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STRUCTURAL EFFECTS IN PHOTOCHEMICAL
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presented by

Yana Cen

has been accepted towards fulfillment
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Peter J. Wagner
Major Professor's Signature

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Date

STRUCTURAL EFFECTS IN PHOTOCHEMICAL HYDROGEN ABSTRACTIONS

By

Yana Cen

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ABSTRACT

STRUCTURAL EFFECTS IN PHOTOCHEMICAL HYDROGEN ABSTRACTIONS

By

Yana Cen

Conformational effects on photocyclization of various 2-alkoxy-3-alkyl phenyl ketones have been investigated. Actual rate constants for triplet reaction were measured as alkyl substituent was varied, the extent of their increase provides direct measures of conformational equilibria. When these rate constants get large enough, photocyclization can be employed as an internal clock for fast reactions, especially in the solid state. Biradical geometries are also constrained, changes in their lifetimes and product ratios were directly correlated with changes in geometry.

Photoinduced carbon-halogen bond cleavage of a series of α-(haloethoxy)acetophenons and β-(haloethoxy)propiophenones has been studied. This involves competition of cleavage with hydrogen abstraction. Comparisons of product ratios and hydrogen abstraction rate constants of these ketones with those of δ-halovalerophenones reveals that the presence of an oxygen in the skeleton of either 1,4 or 1,5-biradicals facilitates the photocleavage process.

Difference in reactivity of both singlet and triplet biradicals derived from α/β-alkoxy aliphatic ketones and the role of environmental and conformational factors in determining the overall efficiency and chemical yield of product formation has been addressed. Steady state kinetics as well as computational study indicate conformational control of reactivity in photocyclization of singlet biradicals.

Photolysis of α-cyclopropylmethoxyacetophenone confirms that an oxygen conjugated to the radical site would lower the rearrangement rate constant from that for cyclopropylethyl radical. Temperature effect on product ratios shows the triplet biradical lives long enough to allow equilibration.

To my parents

ACKNOWLEDGMENTS

'The roles of a teacher are preaching the right way; passing on knowledge and solving questions.' First and foremost, I would like to thank my advisor, Professor Wagner for his guidance, patience, great sense of humor and innumerable entertaining discussions during the course of this work.

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'When I walk along with two others, they may serve as my teachers.' I would like to thank all my colleagues in Wagner's group for creating a friendly and stimulating working environment. I owe special thanks to Dr. Ali Zand for continued encouragement and useful discussions.

Special thanks are given to all my friends at MSU for their friendship and help. Their support made my graduate career much more enjoyable.

Last, but not least, my appreciation is extended to my parents for their continued support, understanding and encouragement during my graduate studies.

'My life is limited, while knowledge is limitless.' It will mold me into a better chemist and guide me to choose the right path.

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Introduction

Photochemistry is chemical change brought by light. For light to be absorbed, the molecule must have an energy level corresponding in energy to that of the radiation. Organic photochemical reactions involve excited electronic states. Depending on functionality, organic compounds can have electronic absorption bands from the far ultraviolet to the visible region of the spectrum. When a molecule absorbs a quantum of light, the electronic configuration changes to correspond to an excited state. After excitation of a molecule, various intramolecular photophysical processes can occur.[1] Jablonski diagram (Figure 1) shows how these processes can be represented and related. There are absorption of a photon by the ground state to produce an excited singlet state, radiative decay processes, namely fluorescence and phosphorescence, and non-radiative decay processes, namely internal conversion and intersystem crossing.

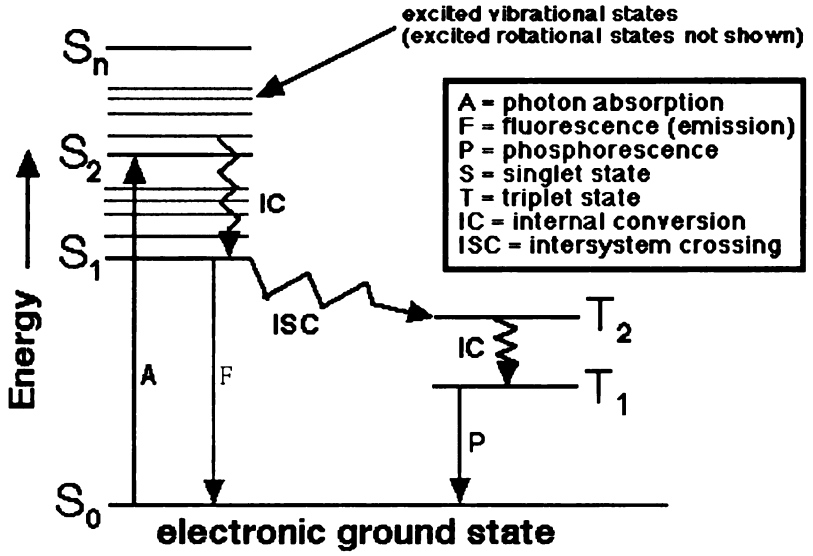


Figure 1. Jablonski Diagram

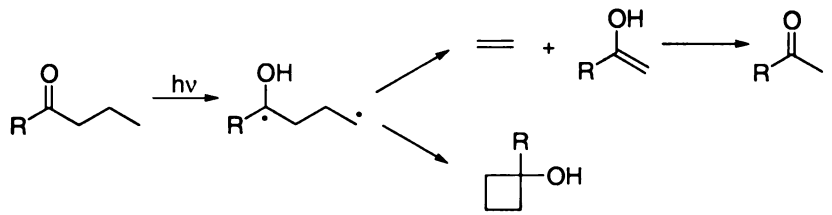
Ketones feature prominently in accounts of the earliest systematic studies of both

synthetic and mechanistic organic photochemistry. Aliphatic ketones absorb weakly at around 280 nm as a result of an n→π* transition that is forbidden on both symmetry and overlap grounds. Intersystem crossing from the n, π* singlet to the corresponding triplet is generally efficient, and because the energy and electronic distribution of the n, π* triplet state are not very different from those of the corresponding singlet, the two states often react in the same overall manner.[2,3] Intersystem crossing is very efficient for aromatic ketones, so that most of their photochemical reactions are the result of triplet-state processes.[4] For many aromatic ketones, the n, π* and π, π* triplet states are similar in energy. This is important because photochemical reaction normally occurs through the lowest state, and the radical-like properties of n, π* states are not shared by π, π* states. This means that the type of product or the efficiency of reaction can be affected quite drastically by substituents that influence the relative energy levels, and even by the nature of the solvent for borderline cases.

n, π* excited states of ketones resemble alkoxy radicals in their ability to abstract a hydrogen atom from a suitable donor. This process can also occur from a position within the ketone molecule, and this generates a biradical that may cyclize by combination of the radical centers.[5] The efficiency of photochemical abstraction from ketones with π, π* lowest triplet is quite low as compared to those with n, π* lowest triplet because reaction takes place from low equilibrium populations of the reactive upper triplet.[6] This underlines the difference in the electronic nature of the two types of excited states.

In an unstrained system a ketone n, π* excited state shows a preference for abstraction from the γ-position, which can be understood on the basis of an energetic preference for reaction by way of a six-atom transition state. γ-Hydrogen abstraction generates a 1,4-

biradical that can cyclize to give a cyclobutanol, and this type of biradical can also undergo cleavage to give an alkene and the enol of a shorter-chain ketone. The overall photoelimination reaction has been known as Norrish type II reaction[7] (Scheme 1).



Scheme 1. Intramolecular γ-Hydrogen Abstraction

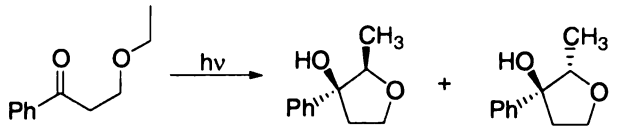
Conformational factors undoubtedly play a large part in determining the cyclization/cleavage ratio for the biradical,[8] mainly because the two singly occupied orbitals in the biradical and the bonding orbital corresponding to the C(α)-C(β) bond that is broken on cleavage need to be aligned in a parallel way for efficient cleavage. Conformational preferences that inhibit this alignment will promote cyclization.

Mechanistic interpretation is complicated by the possibility of reverse hydrogen transfer in the biradical to give ground state of the starting ketone, and it is essential to compare reactivities in terms of rate constant rather than overall quantum yields.

The nature of the solvent has a considerable effect in the quantum yield.[9] In hydrogen-bonding solvents the hydroxyl group is more strongly solvated, and reverse hydrogen transfer from oxygen to carbon is hindered. Product formation therefore increases in efficiency.

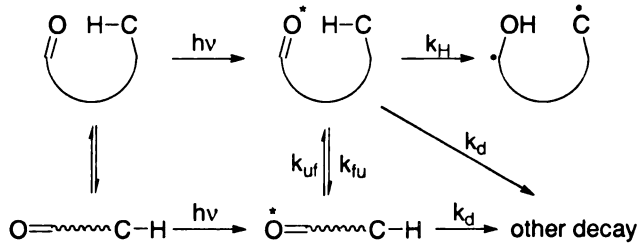
The predominant formation of 1,4-biradical in photoinduced internal hydrogen abstraction of ketones can be explained in terms of preferred 1,5-hydrogen transfer in radical chemistry. However, δ-hydrogen abstraction does compete with γ-hydrogen abstraction: either in a cyclic system with conformational restraint,[10] or in ketones that

have no γ-hydrogen and very reactive δ-C-H bonds (Scheme 2).[11]



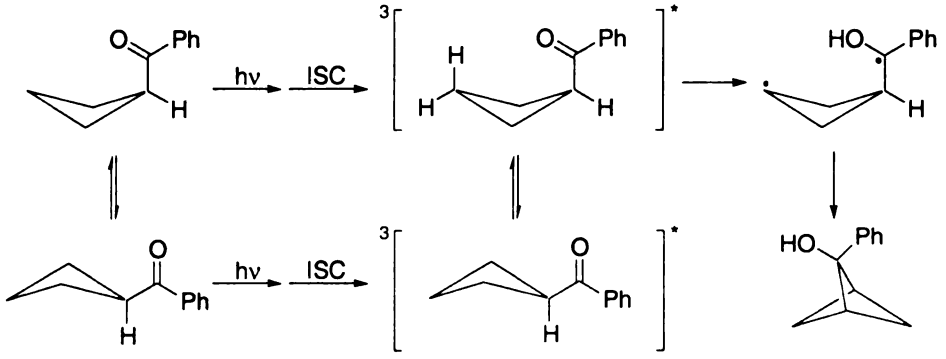
Scheme 2. Intramolecular δ-Hydrogen Abstraction

The rate constant for hydrogen abstraction and the behavior of 1, x-biradicals have revealed the strong influence of conformational effects on such intramolecular processes. The competition between conformational change, reaction and decay provides three boundary conditions:[12] (1) conformational equilibrium (2) ground state control (3) rotational control (Scheme 3).



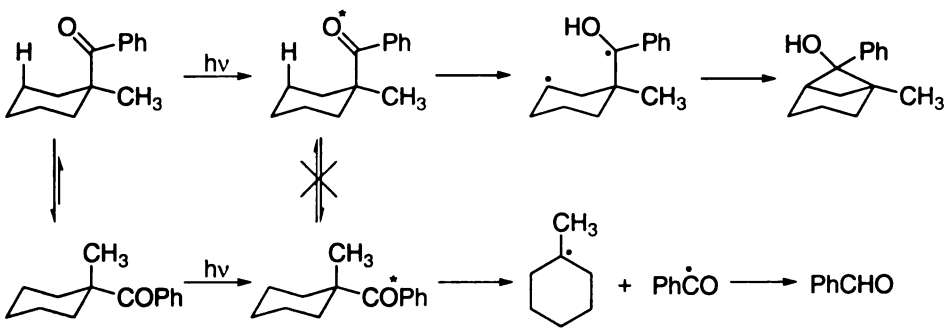
Scheme 3. Conformational, Rotational and Ground State Control of Reactivity

Alexander has reported that an excited state equilibrium between the two triplet ketone conformers is an important factor in the photochemistry of benzoylcyclobutanes[13] (Scheme 4).



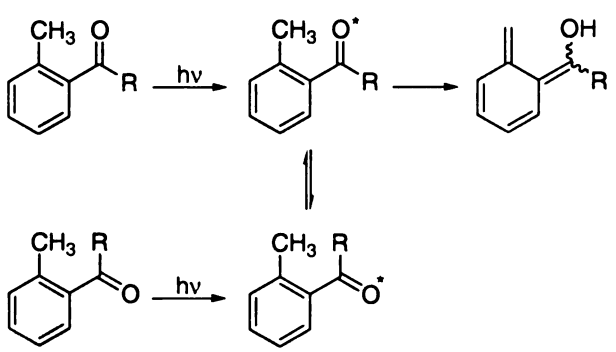
Scheme 4. Conformational Control of Reactivity

Lewis reported that for 1-methylcyclohexyl phenyl ketones, there exist two different ketone triplets each leading to different photoproducts[14] (Scheme 5): the ketone conformer with the benzoyl group in an axial position undergoes γ-hydrogen abstraction followed by cyclization; while the other conformer having the benzoyl group in an equatorial position undergoes acyl cleavage giving rise to benzaldehyde. It has been found that the ratio of products from the two pathways is entirely dependent upon the ground state population of each ketone conformer.



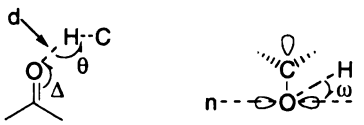
Scheme 5. Ground State Control of Reactivity

Another type of conformational effect, rotational control, is found in the photoenolization of *o*-alkylphenyl ketones.[12,15] Wagner has proposed a mechanism involving two kinetically distinct ketone rotamers, designated syn and anti (Scheme 6). The anti triplet must first rotate into the syn conformer before enolization can occur.



Scheme 6. Rotational Control of Reactivity

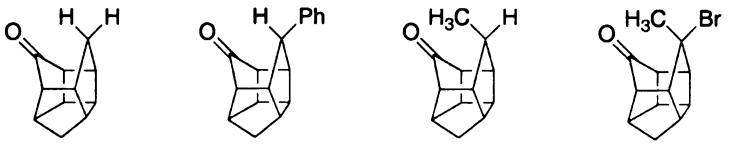
Four ground state parameters: d, the distance between O and H; η, the O-H-C angle; ν, the C=O-H angle; and ω, the dihedral angle that the O-H vector makes with respect to the nodal plane of the carbonyl have been considered to be the most important in determining the rate and efficiency of hydrogen abstraction. Scheffer suggests the theoretically 'ideal' values for these parameters shown in Scheme 7.[16] The fact that a few ketones react with larger values of d probably reflects a varying degree of molecular flexibility in different structures. The value of θ obviously can vary significantly from the linear arrangement thought to be preferable. Likewise, the value of ω can depart from the 'ideal' 0°. Both of these have long been known from the reactivity of many steroidal ketones. The meaning of Δ is the least clear since n, π* only lengthens carbonyl bonds.



ideal: Δ= 90-120° θ= 180° ω= 0° d≤2.7 Å

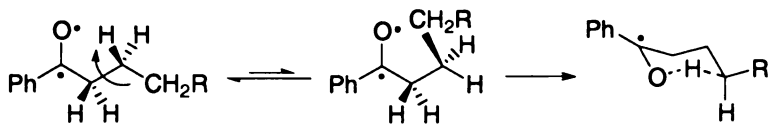
Scheme 7. Orientational Requirements for Hydrogen Abstraction

Sauers has compared the strain energies calculated for the transition states for intramolecular hydrogen abstraction in a variety of cyclic and polycyclic ketones with the observed quantum efficiencies.[17] Several unreactive ketones (Scheme 8) have hydrogens close enough to the carbonyl for reaction but at an angle ω of 90°.[18] The short triplet lifetimes of these ketones were attributed to a reversible Norrish type I cleavage that generates very short lives biradicals.



Scheme 8. Effect of Dihedral Angle on Reactivity

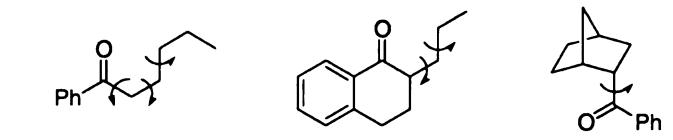
Simple straight chain ketones normally have their largest α-substituent eclipsing the carbonyl. The most populated conformer is in a geometry very close to that required for reaction, requiring only rotation around the β-C—γ-C bond. The ketone can attain a chair or twist-chair transition state geometry quite easily (Scheme 9).[19] This angle is much less than the linear arrangement calculated by theoretical models. It was proposed that the torsional strain present in the cycloheptane-like transition state for 1,6-hydrogen transfer is responsible for the slow rate of δ-hydrogen abstraction in straight chain system. Wagner also suggested that coplanar hydrogen abstraction is not a strict requirement for the type II process and proposed a $\cos^2\omega$ dependence for abstraction.[20]



Scheme 9. Chair-Like Transition State for Hydrogen Abstraction

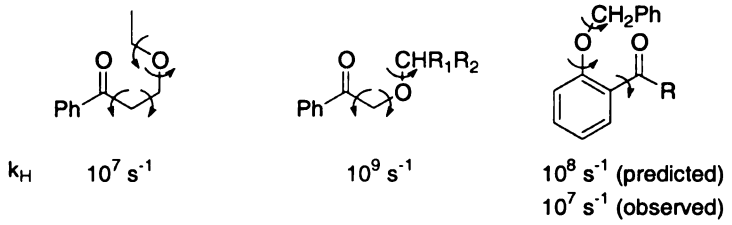
Intramolecular photochemical γ-hydrogen abstraction has been found to be much faster in cyclic ketones than in acyclic ones.[21] This is due to an immobilization of the possible rotations involved in the formation of the six-membered transition state required for γ-hydrogen abstraction.[22] 2-Benzoylnorborane requires about the same activation energy for hydrogen abstraction as valerophenone (3.6 ± 0.2 kcal/mol). However, the activation entropy for hydrogen abstraction in 2-benzoylnorborane is approximately 8 eu more than for valerophenone (Scheme 10). 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.

