 500 ml) and formaldehyde solution (Mallinkrodt, 35% formaldehyde, 32 ml). The mixture was heated to 55°C and hydrogen chloride bubbled into the solution through a gas dispersion tube. After 3 hr, another 32 ml of formaldehyde solution were added and the reaction heated for another 3.5 hr. The reaction mixture was cooled to room temperature and extracted with benzene (3 x 400 ml). The benzene extracts were combined, dried (Na_2SO_4), and the solvent removed on a rotary evaporator. Vacuum distillation of the resulting liquid (0.6 Torr, 100-120°C) afforded 73.6 g of 2,4,6-trimethylbenzyl chloride.
^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.8 (s, 2H, Ar-H's), 4.6 (s, 2H, $C\underline{H}_2$-Cl), 2.4 (s, 6H, 2,6-$C\underline{H}_3$'s), 2.2 (s, 3H, 4-CH_3) ppm.

2,4,6-Trimethylbenzyl chloride (71.3 g, 0.43 mole) was added dropwise to a mixture of sodium cyanide (Mallinkrodt, 37.3 g, 0.76 mole) in 54 ml distilled water and 78 ml ethanol. The mixture was heated on a steam bath with stirring for 5 hr. After the solution had cooled to room temperature, it was extracted with benzene (3 x 200 ml).

The benzene extracts were combined, dried (Na_2SO_4), and the solvent removed on a rotary evaporator. Vacuum distillation of the resulting residue provided 36.9 g (54% yield) of α-mesitylacetonitrile.

^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.9 (s, 2H, Ar-H's), 3.6 (s, 2H, $C\underline{H}_2$-CN), 2.4 (s, 6H, 2,6-CH_3's), 2.2 (s, 3H, 4-CH_3) ppm.

α-Mesitylacetophenone (α-MAP) - Phenyl lithium (Aldrich, 1.9 M, 36.0 ml, 69.7 mmole) was added dropwise to a stirred solution of α-mesitylacetonitrile (10.0 g, 62.9 mmole) in 250 ml anhydrous ether at room temperature under nitrogen. After the addition of phenyl lithium was complete, the reaction was refluxed for 3 hr. The solution was then cooled to room temperature and extracted (3 x 200 ml) with dilute hydrochloric acid. The acidic extracts were combined and refluxed for 4 hr. After this solution had cooled to room temperature, it was extracted with ether (3 x 200 ml), the ether extracts were combined and dried (Na_2SO_4). The solvent was removed on a rotary evaporator to afford 9.2 g (61% yield) of cream colored crystals. Recrystallization of these crystals afforded pure α-MAP as white needles.

m.p. 146.5-148°C (lit. 147-148°C).[123]

^{1}H-nmr (60 MHz, $CDCl_3$): δ=7.8-8.2 (m, 5H, Ar-H's), 6.8 (d, 2H, mesityl-H's), 4.3 (s, 2H, $C\underline{H}_2$Ar), 2.3 (s, 3H, 4-CH_3),

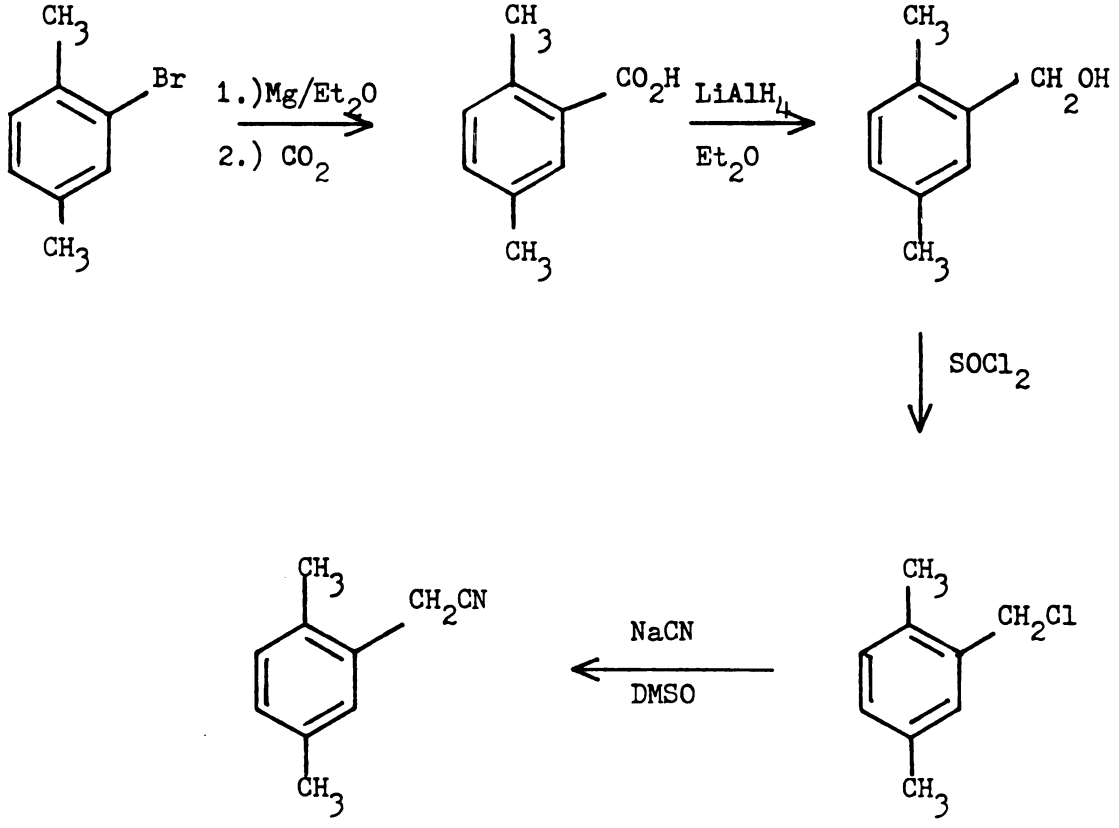
2.2 (s, 6H, 2,6-CH_3's) ppm.

<u>^{13}C-nmr (250 MHz, $CDCl_3$)</u>: δ=197.1 (C=O), 137.1, 136.8, 136.3, 133.1, 129.5, 129.2, 128.8, 128.6, 128.0, 39.23, 20.90, 20.24 ppm.

<u>mass spectrum</u>: (m/e) 238 (M+), 223, 209, 147 (Base), 119, -05, 91, 77.

<u>i.r. (CCl_4)</u>: 1700 cm^{-1} (C=O).

α-(2,5-Dimethylphenyl)acetophenone was prepared by the reaction of phenyl magnesium bromide with 2,5-dimethylbenzyl cyanide, prepared from 2-bromo-<u>p</u>-xylene by the following route.



2,5-Dimethylbenzoic Acid - 2-Bromo-p-xylene (Aldrich, 27.6 ml, 0.200 mole) in 50 ml anhydrous ether was added dropwise to magnesium turnings (MCB, 5.3 g, 0.220 mole) and 50 ml anhydrous ether at room temperature under a nitrogen atmosphere. After the addition was complete, the mixture was refluxed under nitrogen for 1 hr to insure complete formation of the Grignard reagent. The solution was cooled to room temperature and poured over 200 g of powdered dry ice. After all of the dry ice had sublimed, the residue was dissolved in 200 ml ether and extracted with 10% potassium hydroxide solution (3 x 150 ml). The aqueous extracts were combined, acidified with concentrated hydrochloric acid, and extracted with ether (3 x 200 ml). The ether extracts were combined, dried (Na_2SO_4), and the solvent removed on a rotary evaporator to afford 2,5-dimethylbenzoic acid as cream colored crystals (23.7 g, 73% yield).

2,5-Dimethylbenzyl Alcohol - A solution of 2,5-dimethylbenzoic acid (23.7 g, 0.158 mole) in 150 ml anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride (Aldrich, 12.7 g, 0.317 mole) in 50 ml anhydrous ether at room temperature under nitrogen. The resulting mixture was refluxed overnight, cooled to room temperature, and the excess lithium aluminum hydride decomposed by careful addition of methanol. Acidic work up afforded 2,5-dimethylbenzyl alcohol as a pale yellow oil (21.5 g, 100% yield).

^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.8-7.2 (m, 3H, Ar-H's), 4.6 (s, 2H, $C\underline{H}_2$-OH), 2.35 (s, 3H, Ar-CH_3), 2.25 (s, 3H, Ar-CH_3) ppm.

2,5-Dimethylbenzyl Chloride - 2,5-Dimethylbenzyl alcohol (21.5 g, 0.158 mole) was added dropwise to a stirred solution of thionyl chloride (MCB, 20 ml) in 150 ml benzene. The solution was refluxed under nitrogen for 3 hr, cooled to room temperature, and poured into 300 ml distilled water. The layers were separated and the aqueous phase extracted with ether (3 x 200 ml). The ether extracts were combined, washed with saturated sodium bicarbonate solution (2 x 200 ml) and dried (Na_2SO_4). The solvent was removed on a rotary evaporator to afford 22.0 g of 2,5-dimethylbenzyl chloride as a brown oil (93%). This oil was not purified, but used directly for the next reaction.

2,5-Dimethylbenzyl Cyanide - A mixture of sodium cyanide (Fisher, 9.9 g, 0.215 mole) in 100 ml dimethyl sulfoxide was heated at 80°C until all of the sodium cyanide had dissolved. 2,5-Dimethylbenzyl chloride (22.0 g, 0.143 mole) was added to this solution and the mixture stirred at this temperature for 4 hr. The mixture was cooled to room temperature and poured into 500 ml distilled water. The resulting solution was extracted with ether (2 x 150 ml). The ether layers were combined, washed with

distilled water (3 x 150 ml), and dried (Na_2SO_4). The solvent was removed on a rotary evaporator to afford 15.3 g of 2,5-dimethylbenzyl cyanide (50% yield) as a brown solid. The crude product was used without further purification. ^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.8-7.2 (m, 3H, Ar-H), 3.5 (s, 2H, $C\underline{H}_2$-CN), 2.3 (s, 3H, Ar-CH_3), 2.1 (s, 3H, Ar-CH_3) ppm.

α-(2,5-Dimethylphenyl)acetophenone (α-(DMP)AP) - A solution of 2,5-dimethylbenzyl cyanide (15.3 g, 0.106 mole) in 50 ml anhydrous ether was added dropwise to a stirred solution of phenyl magnesium bromide (prepared from 3.1 g magnesium turnings and 13.4 ml bromobenzene in 100 ml anhydrous ether) under a nitrogen atmosphere at room temperature. The resulting mixture was refluxed under nitrogen for 4 hr, cooled to room temperature and extracted with hydrochloric acid (concentrated HCl:water, 1:1) (3 x 200 ml). The acidic extracts were combined and refluxed for 6 hr. After the solution had cooled to room temperature, it was extracted with ether (3 x 200 ml). The ether extracts were combined, washed with saturated sodium bicarbonate (2 x 200 ml) and dried (Na_2SO_4). The ether was removed on a rotary evaporator to afford 7.0 g of crude product (29.5% yield). The crude product was chromatographed on 50 g alumina using petroleum ether as the eluent to afford pure α-(DMP)AP.

m.p. 52-53°C.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.9-8.2 (m, 8H, Ar-H's), 4.62 (s, 2H, Ar-CH_2), 2.8 (s, 3H, Ar-CH_3), 2.21 (s, 3H, Ar-CH_3) ppm.

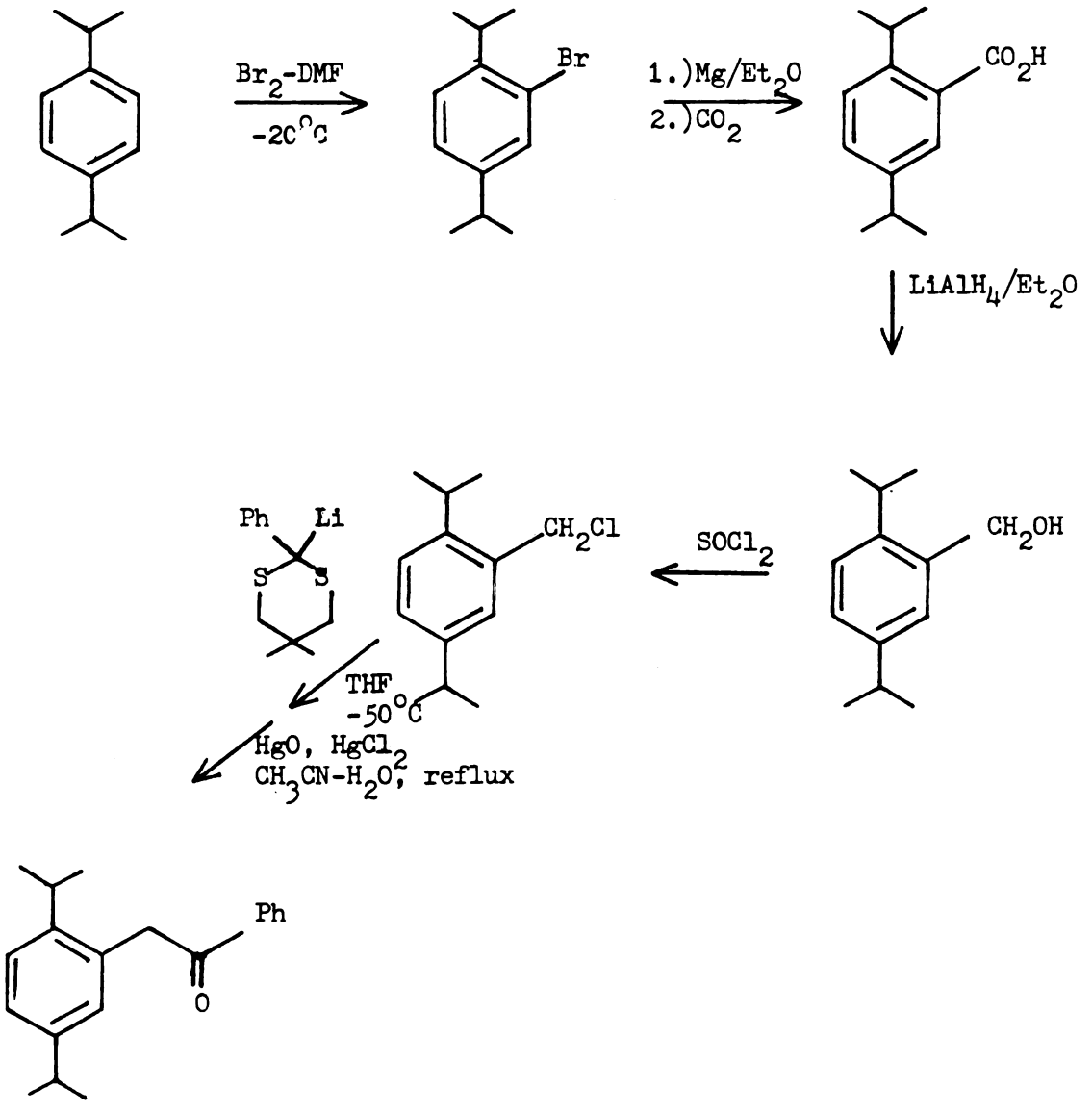
^{13}C-nmr (250 MHz, $CDCl_3$): δ=198.0 (C=O), 135.5, 133.3, 133.1, 131.0, 130.3, 128.7, 128.0, 43.36, 20.83, 19.21 ppm.

mass spectrum: (m/e) 224 (M+), 119, 105 (Base), 91, 77.

i.r. (CCl_4): 1690 cm^{-1} (C=O).

α-(2,5-Diisopropylphenyl)acetophenone was prepared from p-diisopropylbenzene by the following route (page 169).