In light of the results above, a comparison of β-ethoxypropiophenone and α-alkoxyacetophenone with *o*-benzyloxyphenyl ketones (Scheme 11) provides an estimated



Scheme 10. Rate Enhancement for γ-Hydrogen Abstraction

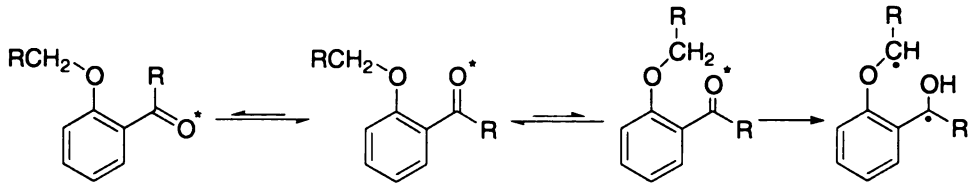
rate constant of at least 10^8 s^{-1}, ten times faster than what is reported.



Scheme 11. Rate Enhancement for δ-Hydrogen Abstraction

Similar result has been reported by Wagner for *o*-alkoxyphenyl ketones.[23] The most important general findings are that acetophenones are much less reactive than benzophenones and give more byproducts; even the benzophenone triplets have small rate constants for δ-hydrogen abstraction. The low rate constants for δ-hydrogen abstraction in these ketones clearly are due to conformational factors, in particular a low equilibrium population of the rotamers in which the alkyl group of the *o*-alkoxy is syn to the carbonyl (Scheme 12). The fact that *o*-benzyloxy ketones are much more reactive than *o*-methoxy ketones, as expected by their relative C-H bond strengths, indicates that reactions are not limited by bond rotation rates but rather involve rotational equilibrium prior to rate-determining hydrogen abstraction. 2,6-Diacyl methoxy and benzyloxy compounds all display triplet reaction rates at least ten times faster than those for monoketones. This fact substantiates the unfavorable rotational equilibrium about the benzene-oxygen bond. The comparable reactivities of 2-alkoxy and 2,6-dialkoxy ketones

indicate that the triplets achieve rotational equilibrium about the benzene-acyl bond before reaction, and this equilibrium favors the reactive rotamer.



Scheme 12. Conformational Equilibrium for *o*-Alkoxyphenyl Ketones

All of the benzophenones studied have n, π^* lowest triplets. The significant lower k_H values observed for the acetophenones reflect their π, π^* lowest triplet configurations. Any further $^3\pi$, π^*-stabilizing substitution would lower rate constants so much that hydrogen abstraction would occur only in very low quantum efficiency.

Blankspoor reported that a methyl group *ortho* to the alkoxy group enhances the quantum yield for reaction of comparable quinines by changing the conformational equilibrium.[24] This effect will be examined in 2-alkoxy-3-alkylbenzophenones and acetophenones for the following reasons: 1) actual rate constants for triplet reaction can be measured as alkyl group is varied, the extent of their increase will provide direct measures of conformational equilibria; 2) biradical geometries also will be constrained, changes in product ratio can then be directly correlated with changes in geometry.

Many free radical processes involve carbon-halogen bond breaking as the rate determining step or as a competing reaction. Compounds which undergo photochemically-induced carbon-halogen bond cleavage are useful as synthetic intermediates and as initiators for free radical polymerizations.[25,26]

Although the photochemical cleavage of carbon-halogen bonds has been known for some time, few attempts have been made to measure or even estimate the rate of bond

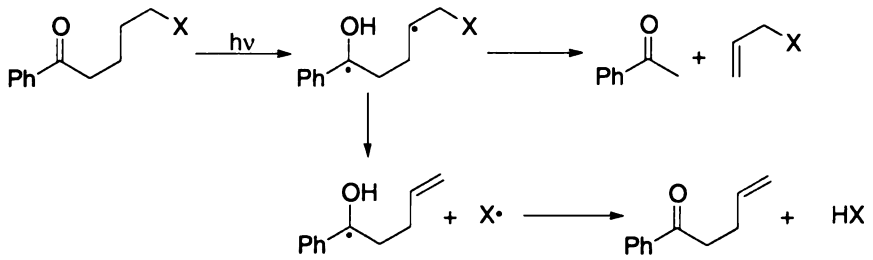
cleavage. The general trend of higher yields and greater ease of reaction for the series: C-I>C-Br>C-Cl>>>C-F is in agreement with bond strengths.[27]

A practical method for measurement of the rates of carbon-halogen cleavage could involve competition of cleavage with some other well-defined photochemical process. By measuring the relative amounts of cleavage versus the competing reaction, the relative rates can be measured. If the competing reaction has rate constants which are known or easily measured, absolute rates for carbon-halogen bond cleavage can be calculated. A further requirement for the competing process is its ability to be incorporated into the same molecule as the carbon-halogen moiety and to react from excited states that also cleave carbon-halogen bonds.

The Norrish type II reaction is ideal for monitoring rate constants of competing excited state reactions. Rate constants for γ-hydrogen abstraction can be determined from maximized quantum yields and triplet lifetimes and can vary depending on structures, thus providing a highly variable clock.[28] The regioselectivity of the reaction makes it easy to monitor both biradical and radical reactions.

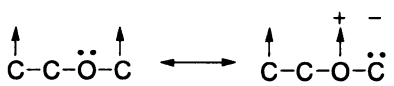
Due to the intense interest in β-haloalkyl radicals,[29,30,31] Wagner's group has studied the photochemistry of several δ-halovalerophenones.[32] They undergo loss of HX competitive with type II elimination (Scheme 13). The halogens are eliminated from 1,4-biradical intermediate involved in type II photoelimination. The results provided the first extensive set of relative β-cleavage rates of radicals.

Another intriguing phenomenon is the large acceleration of 1,4-biradical decay caused by an oxygen atom between the two radical sites.[33] A probable contributor to the lifetime-shortening effect of β-oxygen is the decreased average distance between the



Scheme 13. Photochemistry of δ-Halovalerophenones

unpaired electrons due to the resonance form (Scheme 14). Other explanations might derive from conformations which provide an angle of approximately 90° between the oxygen 2p orbital and the half-filled p orbital at the adjacent terminus. Such conformations will provide maximal spin orbital coupling. Some behavior of 1,5-biradicals is very similar to that of 1,4-biradicals, such as they do have shorter lifetime with an oxygen atom as part of the skeleton, which is ascribed to different conformational freedoms of the biradicals.

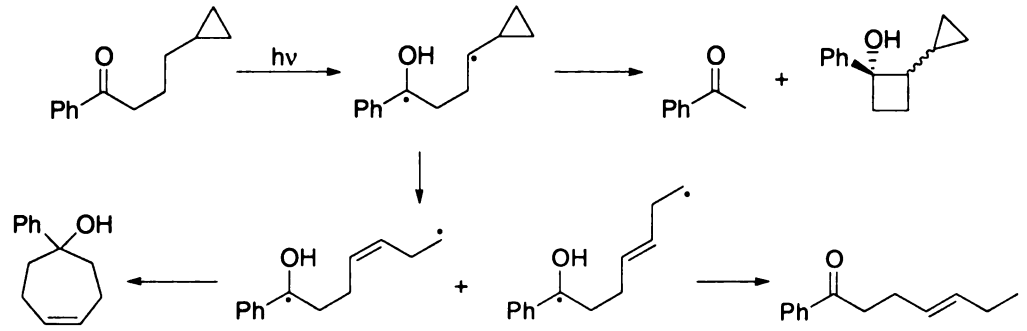


Scheme 14. Resonance Structures of 1, 4-Biradical

We have studied the photobehavior of several α-haloethoxyacetophenones and β-haloethoxypropiophenones at various environments to gain better understanding of the factors that control the β-haloelimination reactivity. These results in conjunction with the results of δ-halovalerophenones have been used to compare and contrast biradical/radical reactivity with an oxygen in skeleton versus their carbon analogues.

The behavior of biradical is of great interest especially whether monoradical reactions of biradicals occur with the same rate constants as those of simple radicals. In the case of intramolecular rearrangement occurred in γ-cyclopropylbutyrophenone (Scheme 15),[34] the rate constant for ring opening is the same in the biradical as in the model

cyclopropylethyl radical. It is believed that the two unpaired electrons are too weakly coupled to affect rate constants for reactions of biradicals with singlet species.



Scheme 15. Photochemistry of γ-Cyclopropylbutyrophenone

One of the most intriguing questions in organic photochemistry is whether the differences in spin multiplicity between singlet and triplet states will be reflected in their reactivity in primary photochemical processes. Yang has shown that in aliphatic ketones that rate of cleavage from the triplet is about one hundred times faster than the singlet.[35] Dialkylketones are known to undergo hydrogen abstraction in both the T_1 and S_1 states.[36,37,38] Photolysis of the optically active ketone (S)-(+)-5-methyl-2-heptanone showed that photoracemization occurs from the triplet state, suggesting the existence of a triplet biradical sufficiently long lived to allow racemization at the γ-carbon.[39] The results obtained with the optically active ketone showed that the total quantum yield of observed events from T_1 is only 0.14. Since Φ_{ISC} was determined to be 0.11 and the quantum yield for reaction from S_1 is 0.07, the remaining quantum yield of 0.79 must represent non radiative decay from S_1. This decay appears to lead to no racemization and is not affected by changes on the solvent, which implies that if it does involve formation of a singlet biradical and subsequent back hydrogen transfer, then the biradical must be extremely short-lived.

It has also been suggested that Norrish type II reaction from S_1 may occur via a concerted pathway.[38] Heller has proposed that the electronic energy might be transferred into vibrational stretching energy of a C-H bond, with further partitioning into a pair of radicals (or biradical) or to a relaxed ground state.[40] Hammond has also postulated that chemical reactions of the excited states are special forms of radiationless decay.[41]

Salem has calculated the activation energies and surface crossing for singlet and triplet state hydrogen abstractions.[42] It has been shown that simple symmetry considerations indicate that the n, π^* singlet of the carbonyl correlates with the singlet biradical product, whereas the ground state correlates with a zwitterionic species. Since the plane of symmetry is not maintained in most hydrogen abstractions, an avoided crossing between the excited and ground state surfaces occur (Figure 2). Hydrogen abstraction therefore requires a radiationless decay which can occur easiest at the point of the smallest energy difference between the two surfaces. Conversion of the electronic energy into vibrational energy populates the ground state at a maximum, from which relaxation to biradical product or to ground state reactant can occur.

Scaiano has studied fluorescence quenching of acetone by several hydrogen donors.[43] They reported the excited singlet of acetone to be 2-10 times more reactive than the triplet toward hydrogen donors. They have ascribed this to a more exothermic reaction from the singlet which results in a lower activation energy for hydrogen abstraction. The lower quantum yield for product formation from the singlet is lower than in the triplet. They attributed this inefficiency to deactivation of the excited state to yield the reactant from an avoided crossing before a radical pair is reached.

It was concluded that the interaction of the singlets with hydrogen donors is not a

chemical reaction but a physical quenching mechanism, where the hydrogen donor causes deactivation by accepting part of the electronic excitation energy as vibrational energy and promoting internal conversion from S_1 to S_0.[37,42]

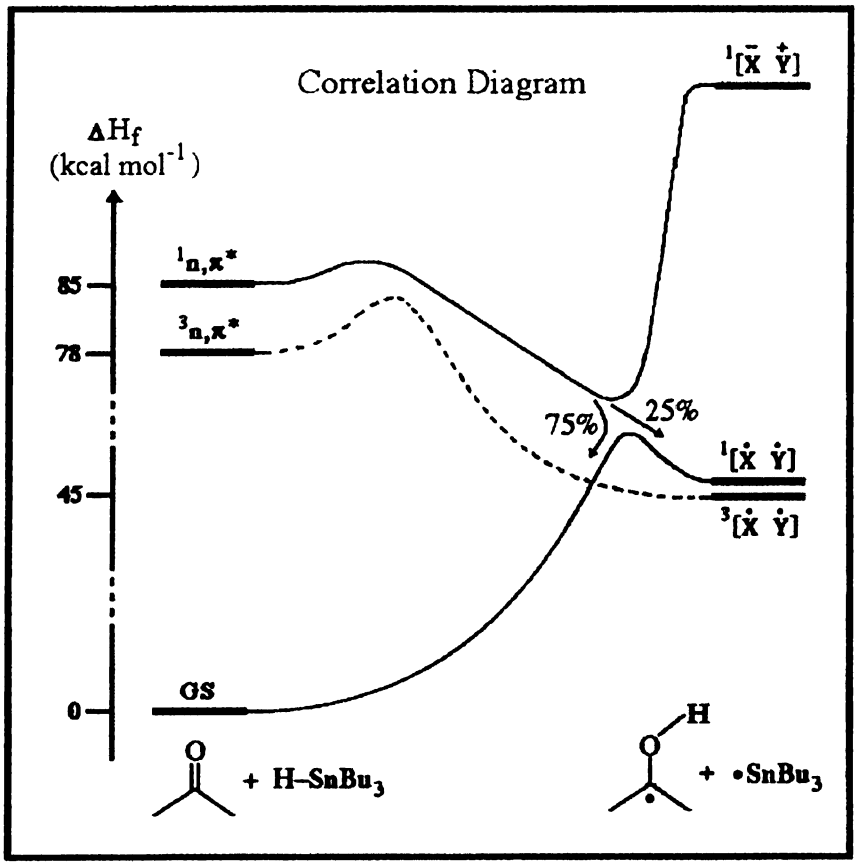
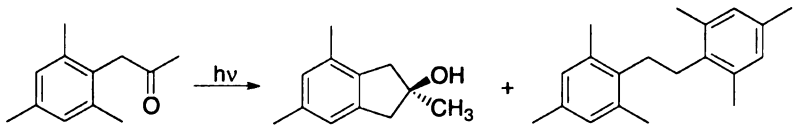


Figure 2. Correlation Diagram

Wagner's group has studied the photobehavior of several α-(*o*-alkylphenyl) and α-(2,4,6-trialkylphenyl)acetones (Scheme 16) at various temperature.[44] Quenching studied indicate that δ-hydrogen abstraction occurs from the singlet while α-cleavage occurs from the triplet; temperature effects on quantum yields demonstrated that there is an enthalpic barrier to hydrogen abstraction at low temperature whereas intersystem crossing has

none; diastereoselectivity indicated conformational control of reactivity in photocyclization of singlet biradicals.

Chandra's group found the presence of ether oxygen in a position β to the carbonyl group in α-alkoxyacetones leads to an overall decrease in the energy of activation and an



Scheme 16. Photochemistry of α-(2,4,6-Trimethylphenyl)acetone

increase in the exothermic nature of the intramolecular γ-hydrogen abstraction process relative to the corresponding alkyl ketones.[45] Their theoretical analysis showed that the singlet 1,4-biradical derived from α-alkoxyacetones can cyclize readily to form 3-oxetanol although experimental results have not been reported.

From a mechanistic point of view, the difference in the reactivity of both singlet and triplet biradicals derived from α/β-alkoxy aliphatic ketones and the role of environmental and conformational factors in determining the overall efficiency and chemical yield of product formation must be addressed. To examine the influence of these factors, we decided to study the photolysis of β-cyclopropylmethoxybutanone and α-cyclopropylmethoxyacetone. By comparing the results for these ketones with their aromatic counterparts, we hope to gain a better understanding of the factors that control singlet state and/or singlet biradical reactivity.

Results

I. General Procedures

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

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

II. Results for 2-Alkoxy-3-alkyl Benzophenones

A. General Preparation of Ketones

The substituted 2-alkoxy-3-alkyl benzophenones were synthesized by ortho-lithiation. The corresponding aromatic ether was allowed to react with *n*-butyl lithium. The aryl lithium species was then reacted with benzaldehyde in diethyl ether. The resulting alcohol was oxidized with PCC to yield the desired benzophenone.

Table 1 provides the structures of the ketones studied.

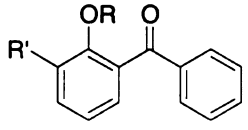


Table 1. 2-Alkoxy-3-alkyl Benzophenones

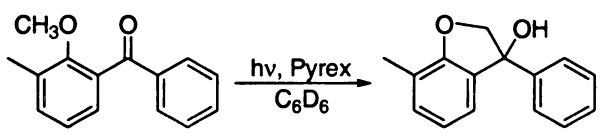
Ketone	R	R'	Abbreviation
2-methoxy-3-methylbenzophenone	CH_3	CH_3	**1**
3-isopropyl-2-methoxybenzophenone	CH_3	$CH(CH_3)_2$	**2**
3-t-butyl-2-methoxybenzophenone	CH_3	$C(CH_3)_3$	**3**
2-ethoxy-3-methylbenzophenone	CH_3CH_2	CH_3	**4**
2-ethoxy-3-isopropylbenzophenone	CH_3CH_2	$CH(CH_3)_2$	**5**
3-t-butyl-2-ethoxybenzophenone	CH_3CH_2	$C(CH_3)_3$	**6**
2-benzyloxy-3-methylbenzophenone	$PhCH_2$	CH_3	**7**
2-benzyloxy-3-isopropylbenzophenone	$PhCH_2$	$CH(CH_3)_2$	**8**
2-benzyloxy-3-t-butylbenzophenone	$PhCH_2$	$C(CH_3)_3$	**9**

B. Identification of Benzofuranols

Irradiation of degassed benzene solution of various 2-alkoxy-3-alkyl benzophenones produced the corresponding substituted 3-hydroxy-2,3-dihydrobenzofuranols as the major products. ***Cis*** and ***trans*** refer to the position of the 2-substituent and the hydroxyl group. Most of the chemical shifts for the hydrogens at C-2 appear between 4.2 and 5.6ppm. The appearance of this resonance was used to gauge the progress of the photochemical reaction. Structural assignments were based on spectral data obtained for these compounds (^{1}H and ^{13}C NMR, IR and mass spectrum). The stereochemical assignments of the dihydrobenzofuranols were based on nOe experiments: irradiation of 3-hydroxy proton caused an enhancement of the C-2 proton signal. This suggests that the benzofuranol has a *trans*-stereochemistry.