2,5-Diisopropylbromobenzene.[124] - p-Diisopropylbenzene (Aldrich, 58 ml, 0.31 mole) was dissolved in 30 ml anhydrous dimethyl formamide and cooled to -20°C (dry-ice/carbon tetrachloride). A solution of bromine (Mallinkrodt, 32 ml, 0.62 mole) in 20 ml dimethyl formamide (NOTE: bromine was added to dimethyl formamide at -20°C to avoid a violently exothermic reaction) was added and the resulting solution stirred at -20°C for 3 hr. The solution was allowed to warm to room temperature and quenched by the addition of 400 ml of a saturated aqueous sodium sulfite solution. This mixture was extracted with carbon tetrachloride (2 x 300 ml). The organic layers were combined and washed with a saturated aqueous sodium bicarbonate solution (300 ml) and 300 ml distilled water. After drying (Na_2SO_4), the solvent



was removed on a rotary evaporator. The resulting liquid was vacuum distilled through a 10 cm Vigreaux column to

provide 49.5 g of the desired bromide (4.0 Torr, 110-115°C, 33% yield).

^{1}H-nmr (60 MHz, $CDCl_3$): δ=7.2 (s, 1H, Ar-H ortho to Br), 7.0 (s, 2H, Ar-H's), 3.2 (m, 1H, $-C\underline{H}(CH_3)_2$ ortho to Br), 2.7 (m, 1H, $-C\underline{H}(CH_3)_2$), 1.3 (d, 12H, $C\underline{H}_3$'s) ppm.

mass spectrum: (m/e) 242 (M+), 227, 211, 199, 183, 171, 161, 146, 131, 115, 103, 91, 80.

2,5-Diisopropylbenzoic Acid - 2,5-Diisopropylbromobenzene (49.5 g, 0.21 mole) in 50 ml anhydrous ether was added dropwise to magnesium turnings (MCB, 5.6 g, 0.23 mole). After addition of the bromide was complete, the mixture was refluxed under nitrogen for 1 hr to insure complete formation of the Grignard reagent. The solution was then cooled to room temperature and poured over 600 g powdered dry ice. After all of the dry ice had sublimed, 300 ml dilute hydrochloric acid was added, and the mixture extracted (3 x 300 ml) with ether. The ether extracts were combined, dried ($MgSO_4$), and the solvent removed on a rotary evaporator to afford 41.6 g (89.1% yield) of 2,5-diisopropylbenzoic acid as cream colored crystals. No further purification was attempted.

2,5-Diisopropylbenzyl Alcohol - A solution of 2,5-diisopropylbenzoic acid (41.6 g, 0.187 mole) in 50 ml anhydrous ether was added dropwise to a stirred suspension

of lithium aluminum hydride (Aldrich, 15.0 g, 0.375 mole) in 100 ml anhydrous ether under nitrogen. After the addition was complete, the mixture was refluxed under nitrogen for 2 hr. The mixture was then cooled in an ice bath and the excess lithium aluminum hydride decomposed by the careful addition of methanol. Distilled water (300 ml) was added and the mixture extracted with ether (2 x 300 ml). The ether extracts were combined, dried (Na_2SO_4), and the so solvent removed on a rotary evaporator to afford 25.4 g of a dark liquid (70.7% yield, 90% pure by glc). ^{1}H-nmr (60 MHz, $CDCl_3$): δ=7.1 (s, 3H, Ar-H's), 4.6 (s, 2H, $C\underline{H}_2OH$), 3.0 (m, 2H, $-C\underline{H}(CH_3)_2$), 1.3 (d, 12H, $C\underline{H}_3$'s) ppm.

2,5-Diisopropylbenzyl Chloride - A solution of thionyl chloride (MCB, 15.0 ml, 0.198 mole) in 50 ml chloroform was added dropwise to a stirred solution of 2,5-diisopropylbenzyl alcohol (25.4 g, 0.12 mole) in 50 ml chloroform. The reaction mixture was refluxed under nitrogen for 6 hr. After the solution had cooled to room temperature, the solvent and excess thionyl chloride were removed under reduced pressure. The residue was dissolved in 300 ml ether and washed with 200 ml of a saturated aqueous sodium bicarbonate solution. The ether was dried (Na_2SO_4) and the solvent removed on a rotary evaporator. Vacuum distillation of the resulting liquid afforded 12.3 g (0.5 Torr, 87-89°C, 44.4% yield) of 2,5-diisopropylbenzyl chloride.

^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.9-7.2 (m, 3H, Ar-H's), 4.6 (s, 2H, CH_2Cl), 2.5-3.5 (m, 2H, $-CH(CH_3)_2$), 1.4 (overlapping d, 12H, CH_3's) ppm.

α-(2,5-Diisopropylphenyl)acetophenone (α-(DIP)AP) - n-Butyl lithium (Aldrich, 1.7 M, 38.0 ml, 64.6 mmole) was added to a stirred solution of 2-phenyl-1,3-dithiane[125] in 100 ml anhydrous tetrahydrofuran under nitrogen ar-50°C. The resulting solution was stirred at -50°C for 6 hr.[126] A solution of 2,5-diisopropylbenzyl chloride (12.3 g, 64.6 mmole) in 100 ml anhydrous tetrahydrofuran was added dropwise and the mixture stirred under nitrogen overnight. The reaction mixture was then poured into 500 ml distilled water and extracted with dichloromethane (2 x 300 ml). The organic extracts were combined and washed with a 10% potassium hydroxide solution (2 x 300 ml). The organic layer was dried (Na_2SO_4) and the solvent removed on a rotary evaporator to afford a pale yellow oil.

This oil was added to a stirred suspension of mercury (II) chloride (Mallinkrodt, 35.0 g, 0.129 mole) and mercury (II) oxide (Mallinkrodt, 28.0 g, 0.192 mole) in 400 ml acetonitrile:water (1:1) under a nitrogen atmosphere.[127] The mixture was refluxed for 4.5 hr, during which time the mixture turned color from milky yellow to milky white. The reaction mixture was cooled, filtered through a pad of Celite, and the solvent removed on a rotary evaporator.

The residue was taken up into 500 ml distilled water and 400 ml dichloromethane. The organic layer was separated and washed with 500 ml of a half-saturated solution of ammonium acetate in water and 500 ml distilled water. The organic phase was dried (Na_2SO_4) and the solvent removed on a rotary evaporator to afford 17.0 g of a pale yellow liquid. Vacuum distillation of this liquid afforded pure α-(DIP)AP (1.0 Torr, 180-185°C, 22% yield).

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.95-8.0 (m, 8H, Ar-H's), 4.32 (s, 2H, $C\underline{H}_2$-Ar), 2.92 (m, 1H, -$C\underline{H}(CH_3)_2$, 2.82 (m, 1H, -$C\underline{H}(CH_3)_2$), 1.19 (d, 6H, -$CH(C\underline{H}_3)_2$ ortho to CH_2CO), 1.17 (d, 6H, -$CH(C\underline{H}_3)_2$) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=197.7 (C=O), 145.8, 136.9, 132.9, 131.4, 128.9, 128.5, 128.1, 125.4, 125.3, 43.06, 33.36, 29.21, 23.82, 23.72 ppm.

mass spectrum: (m/e) 280 (M+), 175, 105 (Base), 77.

i.r. (CCl_4): 1700 cm^{-1} (C=O).

α-(2,4,6-Triisopropylphenyl)acetophenone was synthesized from the reaction of phenyl magnesium bromide and α-2,4,6-triisopropylbenzyl cyanide, prepared following the same procedure used to prepare 2,5-dimethylbenzyl cyanide.

2,4,6-Triisopropylbromobenzene - A solution of 1,3,5-triisopropylbenzene in anhydrous dimethyl formamide was brominated at -20°C with bromine-dimethyl formamide solution

following the procedure described for 2,5-diisopropylbromobenzene. Vacuum distillation of the crude product afforded the desired bromide (b.p. 100°C, 1.0 Torr) in 78% yield.

2,4,6-Triisopropylbenzoic Acid - 2,4,6-Triisopropylbenzoic acid was prepared by the carboxylation of 2,4,6-triisopropylphenyl magnesium bromide with dry ice following the procedure described for 2,5-diisopropylbenzoic acid. The usual work up afforded 14.0 g of the desired acid (53.3% yield).

2,4,6-Triisopropylbenzyl Alcohol - Borane-THF complex in tetrahydrofuran (Aldrich, 1.0 M, 200 ml) was added dropwise to a stirred solution of 2,4,6-triisopropylbenzoic acid (14.0 g, 56.5 mmole) in 50 ml anhydrous tetrahydrofuran under a nitrogen atmosphere. The resulting solution was stirred overnight under nitrogen and then poured into 400 ml of a 20% aqueous potassium hydroxide solution. The aqueous and organic phases were separated and the aqueous phase extracted with ether (2 x 200 ml). The organic extracts were combined, dried ($MgSO_4$), and the solvent removed on a rotary evaporator to afford 2,4,6-triisopropylbenzyl alcohol as a colorless liquid (13.2 g, 56.5 mmole, 100% yield).

^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.9 (s, 2H, Ar-H's), 5.6 (s, 2H, $C\underline{H}_2$-OH), 2.8-3.8 (m, 3H, $-C\underline{H}(CH_3)_2$), 3.5 (br s, 1H, OH), 1.3 (d, 18H, $C\underline{H}_3$'s) ppm.

2,4,6-Triisopropylbenzyl Chloride - 2,4,6-Triisopropylbenzyl chloride was prepared from 2,4,6-triisopropylbenzyl alcohol and thionyl chloride according to the usual procedure. Normal work up afforded the desired chloride in 76% yield as a pale yellow oil.
i.r. (neat): shows no -OH at 3500 cm^{-1}.
mass spectrum: 252 (M+).

2,4,6-Triisopropylbenzyl Cyanide - 2,4,6-Triisopropylbenzyl cyanide was prepared from 2,4,6-triisopropylbenzyl chloride and sodium cyanide following the procedure used to prepare 2,5-dimethylbenzyl cyanide. The solvent was removed after the usual work up to afford 8.0 g of a dark oil which solidified upon standing (75.3% yield). No further purification was attempted.
^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.9 (s, 2H, Ar-H's), 3.7 (s, 2H, $C\underline{H}_2$-CH), 2.5-3.4 (m, 3H, $-CH(CH_3)_2$), 1.4 (d, 12H, $-C\underline{H}(CH_3)_2$'s ortho to CH_2CN), 1.2 (d, 6H, $-C\underline{H}(CH_3)_2$ para to $C\underline{H}_2CN$) ppm.

α-(2,4,6-Triisopropylphenyl)acetophenone (α(TIP)AP) - α-(2,4,6-Triisopropylphenyl)acetophenone was prepared from the reaction of phenyl magnesium bromide with 2,4,6-triisopropylbenzyl cyanide following the procedure used to prepare α-(2,5-dimethylphenyl)acetophenone. Removal of the solvent following the usual work up afforded 3.0 g of

a brown oil which solidified upon standing (24.6% yield). Recrystallization of this solid from methanol afforded pure α-(DIP)AP as white crystals.

m.p. 101.5-102.5°C (lit. 113.5-114.5°C).[128]

^{1}H-nmr (250 MHz, $CDCl_3$): δ=8.1 (d, 2H, Ar-H's ortho to CO), 7.55 (m, 3H, other phenone H's), 7.05 (s, 2H, -phenyl H's), 4.46 (s, 2H, $C\underline{H}_2$-CO), 2.86 (m, 3H, -$C\underline{H}(CH_3)_2$'s), 1.23 (overlapping d's, 18H, -$C\underline{H}(CH_3)_2$) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=197.7 (C=O), 147.1, 137.1, 133.1, 128.7, 128.0, 126.5, 120.9, 37.63, 34.19, 30.25, 23.98 ppm.

mass spectrum: (m/e) 322 (M+), 217, 203, 105 (Base.

i.r. (CCl_4): 1710 cm^{-1} (C=O).

2-(o-Tolyl)ethanol - A solution of o-tolylacetic acid (Aldrich, 10.0 g, 66.7 mmole) in 150 ml anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride (Aldrich, 5.1 g, 0.133 mole) in 100 ml anhydrous ether at room temperature under nitrogen. The mixture was refluxed for 6 hr, cooled to 0°C, and the excess lithium aluminum hydride decomposed by the careful addition of acetone. The reaction mixture was poured into 400 ml distilled water, acidified with concentrated hydrochloric acid, and extracted with ether (2 x 200 ml). The ether extracts were combined, washed with saturated aqueous sodium bicarbonate, and dried (Na_2SO_4). Removal of the

solvent afforded 8.2 g of 2-(o-tolyl)ethanol (91% yield) as a pale yellow oil. No further purification was attempted.

^{1}H-nmr (60 MHz, $CDCl_3$): δ=7.0 (s, 4H, Ar-H's), 3.7 (t, 2H, CH_2-OH), 2.8 (t, 2H, CH_2-Ar), 2.5 (br, s, 1H, OH), 2.3 (s, 3H, Ar-CH_3) ppm.

α-(o-Tolyl)acetaldehyde - Chromium trioxide (Fisher, 18.1 g, 0.181 mole) was added to a stirred solution of pyridine (Fisher, 28 ml) in 300 ml dichloromethane.[129] The orange colored solution was stirred for an additional 15 min, after which a solution of 2-(o-tolyl)ethanol (4.1 g, 30.2 mmole) in 25 ml dichloromethane was added. The resulting green solution was stirred for 30 min. The methylene chloride was decanted from the inorganic precipitate and the precipitate washed with ether (3 x 150 ml). The organic solutions were combined and washed with 350 ml of a saturated sodium bicarbonate solution. After drying ($MgSO_4$) the solvent was removed on a rotary evaporator to afford 3.3 g of α-(o-tolyl)acetaldehyde (70% yield).

^{1}H-nmr (60 MHz, $CDCl_3$): δ=9.4 (s, 1H, CHO), 7.1 (s, 4H, Ar-H's), 3.6 (d, 2H, CH_2CHO), 2.2 (s, 3H, Ar-CH) ppm.

mass spectrum: (m/e) 134 (M+), 91 (Base), 77.

i.r. (neat): 1725 cm^{-1} (C=O).

α-(o-Tolyl)acetone - n-Butyl lithium (Aldrich, 1.7 M, 90 ml) was added to a stirred solution of 2-methyl-1,3-dithiane[127] (20.2 g, 0.151 mole) in 100 ml anhydrous tetrahydrofuran under nitrogen at -20°C. This solution was maintained at -20°C for 1.5 hr, whereupon it was cooled to -70°C. A solution of α-bromo-o-xylene (Aldrich, 27.7 g, 0.174 mole) in 50 ml tetrahydrofuran was added dropwise and the solution stirred at -70°C for an additional 2 hr.[126] The solution was warmed to room temperature and poured into 300 ml distilled water. The layers were separated, and the aqueous layer was extracted with 200 ml ether. The organic layers were combined, washed with 300 ml of a saturated sodium bicarbonate solution, dried ($MgSO_4$), and the solvent removed on a rotary evaporator.

The resulting pale yellow oil was added to a vigorously stirred suspension of mercury (II) oxide (Mallinkrodt, 71.9 g, 0.332 mole), mercury (II) chloride (Mallinkrodt, 90.1 g, 0.332 mole) in 400 ml acetonitrile:water (1:1). The resulting mixture was stirred at reflux under nitrogen for 6 hr. After it had cooled to room temperature, the solution was filtered through a pad of Celite. The filtrate was concentrated and the residue dissolved in 400 ml dichloromethane and 400 ml water containing 30 ml concentrated hydrochloric acid. The layers were separated and the aqueous layer extracted with 200 ml dichloromethane. The organic layers were combined, washed with 300 ml of a saturated

sodium bicarbonate solution, and dried ($MgSO_4$). The solvent was removed on a rotary evaporator and the resulting liquid vacuum distilled (b.p. 104-114°C, 12.0 Torr; lit. b.p. 110-113°C, 14 Torr)[104] to afford 5.0 g (22% yield) of pure α-(o-tolyl)acetone. Spectral data matched that in the literature.[104]

^{1}H-nmr (60 MHz, $CDCl_3$): δ=7.0 (s, 4H, Ar-H's), 3.5 (s, 2H, $C\underline{H}_2CO$), 2.2 (s, 3H, $CO-C\underline{H}_3$), 2.1 (s, 3H, $Ar-C\underline{H}_3$) ppm.
mass spectrum: (m/e) 148 (M+), 133, 119, 105, 91, 77, 43.

α-(o-Benzyloxyphenyl)acetophenone was prepared from o-benzyloxybenzyl chloride and 2-lithio-2-phenyl-1,3-dithiane following the procedure used to prepare α-(2,5-diisopropylphenyl)acetophenone.

o-Benzyloxybenzyl Chloride - o-Benzyloxybenzaldehyde[135] (20.0 g, 94.3 mmole) in 50 ml anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride (Aldrich, 2.0 g, 48.8 mmole) in 100 ml anhydrous ether at room temperature under nitrogen. This solution was refluxed overnight, cooled to room temperature, and the excess lithium aluminum hydride decomposed by the careful addition of methanol. The resulting mixture was poured into 400 ml distilled water and 50 ml concentrated hydrochloric acid. This solution was extracted with ether (3 x 150 ml). The ether extracts were combined, washed with 300 ml of an aqueous sodium bicarbonate solution, and

dried (Na_2SO_4). The solvent was removed on a rotary evaporator to afford 20 g of o-benzyloxybenzyl alcohol as a pale yellow oil.

Thionyl chloride (MCB, 22 ml) in 20 ml benzene was added dropwise to a solution of the crude alcohol in 100 ml benzene. The resulting solution was refluxed under nitrogen for 6 hr. After the solution had cooled to room temperature, the solvent and excess thionyl chloride were removed under reduced pressure. Vacuum distillation of the resulting residue afforded 4.0 g of o-benzyloxybenzyl chloride (20% overall yield, b.p. 128-138°C at 0.1 Torr). ^{1}H-nmr (60 MHz, $CDCl_3$): δ=6.6-7.5 (m, 9H, Ar-H's), 5.0 (s, 2H, O-CH_2Ph), 4.5 (s, 2H, CH_2-Cl) ppm.
mass spectrum: (m/e) 232 (M+), 197.91 (Base), 78.

Note: no peak at 214 (corresponding to the molecular weight of the alcohol) was observed.

α-(o-Benzyloxyphenyl)acetophenone (α-(o-BzOPh)AP - n-Butyl lithium (Aldrich, 1.7 M, 11.1 ml, 18.9 mmole) was added dropwise to a stirred solution of 2-phenyl-1,3-dithiane[125] (3.4 g, 17.2 mmole) in 100 ml anhydrous tetrahydrofuran at -75°C under nitrogen.[126] The resulting solution was warmed to -50°C and stirred at this temperature for 6 hr. o-Benzyloxybenzyl chloride (4.0 g, 17.2 mmole) in 50 ml anhydrous tetrahydrofuran was added dropwise and the reaction mixture allowed to warm to 0°C. After the solution had stirred overnight, it was poured

into 500 ml distilled water, and extracted with methylene chloride (2 x 200 ml). The organics were combined and washed, first with 500 ml distilled water, then an aqueous 5% potassium hydroxide solution, and finally with distilled water (2 x 200 ml). The methylene chloride solution was dried ($MgSO_4$) and the solvent removed on a rotary evaporator to afford a pale yellow oil.

This oil was added to a vigorously stirred suspension of mercury (II) chloride (MCB, 10.3 g, 37.8 mmole) and mercury (II) oxide (MCB, 8.2 g, 37.8 mmole) in 250 ml acetonitrile-distilled water (9:1) at room temperature under nitrogen. This mixture was refluxed under nitrogen for 4.5 hr, cooled to room temperature, and filtered through a pad of Celite. The filtrate was concentrated on a rotary evaporator and the residue taken up into 500 ml distilled water and 400 ml methylene chloride. The layers were separated and the organic layer washed first with 500 ml of a half-saturated aqueous ammonium acetate and then with 500 ml distilled water. The methylene chloride solution was dried ($MgSO_4$) and the solvent removed on a rotary evaporator to afford 6.0 g of a bright yellow oil which crystallized upon standing. Recrystallization of this solid from ethanol afforded pure α-(o-BzOPh)AP as cream colored crystals.

m.p. 102-104°C.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.8-8.1 (m, 14H, Ar-H's),

5.02 (s, 2H, O-$C\underline{H}_2$Ph), 4.28 (s, 2H, $C\underline{H}_2$-CO) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ=197.9 (C=O), 156.2, 136.8, 132.8, 131.1, 128.3, 127.8, 127.6, 127.1, 124.1, 120.8, 111.8, 69.85 (O-CH_2Ph), 39.95 ppm.
i.r. (CCl_4): 1680 cm^{-1} (C=O), 1280 cm^{-1} (Ar-O-C).
mass spectrum: (m/e) 302 (M+), 211, 105, 91 (Base), 77.

2-Keto-[2,2]-Paracyclophane (2-KPCP) - 2-Keto-[2,2]-paracyclophane was synthesized according to the procedure described by Cram and Hegelson.[63] Thus, a solution of [2,2]-paracyclophane (Union Carbide, 9.5 g, 45.6 mmole), N-bromosuccinimide (MCB, 13.0 g, 73.0 mmole) and benzoyl peroxide (Fisher, 100 mg) in 300 ml anhydrous carbon tetrachloride was refluxed under nitrogen for 10 hr. During this time, the solution was irradiated with a high intensity visible lamp. The solution was then cooled to room temperature and filtered. The filtrate was concentrated on a rotary evaporator and the residue dissolved in 70 ml benzene. The benzene solution was adsorbed on a 1.5 Kg silica gel column, and the column eluted with ether-pentane (1:1) to provide 2.0 g of cream colored crystals. Recrystallization of these from hot ethanol afforded pure 2-KPCP. Spectral data agrees with that in the literature.[63]
m.p. 198-201°C (lit. m.p. 195-196°C).[63]
^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.4-6.6 (m, 4H, Ar-H's), 3.87 (s, 1H, $C\underline{H}_2$CO), 3.09 (s, 2H, Ar-$C\underline{H}_2$) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=141.8, 139.4, 138.7, 135.2, 133.5, 132.7, 129.3, 53.73, 35.07, 34.59 ppm.

5. Equipment and Procedures

a. Photochemical Glassware - All volumetric glassware (pipettes and volumetric flasks) used were Class A type. This glassware was rinsed with acetone (3x), then with distilled water (3x), and boiled in a solution of Alconox laboratory detergent in distilled water for 12 hr. The glassware was carefully rinsed with distilled water, and soaked in distilled water for 2 days, with the water being changed every 8-12 hr. This method was also used to clean the syringes and the Pyrex tubes used for irradiations. After the final distilled water rinse, the glassware was dried in an oven (reserved specifically for photochemical glassware) at 150°C.

Ampoules used for irradiations were made by heating 13 x 100 mm Pyrex 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 a uniform 15 cm length.

b. Sample Preparations - All solutions were prepared either by directly weighing the desired material into volumetric flasks or by dilution of a stock solution. Equal volumes (2.8 ml) of sample were placed via syringe into each ampoule. Internal standards used for glc analyses were weighed directly into the ketone stock solutions.

c. Degassing Procedures - Filled irradiation tubes were attached to a vacuum line (10^{-4} Torr). 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 5-10 min. The vacuum was removed and the tubes allowed to thaw at room temperature. This freeze - pump - thaw cycle was repeated a total of three times. After the tubes had been thawed at the conclusion of the third cycle they were refrozen, evacuated for 5 min, and sealed with an oxygen-natural gas torch while still under vacuum.

d. Irradiation Procedures - All samples were irradiated in parallel with actinometer solutions in a Merry-Go-Round apparatus[130] immersed in a water bath at approximately 25°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_3 in 1% aqueous potassium carbonate) was used to isolate the 313 nm emission band. A Corning 7-83 filter was used to isolate the 366 nm emission band.

Preparative scale photolyses of α-(o-alkylphenyl)acetophenones were performed using a Hanovia medium pressure mercury lamp filtered through Pyrex. Samples (100 mg) dissolved in 500 ml spectral grade cyclohexane were irradiated at room temperature under a steady stream of nitrogen.

Preparative scale photolyses of o-alkoxyphenyl ketones were performed in a Merry-Go-Round apparatus at 313 nm. Samples (200 mg) were dissolved in 10 ml benzene and degassed by the freeze - pump - thaw method described previously.

e. Laser Flash Spectroscopy - Ketone samples (10^{-2} M in benzene or Aldrich Gold Lable methanol) were placed in 5 mm Supracil cells and degassed with a steady stream of nitrogen for approximately 3 min. Laser excitation was accomplished with a Molectron UV-24 nitrogen laser (337.1 nm, 8 nsec pulse, up to 10 mJ). The spectroscopic system allowed analysis of transient absorptions in the 10 nsec. to 100 μsec time scale. All data acquisition and processing was handled by a PDP 11/03L computer, which also controlled the experiments. These experiments were performed at the

National Research Council of Canada, Chemistry Division at Ottawa under the supervision of Dr. J. C. Scaiano and Mr. S. E. Sugamori. Details of the experimental apparatus have been described elsewhere.[131]

f. Analysis Procedures - All gas chromatographic analyses were performed on either a Varian Hy-Fi Model 600 or a Varian Aerograph Model 1400 Gas Chromatogram equipped with a flame ionization detector. Gas chromatograms were connected to either a Leeds and Northrup recorded and Inforronics CRS 309 Digital Integrator or a Hewlett-Packard Model 6080 Integrating Recorder.

Analyses by HPLC were performed on a Beckman Model 332 Gradient Liquid Chromatograph System equipped with a Perkin-Elmer LC-75 Ultraviolet-Visible Detector and a DuPont 860 Column Compartment. Either an Altex Ultrasphere ODS-18 Reverse Phase column or an Altex Ultrasphere Si Absorption Phase column were employed for separations. Solvents used were of either HPLC Grade or Spectral Grade and were filtered through a 0.45 μm Nylon 66 membrane prior to use. The HPLC system was connected to a Hewlett-Packard Model 6080 Integrating Recorder.

For gas chromatography, all samples were introduced by on-column injection with a carrier gas (nitrogen) flow rate of 40 ml/min. The following 1/8" o.d. aluminum columns were used -

- Column #1 - 6' 3% OV-101 on Chromsorb G
- Column #2 - 6' 3% QF-1 on Chromsorb G
- Column #3 - 25' 25% 1,2,3-Tris(2-cyanoethyl)propane on Chromsorb P
- Column #4 - 5' 20% SE-30 on Chromsorb G

Response factors for each of the photoproducts and their respective internal standards were obtained by gas chromatography and calculated from the following equation -

$$R.F. = \frac{A_{std}}{A_{photo}} \times \frac{moles_{photo}}{moles_{std}}$$

These response factors are presented in Table 30.

For convenience sake, benzene was used as the internal standard in all HPLC analyses. The response factors for HPLC were calculated from the following equation -

$$R.F. = \frac{A_{C_6H_6}}{A_{photo}} \times [photo] \ .$$

These response factors are summarized in Table 31.

g. Calculation of Quantum Yields - The intensity of light absorbed by samples was determined by valerophenone actinometry.[132] Thus, a degassed 0.10 M valerophenone

Table 30. Gas Chromatographic Response Factors for Various Photoproducts.

Standard/Photoproduct	Conditions[a]	R.F.
Eicosane (C_{20})/2-Phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran	2, 220°C	1.33
Docosane (C_{22})/o-Benzyloxyacetophenone	2, 220°C	1.59
Tetracosane (C_{24})/2,3-Diphenyl-3-hydroxy-2,3-dihydrobenzofuran	2, 180°C	1.20
Heneicosane (C_{21})/3-Phenyl-3-hydroxy-2,3-dihydrobenzofuran	2, 180°C	1.50
Hexacosane (C_{26})/2,3-Diphenyl-3-hydroxy-7-benzyloxy-2,3-dihydrobenzofuran	1, 250°C	0.96
Hexacosane (C_{26})/2,3-Diphenyl-3-hydroxy-5-methyl-2,3-dihydrobenzofuran	2, 205°C	1.24
Heneicosane (C_{21})/2-Phenyl-2-hydroxyindane	2, 185°C	1.40
Pentadecane (C_{15})/Acetophenone	2, 120°C	1.88

[a] Conditions = (Column, Column Temperature).

Table 31. HPLC Response Factors for Various Photoproducts.

Photoproduct	R.F.
2,3-Diphenyl-3-hydroxy-2,3-dihydrobenzofuran	0.038, 0.0397[a,b]
3-Phenyl-3-hydroxy-2,3-dihydrobenzofuran	0.0345[b]
2-Phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran	0.0362[b]
2,3-Diphenyl-3-hydroxy-7-benzoyl-2,3-dihydrobenzofuran	0.0128, 0.0142[a,c]
2-Phenyl-3-methyl-3-hydroxy-7-acetyl-2,3-dihydrobenzofuran	0.190[c]
3-Phenyl-3-hydroxy-7-benzoyl-2,3-dihydrobenzofuran	0.0139[c]
4,6-Dimethyl-2-phenyl-2-hydroxyindane	0.081[d]
5-Methyl-2-phenyl-2-hydroxyindane	0.0535[b]
1,1-Dimethyl-2-phenyl-5-isopropyl-2-hydroxyindane	0.058[b]
1,1-Dimethyl-2-phenyl-4,6-diisopropyl-2-hydroxyindane	0.133[b]
Acetophenone	0.0943[b]

[a]R.F. of cis and trans isomers, respectively.

[b]Ultrasphere Si Column, Hexane:Ethyl Acetate (95:5), 270 nm detector.

[c]Ultrasphere Si Column, Hexane:Ethyl Acetate (90:10), 270 nm detector.

[d]Ultrasphere ODS-18 Column, Acetonitrile:Water, 270 nm detector.

solution was irradiated in parallel with the samples to be analyzed. Upon completion of the irradiation the valerophenone sample was analyzed for acetophenone, using the following equation -

$$AP = (R.F.[\text{int. std.}]\ (A_{AP}/A_{std}) \quad .$$

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

$$I\ (\text{ein}\ l^{-1}) = \frac{[AP]}{0.33} \quad .$$

6. Sensitization Studies

The sensitized isomerization of either cis-piperylene or trans-stilbene by triplet ketone were monitored by gas chromatography. Cis- and trans-stilbene were analyzed on a 6' column containing 20% SE-30 on Chromsorb G maintained at 180°C. Cis- and trans-piperylene were analyzed on a 25' column containing 25% 1,2,3-tris(cyanoethoxy)propane held at 60°C. The area percents of the newly isomerized alkene were calculated from the g.c. peak areas by the following equation -

$$\beta = \frac{A_x}{A_x + A_y}$$

where A_x = area of newly isomerized alkene

A_y = area of unisomerized alkene.

This area percent was corrected for any reisomerization of the alkene product, using -

$$\beta' = \alpha \ln \frac{\alpha}{\alpha - \beta}$$

where α = photostationary state of isomerized alkene

β' = corrected area percent of isomerized alkene

α = 0.55 for cis-piperylene[48]

0.596 for trans-stilbene.[48]

The concentration of the newly isomerized alkene can be calculated from β', since -

$$[\text{isom. alkene}] = \beta'[\text{alkene}]^\circ$$

where $[\text{alkene}]^\circ$ = initial concentration of alkene.