C. Individual Ketones

1. *2-Methoxy-3-methylbenzophenone* (Benzophenone 1)



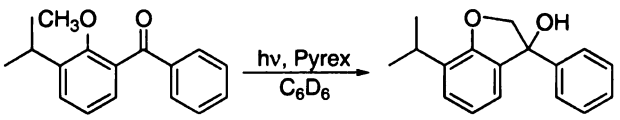
1 **26**

Scheme 17. Photochemistry of Benzophenone 1

Irradiation of a 0.048 M benzene-d_6 solution gave only one product, benzofuranol **26** (Scheme 17), in quantitative yield. The reaction was complete (100% conversion) after 20 minutes of irradiation. The formation of **26** was independent of light source and was formed by irradiation with either a medium pressure mercury arc lamp (Pyrex filtered) or in a Rayonet reactor (300nm lamps). The quantum yield for **26** formation was measured at 313 nm by GC and found to be 0.51 (7.3% conversion). The singlet at 3.36ppm for 2-

methoxy group disappeared at the same rate as the growth of two doublets at 4.27ppm (J= 10.2 Hz) and 4.42ppm (J= 9.9 Hz) in benzene-d_6.

2. *3-Isopropyl-2-methoxybenzophenone* (Benzophenone 2)

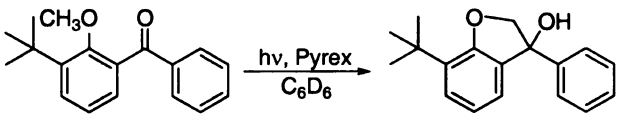


2 **27**

Scheme 18. Photochemistry of Benzophenone 2

Irradiation of a 0.039 M benzene-d_6 solution of **2** gave quantitatively benzofuranol **27** (Scheme 18). The reaction was complete (100% conversion) after 20 minutes of irradiation with Pyrex filtered light. During the course of the reaction the methyl signal at 3.60ppm disappeared with the simultaneous formation of two new signals at 4.29 and 4.38ppm. The quantum yield for **27** formation was measured at 313 nm by GC and found to be 0.64 (8.4% conversion).

3. *3-t-Butyl-2-methoxybenzophenone* (Benzophenone 3)



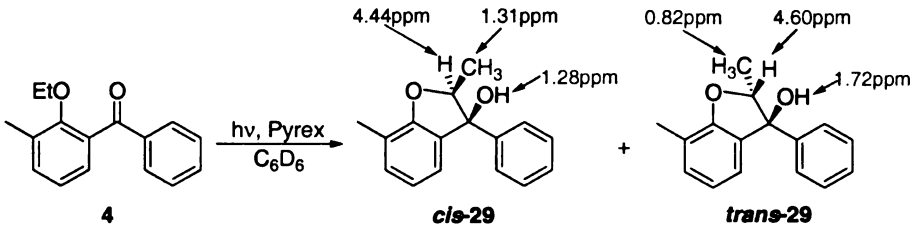
3 **28**

Scheme 19. Photochemistry of Benzophenone 3

Irradiation of 0.039 M **3** in benzene-d_6 at room temperature gave benzofuranol **28** quantitatively within 15 minutes (Scheme 19). The quantum yield for **28** formation was measured at 313 nm by GC and found to be 0.79 (6.6% conversion). The methyl singlet

at 3.55ppm disappeared at the same rate as the growth of two doublets at 4.28 and 4.44ppm in benzene-d_6.

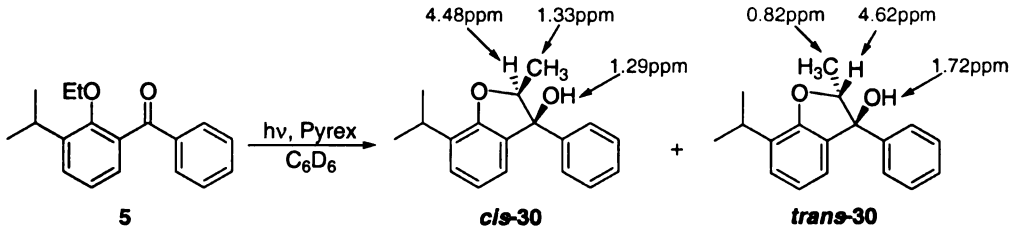
4. *2-Ethoxy-3-methylbenzophenone* (Benzophenone 4)



Scheme 20. Photochemistry of Benzophenone 4

Irradiation of a 0.040 M solution of **4** at room temperature in benzene-d_6 resulted in formation of two products (Scheme 20). Preparative scale irradiation in benzene followed by column chromatography using 2% ethyl acetate in hexanes, resulted in isolation of photoproducts which were identified by their NMR spectra (in C_6D_6) as two isomeric benzofuranols (***cis*-29** and ***trans*-29**). Methyl doublets were most informative because it is generally accepted that a methyl *cis* to the phenyl is significantly shielded relative to the one *trans*. The chemical shift of methyl group of *trans* isomer was shifted much more upfield than that of *cis* isomer. It was also noteworthy that the methine hydrogen *cis* to the phenyl was more shielded than the one *trans* to phenyl. NOe experiments were also performed. Irradiation of the methine quartet of one isomer at 4.60ppm caused an enhancement of the OH signal at 1.72ppm. However, irradiation of the methine quartet of the other isomer at 4.44ppm did not result in signal enhancement of the OH hydrogen at 1.28ppm. Thus, the former was assigned as the *trans* while the latter was assigned as the *cis* isomer. The ratio of the two isomeric benzofuranols were 3.3:1, 4.5:1 and 4.9:1 at -78°C, 0°C and 25°C, respectively.

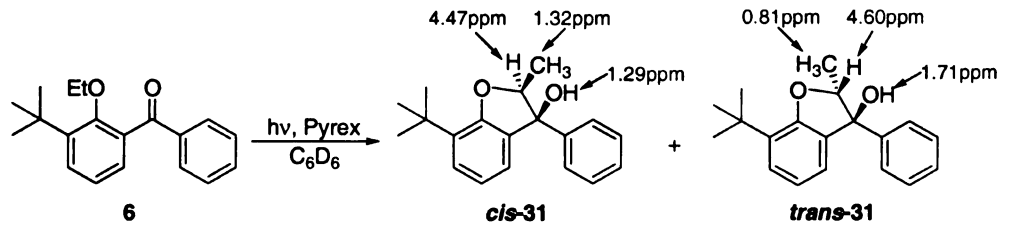
5. *2-Ethoxy-3-isopropylbenzophenone* (Benzophenone 5)



Scheme 21. Photochemistry of Benzophenone 5

Irradiation of **5** in benzene (Scheme 21) resulted in formation of two isomeric benzofuranols (***cis*-30** and ***trans*-30**). Preparative scale irradiation in benzene followed by column chromatography (hexanes: ethyl acetate 40:1) resulted in isolation of the photoproducts which were identified by their corresponding NMR spectra. Stereochemical assignment of the two isomers was made using nOe experiments. Irradiation of the methine quartet signal in the *trans* isomer at 4.62ppm resulted in enhancement of the OH signal at 1.72ppm, while similar irradiation in the *cis* isomer resulted in no such enhancement. The product ratios were determined by NMR analysis. The ratio of the two isomeric benzofuranols were 2.9:1, 4.2:1 and 4.5:1 at -78°C, 0°C and 25°C, respectively. Irradiation of crystalline **5** resulted in a 1.8:1 *cis/trans* benzofuranol ratio.

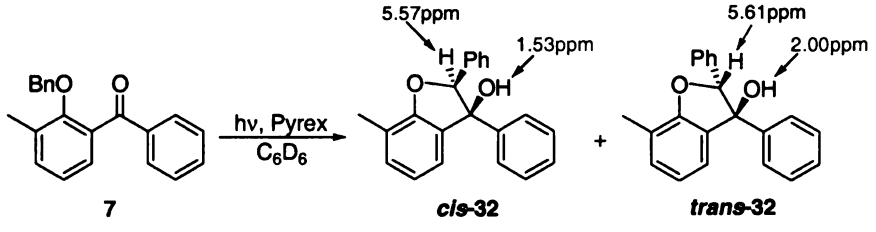
6. *3-t-Butyl-2-ethoxybenzophenone* (Benzophenone 6)



Scheme 22. Photochemistry of Benzophenone 6

Irradiation of a 0.037 M solution of **6** in benzene-d_6 at room temperature resulted in formation of two products (Scheme 22). Preparative scale irradiation in benzene followed by column chromatography, using 2% ethyl acetate in hexanes, resulted in isolation of photoproducts which were identified by their NMR spectra (in C_6D_6) as two isomeric benzofuranols (***cis*-31** and ***trans*-31**). The chemical shift of methyl group of *trans* isomer was shifted much more upfield than that of *cis* isomer. It was also noteworthy that the methine hydrogen *cis* to the phenyl was more shielded than the one *trans* to phenyl. NOe experiments were also performed. Irradiation of the methine quartet of one isomer at 4.60ppm caused an enhancement of the OH signal at 1.71ppm. However, irradiation of the methine quartet of the other isomer at 4.47ppm did not result in signal enhancement of the OH hydrogen at 1.29ppm. Thus, the former was assigned as the *trans* while the latter was assigned as the *cis* isomer. The ratio of the two isomeric benzofuranols were 1:2.7, 1.3:1, 1.9:1 and 2.4:1 at -78°C, -20°C, 0°C and 25°C, respectively.

7. *2-Benzyloxy-3-methylbenzophenone* (Benzophenone 7)

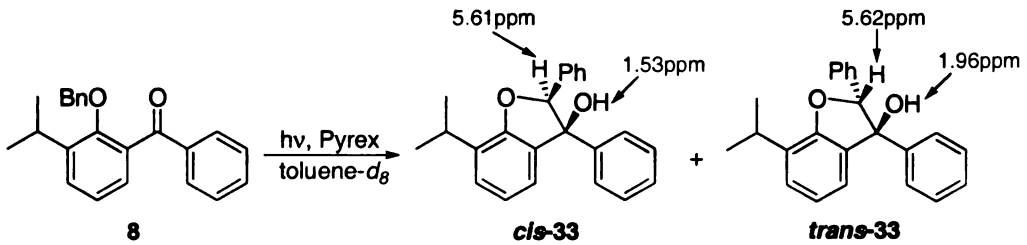


Scheme 23. Photochemistry of Benzophenone 7

Irradiation of **7** in benzene-d_6 resulted in formation of two products (Scheme 23) which were identified as two isomeric benzofuranols (***cis*-32** and ***trans*-32**) by their NMR spectra. Preparative scale irradiation in benzene followed by column chromatography (hexanes: ethyl acetate 30:1~20:1) resulted in separation of photoroducts. The product

ratios were determined by comparing the NMR integration of the methine singlets at 5.57ppm and 5.61ppm of two isomers. Stereochemical assignment of the two isomers was made using nOe experiments. Irradiation of the methine singlet signal in the *trans* isomer at 5.61ppm resulted in enhancement of the OH signal at 2.00ppm, while similar irradiation in the *cis* isomer resulted in no such enhancement. It was also noteworthy that the OH hydrogen *cis* to the phenyl was more shielded than the one *trans* to phenyl. Irradiation of **7** at -78°C, -20°C, 0°C and 25°C resulted in a 2.4:1, 3.8:1, 4.0:1 and 4.7:1 ratio, respectively.

8. *2-Benzyloxy-3-isopropylbenzophenone* (Benzophenone 8)

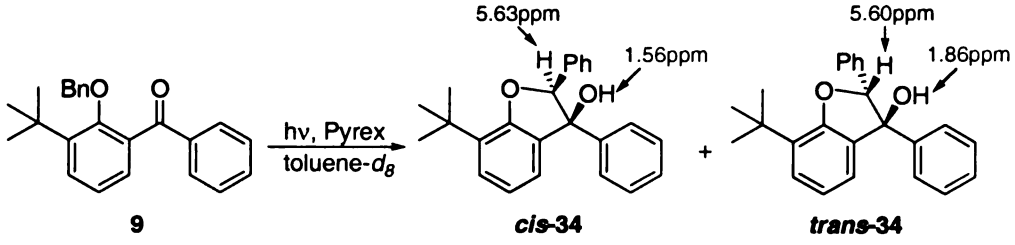


Scheme 24. Photochemistry of Benzophenone 8

Benzophenone **8** (0.031 M) in deuterated toluene was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp. The reaction was complete within 20 minutes and two isomeric benzofuranols (***cis*-33** and ***trans*-33**) formed (Scheme 24). The product ratios were determined by comparing the NMR integration of the OH singlets at 1.53ppm and 1.96ppm of two isomers. Stereochemical assignment of the two isomers was made using nOe experiments. Irradiation of the methine singlet signal in the *trans* isomer at 5.62ppm resulted in enhancement of the OH signal at 1.96ppm, while similar irradiation in the *cis* isomer resulted in no such enhancement. It was also noteworthy that the OH hydrogen *cis* to the phenyl was more shielded than the one *trans* to phenyl.

Irradiation of **8** at -78°C, -20°C, 0°C and 25°C resulted in a 1.8:1, 2.6:1, 2.9:1 and 3.4:1 ratio, respectively.

9. *2-Benzyloxy-3-t-butylbenzophenone* (Benzophenone 9)



Scheme 25. Photochemistry of Benzophenone 9

Irradiation of **9** in toluene-d_8 (Scheme 25) resulted in formation of a mixture of two isomeric benzofuranols (***cis*-34** and ***trans*-34**). Preparative scale irradiation in benzene followed by column chromatography (hexanes: ethyl acetate 30:1~20:1) resulted in separation of the benzofuranols. The product ratios were measured by NMR analysis to be 1:2.7, 1:1.2, 1:1 and 1.4:1 at -78°C, -20°C, 0°C and 25°C, respectively. They were determined by NMR integration of the OH singlet signal of the *cis*-isomer at 1.56ppm to that of the *trans*-isomer at 1.86ppm. Stereochemical assignment of the two isomers was made using nOe experiments. Irradiation of the methine singlet signal in the *trans* isomer at 5.60ppm resulted in enhancement of the OH signal at 1.86ppm, while similar irradiation in the *cis* isomer resulted in no such enhancement. It was also noteworthy that the OH hydrogen *cis* to the phenyl was more shielded than the one *trans* to phenyl.

III. Results for 2-Alkoxy-3-alkyl Acetophenones

A. General Preparation of Ketones

The substituted 2-alkoxy-3-alkyl acetophenones were synthesized by ortho-lithiation. The corresponding aromatic ether was allowed to react with *n*-butyl lithium. The aryl lithium species was then reacted with acetaldehyde in diethyl ether. The resulting alcohol was oxidized with PCC to yield the desired acetophenone.

Table 2 provides the structures of the ketones studied.

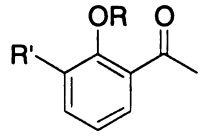
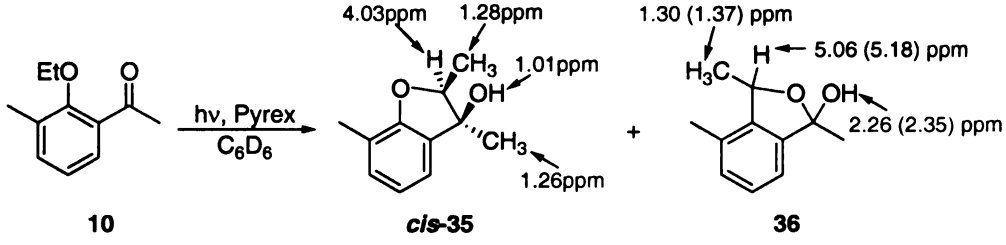


Table 2. 2-Alkoxy-3-alkyl Acetophenones

Ketone	R	R'	Abbreviation
2-ethoxy-3-methylacetophenone	CH_3CH_2	CH_3	**10**
2-ethoxy-3-isopropylacetophenone	CH_3CH_2	$CH(CH_3)_2$	**11**
3-t-butyl-2-ethoxyacetophenone	CH_3CH_2	$C(CH_3)_3$	**12**
2-benzyloxy-3-methylacetophenone	$PhCH_2$	CH_3	**13**
2-benzyloxy-3-isopropylacetophenone	$PhCH_2$	$CH(CH_3)_2$	**14**
2-benzyloxy-3-t-butylacetophenone	$PhCH_2$	$C(CH_3)_3$	**15**

B. Identification of Photoproducts

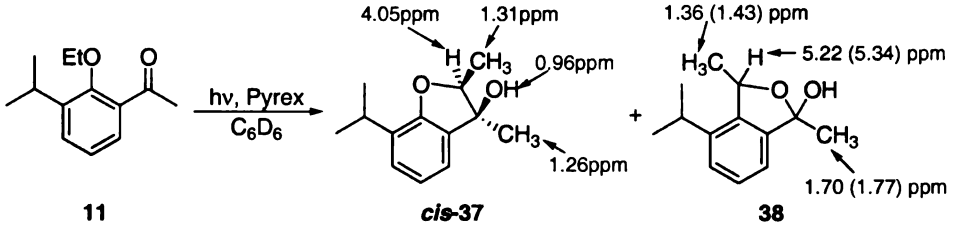
1. *2-Ethoxy-3-methylacetophenone* (Acetophenone 10)



Scheme 26. Photochemistry of Acetophenone 10

The photobehavior of **10** at room temperature was conversion dependent. At low conversion ***cis*-35** and two isomeric hemiketals (**36**) were the major products (Scheme 26). The two hemiketals were identified by the following NMR signals in benzene: methyl doublets at 1.30 and 1.37ppm, methine quartets at 5.06 and 5.18ppm, OH singlets at 2.26 and 2.35ppm. At high conversion the benzofuranol was the only observable photoproduct. The *cis*-stereochemistry was assigned based on nOe experiment: irradiation of the methine quartet at 4.03ppm caused an enhancement of the methyl singlet at 1.26ppm. Preparative scale irradiation was carried out upon low conversion of the starting ketone, stability of the two hemiketals allowed them to be isolated by column chromatography on deactivated silica gel. They were obtained as a 1:1 mixture.