Actinometer solutions were prepared from a stock solution of acetophenone or benzophenone and an appropriate concentration of alkene. Concentrations of acetophenone or

benzophenone were adjusted such that the absorbance of the actinometer at 313 nm (for piperylene) or 366 nm (for stilbene) was identical to that of the ketone solutions studied. If the concentration of alkene used was greater than 0.5 M, separate actinometers were used for each of the ketone solutions in the experiment, such that each sample in the experiment had an actinometer of identical alkene concentration. This was done to correct for any changes in the characteristics of the solvent that might occur in such a high concentration of alkene. In all other cases, the concentration of alkene used in the actinometer was a value in the middle of the range of concentrations used for ketone solutions. The intensity of absorbed light can be calculated from -

$$(\text{ein. light})l^{-1} = \frac{\beta'_{act}[\text{alkene}]_{act}}{\alpha}$$

Thus the quantum yield for the ketone sensitized isomerization can be represented by -

$$\phi_{isom} = \frac{\beta'[\text{alkene}]^{\circ}}{\beta'_{act}[\text{alkene}]^{\circ}_{act}}$$

A straight line was obtained from a plot of α/ϕ_{isom} versus $[\text{alkene}]^{-1}$. This line had an intercept of ϕ_{isc}^{-1},

the reciprocal of the intersystem crossing quantum yield for the ketone sensitizer. The ratio of the intercept to the slope equals $k_q\tau_T$, where τ_T is the lifetime of the ketone sensitizer triplet.

B. Isolation and Identification of Photoproducts

In most cases, photoproducts were obtained by preparative scale photolysis of 0.01 to 0.1 M solutions of the appropriate ketone in spectral grade cyclohexane or heptane under a nitrogen atmosphere. A medium pressure Hanovia mercury vapor lamp was used as the irradiation source. For o-alkoxyphenyl ketones, this light was filtered through uranium glass. A Pyrex filter was used for the irradiation of α-(o-alkylphenyl)acetophenones.

Photoproducts from o-alkoxyphenyl ketones were isolated by flash chromatography[88] on ICN Silica Gel (0.032 to 0.063 mm) using hexanes:ethyl acetate (95:5) as the eluent. Photoproducts from α-(o-alkylphenyl)acetophenones were formed innearly quantitative yields and did not require any further purification.

Structural assignments were based upon standard spectroscopic techniques - ^1H and ^{13}C nmr spectroscopy, infrared spectroscopy, and mass spectrometry. ^1H nmr spectra were recorded on either a Varian T-60 Nuclear Magnetic Resonance Spectrometer or on a Bruker WM-250 250 MHz Fourier Transform Nuclear Magnetic Resonance Spectrometer. ^{13}C

nmr spectra were recorded on the Bruker WM-250 instrument. All spectra were calibrated using tetramethylsilane as an internal standard (δ=0.0 ppm). Infrared spectra were recorded on a Perkin-Elmer Model 237 B Grating Infrared Spectrophotometer. Mass spectra were recorded on a Finnigan 4000 GC/MS using the direct inlet mode. This instrument was operated by Mr. Ernest A. Oliver. Ultraviolet-visible absorption spectra were recorded on a Varian Carey 219 Spectrophotometer. Melting points were recorded on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected.

o-Benzyloxyacetophenone - Irradiation of a 0.1 M solution of o-benzyloxyacetophenone in spectral grade heptane (100% ketone conversion) afforded containing 2M pyridine afforded a mixture of three photoproducts. These three products were separated by flash chromatography and are listed in order of elution.

Z-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.9-7.55 (m, 9H, Ar-H's), 5.3 (s, 1H, O-CHPh), 1.7 (s, 3H, CH_3), 1.45 (br s., 1H, OH) ppm. i.r. (neat): 3470 cm^{-1} (OH), 3080, 3060, 3030 cm^{-1} (Ar-CH), 2960, 2910, 2870 cm^{-1} (sat. C-H), 1260 cm^{-1} (Ar-O-C). mass spectrum: (m/e) 266 (M+), 208, 121, 105, 91 (Base), 77.

E-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.9-7.9 (m, 9H, Ar-H's), 5.52 (s, 1H, O-CH-Ph), 2.48 (s, 1H, OH), 1.11 (s, 3H, CH_3) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ=159.4, 134.9, 132.0, 130.4, 128.8, 128.6, 127.1, 123.9, 121.5, 110.7, 92.90, 78.20, 25.14 ppm.
i.r. (CCl_4): 3580 cm^{-1} (OH), 3060, 3030 cm^{-1} (Ar-CH), 2970, 2950 cm^{-1} (sat. C-H), 1260 cm^{-1} (Ar-O-C).
mass spectrum: (m/e) 226 (M+), 208 (Base), 121, 105, 91, 77.

2-Acetylbenzophenone

^{1}H-nmr (250 MHz, $CDCl_3$): δ=7.25-7.95 (m, 9H, Ar-H's), 2.52 (s, 3H, CH_3) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ198.6, 197.9 (C=O), 141.0, 137.7, 137.3, 133.0, 132.2, 129.8, 129.4, 129.3, 128.5, 128.4, 120.4, 112.7, 27.39 (CH_3)ppm.
i.r. (CCl_4): 1680, 1660 cm^{-1} (C=O), (lit. 1680, 1660 cm^{-1}).[136]
mass spectrum: (m/e) 224 (M+), 209, 181, 147, 105, 77.
m.p.: 78-80°C (lit. 99°C).[133]

o-Benzyloxybenzophenone - Irradiation of a 0.2 M solution of o-benzyloxybenzophenone in heptane containing 2 M pyridine (100% ketone conversion) resulted in the formation of three compounds (by HPLC). The first and last peaks were isolated by flash chromatography. The middle peak

was unstable to chromatographic conditions. The two compounds isolated are listed in order of elution.

Z-2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.6-7.9 (m, 14H, Ar-H's), 5.66 (s, 1H, O-C<u>H</u>-Ph), 1.95 (br s, 1H, OH).
^{13}C-nmr (250 MHz, $CDCl_3$): δ=160.3, 142.9, 134.0, 130.7, 129.6, 128.8, 128.5, 128.3, 127.7, 127.6, 127.0, 126.8, 125.5, 122.0, 110.8, 95.3, 83.2 ppm.
i.r. (CCl_4): 3500 cm^{-1} (OH), 3080, 3060, 3030 cm^{-1} (Ar-C-H), 2960, 2910 cm^{-1} (sat. C-H), 1275 cm^{-1} (Ar-O-C).
mass spectrum: (m/e) 288 (M+), 270, 181, 121, 105, 91 (Base), 84, 77.

E-2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.9-7.46 (m, 14H, Ar-H's), 5.77 (s, 1H, O-C<u>H</u>-Ph), 2.62 (br, s, 1H, OH) ppm.
i.r. (CH_2Cl_2): 3570 cm^{-1} (OH), 3010 cm^{-1} (Ar-CH), 2945 cm^{-1} (Sat. C-H), 1225 cm^{-1} (Ar-O-C).
mass spectrum: (m/e) 288 (M+), 270, 181, 121, 105, 91 (Base) 84,77.

o-Methoxybenzophenone - Irradiation of 0.2 M solution of o-methoxybenzophenone in spectral grade heptane containing 2 M pyridine (100% ketone conversion) afforded a

mixture of two photoproducts. These photoproducts were isolated by flash chromatography and are listed in the order of their elution.

o-Methoxybenzhydrol.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.7=8.1 (m, 9H, Ar-H's), 5.45 (s, 1H, C<u>H</u>-OH), 3.35 (s, 3H, O-CH_3) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ=167.1, 157.7, 145.5, 134.9, 132.3, 129.2, 127.9, 126.1, 125.6, 120.0, 113.4, 82.7 (<u>C</u>H-OH), 56.16 (O-CH_3) ppm.
i.r. (CCl_4): 3500 cm^{-1} (OH), 3040, 3010 cm^{-1} (Ar-CH), 2950, 2925 cm^{-1} (sat. C-H).
mass spectrum: (m/e) 213, 195 (Base), 135, 121, 105, 77.
m.p.: 177-178°C (lit. 141).[134]

3-Phenyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.88-7.50 (m, 9H, Ar-H's), 4.48, 4.66 (AB quartet, J=10.29 Hz, 2H, O-C<u>H</u>$_2$-), 1.42 (br, s, 1H, OH) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ=166.8, 142.5, 132.2, 130.6, 128.3, 127.-, 126.1, 124.4, 121,4, 110.8, 86.13, 82.59 ppm.
i.r. (neat): 3430 cm^{-1} (OH), 3080, 3060, 3030 cm^{-1} (Ar-CH), 2980, 2950, 2890 cm^{-1} (sat. C-H), 1225 cm^{-1} (Ar-O-C).
mass spectrum: (m/e) 212 (M+) (Base), 194, 181, 165, 121, 105, 91, 77.

o-Benzyloxy-5-methylbenzophenone - A degassed solution of o-benzyloxy-5-methylbenzophenone was irradiated at 313 nm (100% ketone conversion). Proton nmr of the crude photolysate revealed it to be mainly 2,3-diphenyl-5-methyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.8-7.4 (m, 14H, Ar-H's), 5.65 (s, 1H, O-CHPh), 2.26 (s, 3H, CH_3), 1.8 (br, s, 1H, OH) ppm.

2,6-Diacetylbenzyloxybenzene - 2-Phenyl-3-methyl-7-acetyl-3-hydroxy-2,3-dihydrobenzofuran was isolated by flash chromatography of the crude photolysate from 2,6-diacetylbenzyloxybenzene in spectral grade cyclohexane (50% ketone conversion). Based upon the proton chemical shift of the methyl protons and the hydroxyl proton it was assigned the Z-stereochemistry. The structural assignment was based upon the following spectral data.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=7.0-8.0 (m, 8H, Ar-H's), 5.46 (s, 1H, O-CHPh), 2.69 (s, 3H, $COCH_3$), 1.77 (s, 3H, $C(OH)CH_3$), 1.48 (br, s, 1H, OH) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ=194.9 (C=O), 190.7, 175.9, 149.6, 130.6, 129.0, 128.8, 128.7, 126.9, 125.7, 121.6, 93.62, 77.30, 31.34, 25.38 ppm.
i.r. (CCl_4): 3560 cm^{-1} (OH), 3050 cm^{-1} (Ar C-H), 2970 cm^{-1} (sat. C-H), 1260 cm^{-1} (Ar-O-C).

mass spectrum: (m/e), 268 (M+), 253, 225, 147 (Base), 119, 105, 91, 77, 43.

2,6-Dibenzoylbenzyloxybenzene - Irradiation (313 nm, 12 hr) of a degassed solution of 2,6-dibenzoylbenzyloxybenzene (50% ketone conversion) in benzene produced a mixture of two photoproducts and starting material. These products were separated by flash chromatography and are listed in the order of elution.

Z-2,3-diphenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=7.0-7.9 (m, 18H, Ar-H's), 5.69 (s, 1H, O-CHPh), 2.19 (br. s, 1H, OH) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ=195.0 (C=O), 142.3, 138.0, 134.5, 133.0, 132.8, 131.7, 129.9, 128.8, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 126.5, 121.6, 95.76, 82.23 ppm.
i.r. (CH_2Cl_2): 3550 cm^{-1} (OH), 3010, 3000 cm^{-1} (Ar C-H), 2900, 2880, cm^{-1} (sat. C-H), 1270 cm^{-1} (Ar-O-C).
mass spectrum: (m/e) 392 (M+), 374, 285 (Base), 181, 105, 91, 77.

E-2,3-diphenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, d_6-acetone): δ=6.8-8.2 (m, 18H, Ar-H's), 5.81 (s, 1H, O-CHPh), 5.70 (s, 1H, OH).
i.r. (CH_2Cl_2): 3570 cm^{-1} (OH), 3020 cm^{-1} (Ar-C-H), 2960,

2900 cm^{-1} (sat. C-H), 1240 cm^{-1} (Ar-O-C).
mass spectrum: (m/e) 392 (M+), 374 (Base), 285, 181, 105, 91, 77.

2,6-Dibenzoylanisole - 3-Phenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran was isolated by flash chromatography from the photolysate of 2,6-dibenzoylanisole in spectral grade cyclohexane (50% ketone conversion). Structural assignment was based upon the following spectral data.

3-Phenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.92-7.99 (m, 13H, Ar-H's), 4.47, 4.65 (AB quartet, J=10.5 Hz, 2H, O-CH_2), 1.2 (br. s, 1H, OH) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ=194.1 (C=O), 157.8, 137.8, 132.8, 132.1, 130.2, 129.9, 128.4, 128.3, 128.2, 127.8, 126.0, 122.3, 122.2, 121.2, 86.76, 81.79 ppm.
i.r. (CH_2Cl_2): 3570 cm^{-1} (OH), 3045 cm^{-1} (Ar C-H), 2950 cm^{-1} (sat. C-HO, 1260 cm^{-1} (Ar-O-CO)
mass spectrum: (m/e) 316 (M+), 298, 221 (Base), 165, 105, 91, 77.

o-Benzyloxyvalerophenone - GC/MS of the photolysate from o-benzyloxyvalerophenone in benzene (313 nm irradiation) contained only o-benzyloxyacetophenone. The mass spectrum of the photoproduct was identical to that of

authentic o-benzyloxyacetophenone. There was also good agreement between the retention times of the photoproduct and authentic sample.

α-(o-Tolyl)acetophenone - α-(o-Tolyl)acetophenone (200 mg) in 300 ml spectral grade cyclohexane was irradiated under a nitrogen atmosphere to 100% ketone conversion (approximately 6 hr). HPLC analysis (Ultrasphere Si column; hexane/ethyl acetate, 95:5; 2.0 ml/min) of the photolysate (200 mg) revealed one major component (>99% pure). The photoproduct was identified as 2-phenyl-2-hydroxyindane on the basis of the following spectral data.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=7.1-7.8 (m, 9H, Ar-H's), 3.49, 3.24 (AB quartet, J=16.4 Hz, 4H, CH_2Ph), 2.15 (br. s, 1H, OH) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=145.8, 140.9, 128.4, 127.2, 126.9, 125.2, 125.0, 83.32, 49.13 ppm.

i.r. (neat): 3770 cm^{-1} (OH), 3080, 3060, 3020 cm^{-1} (Ar C-H), 2920, 2850 cm^{-1} (sat. C-H).

mass spectrum: (m/e) 210 (M+), 192, 105 (Base), 91, 77.

α-(2,5-Dimethylphenyl)acetophenone - α-(2,5-dimethylphenyl)acetophenone (200 mg) in 300 ml spectral grade cyclohexane was irradiated under a nitrogen atmosphere to 100% ketone conversion. Removal of the solvent on a rotary evaporator afforded 200 mg of crude photolysate (colorless

oil) which HPLC analysis (same conditions as α-TAP) revealed to contain one major component (>99% pure). Spectral analysis of the crude photolysate identified the photoproduct as 2-phenyl-5-methyl-2-hydroxyindane. Structural assignment was based upon the following spectral data.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.88-7.41 (m, 8H, Ar-H's), 3.29, 3.02 (AB quartet, J=16.28 Hz, 4H, $C\underline{H}_2$-Ph), 2.21 (s, 3H, Ar-$C\underline{H}_3$) ppm.
^{13}C-nmr (250 MHz, $CDCl_3$): δ=145.9, 141.2, 138.0, 136.4, 128.3, 128.25, 127.6, 127.0, 125.7, 125.2, 124.7, 83.36, 49.04, 48.77, 21.18 ppm.
i.r. (neat): 3540, 3420 cm^{-1} (OH), 3080, 3060, 3030, 3010 cm^{-1} (Ar-C-H), 2940, 2920 cm^{-1} (sat. C-H).
mass spectrum: (m/e) 224 (M+), 206, 191, 119, 105 (Base), 91, 77.

α-Mesitylacetophenone - α-Mesitylacetophenone (200 mg) in 300 ml spectral grade cyclohexane was irradiated under a nitrogen atmosphere to 100% ketone conversion (12 hr). The solvent was removed on a rotary evaporator to afford 200 mg of a pale yellow oil. HPLC analysis of this oil revealed one major component in >99% purity. Spectral analysis identified the photoproduct as 2-phenyl-4,6-dimethyl-2-hydroxyindane on the basis of the following data.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.81-7.49 (m, 7H, Ar-H's), 3.29, 3.02 (AB quartet, J=16.3 Hz, 4H, $C\underline{H}_2Ph$), 2.27 (s, 3H, Ar-CH_3), 2.16 (s, 3H, Ar-$C\underline{H}_3$), 1.26 (br. s, 1H, OH) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=147.6, 140.8, 136.7, 136.4, 133.7, 128.5, 128.1, 126.8, 125.0, 122.8, 82.76, 49.27, 47.60, 21.09, 18.84 ppm.

i.r. (neat): 3520, 3370 cm^{-1} (OH), 3080, 3060, 3020 cm^{-1} (Ar C-H), 2960, 2920, 2860 cm^{-1} (sat. C-H).

mass spectrum: (m/e) 238 (M+), 220, 133, 105 (Base), 91, 77.

α-(2,5-Diisopropylphenyl)acetophenone - α-(2,5-Diisopropylphenyl)acetophenone (200 mg) in 300 ml spectral grade cyclohexane was irradiated to 100% ketone conversion (12 hr) under a nitrogen atmosphere. The solvent was removed on a rotary evaporator to afford 200 mg of a pale yellow oil. HPLC analysis of the oil showed only one major component in >99% purity. Spectral analysis of the crude photolysate identified the photoproduct as 1,1-dimethyl-2-phenyl-5-isopropyl-2-hydroxyindane on the basis of the following data.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=7.1-7.7 (m, 8H, Ar-H's), 3.29, 2.99 (AB quartet, J=16.01 Hz, 2H, $C\underline{H}_2Ph$), 2.90 (m, 1H, -$C\underline{H}$-$(CH_3)_2$), 2.03 (br. s, 1H, OH), 1.35 (s, 3H, $C\underline{H}_3$), 1.28 (d, 6H, -$CH(CH_3)_2$), 0.76 (s, 3H, $C\underline{H}_3$) ppm.

^{13}C-nmr (250 MHz, $CDCl_3$): δ=147.4, 141.9, 138.8, 127.6, 127.0, 126.4, 125.2, 123.2, 123.1, 122.6, 87.23, 43.98, 33.88, 27.80, 24.11, 19.53 ppm.
i.r. (neat): 3420 cm^{-1} (OH), 3080, 3060 cm^{-1} (Ar C-H), 2960, 2860 cm^{-1} (sat. C-H).
mass spectrum: (m/e) 280 (M+), 161, 105 (Base), 91, 77.

α-(2,4,6-Triisopropylphenyl)acetophenone - α-(2,4,6-Triisopropylphenyl)acetophenone (200 mg) in 300 ml spectral grade cyclohexane was irradiated to 100% ketone conversion (24 hr). HPLC analysis of the pale yellow oil (200 mg) obtained after the solvent had been removed indicated only one major component in 95% purity. Spectral analysis of the crude photolysate identified the photoproduct as 1,1-dimethyl-2-phenyl-4,6-diisopropyl-2-hydroxyindane on the basis of the following spectral evidence.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.9-7.63 (m, 7H, Ar-H's), 3.81, 3.08 (AB quartet, J=16.1 Hz, 2H, $C\underline{H}_2Ph$), 2.92 (m, 2H, $-C\underline{H}(CH_3)_2$), 2.14 (br. s, 1H, OH), 1.36 (s, 3H, $C\underline{H}_3$), 1.29 (d, 6H,$-CH(C\underline{H}_3)_2$),0.78 (s, 3H, CH_3).
^{13}C-nmr (250 MHz, $CDCl_3$): δ=148.4, 144.8, 140.8, 133.6, 127.7, 127.1, 126.6, 124.1, 121.5, 118.4, 87.21, 51.62, 42.19, 34.39, 31.06, 28.09, 24.28, 23.07, 22.90, 19.62.
i.r. (neat): 3420 cm^{-1} (OH), 3080, 3060, 3020 cm^{-1} (Ar C-H), 2970, 2900, 2860 cm^{-1} (sat. C-H).
mass spectrum: (m/e) 322 (M+), 231, 217, 203 (Base), 105, 91,77.

α-(o-Benzyloxyphenyl)acetophenone - A solution of 100 mg α-(o-benzyloxyphenyl)acetophenone in 300 ml spectral grade cyclohexane was irradiated under a nitrogen atmosphere to 100% ketone conversion (24 hr). HPLC analysis (Ultrasphere ODS-18 column; acetonitrile/water; 2.0 ml/min) revealed one major component in the crude photolysate (80% pure). Homodecoupled ^{1}H-nmr revealed the presence of two AB quartets. Spectral analysis of the crude photolysate identified the photoproduct as a mixture of Z and E-2,3-diphenyl-3-hydroxy-3,4-dihydrobenzopyran (Z/E = 1.6:1 by proton nmr). The structural assignment was based upon the following spectral data.

^{1}H-nmr (250 MHz, $CDCl_3$): δ=6.7-7.5 (m, 14H, Ar-H's), 5.15 (overlapping s's, 2H, O-C<u>H</u>Ph); 3.67, 300 (AB quartet, E-isomer, J=17.11 Hz, 2H, Ar-C<u>H</u>$_2$); 3.44, 3.08 (AB quartet, Z-isomer, J=16.33 Hz, 2H, Ar-C<u>H</u>$_2$), 1.26 (br. s, 1H, OH). (Homodecoupling experiments helped to unravel both AB systems in the ^{1}H-nmr.)

^{13}C-nmr (250 MHz, $CDCl_3$): δ=154.1, 137.3, 130.1, 129.9, 128.0, 127.9, 127.5, 127.3, 127.1, 126.4, 125.4, 121.3, 121.1, 116.7, 116.5, 84.65, 83.00, 72.08, 40.53, 36.77 ppm.

i.r. (CCl_4): 3580 cm^{-1} (OH), 3080, 3060, 3030 cm^{-1} (Ar C-H), 2950, 2920 cm^{-1} (sat. C-H), 1280 cm^{-1} (Ar-O-C).

mass spectrum: (m/e) 302 (M+), 284, 211, 196, 183, 165, 152, 133, 105 (Base),91, 77.

α-(o-Tolyl)acetone and α-(o-Tolyl)acetaldehyde - 1,2-Di(o-tolyl)ethane was the only photoproduct visible in the proton nmr spectrum of the crude photolysate from either α-(o-tolyl)acetone or α-(o-tolyl)acetaldehyde in spectral grade cyclohexane. Structural assignment was based upon both the proton nmr and the mass spectrum of the crude photolysate.

^{1}H-nmr (60 MHz, $CDCl_3$): δ= 7.0 (s, 4H, Ar-H's), 2.8 (s, 2H, Ar-CH_2), 2.1 (s, 3H, Ar-CH_3) ppm.
mass spectrum: (m/e) 210 (M+), 105 (Base).

APPENDIX

The tables in this Appendix contain the raw data from quantum yield measurements, Stern-Volmer quenching, and sensitization studies. Analysis conditions, appropriate concentrations of the materials used, as well as other pertinent experimental conditions are also furnished. In all cases, g.c. or HPLC peak areas are the average of at least two injections.

Table 32. Quenching of o-Benzyloxyacetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau_1$ = 1750 M^{-1} GC Analysis: 5' 3% QF-1 on Chrom. G

$k_q\tau_2$ = 2420 M^{-1} Column at 220°C.

	A_{photo}/A_{std}		$\phi°/\phi$	
[Q], 10^{-3} M	#1	#2	#1	#2
0.0	0.149[b]	1.18[b,c]	----	----
0.303	0.103	0.703	1.45	1.68
0.606	0.0753	0.566	1.98	1.68
1.21	0.0476	0.301	3.13	3.92
1.82	0.0347	0.188	4.29	6.28
2.42	0.0253	0.118	5.89	10.0

[a] [Ketone] = 0.0388 M, $[C_{20}] = 1.29 \times 10^{-3}$ M, [VP] = 0.110 M, $[C_{15}] = 7.92 \times 10^{-3}$ M.

[b] Actinometer (VP): moles AP = 6.68×10^{-3}; I = 0.0202 ein l^{-1}

moles photoproduct #1 = 2.56×10^{-4}; ϕ = 0.0177

moles photoproduct #2 = 2.02 x10^{-3}; ϕ = 0.100

[c] photoproduct #1 = Z-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran; photoproduct #2 = 2-Acetylbenzophenone.

Table 33. Quenching of o-Benzyloxyacetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a,b]

$k_q\tau$ = 1640 M^{-1} HPLC Analysis: Ultrasphere Si Column, 270 nm
Hexane: EtOAc (95:5)
Flow: 2.0 ml/min

[Q], 10^{-3} M	$(A_{photo}/A_{benzene})$ x 100	$\phi°/\phi$
0.0	2.15	----
0.441	1.41	1.52
0.881	0.919	2.34
1.76	0.538	4.00
2.64	0.326	6.61
3.53	0.222	9.68

[a][Ketone] = 0.034 M.

[b]Quenching of the formation of Z-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 34. Quantum Yield Determination for Photoproducts from o-Benzyloxyacetophenone in Benzene at 25°C.[a]

HPLC Analysis: Ultrasphere Si, 270 nm

Hexane: EtOAc (95:5)

Flow: 2.0 ml/min

	$A_{photo}/A_{benzene}$		mmoles photo			
Tube	#1[c]	#2[c]	#1[c]	#2[c]	$\phi^{c}_{\#1}$	$\phi^{c}_{\#2}$
A	0.0190	0.0303				
B	0.0171	0.0355				
Average	0.0181	0.0329	0.653	1.07	0.027	0.059
VP	0.101		9.53[b]			

[a] [Ketone] = 0.0381 M; [VP] = 0.111 M.

[b] $I = 0.0289$ ein l^{-1}.

[c] #1 = Z-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran.

#2 = 2-Acetylbenzophenone.

Table 35. Quenching of o-Benzyloxyacetophenone in Benzene Containing 1.02 M Pyridine with 2,5-Dimethyl-2,4-Hexadiene at 25°C.[a]

$k_q\tau_1$ = 2250 M^{-1} HPLC Analysis: Ultrasphere Si, 270 nm

$k_q\tau_2$ = 1920 M^{-1} Hexane: EtOAc (95:5)

$k_q\tau_3$ = 2250 M^{-1} Flow: 2.0 ml/min

[Q], 10^{-3} M	A_{photo}/A_{std}			$\phi°/\phi$		
	#1[b]	#2[b]	#3[b]	#1[b]	#2[b]	#3[b]
0.0	0.115	0.0675	0.0361	----	----	----
0.383	0.0726	0.0442	0.0246	1.58	1.53	1.47
0.766	0.0428	0.0286	0.0165	2.41	2.36	2.19
1.53	0.0260	0.0155	0.00927	4.42	4.35	3.89
2.30	0.0177	0.0105	0.00637	6.50	6.43	5.67
3.06	0.0145	0.00845	0.00514	7.93	7.99	7.02

[a][Ketone] = 0.0402 M.

[b]#1 = Z-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran.

#2 = E-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran.

#3 = 2-Acetylbenzophenone.

Table 36. Effects of Pyridine on Photoproduct Quantum Yield for o-Benzyloxyacetophenone in Benzene at 25°C.[a]

HPLC Analysis: Ultrasphere Si, 270 nm

Hexane: EtOAc (95:5)

Flow: 2.0 ml/min

[Pyr], M	A_{photo}/A_{std}	ϕ
0.0	0.0130	0.0226
0.544	0.0360	0.0624
1.09	0.0550	0.0958
1.63	0.0670	0.116
2.18	0.0821	0.143

[a][Ketone] = 0.0197 M, photoproduct = Z-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 37. Quenching of o-Benzyloxybenzophenone in Benzene with 2,5-Dimethyl-2,4-Hexadiene at 25°C.[a]

$k_q\tau$ = 100.1 M^{-1} GC Analysis: 5' 3% QF-1 on Chrom G 180°C

[Q], 10^{-2} M	A^b_{photo}/A_{std}	$\phi°/\phi$
0.0	12.65	----
0.518	7.85	1.61
1.04	6.47	1.96
2.07	4.02	3.15
3.11	3.08	4.11

[a][Ketone] = 0.038 M, $[C_{24}]$ = 7.87 x 10^{-4} M, 313 nm

[b]Z and E 2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran have the same retention.

Table 38. Quenching of o-Benzyloxybenzophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 112.4 M^{-1}

[Q], 10^{-2} M	A^b_{photo}/A_{std}	$\phi°/\phi$
0.0	6.71	----
0.487	4.38	1.53
0.974	3.17	2.11
1.95	2.04	3.29
2.92	1.50	4.48
3.90	1.28	5.24

[a][Ketone] = 0.0408 M, $[C_{24}]$ = 9.82 x 10^{-4} M, 313 nm.

[b]Z and E-2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 39. Quantum Yield for Photoproduct from o-Benzyloxybenzophenone in Benzene at 25°C.[a]

GC Analysis: 5' 3% QF-1 on Chrom G

180°C

Sample	$A_{photo}/_{std}$	Moles Photoproduct	ϕ^{c}_{pdt}
A	7.60	0.014	
B	7.63	0.0138	
Average	7.62	0.0139	0.938
VP	0.260	4.89×10^{-3}[b]	

[a][Ketone] = 0.0395 M, $[C_{24}] = 1.36 \times 10^{-3}$ M; [VP] = 0.111 M, $[C_{15}]$ = 0.01 M; 313 nm.

[b]I = 0.0148 ein l^{-1}.

[c]E and Z- 2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 40. Quantum Yield for Photoproduct from o-Benzyloxybenzophenone in Benzene at 25°C.[a]

HPLC Analysis: Ultrasphere Si, 270 nm

Hexane: EtOAc (93:7)

Flow: 1.0 ml/min

	$A_{photo}/A_{benzene}$		moles photo			
Sample	#1[c]	#2[c]	#1[c]	#2[c]	$\phi^{c}_{\#1}$	$\phi^{c}_{\#2}$
A	0.434	0.0543				
B	0.375	0.0466				
Average	0.405	0.0504	0.0154	0.002	0.831	0.108
VP	0.0599		0.00611[b]			

[a][Ketone] = 0.04 M, [VP] = 0.108 M, 313 nm. [b]I = 0.0185 ein l^{-1}

[c]#1 = Z-2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran.
#2 = E-2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 41. Quenching of o-Benzyloxybenzophenone with n-Octyl Mercaptan in Benzene at 25°C.[a]

$k_q\tau = 0.58$[b] M^{-1} GC Analysis: 5' 3% QF-1 on Chrom G 180°C

[Q], M	A^{c}_{photo}/A_{std}	$\phi°/\phi$
0.0	7.60	----
0.159	6.78	1.12
0.319	6.15	1.24
0.638	5.65	1.35
0.957	4.90	1.55
1.28	4.46	1.71

[a] [Ketone] = 0.0395 M, $[C_{24}] = 1.36 \times 10^{-3}$ M, 313 nm.
[b] τ = 40 nsec assuming $k_q = 1.4 \times 10^{7} M^{-1}s^{-1}$.
[c] Both E and Z benzofuranols.