2. *2-Ethoxy-3-isopropylacetophenone* (Acetophenone 11)



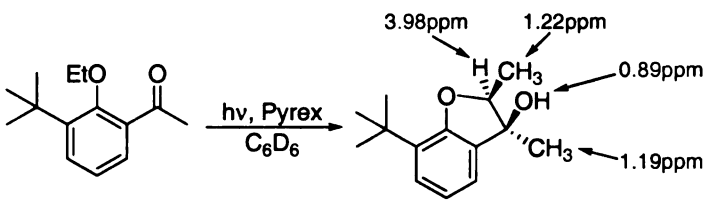
11 ***cis*-37** **38**

Scheme 27. Photochemistry of Acetophenone 11

The photobehavior of **11** at room temperature was conversion dependent. At low conversion ***cis*-37** and two isomeric hemiketals (**38**) were the major products (Scheme 27). The two hemiketals were identified by the following NMR signals in benzene: methyl doublets at 1.36 and 1.43ppm, methine quartets at 5.22 and 5.34ppm, allylic methyl singlets at 1.70 and 1.77ppm. At high conversion the benzofuranol was the only observable photoproduct. The *cis*-stereochemistry was assigned based on nOe experiment: irradiation of the methine quartet at 4.05ppm caused an enhancement of the

methyl singlet at 1.26ppm. Preparative scale irradiation was carried out upon low conversion of the starting ketone. The two hemiketals could not be isolated due to a rapid decomposition on silica gel.

3. *3-t-Butyl-2-ethoxyacetophenone* (Acetophenone 12)



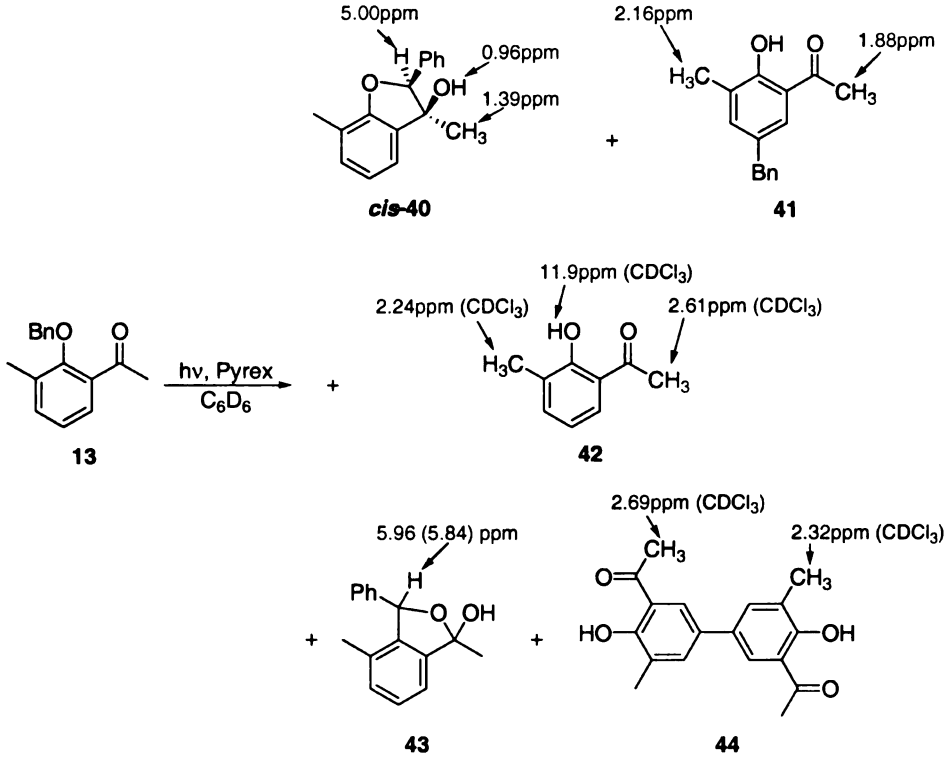
Scheme 28. Photochemistry of Acetophenone 12

Benzophenone **12** (0.025 M) in deuterated benzene was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp. The reaction was complete within 30 minutes and only one product (***cis*-39**) formed (Scheme 28). The stereochemical assignment was made based on nOe experiment: irradiation of the methine quartet at 3.98ppm caused an enhancement of the methyl singlet at 1.19ppm.

4. *2-Benzyloxy-3-methylacetophenone* (Acetophenone 13)

Irradiation of a 0.019 M solution of **13** at room temperature in benzene-d_6 resulted in formation of a mixture of products (Scheme 29). Preparative scale irradiation in benzene followed by column chromatography, using 3% ethyl acetate in hexanes, resulted in isolation of photoproducts which were identified by their NMR spectra (C_6D_6 or $CDCl_3$) as one benzofuranol (***cis*-40**), one benzyl transfer product (**41**), one debenzylation product (**42**), dimerized hydroxyacetophenone (**44**). The two hemiketals (**43**) formed during the irradiation could not be isolated due to rapid decomposition on silica gel, their presence

was confirmed by the two singlets at 5.84 and 5.96ppm in the NMR spectrum of the reaction mixture. The chemical shift of the OH signal from the benzofuranol indicated a *cis* configuration relative to the 2-phenyl, nOe experiment was also performed: irradiation of benzylic methine signal at 5.00ppm caused an enhancement of the methyl singlet at 1.39ppm.

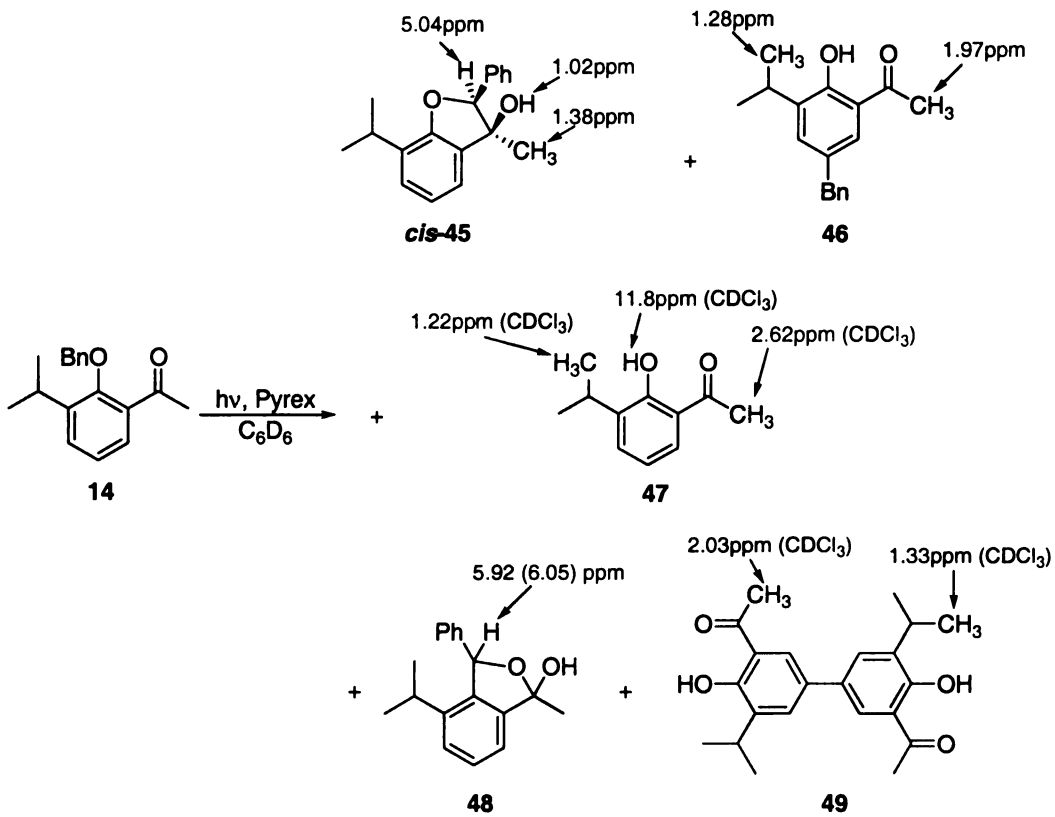


Scheme 29. Photochemistry of Acetophenone 13

5. *2-Benzyloxy-3-isopropylacetophenone* (Acetophenone 14)

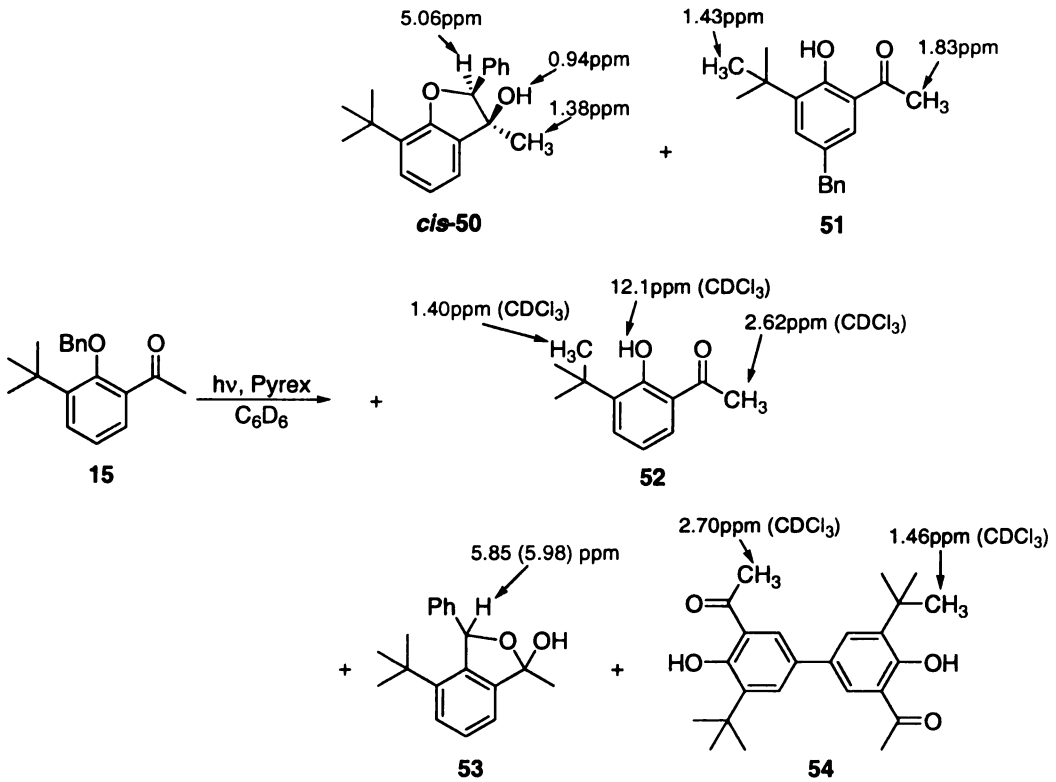
Irradiation of a 0.020M solution of **14** at room temperature in benzene-d_6 resulted in formation of a mixture of products (Scheme 30). Preparative scale irradiation in benzene followed by column chromatography, using 3% ethyl acetate in hexanes, resulted in isolation of photoproducts which were identified by their NMR spectra (C_6D_6 or $CDCl_3$)

as one benzofuranol (***cis*-45**), one benzyl transfer product (**46**), one debenzylation product (**47**), dimerized hydroxyacetophenone (**49**). The two hemiketals (**48**) formed during the irradiation could not be isolated due to rapid decomposition on silica gel, their presence was confirmed by the two singlets at 5.92 and 6.05ppm in the NMR spectrum of the reaction mixture. The chemical shift of the OH signal from the benzofuranol indicated a *cis* configuration relative to the 2-phenyl, nOe experiment was also performed: irradiation of benzylic methine signal at 5.04ppm caused an enhancement of the methyl singlet at 1.38ppm.



Scheme 30. Photochemistry of Acetophenone 14

6. *2-Benzyloxy-3-t-butylacetophenone* (Acetophenone 15)



Scheme 31. Photochemistry of Acetophenone 15

Irradiation of a 0.018M solution of **15** at room temperature in benzene-d_6 resulted in formation of a mixture of products (Scheme 31). Preparative scale irradiation in benzene followed by column chromatography, using 1% ethyl acetate in hexanes, resulted in isolation of photoproducts which were identified by their NMR spectra (C_6D_6 or $CDCl_3$) as one benzofuranol (***cis*-50**), one benzyl transfer product (**51**), one debenzylation product (**52**), dimerized hydroxyacetophenone (**54**). The two hemiketals (**53**) formed during the irradiation could not be isolated due to rapid decomposition on silica gel, their presence was confirmed by the two singlets at 5.85 and 5.98ppm in the NMR spectrum of the reaction mixture. The chemical shift of the OH signal from the benzofuranol indicated a *cis* configuration relative to the 2-phenyl, nOe experiment was also performed: irradiation

of benzylic methine signal at 5.06ppm caused an enhancement of the methyl singlet at 1.38ppm.

IV. Results for α-(Haloethoxy)acetophenones

A. General Preparation of Ketones

α-(Haloethoxy)acetophenones were prepared by basic condition ring opening of styrene oxide, tosylation with tosyl chloride, Dess-Martin oxidation and substitution with halides. α-(2-bromo-2-methylpropoxy)acetophenone was prepared by basic condition ring opening of styrene oxide, PCC oxidation followed by Markovnikov addition of HBr to alkene.

Table 3 provides the structures of the ketones studied.

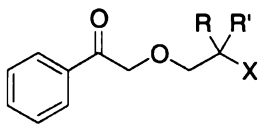


Table 3. α-(Haloethoxy)acetophenones

Ketone	X	R	R'	Abbreviation
α-(chloroethoxy)acetophenone	Cl	H	H	**16**
α-(bromoethoxy)acetophenone	Br	H	H	**17**
α-(iodoethoxy)acetophenone	I	H	H	**18**
α-(2-bromo-2-methylpropoxy)acetophenone	Br	CH_3	CH_3	**19**

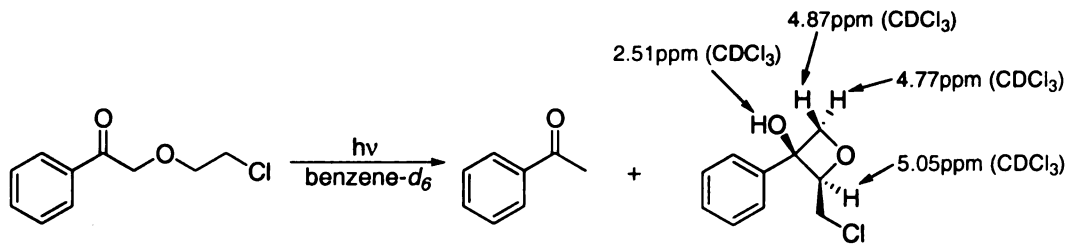
B. Identification of Photoproducts

NMR scale irradiations were carried out using 0.03~0.04M solutions of ketones in

deuterated benzene or methanol. The solutions were irradiated through a Pyrex filter (>290nm). In C_6D_6 with the presence of pyridine, most ketones underwent loss of HX competitive with type II elimination. In the case of **16**, oxetanol and acetophenone were detected after irradiation. Irradiations in benzene-d_6 without pyridine or in methanol-d_4 always resulted in formation of a complex mixture of several products due to competitive reactions and secondary reactions. Preparative irradiations were carried out in benzene with or without pyridine.