Table 42. Quenching of o-Benzyloxybenzophenone with n-Octyl Mercaptan in Benzene at 25°C.[a]

$k_q\tau = 0.612$ M^{-1}

[Q], M	A^{c}_{photo}/A_{std}	$\phi°/\phi$
0.0	17.26	----
0.153	15.13	1.14
0.306	13.37	1.29
0.612	11.47	1.51
0.918	10.09	1.72
1.224	10.02	1.78

[a] [Ketone] = 0.0411 M $[C_{24}] = 4.79 \times 10^{-4}$ M, 313 nm.
[b] τ = 40.1 nsec. [c] Both E and Z benzofuranols.

Table 43. Quenching of o-Benzyloxybenzophenone by 2,5-Dimethyl-2,4-Hexadiene in 1,4-Dioxane at 25°C.[a]

$k_q\tau$ = 51.5 M^{-1} GC Analysis: 5' 3% QF-1 on Chrom G 180°C

[Q], 10^{-2} M	A^c_{photo}/A_{std}	$\phi°/\phi$
0.0	5.77[b]	----
0.645	4.31	1.34
1.29	3.17	1.82
2.58	2.48	2.31
3.87	1.95	2.96
5.16	1.53	3.77
VP	0.383[b]	

[a] [Ketone] = 0.043 M, $[C_{24}]$ = 6.21 x 10^{-4} M, [VP] = 0.103 M, $[C_{15}]$ = 4.76 x 10^{-3} M, 313 nm.

[b] [AP] in aceinometer = 3.43 x 10^{-3} M; I = 0.0104 ein l^{-1} [Photoproduct] = 4.78 x 10^{-3} M; ϕ_{pdt} = 0.46.

[c] Both E and Z benzofuranols.

Table 44. Quenching of o-Benzyloxy-5-Methylbenzophenone by 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 160 M^{-1} GC Analysis: 5' 3% QF-1 on Chrom G 205°C

[Q], 10^{-2} M	A^c_{photo}/A_{std}	$\phi°/\phi$
0.0	0.787[b]	----
0.768	0.338	2.33
1.54	0.220	3.58
3.07	0.134	5.87
4.61	0.103	7.63
6.14	0.0707	11.13
VP	0.206[b]	

[a] [Ketone] = 0.0395 M, $[C_{26}]$ = 7.6 x 10^{-4} M, [VP] = 0.108 M, $[C_{15}]$ = 0.0118 M, 313 nm.

[b] [AP] = 4.57 x 10^{-3} M; I = 0.0138 ein l^{-1}, [Photoproduct] = 7.87 x 10^{-3} M; ϕ_{pdt} = 0.57.

[c] 2,3-diphenyl-5-methyl-3-hydroxy-2,3-dihydrobenzofuran, stereochemistry of the photoproduct is undetermined.

Table 45. Quenching of o-Benzyloxy-5-Methylbenzophenone in Benzene with 2,5-Dimethyl-2,4-Hexadiene at 25°C.[a]

$k_q\tau$ = 169 M^{-1}. GC Analysis: 5' 3% QF-1 on Chrom G 205°C

[Q], 10^{-2} M	mmoles photoproduct[c]	$\phi°/\phi$
0.0	7.67[b]	----
0.552	3.92	1.96
1.10	2.61	2.94
2.21	1.54	4.98
3.31	1.18	6.50
4.42	0.901	8.81
VP	4.87[b]	

[a] [Ketone] = 0.0402 M, $[C_{26}]$ = 1.44 x 10^{-3} M, [VP] = 0.110 M, $[C_{15}]$ = 5.57 x 10^{-3} M.

[b] [AP] = 4.87 x 10^{-3} M; I = 0.0148 ein l^{-1}, [Photoproduct] = 7.67 x 10^{-3} M; ϕ_{pdt} = 0.520.

[c] 2,3-Diphenyl-5-methyl-3-hydroxy-2,3-dihydrobenzofuran, photoproduct stereochemistry is undetermined.

Table 46. Quenching of 2,2'-Dibenzyloxybenzophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a,c]

$k_q\tau$ = 71.7 M^{-1} GC Analysis: 6' 5% OV-101 on Chrom G 250°C

[Q], M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	2.04[b]	----
0.0188	0.982	2.08
0.0377	0.607	3.36
0.0753	0.318	6.43
0.113	0.239	8.91
0.151	0.174	11.59
VP	0.170[b]	

[a] [Ketone] = 0.0387 M; $[C_{26}] = 1.37 \times 10^{-3}$ M; [VP] = 0.108 M; $[C_{15}] = 6.13 \times 10^{-3}$ M, 313 nm.

[b] [AP] = 1.95×10^{-3} M; I = 5.92×10^{-3} ein l^{-1}, [Photoproduct] = 2.69×10^{-3} M; ϕ_{pdt} = 0.455.

[c] Photoproduct assumed to be 2-phenyl-3-(o-benzyloxyphenyl)-3-hydroxy-2,3-dihydrobenzofuran.

Table 47. Quenching of 2,2'-Dibenzyloxybenzophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a,c]

$k_q\tau$ = 65.8 M^{-1} GC Analysis: 6' 5% OV-101 on Chrom G 250°C

[Q], M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	2.04[b]	----
0.0196	0.982	2.08
0.0391	0.597	3.42
0.0782	0.354	5.76
0.117	0.241	8.48
VP	0.196[b]	

[a] [Ketone] = 0.0406 M, $[C_{26}]$ = 1.31 x 10^{-3} M, [VP] = 0.106 M, $[C_{15}]$ = 5.00 x 10^{-3} M, 313 nm.

[b] [AP] = 1.84 x 10^{-3} M; I = 5.58 x 10^{-3} ein l^{-1}, [Photoproduct] = 2.57 x 10^{-3} M; ϕ = 0.461.

[c] Photoproduct was assumed to be 2-phenyl-3-(o-benzyloxyphenyl)-3-hydrogen-2,3-dihydrobenzofuran.

Table 48. Quenching of o-Methoxybenzophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a,c]

$k_q\tau$ = 2330 M^{-1} GC Analysis: 6' 3% QF-1 on Chrom G 180°C

[Q], 10^{-4} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	2.70[b]	----
0.205	2.60	1.01
0.408	2.54	1.06
0.816	2.27	1.19
1.22	2.08	1.30
1.63	1.94	1.39
VP	0.191[b]	

[a] [Ketone] = 0.0405 M, $[C_{21}]$ = 1.32 x 10^{-3} M, [VP] = 0.114 M, $[C_{15}]$ = 0.0139 M, 313 nm.

[b] [AP] = 5.00 x 10^{-3} M; I = 0.0152 ein l^{-1}, [Photoproduct] = 5.35 x 10^{-3} M; ϕ = 0.352.

[c] Photoproduct = 3-phenyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 49. Quenching of o-Methoxybenzophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a,c]

$k_q\tau$ = 2810 M^{-1} GC Analysis: 6' 3% QF-1 on Chrom G 180°C

[Q], 10^{-3} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	3.78[b]	----
0.183	2.66	1.48
0.366	2.09	1.88
0.732	1.26	3.11
1.10	0.906	4.42
1.46	0.709	5.61
VP	0.959[b]	

[a][Ketone] = 0.0411 M, $[C_{21}]$ = 1.39 x 10^{-3} M, [VP] = 0.103 M, $[C_{15}]$ = 2.55 x 10^{-3} M, 313 nm.

[b][AP] = 4.6 x 10^{-3} M; I = 0.0139 ein l^{-1}, [Photoproduct] = 5.63 x 10^{-3} M; ϕ = 0.404.

[c]Photoproduct = 3-phenyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 50. Quantum Yield for Photoproduct from o-Methoxybenzophenone in Benzene at 25°C.[a]

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (95:5)
Flow: 2.0 ml/min
270 nm

Sample	A_{photo}/A_{std}	mmoles photo.[c]	ϕ
A	0.158		
B	0.172		
Average	0.161	5.54	0.299
VP	0.0599	6.11[b]	

[a][Ketone] = 0.0370 M; [VP] = 0.099 M, 313 nm.

[b]$I = 0.0185$ ein l^{-1}.

[c]Photoproduct = 3-phenyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 51. Quenching of o-Benzyloxyvalerophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a,c]

$k_q\tau$ = 273 M^{-1} GC Analysis: 5' 3% QF-1 on Chrom G 220°C

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	3.88[b]	----
0.347	1.75	2.22
0.694	1.26	3.08
1.39	0.751	5.17
2.08	0.483	8.03
2.78	0.438	8.85
VP	0.699[b]	

[a][Ketone] = 0.0401 M, $[C_{22}]$ = 1.26 x 10^{-3} M, [VP] = 0.105 M, $[C_{15}]$ = 0.0103 M, 313 nm.

[b][AP] = 0.0135 M; I = 0.0409 ein l^{-1}, [Photoproduct] = 7.77 x 10^{-3} M; ϕ = 0.19.

[c]Photoproduct = o-benzyloxyzcetophenone.

Table 52. Quenching of o-Benzyloxyvalerophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a,c]

$k_q\tau$ = 309 M^{-1} GC Analysis: 5' 3% QF-1 on Chrom G 220°C

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.692[b]	----
0.182	0.319	2.16
0.364	0.231	2.99
0.727	0.152	4.54
1.09	0.117	5.90
1.45	0.0913	7.56
VP	0.0917[b]	

[a] [Ketone] = 0.041 M, $[C_{22}]$ = 2.45 x 10^{-3} M, [VP] = 0.105 M, $[C_{15}]$ = 0.0196 M.

[b] [AP] = 3.38 x 10^{-3} M; I = 0.0102 ein l^{-1}, [Photoproduct] = 2.69 x 10^{-3} M; ϕ = 0.260.

[c] Photoproduct = o-benzyloxyacetophenone.

Table 53. Quenching of o-Benzyloxyvalerophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a,c]

$k_q\tau$ = 295 M^{-1} GC Analysis: 5' 3% QF-1 on Chrom G 220°C

[Q], 10^{-3} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	2.37[b]	----
1.08	1.55	1.53
2.16	1.11	2.14
4.32	0.886	2.67
6.48	0.668	3.55
8.64	0.678	3.50
VP	0.292[b]	

[a][Ketone] = 0.0392 M, $[C_{22}]$ = 1.4 x 10^{-3} M, [VP] = 0.103 M, $[C_{15}]$ = 0.0109 M, 313 nm.

[b][AP] - 5.98 x 10^{-3} M; I = 0.0181 ein l^{-1}, [Photoproduct] = 5.27 x 10^{-3} M; ϕ = 0.291.

[c]Photoproduct = o-benzyloxyacetophenone.

Table 54. Effects of Pyridine on Quantum Yield for o-benzyloxyacetophenone Formation from o-Benzyloxyvalerophenone in Benzene at 25°C.[a]

HPLC Analysis: Ultrasphere Si

Hexane: EtOAc (95:5)

Flow: 1.7 ml/min

270 nm

[Pyr], M	A_{photo}/A_{std}	ϕ_{II}
0.0	0.0456	0.300
0.226	0.0675	0.444
0.453	0.0768	0.505
0.679	0.0783	0.515
0.906	0.0799	0.526

[a][Ketone] = 0.0195 M, 313 nm.

Table 55. Quenching of 2,6-Dibenzoylbenzyloxybenzene in Benzene with 2,5-Dimethyl-2,4-Hexadiene at 25°C.[a]

$k_q\tau_1$ = 14.7 M^{-1}

$k_q\tau_2$ = 13.4 M^{-1}

HPLC Analysis: Ultrasphere Si

Hexane: EtOAc (9:1)

Flow: 2.2 ml/min

270 nm

	A_{photo}/A_{std}		$\phi°/\phi$	
[Q], M	#1	#2	#1	#2
0.0	0.361[b]	0.0990[b]	----	----
0.0192	0.219	0.0654	1.58	1.51
0.0394	0.195	0.0595	1.76	1.67
0.0789	0.143	0.0436	2.40	2.27
0.118	0.124	0.0377	2.77	2.63
0.158	0.100	0.0308	3.42	3.22
VP	0.0192[b]			

[a] [Ketone] = 0.0411 M, [VP] = 0.112 M, 313 nm.

[b] [AP] = 1.81 x 10^{-3} M; I = 5.49 x 10^{-3} ein l^{-1}, [Photoproduct 1] = 4.62 x 10^{-3} M; ϕ = 0.842, [Photoproduct 2] = 1.41 x 10^{-3} M; ϕ = 0.257. Photoproduct #1 = Z-2,3-diphenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran. Photoproduct #2 = E-isomer.

Table 56. Quenching of 2,6-Dibenzoyloxybenzene in Benzene with 2,5-Dimethyl-2,4-Hexadiene at 25°C.[a]

$k_q\tau_1$ = 14.2 M^{-1}

$k_q\tau_2$ = 13.5 M^{-1}

HPLC Analysis: Ultrasphere Si

Hexane: EtOAc (9:1)

Flow: 2.2 ml/min

270 nm

	A_{photo}/A_{std}		$\phi°/\phi$	
[Q], M	#1	#2	#1	#2
0.0	0.142[b]	0.0420[b]	----	----
0.0226	0.0818	0.0252	1.74	1.67
0.0452	0.0652	0.0201	2.18	2.09
0.0904	0.0462	0.0147	3.03	2.87
0.136	0.0393	0.0123	3.61	3.41
0.181	0.0302	0.0095	4.70	4.42
VP	0.0069[b]			

[a] [Ketone] = 0.0207 M, [VP] = 0.102 M.

[b] [SP = 6.51 x 10^{-4} M; I = 1.97 x 10^{-3} ein l^{-1}, [Photoproduct 1] = 1.82 x 10^{-3} M; ϕ = 0.92, [Photoproduct 2] = 6.17 x 10^{-4} M; ϕ = 0.31, Photoproduct #1 = Z-Benzofuranol; photoproduct #2 = E-Benzofuranol.

Table 57. Quenching of 2,6-Diacetylbenzyloxybenzene with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 69.5 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (9:1)
Flow: 2.0 ml/min
270 nm

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.0239[b]	----
0.943	0.0117	1.86
1.89	0.0085	2.57
3.77	0.00579	3.77
5.60	0.00426	5.12
7.54	0.00337	6.48
VP	0.00916 M AP[b]	

[a][Ketone] = 0.02 M, [VP] = 0.110 M.

[b][AP] = 0.00916 M; I = 0.0267 ein l^{-1}, [Photoproduct] = 4.53 x 10^{-3} M; ϕ = 0.163; Photoproduct = Z-2-phenyl-3-methyl-7-acetyl-3-hydroxy-2,3-dihydrobenzufuran.

Table 58. Quenching of 2,6-Diacetylbenzyloxybenzene in Benzene with 2,5-Dimethyl-2,4-Hexadiene at 25°C.[a]

$k_q\tau$ = 76.1 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (9:1)
Flow: 2.0 ml/min
270 nm

[Q], 10^{-2} M	(A_{photo}/A_{std}) x 100	$\phi°/\phi$
0.0	1.74[b]	----
0.973	0.917	1.90
1.95	0.650	2.68
3.89	0.429	4.06
5.84	0.318	5.48
7.79	0.243	7.16
VP	6.23×10^{-3} M AP[b]	

[a][Ketone] = 0.0193 M, [VP] = 0.107 M, 313 nm.

[b][AP] = 6.23×10^{-3} M; I = 0.0189 ein l^{-1}, [Photoproduct] = 3.31×10^{-3} M; ϕ = 0.175; Photoproduct = Z-benzofuranol.