C. Individual Ketones

1. *α-(Chloroethoxy)acetophenone* (16)

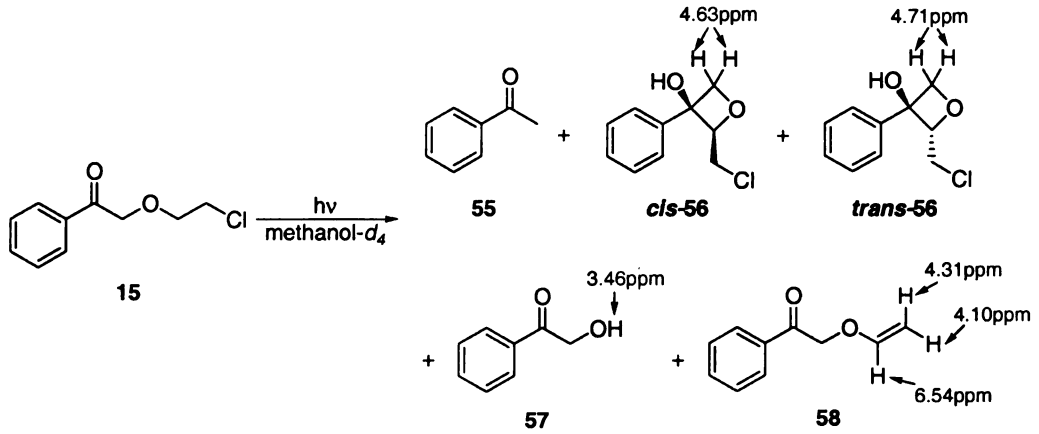


16 **55** ***cis*-56**

Scheme 32. Photochemistry of 16 in Benzene

Irradiation of **16** in benzene-d_6 (Scheme 32) resulted in formation of two products which were identified as acetophenone (**55**) and an oxetanol (***cis*-56**) by their NMR spectra. Preparative scale irradiation in benzene followed by column chromatography (hexanes: ethyl acetate 40:1~20:1) resulted in separation of photoproducts. The product ratio was determined by comparing the NMR integration of the methyl singlet of acetophenone at 2.06ppm to that of the methine signal of the oxetanol at 4.82ppm. Irradiation with the presence of pyridine gave the same outcome as the one without pyridine. During the reaction process, the solutions kept water-white. The *cis*-

stererochemistry of the oxetanol was determined by performing nOe experiment: irradiation of the methine signal at 5.05ppm caused an enhancement of one of the aryl proton signals (7.53ppm).

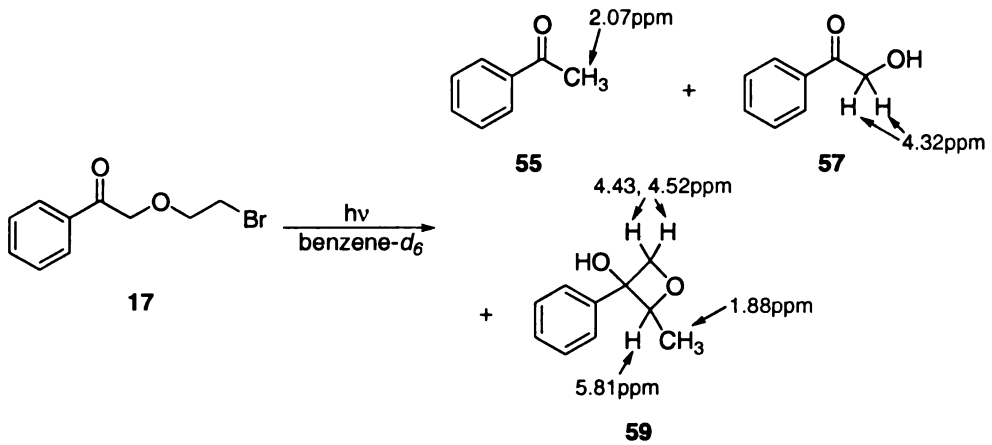


Scheme 33. Photochemistry of 16 in Methanol

The behavior of **16** in deuterated methanol is conversion dependent. At low conversion, irradiation resulted in formation of a mixture of compounds (Scheme 33). **58** was identified by the following NMR signals in methanol: two vinyl protons at 4.31 and 4.10ppm, a vinylidene proton at 6.54ppm. **57** showed a triplet at 3.46ppm corresponding to the OH proton. The two isomeric oxetanols (**56**) were identified by the triplets at 4.63 and 4.71ppm corresponding to the methylenes on the four-membered rings. At high conversion, the signals corresponding to **58** disappeared. The *cis*:*trans* oxetanol ratio decreased as irradiation time increased, ranging from 1.5:1 to 1.3:1. No attempt was made to isolate the products.

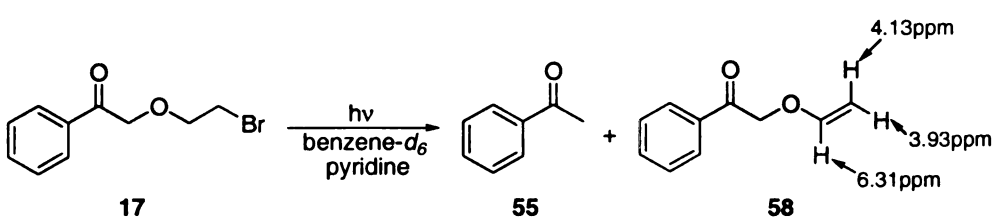
2. *α-(Bromoethoxy)acetophenone* (17)

The behavior of **17** was environment dependent. Irradiation of **17** in benzene or toluene



Scheme 34. Photochemistry of 17 in Benzene Without Additive

without pyridine resulted in formation of a mixture of compounds (Scheme 34). Preparative scale irradiation followed by column chromatography (hexanes: ethyl acetate 8:1) resulted in the separation of photoproducts. The structural assignments of **55** and **57** were based on their NMR spectra as well as comparison with authentic samples of **55** and **57**. The oxetanol (**59**) formed was identified by the following signals in the NMR spectrum of the photolysis mixture: a methine quartet at 5.81ppm (J= 5.4 Hz), a methyl doublet at 1.88ppm (J= 5.4 Hz), two doublets at 4.43 and 4.52ppm corresponding to two methylene protons.



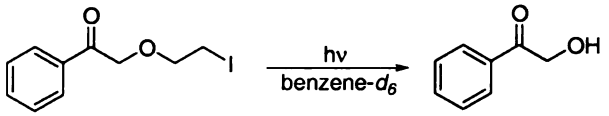
Scheme 35. Photochemistry of 17 in Benzene With Pyridine

When the irradiation was carried out in benzene-d_6 with the presence of pyridine resulted in the formation of two products (Scheme 35): **55** and **58**. They were isolated by preparative irradiation followed by column chromatography (hexanes: ethyl acetate 20:1)

and identified by their NMR spectra. The product ratio was determined by comparing the NMR integration of the methyl singlet of **55** to that of the vinylidene quartet of **58**.

Irradiation of **17** in deuterated methanol resulted in formation of a complex mixture. Their structures were uninterpretable due to signal overlap.

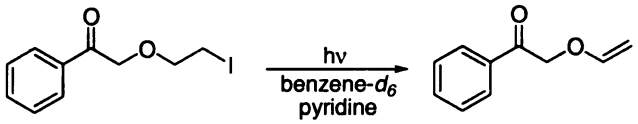
3. *α-(Iodoethoxy)acetophenone* (18)



18 **57**

Scheme 36. Photochemistry of 18 in Benzene Without Additive

The behavior of **18** was also environment dependent. Irradiation of **18** in deuterated benzene gave only one product (Scheme 36): **57**, and the solution turned dark red after irradiation. In the same solvent with pyridine, photolysis resulted in formation of **58**, and the solution remained colorless with some white precipitates (Scheme 37).



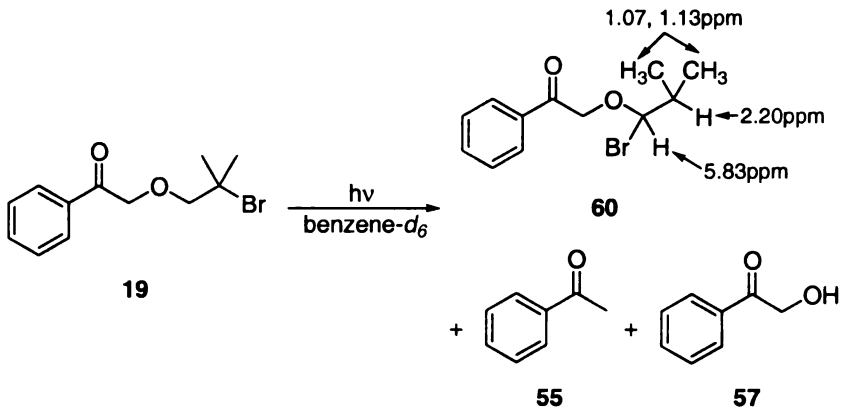
18 **58**

Scheme 37. Photochemistry of 18 in Benzene With Pyridine

4. *α-(2-Bromo-2-methylpropoxy)acetophenone* (19)

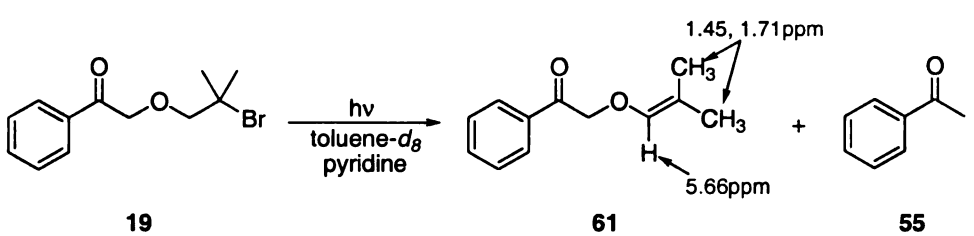
The NMR scale photoreaction of **19** in benzene-d_6 yielded three photoproducts: **55**, **57** and **60** (Scheme 38). Structural assignment of **60** was based on the following signals in the NMR spectrum of the photolysis mixture: two methyl doublets at 1.07 and 1.13ppm (J= 6.6 Hz), a methine multiplet at 2.20ppm, another methine doublet at 5.83ppm (J= 3.6

Hz), two doublets at 4.53 and 4.54ppm corresponding to the methylene protons. No attempt was made to isolate the products.



Scheme 38. Photochemistry of 19 in Benzene Without Additive

The NMR scale reaction was also carried out in deuterated toluene with the presence of pyridine. Irradiation gave two major products (Scheme 39): **55** and **61**. The structure of **61** was determined by the following signals in the NMR spectrum of the photolysis mixture: two methyl singlets at 1.45 and 1.71ppm, a vinylidene signal at 5.66ppm and a singlet at 4.35ppm corresponding to the methlyene protons. During the irradiation the solution remained colorless with the formation of some white precipitates. No attempt was made to isolate the products.



Scheme 39. Photochemistry of 19 in Benzene With Pyridine

V. Results for β-(Haloethoxy)propiophenones

A. General Preparation of Ketones

β-(Haloethoxy)propiophenones were prepared by Michael addition of ethylene glycol to phenyl vinyl ketone, tosylation with tosyl chloride followed by substitution with halides.

Table 4 provides the structures of the ketones studied.

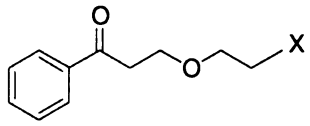


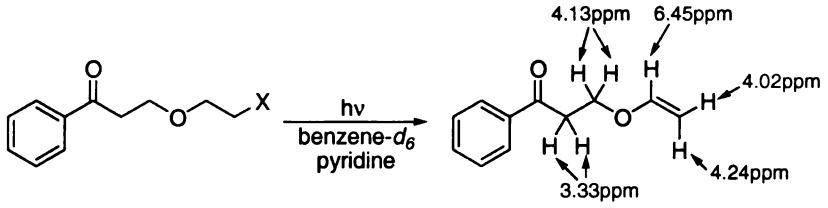
Table 4. β-(Haloethoxy)propiophenones

Ketone	X	Abbreviation
β-(chloroethoxy)prpiophenone	Cl	**20**
β-(bromoethoxy)propiophenone	Br	**21**
β-(iodoethoxy)propiophenone	I	**22**

B. Identification of Photoproducts

NMR scale irradiations were carried out using 0.03 M solutions of ketones in deuterated benzene with the presence of pyridine. The solutions were irradiated through a Pyrex filter (>290 nm). The ketones underwent loss of HX to yield **62** (Scheme 40). Its structure was determined by the following NMR signals: two triplets at 3.33 and 4.13ppm corresponding to two methylenes, two vinyl protons at 4.02 and 4.24ppm, and a vinylidene signal at 6.45ppm. All the reaction solutions remained colorless during the irradiation with the formation of white precipitates. As for **20**, NMR scale reaction was also carried out in methanol-d_4 with pyridine. Results were conversion dependent: at low conversion, the only observable product was **62**; at high conversion, the irradiation gave a

complex mixture. Preparative irradiation was carried out in benzene with pyridine.



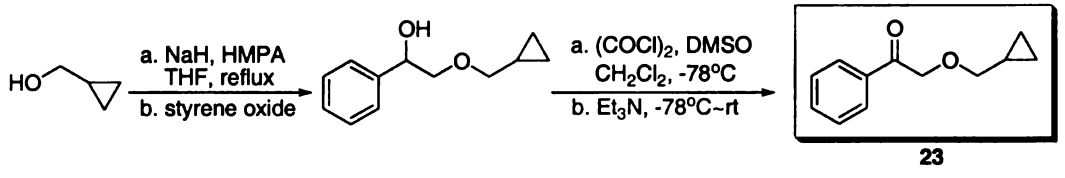
20, 21 or 22 **62**

Scheme 40. Photochemistry of β-(Haloethoxy)propiophenone

VI. Results for α-Cyclopropylmethoxyacetophenone (23)

A. General Preparation

Cyclopropylmethanol was treated with sodium hydride in THF solution with the presence of HMPA, then styrene oxide was added dropwise to this solution to afford a benzylic alcohol. The following Swern oxidation gave desired product **23** (Scheme 41).



23

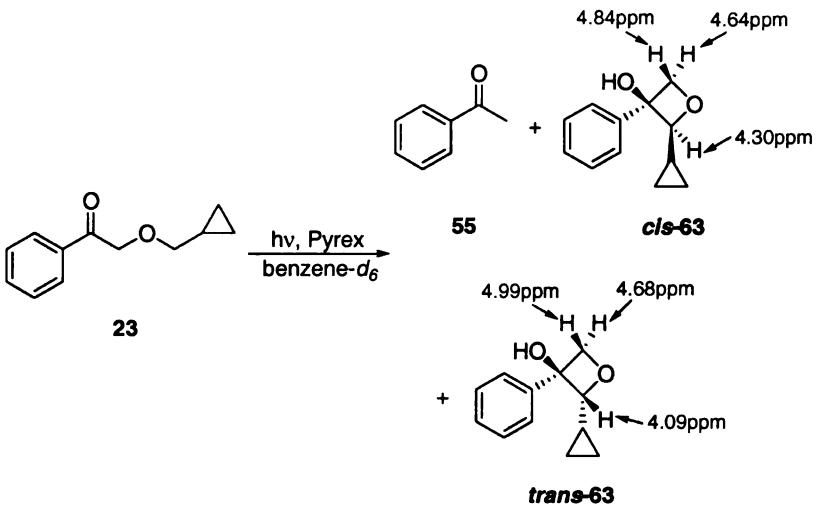
Scheme 41. Synthesis of 23

B. Irradiation Conditions

NMR scale irradiations were carried out using 0.04~0.05 M solutions of **23** in deuterated benzene, toluene, acetonitrile and methanol. The solutions were irradiated through a Pyrex filter. The ketone was irradiated at -70°, -15°, 25° and 80°C to determine the effect of temperature on product ratios. The desired temperatures were attained by dry

ice-acetone, NaCl-ice, water (at RT) and heated silicon oil baths, respectively. Preparative irradiations were carried out in *t*-butanol and methanol.

C. Identification of Photoproducts

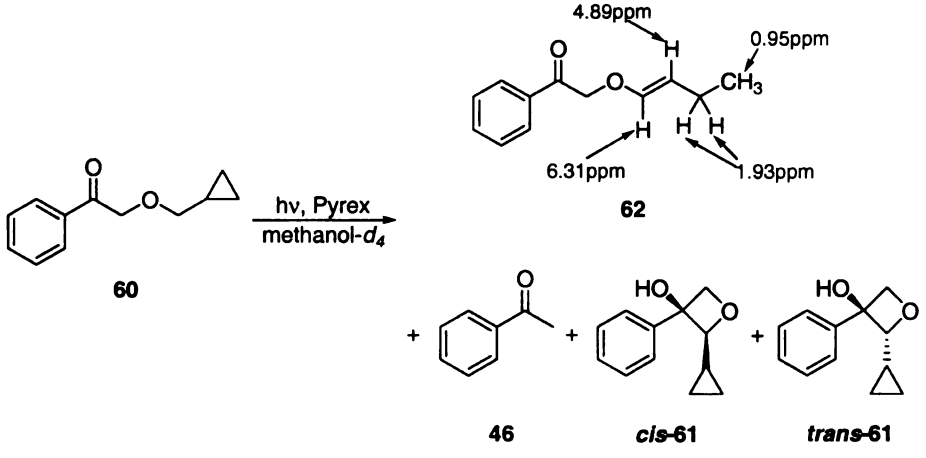


Scheme 42. Photochemistry of 23 in Benzene

Acetophenone **23** (0.035 M) in deuterated benzene was irradiated with Pyrex-filtered light from a medium pressure mercury arc lamp. The reaction resulted in formation of three products (Scheme 42): two isomeric oxetanols (**63**) and acetophenone (**55**). The reaction was repeated at different temperaures and product ratios were determined by NMR. The stereochemical assignments of the two oxetanols were based on nOe experiment: irridiation of the methine doublet at 4.09ppm in the minor isomer caused an enhancement of the OH signal, irridiation of the methine doublet at 4.30ppm in the major isomer caused an enhancement of one of the aryl proton signals. It was also noteworthy that the methine hydrogen *cis* to the phenyl was less shielded than the one *trans* to phenyl. These data strongly suggest that the minor isomer has a *trans*-stereochemistry,

and the major isomer has a *cis*-stereochemistry. Irradiation in deuterated toluene and acetonitrile resulted in the same three products. Temperature effect has also been investigated at various temperature in toluene. The diastereomeric ratio of oxetanols was determined by NMR integration of the methine doublet signals corresponding to each isomer. Preparative irradiation was conducted in *t*-butanol followed by column chromatography on deactivated silica gel.

NMR scale irradiation was also carried out in methanol-d_4 and four products formed (Scheme 43). Besides two isomeric oxetanols (**63**) and **55**, a rearrangement product **64** was also observed. Its structure was determined by the following NMR signals: a methyl triplet at 0.95ppm, a doublet of quartet at 1.93ppm corresponding to the methylene protons, two vinylidene signals at 4.89 and 6.31ppm. The *E*-stereochemistry of the double bond was determined by coupling constant of the two vinylidene protons (J= 12.5 Hz). Preparative irradiation in methanol followed by column chromatography on deactivated silica gel resulted in the isolation of photoproducts.



Scheme 43. Photochemistry of 23 in Methanol

VII. Results for α-Cyclopropylmethoxyacetone (24)

A. General Preparation

Cyclopropylmethanol was treated with sodium hydride in THF solution with the presence of HMPA, then propylene oxide was added dropwise to this solution to afford a secondary alcohol. The following Swern oxidation gave desired product **24**.

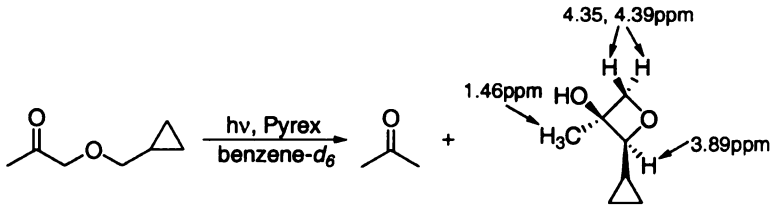
B. Irradiation Conditions

NMR scale irradiations were carried out using 0.04 M solutions of **24** in deuterated benzene, acetonitrile and methanol. The solutions were irradiated through a Pyrex filter. Preparative irradiations were carried out in benzene and methanol.

C. Identification of Photoproducts

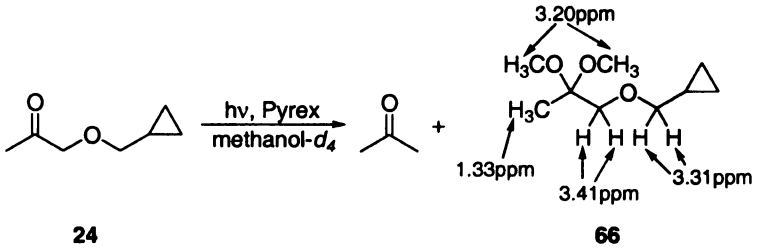
Irradiation of **24** in benzene-d_6 resulted in the formation of acetone and an oxetanol (***cis*-65**) (Scheme 44). The product ratio was determined by NMR integration of the methine doublet signal of the oxetanol and the methyl singlet signal of acetone. The structural assignment of the oxetanol (***cis*-65**) was accomplished by performing nOe experiments. Irridiation of the methine doublet at 3.89ppm caused an enhancement of the methyl signal, this suggests that this oxetanol has a *cis*-stereochemistry. Photolysis of **24** in deuterated acetonitrile gave the same two products. Preparatory scale reaction was conducted in benzene, the following column chromatography resulted in the isolation of products.

The behavior of **24** in methanol-d_4 was quite different from that in benzene or



Scheme 44. Photochemistry of 24 in Benzene

acetonitrile. Irradiation also gave two products (Scheme 45): acetone and an acetal (**66**). The acetal has the following NMR signals in $CDCl_3$: methyl singlet at 1.33ppm, methoxy signal at 3.20ppm, two methylene signals at 3.31 and 3.41ppm. Considering the acidity of deuterated methanol, the preparative reaction was conducted in purified methanol. However, the same result as that of the NMR scale reaction was obtained. The following column chromatography resulted in the isolation of **66**.



Scheme 45. Photochemistry of 24 in Methanol

VIII. Results for β-Cyclopropylmethoxybutanone (25)

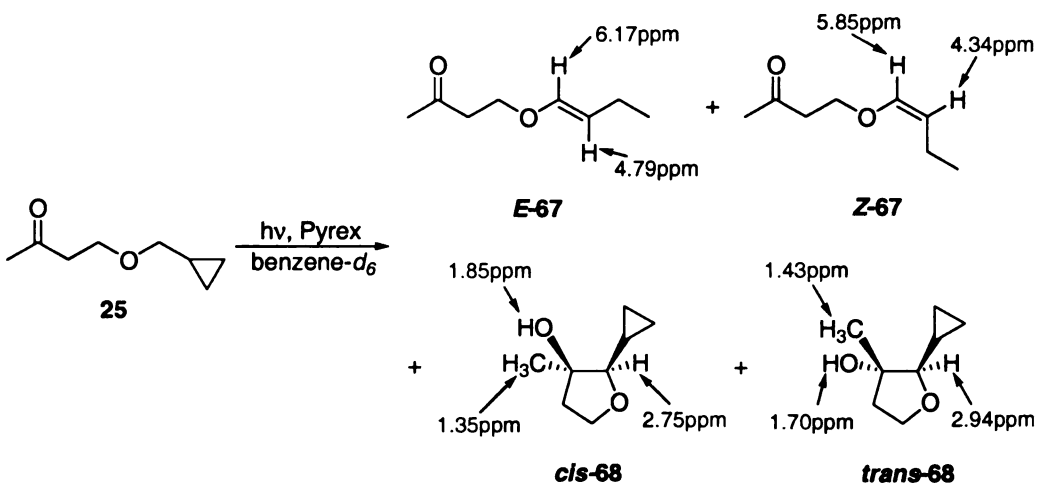
A. General Preparation

25 was prepared by Michael addition of cyclopropylmethanol to methyl vinyl ketone under basic condition.

B. Irradiation Conditions

NMR scale irradiations were carried out using 0.04~0.06 M solutions of **25** in deuterated benzene, toluene and methanol. The solutions were irradiated through a Pyrex filter. The ketone was irradiated at -78°, 25° and 0°C to determine the effect of temperature on product ratios. The desired temperatures were attained by dry ice-acetone, ice water and water (at RT), respectively. Preparative irradiation was carried out in benzene.

C. Identification of Photoproducts

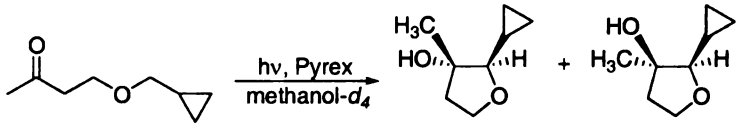


Scheme 46. Photochemistry of 25 in Benzene

25 (0.038 M) in deuterated benzene was irradiated with Pyrex-filtered light from a medium pressure mercury arc lamp. The reaction resulted in formation of four products (Scheme 46): two isomeric tetrahydrofuranols (**68**) and two isomeric 4-butenyloxybutanones (**67**). The stereochemical assignments of the two THFs were based on nOe experiment: irradiation of the methine doublet at 2.75ppm in the major isomer caused an enhancement of the methyl signal, irradiation of the methine signal at 2.94ppm

in the minor isomer caused an enhancement of the OH signal. These data suggest that the major isomer has a *cis*-stereochemistry and the minor isomer has a *trans*-stereochemistry. The stereochemical assignments of the two 4-butenyloxybutanones were determined by coupling constant of the two vinylidene protons: the coupling constant for *E*-isomer was 12.6 Hz, for *Z*-isomer was 6.9 Hz. Irradiation in deuterated toluene resulted in the same four products. Product ratio was determined by NMR integration of the vinyl proton signals of **67** and the methine signals (doublets) of the THFs. Preparative irradiation conducted in benzene followed by column chromatography resulted in isolation of photoproducts.

NMR scale irradiation was also carried out in methanol-d_4 and two isomeric THFs (**68**) formed (Scheme 47).



25 ***trans*-68** ***cis*-68**

Scheme 47. Photochemistry of 25 in Methanol

Discussion

I. Conformational Effect on Photobehavior of Substituted Phenyl Ketones

A. Substituted Benzophenones

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 $M^{-1}s^{-1}$.[46,47] Wagner has shown that energy transfer is sensitive to the degree of steric congestion *ortho* to the carbonyl.[23] k_q values were measured by nanosecond laser flash spectroscopy for a number of *o*-alkoxyphenyl ketones, having *o*-alkoxy substituents of various sizes. Most ketones have k_q values on the order of 2.9 x 10^9 $M^{-1}s^{-1}$. The steric bulk of the *o*-alkoxy substituents prevent complete overlap of the π-orbitals of ketone and quencher. The result is a lower than normal k_q value for those ketones.

Reciprocal triplet lifetimes were calculated from the slopes of Stern-Volmer quenching plots ($k_q\tau$) assuming that k_q= 2.9 x 10^9 $M^{-1}s^{-1}$ for all ketones. These reciprocal triplet lifetimes are presented in Table 5.

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

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

Wagner has found k_d values for *o*-alkoxybenzophenones on the order of 1.7 x 10^5 s^{-1}.[48] There is no known reason why k_d values should be sensitive to an extra alkyl substituent, i.e., k_d's for 2-alkoxy-3-alkyl benzophenones and *o*-alkoxybenzophenones should be equal. δ-Hydrogen abstraction rate constants calculated from reciprocal triplet lifetimes and assumed k_d value are presented in Table 6.

Table 5. Kinetic Results on 2-Alkoxy-3-alkyl Benzophenones in Benzene at 25°C

Ketone	R	R'	$k_q\tau^a$, M^{-1}	τ^b, ns
1	CH_3	CH_3	629.7	217
2	CH_3	$CH(CH_3)_2$	673	232
3	CH_3	$C(CH_3)_3$	333.3	114.9
4	CH_3CH_2	CH_3	91.6	31.6
5	CH_3CH_2	$CH(CH_3)_2$	105.5	36.4
6	CH_3CH_2	$C(CH_3)_3$	65.7	22.7
7	$PhCH_2$	CH_3	19.1	6.6
8	$PhCH_2$	$CH(CH_3)_2$	60	20.7
9	$PhCH_2$	$C(CH_3)_3$	11	3.8

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

[b]$k_q = 2.9 \times 10^9\ M^{-1}s^{-1}$.

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

$$\Phi = \Phi_{isc} k_H \tau \alpha$$

where Φ_{isc} = intersystem crossing quantum yield

k_H = rate constant for δ-hydrogen abstraction

τ = ketone triplet lifetime

α = efficiency with which biradical converts to product

Intersystem crossing quantum yield for aromatic ketone is 1.0. If α is 1.0, then $\Phi\tau^{-1}$ equals k_H. If α is less than unity, this product represents a lower limit for k_H. Values calculated from both assumptions are presented in Table 6.

Table 6. k_H Values for 2-Alkoxy-3-alkyl Benzophenones in Benzene at 25°C

Ketone	R	R'	Φ^a	τ^{-1} 10^6 s^{-1}	k_H^b 10^6 s^{-1}	k_H^c 10^6 s^{-1}
1	CH_3	CH_3	0.51	4.61	4.44	2.35
2	CH_3	$CH(CH_3)_2$	0.64	4.31	4.14	2.76
3	CH_3	$C(CH_3)_3$	0.79	8.70	8.53	6.87
4	CH_3CH_2	CH_3	0.47	31.6	31.4	14.9
5	CH_3CH_2	$CH(CH_3)_2$	0.53	27.5	27.3	14.6
6	CH_3CH_2	$C(CH_3)_3$	0.75	44.1	43.9	33.1
7	$PhCH_2$	CH_3	0.68	151.5	151.3	103.0
8	$PhCH_2$	$CH(CH_3)_2$	0.74	48.3	48.1	35.7
9	$PhCH_2$	$C(CH_3)_3$	0.90	263.2	263.0	236.9

[a]Total quantum yield.

[b]Calculated from $1/\tau$, assuming $k_d = 1.7 \times 10^5$ s^{-1}.

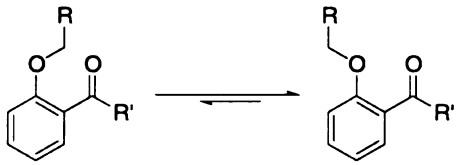
[c]Product of Φ and $1/\tau$.

Discrepancies between the two calculated k_H values may come when α is less than one. Biradical inefficiencies are well known in ketone photochemistry, that is probably the case for these ketones.

δ-Hydrogen abstraction rate constants are sensitive to the reactivity of the alkoxy hydrogens. Benzophenone **7** is 34 times more reactive than **1** and 4.8 times more reactive than **4**, reflecting the greater reactivity of a benzylic hydrogen in comparison with a primary or secondary hydrogen. The same trend has also been observed for 3-isopropyl- and 3-t-butylbenzophenones.

Previous study in our group showed that *o*-alkoxyphenyl ketones undergo slow δ-

hydrogen abstraction from their triplets because the alkoxy group prefers a conformation unfavorable to reaction, as shown in Scheme 48.[23] Blankespoor reported that a methyl group *ortho* to the alkoxy group enhances the quantum efficiency for reaction of comparable anthraquinones by changing the conformational equilibrium.[24] This effect has been examined in 2-alkoxy-3-alkyl benzophenones.

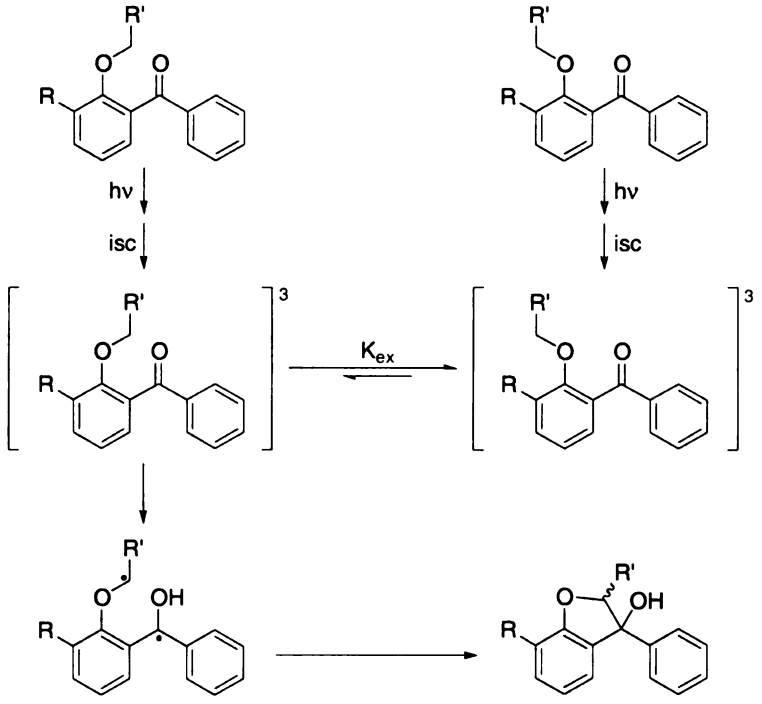


syn, syn anti, syn

Scheme 48. Conformational Equilibrium of *o*-Alkoxyphenyl Ketones

For *o*-alkoxybenzophenones, coplanarity of the alkoxy substituted benzene ring with the carbonyl and rotation about the acyl-phenyl bond do not have significant effect on the rate of hydrogen abstraction. 2,6-Diacylalkoxybenzenes have been used as models for the (syn, syn) conformer, the large k_H values for these compounds indicate that the alkoxy group rotation is important to the overall hydrogen abstraction mechanism, and the interconversion of the two conformers resulting from such a rotation is due to excited state equilibrium.

The preferred excited state conformation of *o*-alkoxybenzophenones is one in which the alkoxy group is rotated away from the carbonyl group, then the alkoxy hydrogens are not as available to the carbonyl oxygen in this arrangement as they would be if the alkoxy group was pointing towards the carbonyl. Hence, δ-hydrogen abstraction may be more efficient for 2-alkoxy-3-alkyl benzophenones than for *o*-alkoxybenzophenones. In all cases, this rate enhancement is observed for 2-alkoxy 3-alkyl benzophenones (Table 6). A mechanism based upon excited state equilibrium is summarized in Scheme 49.



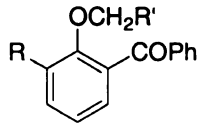
Scheme 49. Excited State Equilibrium of 2-Alkoxy-3-alkyl Benzophenones

The ^{13}C NMR chemical shifts of the alkoxy carbons in 3-substituted 2-alkoxybenzophenones are 6 to 7ppm downfield relative to those of their *o*-alkoxybenzophenone counterparts (Table 7). In this system, increasing bulky alkyl substituents force the alkoxy group out of the plane of the benzene ring, thereby disrupting conjugation of the alkoxy oxygen with the aromatic system. This loss of conjugation is manifested by the higher chemical shift values of the alkoxy carbons of theses compounds.