Table 59. Quenching of 2,6-Dibenzoylanisole with 2,5-Dimethyl-2,4-hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 247 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (9:1)
Flow: 2.0 ml/min
270 nm

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.391	----
0.197	0.234	1.67
0.393	0.185	2.11
0.787	0.126	3.10
1.18	0.0990	3.95
1.57	0.0765	5.11

[a][Ketone] = 0.0191 M, 313 nm. Photoproduct = 3-phenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 60. Quenching of 2,6-Dibenzoylanisole with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 206 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (9:1)
Flow: 2.0 ml/min
270 nm

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.912	----
0.201	0.568	1.61
0.402	0.427	2.14
0.804	0.311	2.93
1.21	0.236	3.86
1.61	0.202	4.51

[a][Ketone] = 0.0219 M, 313 nm. Photoproduct = 3-phenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 61. Quantum Yield for Photoproduct Formation from 2,6-Dibenzoylanisole in Benzene at 25°C.[a]

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (9:1)
Flow: 2.0 ml/min
270 nm

Sample	A_{photo}/A_{std}	mmoles photo.	ϕ_{pdt}
A	0.406		
B	0.398		
Average	0.400	5.56	0.77
VP	0.0253	2.39[b]	

[a] [Ketone] = 0.0205 M; [VP] = 0.105 M, 313 nm.

[b] $I = 7.24 \times 10^{-3}$ ein l^{-1}; photoproduct = 3-phenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran.

Table 62. Quenching of α-(o-Tolyl)acetophenone with 2,5-Dimethyl-2,4-hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 29.3 M^{-1} GC Analysis: 6' 3% QF-1 on Chrom G 185°C

[Q], 10^{-2} M	mmoles photoproduct	$\phi°/\phi$
0.0	2.33[b]	----
0.937	1.87	1.25
1.87	1.57	1.49
3.75	1.05	2.22
5.62	0.878	3.65
7.49	0.563	4.14
VP	0.854[b]	

[a][Ketone] = 0.0261 M, $[C_{21}]$ = 9.59 x 10^{-4} M, [VP] = 0.124 M, $[C_{15}]$ = 0.0105 M, 313 nm.

[b]I = 2.85 x 10^{-3} ein l^{-1}; photoproduct = 2-phenyl-2-hydroxyindane.

Table 63. Quenching of α-(o-Tolyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 31.8 M^{-1}

[Q], 10^{-2} M	mmoles photoproduct	$\phi°/\phi$
0.0	3.68[b]	----
0.843	2.77	1.33
1.69	2.21	1.67
3.37	1.69	2.18
5.06	1.50	2.46
6.74	1.17	3.15

[a][Ketone] = 0.025 M, $[C_{24}]$ = 7.69 x 10^{-4} M; photoproduct = 2-phenyl-2-hydroxyindane.

Table 64. Quenching of α-(2,5-Dimethylphenyl)acetophenone with 2,5-Dimethyl-2,4-hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 18.8 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (95:5)
Flow: 2.0 ml/min
270 nm

[Q], M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.109	----
0.032	0.0724	1.51
0.064	0.0512	2.13
0.128	0.0339	3.22
0.192	0.0226	4.82
0.256	0.0163	6.69

[a][Ketone] = 0.0253 M, 313 nm; photoproduct = 2-phenyl-5-methyl-2-hydroxyindane.

Table 65. Quenching of α-(2,5-Dimethylphenyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 19.6 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (95:5)
Flow: 2.0 ml/min
270 nm

[Q], M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.110[b]	----
0.0325	0.0720	1.52
0.0651	0.0524	2.10
0.130	0.0380	3.33
0.195	0.0234	4.70
0.260	0.0164	6.71
VP	0.0315[b]	

[a][Ketone] = 0.0244 M, [VP] = 0.105 M, 313 nm.

[b][AP] = 2.97 x 10^{-3} M; I = 0.009 ein l^{-1}; [Photoproduct] = 5.08 x 10^{-3} M; ϕ = 0.653; photoproduct = 2-phenyl-5-methyl-2 hydroxyindane.

Table 66. Quenching of α-Mesitylacetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 4.45 M^{-1}

HPLC Analysis: Ultrasphere ODS-18

CH_3CN - H_2O

Flow: 2.0 ml/min

270 nm

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.559	----
0.889	0.517	1.08
1.78	0.490	1.14
3.56	0.481	1.16
5.33	0.446	1.25
7.11	0.405	1.38

[a][Ketone] = 0.0225 M, 313 nm; photoproduct = 2-phenyl-4,6-dimethyl-2-hydroxyindane.

Table 67. Quenching of α-Mesitylacetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 4.73 M^{-1}

HPLC Analysis: Ultrasphere ODS-18

CH_3CN - H_2O

Flow: 2.0 ml/min

270 nm

[Q], M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.570	----
0.0335	0.487	1.17
0.0670	0.419	1.36
0.134	0.365	1.56
0.201	0.286	2.01
0.268	0.251	2.27

[a][Ketone] = 0.0221 M, 313 nm; photoproduct = 2-phenyl-4,6-dimethyl-2-hydroxyindane.

Table 68. Quantum Yield for Photoproduct from α-Mesityl-acetophenone in Benzene at 25°C.[a]

Sample	A_{photo}/A_{std}	mmoles photoprod.	ϕ_{pdt}
A	0.0101		
B	0.00965		
Average	0.00987	7.99	0.471
VP	0.0600	5.66[b]	

[a][Ketone] = 0.025 M, [VP] = 0.104 M, 313 nm.

[b]I = 0.0172 ein l^{-1}; photoproduct = 2-phenyl-4,6-dimethyl-2-hydroxyindane.

Table 69. Effects of Pyridine on Quantum Yield for Photoproduct from α-Mesitylacetophenone in Benzene at 25°C.[a]

[Pyridine], M	A_{photo}/A_{std}	ϕ_{pdt}
0.0	0.0267	0.44
0.117	0.0279	0.46
0.233	0.0295	0.486
0.467	0.0309	0.509
0.700	0.0308	0.508
0.933	0.0329	0.542

[a][Ketone] = 0.0231 M, 313 nm; photoproduct = 2-phenyl-4,6-dimethyl-7-hydroxyindane.

Table 70. Quenching of α-(2,5-Diisopropylphenyl)acetophenone with 2,5-Dimethyl-2,4-hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 3.44 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (95:5)
Flow: 2.0 ml/min
270 nm

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.216	----
0.93	0.192	1.13
1.86	0.181	1.20
3.72	0.184	1.17
5.58	0.168	1.29
7.44	0.158	1.37

[a][Ketone] = 0.0263 M, 313 nm; photoproduct = 1,1-Dimethyl-2-phenyl-5-isopropyl-2-hydroxyindane.

Table 71. Quenching of α-(2,5-Diisopropylphenyl)acetophenone in Benzene with 2,5-Dimethyl-2,4-Hexadiene at 25°C.[a]

$k_q\phi$ = 3.27 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (95:5)
Flow: 2.0 ml/min
270 nm

[Q], M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.107[b]	----
0.081	0.0794	1.29
0.162	0.0722	1.41
0.324	0.0514	1.98
0.486	0.0403	2.53
0.648	0.0326	3.13
VP	4.96×10^{-3} M AP	

[a][Ketone] = 0.025 M; [VP] = 0.105 M, 313 nm.

[b]I = 0.0150 ein l^{-1}; [Photoproduct] = 6.23×10^{-3} M; ϕ = 0.415; photoproduct = 1,1-Dimethyl-2-phenyl-5-isopropyl-2-hydroxyindane.

Table 72. Quenching of α-(2,4,6-Triisopropylphenyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 3.51 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (99:1)
Flow: 2.0 ml/min
270 nm

[Q], M	A_{photo}/A_{std} x 100	$\phi°/\phi$
0.0	1.53[b]	----
0.123	0.915	1.67
0.246	0.777	1.97
0.492	0.533	2.87
0.737	0.402	3.81
0.983	0.330	4.64
VP	0.839[b]	

[a][Ketone] = 0.0259 M; [VP] = 0.103 M, [C_{15}] = 0.01 M, 313 nm.

[b][AP] = 0.058 M; I = 0.0478 ein l^{-1}; [Photoproduct] = 2.03 x 10^{-3} M; ϕ = 0.0425; photoproduct = 1,1-Dimethyl-2-phenyl-4,6-diisopropyl-2-hydroxyindane.

Table 73. Quenching of α-(2,4,6-Triisopropylphenyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau$ = 2.98 M^{-1}

HPLC Analysis: Ultrasphere Si
Hexane: EtOAc (99:1)
Flow: 2.0 ml/min
270 nm

[Q], M	A_{photo}/A_{std} x 100	$\phi°/\phi$
0.0	1.30[b]	----
0.126	0.743	1.75
0.252	0.622	2.09
0.504	0.460	2.83
0.756	0.378	3.44
1.01	0.299	4.35
VP	0.672[b]	

[a][Ketone] = 0.0229 M; [VP] = 0.103 M; [C_{15}] = 0.0115 M, 313 nm.

[b][AP] = 0.0145 M; I = 0.0439 ein l^{-1}; [Photoproduct] = 1.73 x 10^{-3} M; ϕ = 0.0394; photoproduct = 1,1-Dimethyl-2-phenyl-4,6-diisopropyl-2-hydroxyindane.

Table 74. Sensitization of the Cis-Trans Isomerization of cis-Piperylene with o-Benzyloxyacetophenone in Benzene at 25°C.[a]

$k_q\tau$ = 62.8 M^{-1} GC Analysis: 25' 25% 1,2,3-Tris-(2-cyanoethyl)propane on Chromsorb P

ϕ_{isc} = 0.97

$[c\text{-}P]^{-1}$, M^{-1}	β_{corr}	ϕ_{c-t}	$0.55/\phi_{c-t}$
23.4	0.203	0.439	1.25
11.7	0.103	0.446	1.23
7.81	0.0741	0.480	1.15
5.95	0.0561	0.485	1.13
4.67	0.0455	0.492	1.12
3.90	0.0383	0.498	1.11
2.92	0.0298	0.516	1.07
AP	0.0423[b]		

[a] [Ketone] = 1.49 x 10^{-3} M; [AP] = 0.102 M, 313 nm.

[b] [c-P] in Actinometer = 0.257 M; I = 0.0109 ein l^{-1}.

Table 75. Sensitization of Cis-Trans Isomerization of cis-Piperylene with o-Benzyloxyacetophenone in Benzene at 25°C.[a]

$k_q \tau = 63.6\ M^{-1}$ GC Analysis: 25' 25% 1,2,3-Tris-(2-cyanoethyl)propane on Chromsorb P

$\phi_{isc} = 1.00$

$[c\text{-}P]^{-1}$, M^{-1}	β_{corr}	$\phi_{c\text{-}t}$	$0.55/\phi_{c\text{-}t}$
23.20	0.0698	0.494	1.18
11.60	0.103	0.485	1.13
7.75	0.0698	0.494	1.11
5.78	0.0548	0.517	1.06
4.63	0.0445	0.527	1.04
3.86	0.0382	0.543	1.01
2.90	0.0387	0.543	1.01
AP	0.0543[b]		

[a] [Ketone] = 1.41×10^{-3} M; [AP] = 0.104 M, 313 nm.

[b] [c-P] in Actinometer = 0.172 M; I = 8.44×10^{-3} ein l^{-1}.

Table 76. Sensitization of Trans-Cis Isomerization of trans-Stilbene with o-Benzyloxybenzophenone in Benzene at 25°C.[a]

$k_q\tau$ = 110 M^{-1} GC Analysis: 6' 20% SE-30 on Chrom G

ϕ_{isc} = 0.97 180°C

$[t\text{-}S]^{-1}$, M^{-1}	β_{corr}	$\phi_{t\text{-}s}$	$0.41/\phi_{t\text{-}s}$
55.0	0.118	0.265	1.55
27.6	0.0771	0.345	1.19
36.6	0.0862	0.289	1.42
18.4	0.0499	0.333	1.23
13.8	0.0388	0.347	1.18
AP	0.0613[b]		

[a][Ketone] = 0.0435 M; [BP] = 0.103 M, 366 nm.

[b][t-S] in Actinometer = 0.0545 M; I = 8.13 x 10^{-3} ein l^{-1}.

Table 77. Sensitization of Trans-Cis Isomerization of trans-Stilbene with o-Benzyloxybenzophenone in Benzene at 25°C.[a]

$k_q\tau$ = 106 M^{-1} GC Analysis: 6' 20% SE-30 on Chrom G

ϕ_{isc} = 0.92 180°C

$[t\text{-}S]^{-1}$, M^{-1}	β_{corr}	$\phi_{c\text{-}t}$	$0.41/\phi_{c\text{-}t}$
93.5	0.173	0.203	2.02
46.7	0.109	0.256	1.60
31.2	0.080	0.282	1.46
23.4	0.0639	0.300	1.37
15.6	0.0472	0.332	1.23
11.7	0.0382	0.359	1.14
BP1	0.170[b]		
BP2	0.0599[b]		

[a] [Ketone] = 0.0392 M; [BP] = 0.104 M, 366 nm.

[b] [t-S] in BP1 = 0.0214 M; [t-S] in BP] = 0.0642 M; I = 9.12 x 10^{-3} ein l^{-1}.

Table 78. Determination of k_q for o-Benzyloxyacetophenone and 2,5-Dimethyl-2,4-hexadiene in Benzene at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 2.91 \times 10^9 M^{-1}s^{-1}$ $\lambda = 420$ nm

[Q], 10^{-3}M	k, $10^6 s^{-1}$
0.0	2.14
0.0279	2.35
0.0558	2.29
0.111	2.35
0.166	2.45
0.275	3.06

[a][Ketone] = 0.014 M; τ_T = 469 nsec (420 nm); τ_T = 438 nsec (390 nm).

Table 79. Determination of k_q for o-Benzyloxyacetophenone and 2,5-Dimethyl-2,4-hexadiene in Benzene at 27°C by Laser Flash Spectroscopy.

$k_q = 1.41 \times 10^9 N^{-1}s^{-1}$

[Q], 10^{-3}M	k, $10^6 s^{-1}$
0.0	2.23
0.0700	3.12
0.140	3.75
0.209	4.15
0.347	5.22
0.517	6.92
0.854	13.80
1.18	18.90

Table 80. Determination of k_q for o-Benzyloxybenzophenone and 2,5-Dimethyl-2,4-hexadiene at 27°C in Benzene by Laser Flash Spectroscopy.[a]

$k_q = 1.94 \times 10^9 M^{-1}s^{-1}$ $\lambda = 550$ nm.

[Q], 10^{-2}M	k, 10^6 s^{-1}
0.0	18.2
1.40	19.9
2.79	22.6
4.17	23.7
6.93	31.20
10.30	37.6

[a][Ketone] = 0.008 M; $\tau_T = 56.2$ nsec $\lambda = 550$ nm
$\tau_T = 48.7$ nsec $\lambda = 390$ nm

Table 81. Determination of k_q for o-Benzyloxyvalerophenone with 2,5-Dimethyl-2,4-hexadiene in Benzene at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 2.94 \times 10^9 M^{-1}s^{-1}$ $\lambda = 380$ nm

[Q], 10^{-3}M	k, $10^6 s^{-1}$
0.0	14.8
0.138	15.6
0.276	16.0
0.415	16.4
0.686	16.9

[a][Ketone] = 0.0128 M; $\tau_T = 79.7$ nsec (380 nm); $\tau_T = 86.1$ nsec (420 nm).

Table 82. Determination of k_q for 2,2'-Dibenzyloxybenzophenone with 2,5-Dimethyl-2,4-hexadiene in Benzene at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 8.27 \times 10^6 M^{-1}s^{-1}$ $\lambda = 570$ nm

[Q], 10^{-3}M	k, $10^6 s^{-1}$
0.00	14.0
6.99	18.3
14.0	27.6
27.9	35.2
41.7	48.9

[a][Ketone] = 4.68×10^{-3}M; τ_T = 66.9 nsec (570 nm); τ_T = 72.8 nsec (570 nm).