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 2-

Table 7. Chemical Shift of the Alkoxy Carbons of 2-Alkoxy-3-alkyl Benzophenones



R	R'	$\delta_{O\text{-}CH_2\text{-}R'}$, ppm
H	H	55.5
CH_3	H	61.8
$CH(CH_3)_2$	H	62.9
$C(CH_3)_3$	H	62.1
H	CH_3	63.9
CH_3	CH_3	70.4
$CH(CH_3)_2$	CH_3	71.4
$C(CH_3)_3$	CH_3	70.8
H	Ph	70.0
CH_3	Ph	76.5
$CH(CH_3)_2$	Ph	77.5
$C(CH_3)_3$	Ph	76.7

alkoxy-3-alkyl benzophenone 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 2-alkoxy-3-alkyl benzophenones. That is, k_H for 2,6-diacylalkoxybenzenes represent the intrinsic k_H values for their corresponding 2-alkoxy-3-alkyl benzophenone analogues. The calculation was based on Winstein –Holness principle.[49] This principle, 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 2-alkoxy-3-alkyl benzophenone)

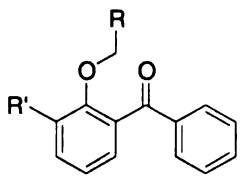
K_{ex} = excited state fractional equilibrium population of the reactive conformer

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 8.

Table 8. Excited State Equilibrium Constants for 2-Alkoxy-3-alkyl Benzophenones in Benzene at 25°C



R	R'	k_H, 10^6 s^{-1}	K_{ex}
H	CH_3	2.35	0.107
H	$CH(CH_3)_2$	2.76	0.126
H	$C(CH_3)_3$	6.87	0.314
H	COPh	21.9	
Ph	CH_3	103.0	0.417
Ph	$CH(CH_3)_2$	35.7	0.145
Ph	$C(CH_3)_3$	236.9	0.959
Ph	COPh	247.0	

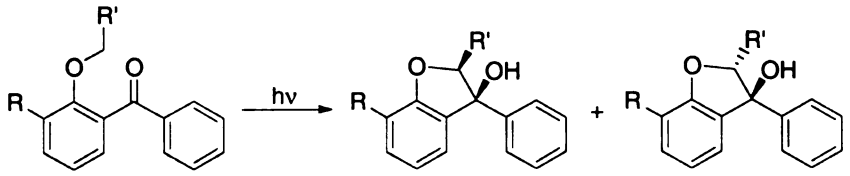
The K_{ex} values for 2-methoxy and 2-benzyloxybenzophenones are quite different. This would seem to indicate that the magnitude of K_{ex} is influenced by the size of the alkoxy substituents.

Excited state equilibrium favors the unreactive conformer in 2-methoxy-3-methylbenzophenone (**1**) by nearly 9:1, that number drops to 3:1 in 3-t-butyl-2-methoxybenzophenone (**3**). The same trend has also been found for their 2-benzyloxy counterparts, especially for 2-benzyloxy-3-t-butylbenzophenone (**9**) the excited state equilibrium highly favors the reactive conformer with a K_{ex} almost equals to 1. Hence, the steric repulsion due to the 3-alkyl groups gets stronger than that due to the carbonyl group with the size of the 3-alkyl substituents.

The hydrogen abstraction rate constants for 3-isopropyl benzophenones do not differ much from their 3-methyl analogues. It is well known that methyl and isopropyl have similar conformational energies,[27] with the value for the isopropyl group (2.1 kcal/mol) being only slightly larger than that of the methyl group (1.8 kcal/mol). The similar values of the two substituents reflect the fact that rotation about the bond between the substituent and the ring allows the isopropyl to adopt a conformation that minimizes the effect of its additional methyl substituents. A t-butyl (>4.5 kcal/mol) substituent experience a strong van der Waals repulsion with the *o*-alkoxy group which cannot be relieved by rotation about the bond to the ring.

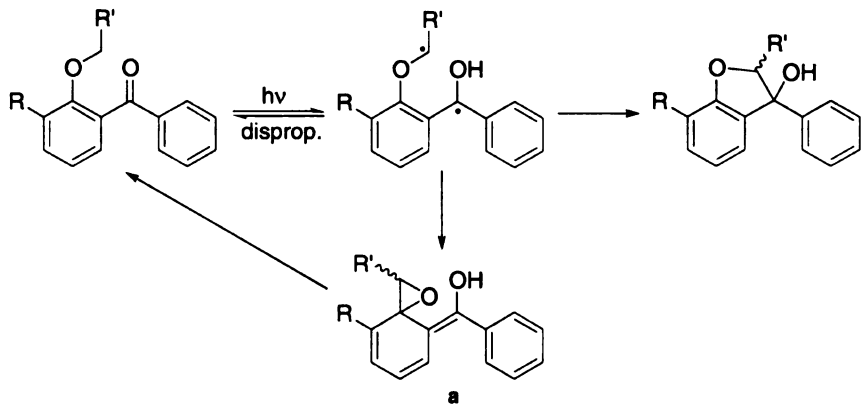
The quantum efficiency for cyclization is lower in methanol than in benzene (Table 9), in sharp contrast to the solvent effects observed on quantum efficiencies of product formation for *o*-alkoxybenzophenones. It is well known that pyridine and other weak Lewis bases, such as t-butyl alcohol, solvate the 1,5-biradical derived from *o*-

Table 9. Solvent Effects on Quantum Yields of 2-Alkoxy-3-alkyl Benzophenones



Solvent	R	R'	Φ_{cis}	Φ_{trans}	Φ_{total}
Benzene	CH_3	H			0.51
Methanol	CH_3	H			0.35
Benzene	$CH(CH_3)_2$	H			0.64
Methanol	$CH(CH_3)_2$	H			0.46
Benzene	$C(CH_3)_3$	H			0.79
Methanol	$C(CH_3)_3$	H			0.51
Benzene	CH_3	CH_3	0.39	0.08	0.47
Methanol	CH_3	CH_3	0.09	0.24	0.33
Benzene	$CH(CH_3)_2$	CH_3	0.43	0.10	0.53
Methanol	$CH(CH_3)_2$	CH_3	0.10	0.28	0.38
Benzene	$C(CH_3)_3$	CH_3	0.53	0.22	0.75
Methanol	$C(CH_3)_3$	CH_3	0.09	0.32	0.41
Benzene	CH_3	Ph	0.56	0.12	0.68
Methanol	CH_3	Ph	0.21	0.47	0.68
Benzene	$CH(CH_3)_2$	Ph	0.57	0.17	0.74
Methanol	$CH(CH_3)_2$	Ph	0.23	0.51	0.74
Benzene	$C(CH_3)_3$	Ph	0.53	0.37	0.90
Methanol	$C(CH_3)_3$	Ph	0.18	0.56	0.74

alkoxybenzophenone and suppress disproportionation of the biradical to starting ketone, resulting in an enhancement of the photocyclization quantum yield.[50] For 2-alkoxy-3-alkylbenzophenones, it may be possible that solvation of the biradical reduces the rate constant for cyclization enough to make some other biradical process competitive. A possible pathway is outlined in Scheme 50. 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 **a**. Methanol would not affect the rate with which the biradical cyclizes to **a**, since such a cyclization does not involve the hydroxyl proton. Rearrangement of **a** to the starting ketone should be fast since it involves a rearomatization of the benzene ring.



Scheme 50. Proposed Mechanism for 2-Alkoxy-3-alkyl Benzophenones

Methanol solvation of the biradical also results in a reverse stereoselectivity for biradical cyclization. In benzene, cyclization of biradicals derived from 2-alkoxy-3-alkylbenzophenones clearly favors formation of the kinetically preferred product. That is, cyclization of these biradicals in hydrocarbon solvent favors the isomer in which the less bulky hydroxyl group is *cis* to the C-2 alkyl (*cis*-isomer). Solvation in methanol increases the steric bulk of the hydroxyl group, since methanol is now hydrogen bonded to the

hydroxyl proton, the hydroxyl group is now comparable in size to a methyl (in 2-ethoxyl-3-alkylbenzophenone derived biradical) or a phenyl (in 2-benzyloxy-3-alkylbenzophenone derived biradical), cyclization proceeds with opposite stereochemical preference.

Our temperature studies along with semiemperical calculations indicates that not only activation enthalpies, but also their entropies (the A factors in the Arrhenius equation, $k = Ae^{-Ea/RT}$), which may reflect the intersystem crossing rates of the biradical rotamers, are responsible for the observed diastereoselectivities.

Table 10. Arrhenius Data for 2-Alkoxy-3-alkyl Benzophenones

Ketone	A_{cis}/A_{trans}	ΔE_a, kcal/mol
4	10.3	0.44
5	10.7	0.51
5	88.3	2.1
7	16.6	0.75
8	10.8	0.70
9	15.7	1.46

Product ratios are influenced by the energies and hydrogen abstraction rates of reactive excited state conformer as well as interconversion and cyclization rates of biradical rotamers. Energies of reactive triplet conformers mirror those of reactive ground state minima since the only significant change in geometry due to n, π^* excitation is a slight lengthening of the C-O bond.[51] The hydrogen abstraction rates are dependent on the orientation of the abstractable hydrogen relative to the nodal plane of the carbonyl group[52] and are assumed to be similar for various conformers. These factors control the

product ratio only when cyclization is faster than interconversion of biradical rotamers (ground state control). When biradicals interconvert faster than they cyclize, which is the case for most triplet biradicals due to their long lifetime, only energies and cyclization rates of various conformers influence product ratios (conformational control). Thus, in cases where the photocyclization is conformationally controlled, the product ratios can be calculated using,[53]

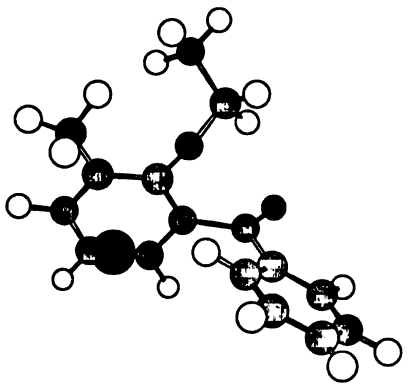
$$cis/trans = (X_{cis}/X_{trans})\cdot(k^{cis}{}_{cyc}/k^{trans}{}_{cyc})$$

where X_{cis} and X_{trans} are the population of the biradicals leading to *cis* and *trans* indanols, $k^{cis}{}_{cyc}$ and $k^{trans}{}_{cyc}$ are the rates of the cyclizations for different conformers. The populations of different rotamers are determined by the difference in their free energies which are presumed to be dominated by enthalpies. There are several known mechanisms for ISC of biradicals.[54] In short biradicals, ISC is mainly driven by spin-orbit coupling, which is known to be very much dependent upon the distance and orientation of radical centers.[55,56,57] The observed diastereoselectivities can be explained by the calculated energies, which reflects the conformational population, and cyclization rates which contain the intersystem crossing term.

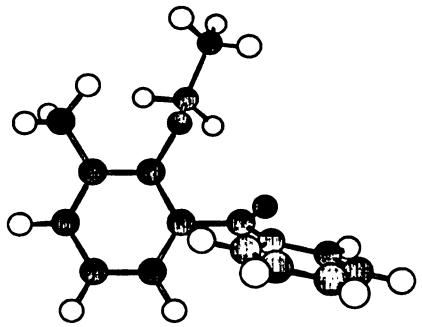
2-Ethoxy-3-methylbenzophenone (4):

Experimental results show the *cis*-benzofuranol to be the major cyclization product under all conditions. Ground state global minimizations indicate the presence of two reactive geometries, a low energy **A** (d=2.40 Å, ω= 68°) in a pro-*cis* and a pro-*trans* geometry **B** (d= 2.51Å, ω= 38°) 0.1 kcal/mol higher in energy.

Arrhenius data for **4** indicate the pro-*trans* precursor to be enthalpically more stable

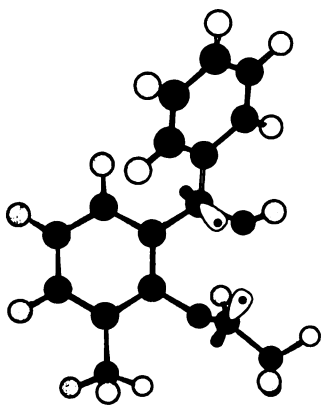


A

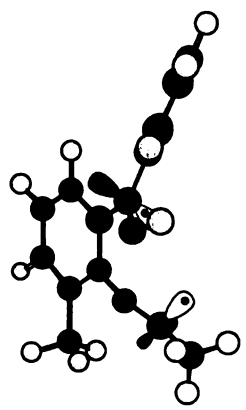


B

than the pro-*cis* one by 0.44 kcal/mol. Global minimization on the biradical from **4** show the presence of two minima within 0.42 kcal/mol of each other. The global minimum **a** is in a pro-*trans* geometry, and pro-*cis* (**b**) geometry is higher in energy than **a** by 0.41 kcal/mol, in good agreement with the experimental values. The difference in A factors can be attributed to a faster cyclization rate of the pro-*cis* precursor, due to its higher energy which in turn means a lower activation energy for cyclization. Therefore, the photocyclization of **4** is believed to be conformationally controlled which means that the biradical lives long enough to allow equilibration. Furthermore, the difference in the A factors indicates that there needs to be an activation energy for cyclization.



a



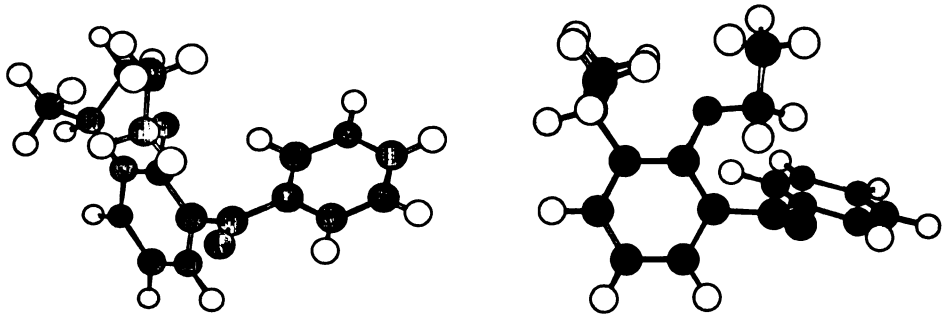
b

Table 11. Temperature Effect on 2-Alkoxy-3-alkylbenzophenones

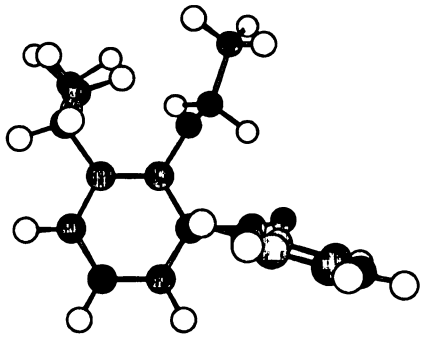
T (°C)	Solvent	4	5	6	7	8	9
		cis:trans	*cis:trans*	*cis:trans*	*cis:trans*	*cis:trans*	*cis:trans*
-78	**Benzene**	**3.29:1**	**2.89:1**	**1:2.67**	**2.39:1**	**1.76:1**	**1:2.71**
-20	**Benzene**			**1.3:1**	**3.77:1**	**2.58:1**	**1:1.22**
0	**Benzene**	**4.53:1**	**4.22:1**	**1.87:1**	**4.04:1**	**2.89:1**	**1.03:1**
25	**Benzene**	**4.90:1**	**4.52:1**	**2.4:1**	**4.7:1**	**3.4:1**	**1.4:1**
25	**Crystal**		**1.76:1**				
25	**Methanol**	**1:2.2**	**1:2.35**	**1:2.5**	**1:1.72**	**1:1.76**	**1:2.6**

2-Ethoxy-3-isopropylbenzophenone (5):

Global minimization (semiempirical- AM1 level) with dihedral drivers around substituted benzene-acyl and ether oxygen-benzene bonds have shown that **5** has three energy minima within 0.5 kcal/mol of each other. In the lowest energy geometry **A**, the closest methylene hydrogen is 2.39 Å away and makes a dihedral angle of 73° with the carbonyl σ plane. The other minimum **B** is 0.45 kcal/mol higher in energy than the global minimum. **B** (d_1=2.52 Å, ω_1= 60°; d_2=2.79 Å, ω_2= 83°) has both methylene hydrogens close enough for abstraction. Another minimum **C**, which lies 0.47 kcal/mol above the global minimum, has a hydrogen 2.32 Å (ω= 56°) from carbonyl oxygen.



A **B**

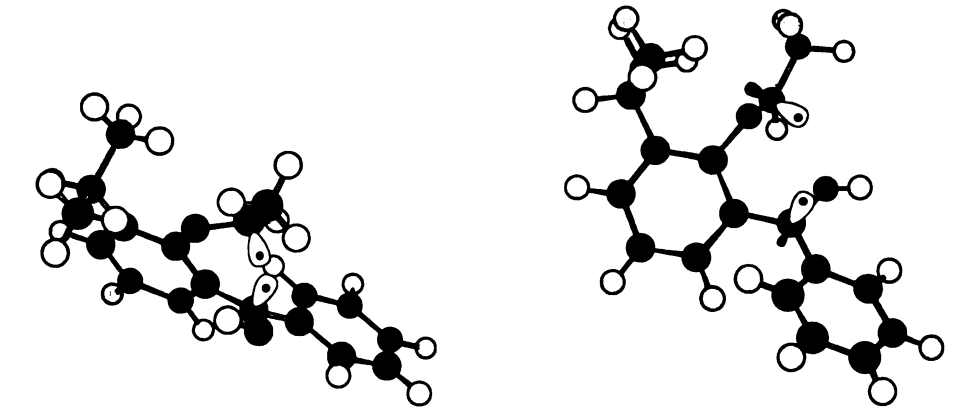


c

The Arrhenius plot is linear which indicates that the biradical conformers are equilibrated at all temperatures. Semiempirical minimizations reveal the presence of four minima within 2.2 kcal/mol of each other. Three of these (**a, b** and **c**) are in the pro-*cis* geometry and the other one (**d**) is in a pro-*trans* geometry. Conformations **b** and **c** are respectively 1.5 and 1.8 kcal/mol higher in energy than **a**. The highest energy conformer (**d**) is 2.2 kcal/mol higher than **a** and will not contribute much to the overall yield of *trans*-benofuranol. Arrhenius data, however, indicate that the conformation leading to *trans* should be 0.51 kcal/mol more stable than the one leading to *cis*. The fact that the global minimum has a pro-*cis* geometry contrasts with the Arrhenius data. It was thought that ground state control might be operative. The rotational energy map for interconversion of **a** and **d** indicates a 6-7 kcal/mol barrier. This barrier is much too large for the interconversion of these biradical conformers to compete with cyclization. Thus, ground state control of reactivity must be operative.