Table 83. Determination of k_q for 2,6-Dimethoxybenzophenone with 2,5-Dimethyl-2,4-hexadiene in Benzene at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 3.26 \times 10^9 M^{-1}s^{-1}$ $\lambda = 420$ nm

[Q], 10^{-3}M	k, $10^6 s^{-1}$
0.00	0.733
0.0696	0.958
0.138	1.14
0.345	1.84
0.686	2.87
1.02	3.94
1.36	5.23

[a][Ketone] = 0.0125 M; τ_T = 1916 nsec (420 nm); τ_T = 1901 nsec (685 nm).

Table 84. Determination of k_q for o-Methoxybenzophenone with 2,5-Dimethyl-2,4-hexadiene in Benzene at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 6.77 \times 10^9 M^{-1}s^{-1}$ $\lambda = 520$ nm

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.00	1.28
0.0692	1.60
0.138	2.30
0.345	3.54
0.686	6.67
1.02	7.79

[a][Ketone] = 0.005 M; τ_T = 783.2 nm (520 nm); τ_T = 1262 nm (400 nm); τ_T = 961.3 nm (380 nm); τ_T = 1003 nm (390 nm).

Table 85. Determination of k_q for o-Methoxybenzophenone and 2,5-Dimethyl-2,4-Hexadiene in Methanol at 27°C by Laser Flash Spectroscopy.

$k_q = 8.24 \times 10^9 M^{-1}s^{-1}$ $\lambda = 700$ nm.

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.0	8.26
0.699	12.10
1.39	18.40
2.09	25.30

[a][Ketone] = 0.005 M; τ_1 = 121.1 nsec - λ = 700 nm; τ_2 = 206.1 nsec - λ = 520 nm.

Table 86. Determination of k_q for 2,6-Dimethoxybenzophenone and 2,5-Dimethyl-2,4-Hexadiene in Methanol at 27°C by Laser Flash Spectroscopy.

$k_q = 4.86 \times 10^9 M^{-1}s^{-1}$ $\lambda = 680$ nm

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.00	6.49
0.0662	8.02
0.345	8.46
0.686	9.09
1.02	11.20
1.69	13.80
3.30	22.00

$\tau_1 = 154.1$ nsec $\lambda = 680$ nm; [Ketone] = 0.0128 M.

Table 87. Determination of k_q for 2,2'-Dibenzyloxybenzophenone and 2,5-Dimethyl-2,4-Hexadiene in Methanol at 27°C by Laser Flash Spectroscopy.

$k_q = 5.37 \times 10^9 M^{-1}s^{-1}$ $\lambda = 700$ nm

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.00	7.86
0.699	11.30
1.40	14.50
2.79	23.80

$\tau_1 = 127.3$ nsec $\lambda = 700$ nm; $\tau_2 = 191.6$ nsec $\lambda = 570$ nm
[Ketone] = 0.004 M.

Table 88. Determination of k_q for o-Benzyloxy-5-Methylbenzophenone and 2,5-Dimethyl-2,4-Hexadiene in Methanol at 27°C by Laser Flash Spectroscopy.

$k_q = 6.64 \times 10^9 M^{-1}s^{-1}$ $\lambda = 700$ nm

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.00	4.12
0.14	5.40
0.279	6.54
0.417	7.32
0.693	8.79

$\tau_1 = 242.7$ nsec $\lambda = 700$ nm [Ketone] = 0.005 M

Table 89. Determination of k_q for o-Benzyloxybenzophenone and 2,5-Dimethyl-2,4-Hexadiene in Methanol at 27°C by Laser Flash Spectroscopy.

$k_q = 5.78 \times 10^9 M^{-1}s^{-1}$ $\lambda = 650$ nm

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.00	20.3
1.40	31.7
2.79	39.4
4.17	44.5

$\tau_1 = 44.7$ nsec $\lambda = 730$ nm $\tau_2 = 49.3$ nsec $\lambda = 650$ nsec

[Ketone] = 0.005 M.

Table 90. Determination of k_q for o-Benzyloxyacetophenone and 2,5-Dimethyl-2,4-Hexadiene in Methanol at 27°C by Laser Flash Spectroscopy.

$k_q = 9.38 \times 10^9 M^{-1}s^{-1}$ $\lambda = 390$ nm

[Q], 10^{-3}M	k, $10^6 s^{-1}$
0.00	1.70
0.0838	1.99
0.112	2.89
0.167	3.43
0.277	4.17
0.414	5.49

$\tau_1 = 587.9$ nsec $\lambda = 390$ nm $\tau_2 = 557.6$ nsec $\lambda = 490$ nm

[Ketone] = 0.01 M.

Table 91. Determination of k_q for o-Benzyloxyvalerophenone and 2,5-Dimethyl-2,4-Hexadiene in Methanol at 27°C by Laser Flash Spectroscopy.

$k_q = 5.32 \times 10^9 M^{-1}s^{-1}$ $\lambda = 400$ nm

[Q], 10^{-} M	k, $10^6 s^{-1}$
0.00	4.07
0.140	4.88
0.279	5.73
0.417	6.25
0.693	9.05

$\tau = 245.5$ nsec $\lambda = 400$ nm [Ketone] = 0.021 M.

Table 92. Determination of k_q for 2-Keto-[2,2]-Paracyclophane and 2,5-Dimethyl-2,4-hexadiene in Benzene at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 1.72 \times 10^9 M^{-1}s^{-1}$ $\lambda = 380$ nm

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.00	0.57
1.40	2.39
2.80	4.42
5.6	10.10

[a][Ketone] = 0.0157 M; τ_T = 1124 nsec (550 nm) τ_T = 1766 nsec (380 nm).

Table 93. Determination of k_q for 2-Keto-[2,2]-Paracyclophane and Methyl Naphthalene in Benzene at 27°C with Laser Flash Spectroscopy.[a]

$k_q = 1.45 \times 10^9 M^{-1}s^{-1}$

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.0	0.404
7.20	1.55
14.40	2.57
21.60	3.55

[a][Ketone] = 0.0157 M.

Table 94. Determination of k_q for 2-Keto-[2,2]-Paracyclophane with Methyl Naphthalene in Benzene at 25°C by Laser Flash Spectroscopy.[a]

$k_q = 1.56 \times 10^9 M^{-1}s^{-1}$

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.0	0.409
0.0719	0.487
0.144	0.771
0.358	1.15
0.713	1.51
1.06	1.87
1.40	2.79

[a][Ketone] = 0.0157 M.

Table 95. Determination of k_q for 2-Keto-[2,2]-Paracyclophane and 1,3-Cyclooctadiene in Benzene at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 1.47 \times 10^8 M^{-1}s^{-1}$ $\lambda = 550$ nm

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.0	0.618
0.298	0.639
0.594	0.702
0.889	0.740
1.48	0.779
2.20	0.903
2.92	0.979
3.63	1.06
4.60	1.36

[a][Ketone] = 0.0157 M.

Table 96. Determination of k_q for 2-Keto-[2,2]-Paracyclophane and 2,5-Dimethyl-2,4-Hexadiene in Methanol at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 2.63 \times 10^9 M^{-1}s^{-1}$

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.0	0.470
0.140	0.676
0.348	1.15
0.693	2.06
1.03	3.11
1.37	3.92

[a][Ketone] = 0.02 M.

Table 97. Determination of k_q for 2-Keto-[2,2]-Paracyclophane and 1,3-Cyclooctadiene in Methanol at 27°C by Laser Flash Spectroscopy.[a]

$k_q = 1.33 \times 10^8 M^{-1}s^{-1}$

[Q], 10^{-3} M	k, $10^6 s^{-1}$
0.0	0.508
0.297	0.420
0.741	0.494
1.48	0.598
2.20	0.721
2.92	0.853

[a][Ketone] = 0.02 M.

Table 98. Arrhenius Data for k_q from 2-Keto-[2,2]-Paracyclophane and 2,5-Dimethyl-2,4-Hexadiene in Methanol.

E_a = 1.818 0.280 kcal/mole
log A = 10.69 0.25

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^9 M^{-1}s^{-1}$	Log k
330.0	3.03	2.56	9.408
265.1	3.77	1.59	9.202
240.2	4.16	1.23	9.090
211.9	4.72	0.645	8.809
193.8	5.16	0.390	8.591
304.2	3.29	2.63	9.420

Table 99. Arrhenius Data for k_q from 2-Keto-[2,2]-Paracyclophane and 1,3-Cyclooctadiene in Methanol.

E_a = 1.194 ± 0.099 kcal/mole
log A = 9.14 ± 0.09

T °K	1/T, 10^{-3} °K^{-1}	k, $10^8 M^{-1}s^{-1}$	log K
194.1	5.15	0.631	7.800
210.0	4.76	0.819	7.913
234.4	4.27	1.03	8.014
256.3	3.90	1.27	8.104
273.2	3.66	1.49	8.174
328.8	3.05	2.33	8.368

Table 100. Arrhenius Data for τ^{-1} for 2,6-Dimethoxybenzophenone in Benzene.

E_a = 3.084 ± 0.257 kcal/mole
log A = 9.09 ± 0.23

T °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
300.1	3.33	6.23	6.795
195.7	5.11	0.461	5.664
218.3	4.58	0.964	5.984
249.7	4.01	2.16	6.335
279.1	3.58	4.62	6.665
318.0	3.15	10.70	7.029

Table 101. Arrhenius Data for τ^{-1} from 2,6-Dimethoxybenzophenone in Chlorobenzene.

E_a = 2.26 ± 0.733 kcal/mole
log A = 8.81 ± 0.54

T °K	1/T, 10^{-3} °K^{-1}	k, $10^7 s^{-1}$	log k
300.9	3.32	1.81	7.258
261.3	3.83	0.734	6.866
268.2	3.73	0.913	6.961
327.1	3.06	1.96	7.292
351.1	2.85	2.23	7.348

Table 102. Arrhenius Data for o-Methoxybenzophenone in Chlorobenzene.

E_a = 4.168 ± 0.647 kcal/mole
log A = 9.21 ± 0.51

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
298.7	3.35	1.49	6.173
239.1	4.18	0.292	5.465
254.7	3.93	0.357	5.553
273.4	3.66	0.680	5.833
317.0	3.16	1.83	6.263
335.6	2.98	3.61	6.558

Table 103. Arrhenius Data for o-Methoxybenzophenone in Methanol.

E_a = 3.049 ± 0.148 kcal/mole
log A = 9.06 ± 0.13

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
299.1	3.34	7.01	6.846
195.9	5.11	0.452	5.655
216.6	4.62	0.944	5.975
250.6	3.99	2.65	6.423
274.2	3.65	3.68	6.566
317.9	3.15	9.10	6.959
334.5	2.99	12.00	7.079

Table 104. Arrhenius Data for o-Benzyloxybenzophenone in Chlorobenzene.

E_a = 2.815 ± 0.759 kcal/mole

log A = 9.20 ± 0.59

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^7 s^{-1}$	log k
300.9	3.32	1.81	7.258
237.4	4.21	0.313	6.496
261.3	3.83	0.734	6.866
268.2	3.73	0.913	6.961
327.1	3.06	1.96	7.292
351.1	2.85	2.23	7.348

Table 105. Arrhenius Data for o-Benzyloxybenzophenone in Methanol.

E_a = 3.57 ± 0.285 kcal/mole

log A = 9.63 ± 0.26

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
300.9	3.32	10.90	7.037
191.7	5.22	0.341	5.533
210.7	4.75	0.728	5.862
236.8	4.22	2.14	6.330
256.4	3.90	4.59	6.662
270.1	3.70	0.569	6.755
326.6	3.06	14.20	7.152

Table 106. Arrhenius Data for o-Benzyloxyacetophenone in Chlorobenzene.

E_a = 3.662 ± 0.601 kcal/mole

log A = 9.03 ± 0.47

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
297.2	3.37	2.38	6.377
239.4	4.18	0.558	5.747
256.8	3.89	0.687	5.837
273.5	3.66	1.05	6.021
318.3	3.14	2.96	6.471
341.1	2.93	5.09	6.707

Table 107. Arrhenius Data for o-Benzyloxyacetophenone in Methanol.

E_a = 3.725 ± 0.695 kcal/mole

log A = 8.98 ± 0.54

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
295.9	3.38	1.41	6.149
244.1	4.10	0.488	5.688
264.8	3.78	0.761	5.881
281.3	3.56	1.06	6.025
316.5	3.16	2.42	6.384
329.7	3.03	3.87	6.588

Table 108. Arrhenius Data for o-Benzyloxyvalerophenone in Chlorobenzene.

E_a = 4.77 ± 0.439 kcal/mole
log A = 10.44 ± 0.34

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
297.0	3.37	8.88	6.948
237.6	4.21	1.14	6.057
256.0	3.91	2.08	6.318
273.1	3.66	3.84	6.584
318.3	3.14	12.00	7.079
335.3	2.98	23.00	7.362

Table 109. Arrhenius Data for o-Benzyloxyvalerophenone in Methanol.

E_a = 4.73 ± 0.105 kcal/mole
log A = 9.96 ± 0.08

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
296.4	3.37	2.99	6.476
229.5	4.36	0.274	5.438
260.8	3.83	0.924	5.966
281.2	3.56	1.88	6.274
317.3	3.15	4.83	6.684
331.9	3.01	6.64	6.822

Table 110. Arrhenius Data for o-Benzyloxy-5-Methylbenzophenone in Chlorobenzene.

E_a = 4.496 ± 0.454 kcal/mole

log A = 10.30 ± 0.36

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
297.6	3.36	11.30	7.053
236.9	4.22	1.27	6.104
255.9	3.91	2.69	6.430
273.8	3.65	5.61	6.749
317.0	3.16	14.50	7.161
336.1	2.98	21.00	7.322

Table 111. Arrhenius Data for o-Benzyloxy-5-Methylbenzophenone in Methanol.

E_a = 3.832 ± 0.233 kcal/mole

log A = 9.32 ± 0.20

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
297.4	3.36	2.94	6.468
194.3	5.15	0.108	5.033
221.4	4.52	0.337	5.528
252.8	3.96	0.899	5.954
281.2	3.56	1.96	6.292
318.2	3.14	4.86	6.687
332.1	3.01	7.41	6.870

Table 112. Arrhenius Data for 2,2'-Dibenzyloxybenzophenone in Chlorobenzene.

E_a = 3.068 ± 0.500 kcal/mole

log A = 9.29 ± 0.39

T, °K	1/T, 10^{-3} °K^{-1}	k, $10^6 s^{-1}$	log k
298.3	3.35	12.70	7.104
239.6	4.17	2.70	6.431
255.6	3.91	4.59	6.662
273.7	3.65	7.51	6.876
316.0	3.17	13.30	7.124
335.5	2.98	17.40	7.241

Table 113. Quenching of α-(o-Benzyloxyphenyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau_T$ = 173 M^{-1} HPLC Analysis: Ultrasphere ODS-18

$CH_3:H_2O$

2.0 ml/min

270 nm

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.00	0.1965	----
0.708	0.0863	2.28
1.42	0.0574	3.43
2.83	0.0417	5.63
4.25	0.0231	8.15

[a][Ketone] = 0.0256 M 313 nm.

Both E and Z- 2,3-diphenyl-3-hydroxy-3,4-dihydrobenzopyran photoproducts appear as one peak.

Table 114. Quenching of α-(o-Benzyloxyphenyl)acetophenone with 2,5-Dimethyl-2,4-Hexadiene in Benzene at 25°C.[a]

$k_q\tau_T$ = 191 M^{-1}

Same analysis conditions as Table 113.

[Q], 10^{-2} M	A_{photo}/A_{std}	$\phi°/\phi$
0.0	0.235	----
1.06	0.0831	2.78
2.13	0.0487	4.75
4.25	0.0240	9.64
6.38	0.0175	13.3

[a][Ketone] = 0.0265 M 313 nm.

Both E- and Z- photoproducts appear as a single peak.

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