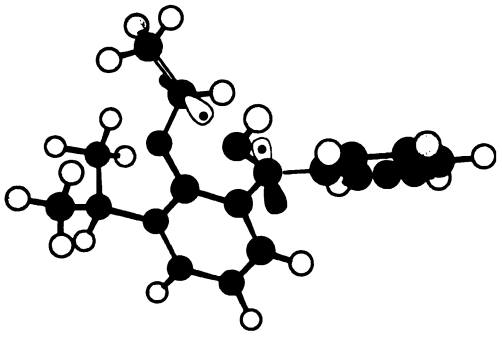
Semiempirical minimizations on the ground state of **5** revealed three minima within 0.5 kcal/mol of each other. If bond rotations are slow as expected and ground state control is operative, then these geometries should give the products in the correct ratios. Arrhenius data predict the two reactive geometries to be different in energy by 0.51

kcal/mol (good agreement with calculated results) with the lower energy geometry resulting in the *trans*-isomer. Indeed, the global ground state minimum is in the pro-*trans* geometry.

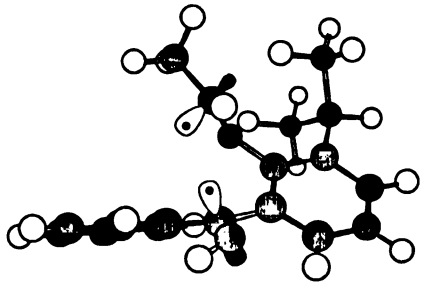


a

b



c

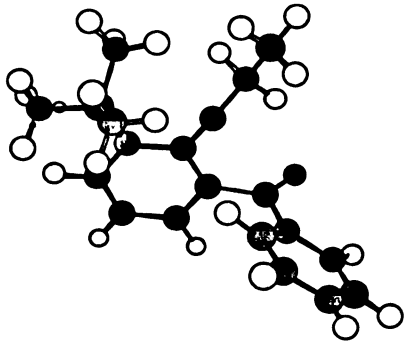


d

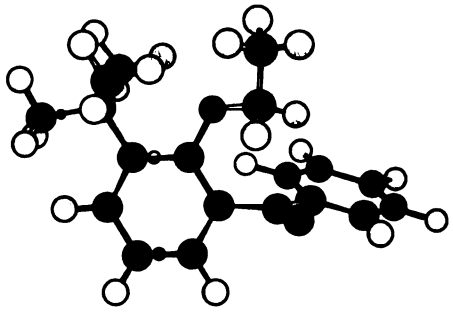
The difference in the A factors is attributed to the difference in rotational entropies of the two conformers. The pro-*cis* conformer has a higher rotational freedom than the pro-*trans* conformer since in the latter phenyl and methyl are cis to each other. Thus, for the ground state control of reactivity, interconversion of the pro-*cis* conformer to the pro-*trans* one is entropically favored while the reverse is entropically disfavored. The fact that quantum yields of formation for the *cis* (0.43) and *trans*-benzofuranols (0.10) indicates that the pro-*cis* biradical is cyclizing more efficiently.

The lower *cis/trans* ratio in solid compared to solution reinforces our assumption that cyclization is faster than interconversion of biradical rotamers (ground state control). In solid, the observed selectivity always reflects a least-motion picture of biradical cyclization. The general conclusion is that low molecular flexibility in crystal may reduce but not totally prevent inversion by rotation. The fact that **5** yields relatively more *trans*-benzofuranol in the crystal confirms that pro-*trans* is the predominant initial biradical geometry.

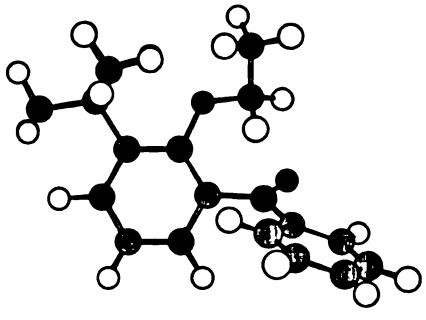
3-t-Butyl-2-ethoxybenzophenone (6):



A



B

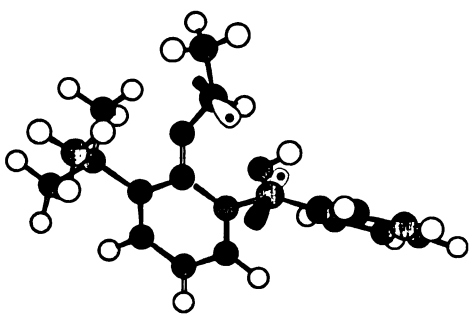


C

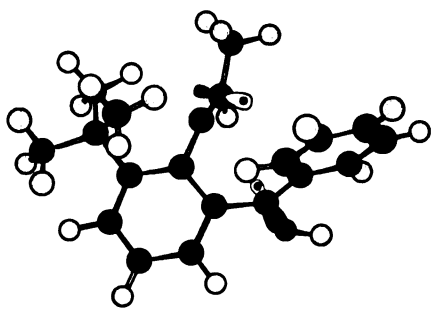
Semiempirical calculations show that in the lowest energy geometry (**A**) of ground state **6**, one of the methylene hydrogens (d= 2.36 Å, ω= 71°) is close to carbonyl oxygen. Another minimum **B** (d_1= 2.50 Å, ω_1= 60°; d_2=2.78 Å, ω_2= 83°) higher in energy than **A**

by 0.35 kcal/mol, has both methylene hydrogens close enough for abstraction. **C** is another local minimum which lies 0.94 kcal/mol higher than the global minimum with one methylene hydrogen abstractable (d= 2.38 Å, ω= 80°).

The photobehavior of **6** is striking in that the *trans*-isomer, the minor benzofuranol formed at room temperature, is the predominant product at low temperatures in hydrocarbon solvent. The Arrhenius data would indicate the pro-*trans* biradical to be more stable than the pro-*cis* by 2.1kcal/mol. Global minimizations on the biradical of **6**, however, show the global minimum (**a**) to have a pro-*cis* geometry, with the closest cyclizable pro-*trans* biradical (**b**) 0.35 kcal/mol higher in energy. Slow bond rotation in the biradical can not compete with cyclization, then the biradicals must react from the geometry in which it is formed and ground state control becomes operative. The lowest energy rotational map for interconversion of the ground state ketone conformers shows 8-9 kcal/mol barriers. The *cis*:*trans* ratio at -78°C thus must be the result of the ground state control. Global minimizations on ground state of these ketones reveal the presence of three minima, with the lowest energy one being in the pro-*trans* geometry. It is thus believed that these three conformers are responsible for the observed *cis*:*trans* ratio at -78°C.



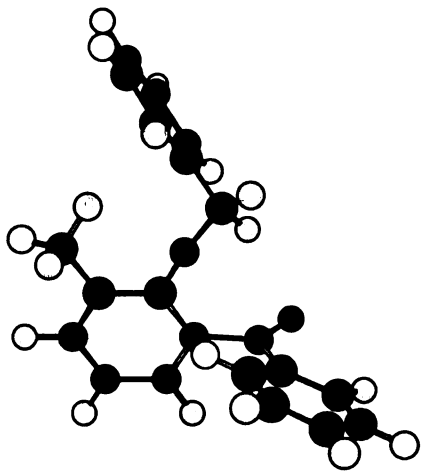
a



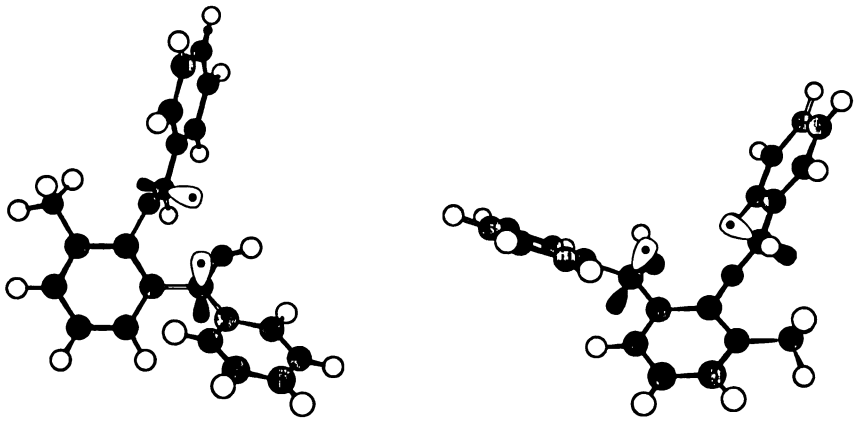
b

2-Benzyloxy-3-methylbenzophenone (7):

Global minimizations (AM1) with dihedral drivers around phenyl-acyl bond and phenyl-ether oxygen bond have revealed the presence of one distinct minimum on the energy surface of 2-BnO-3-MeBP. The lowest energy minimum has one of the methylene hydrogens (d= 2.41 Å, ω= 63°) close enough for abstraction. The global minimum has a pro-*cis* geometry.



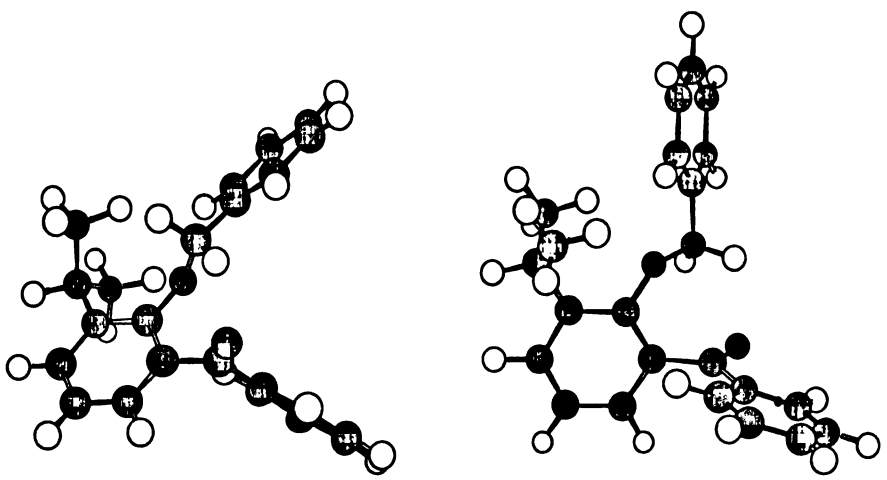
The Arrhenius plot is linear which indicates that the biradical conformers are equilibrated at all temperatures. Semiempirical minimizations reveal the presence of two minima (**a** and **b**) within 0.4 kcal/mol of each other. The global minimum **a** is in the pro-*trans* geometry while **b** is in the pro-*cis* geometry. The calculated enthalpic difference between the two biradical rotamers is half of the measured value. It is believed that reactivity is rotationally controlled, with the discrepancy between the calculated and measured values attributed to over estimation of calculated pro-*trans* energy. The large difference in the A factors may be attributed to: 1) the pro-*cis* biradical cyclizing faster than the pro-*trans* biradical and 2) a larger entropic loss for the pro-*trans* relative to pro-*cis* biradical due to two phenyl groups ending up *cis* to each other in the *trans* –isomer.



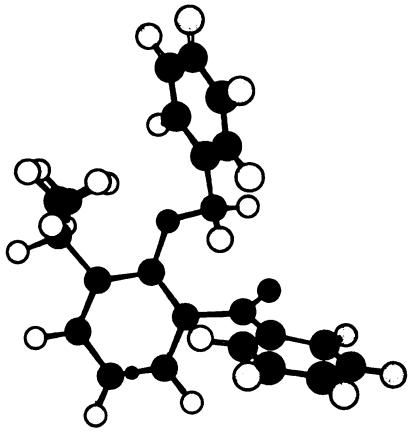
a b

2-Benzyloxy-3-isopropylbenzophenone (8):

The lowest energy geometry of **8 A** is in a pro-*trans* geometry. In this geometry, the closest methylene hydrogen is 2.36 Å away and makes a dihedral angle of 69° with the carbonyl σ plane. Global minimizations with dihedral drivers (15° increments) around benzene-acyl bond and benzene-ether oxygen bond reveal two other minima. **B** lies 0.19 kcal/mol above the global minimum with both methylene hydrogens (d_1= 2.43 Å, ω_1= 43°; d_2= 2.53 Å, ω_2= 85°) close enough for abstraction. Another minimum **C** 0.96 kcal/mol higher in energy than **A** has the closest methylene hydrogen 2.39 Å from

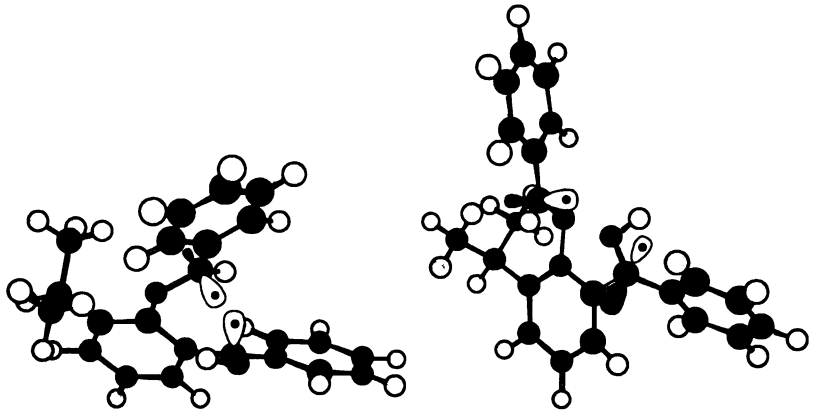


A B

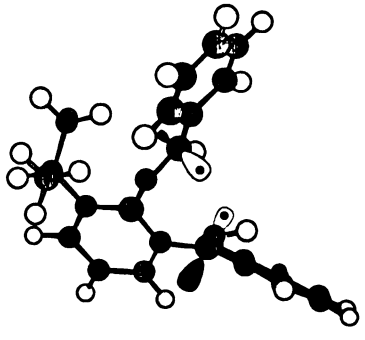


C

carbonyl oxygen and makes a dihedral angle of 79° with the nodal plane of carbonyl.



a **b**



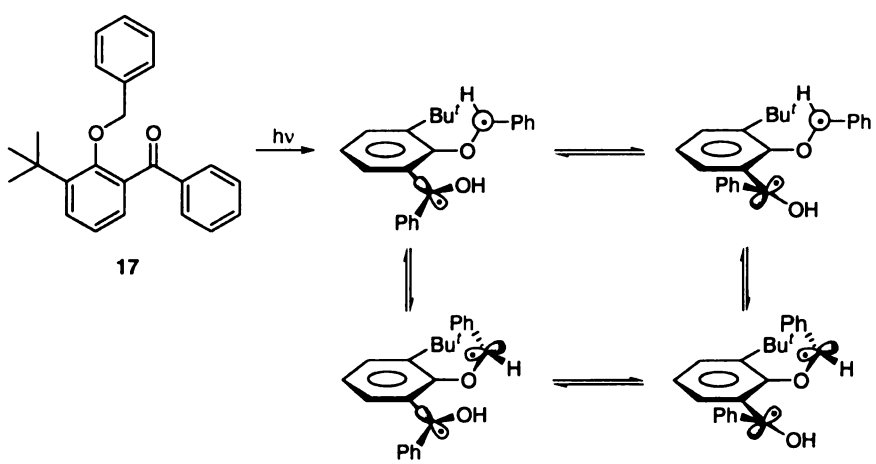
c

Arrhenius data for **8** indicate that the conformation leading to *trans*-benzofuranol

should be 0.7 kcal/mol more stable than that one leading to *cis*-isomer. Our minimizations, however, reveal the presence of three minima within 1.3 kcal/mol of each other. Two of these (**a** and **c**) are in the pro-*cis* and the other one (**b**) is in a pro-*trans* geometry. Comformations **b** and **c** are 0.95 and 1.29 kcal/mol higher in energy than global minimum **a**, respectively. Conversion of **a** to conformer **b** suffers from relatively high barrier (10 kcal/mol). This means that at low temperature biradical interconversion can not compete with cyclization which in turn means that ground state control is operative. The difference in the A factors is attributed to a more efficient cyclization of the pro-*cis* conformer.

2-Benzyloxy-3-t-butylbenzophenone (9):

The lack of stereoselectivity in photocyclization of **9** is similar to earlier results from our group. The two biradical geometries with phenyl tilted up or down are very similar in energy but have different orbital orientation which leads to different cyclization rates (Scheme 51).

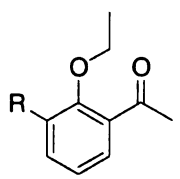


Scheme 51. Biradical Geometries of 9

B. Substituted Acetophenones

Previous study showed that *o*-benzyloxybenzophenone is approximately fifty times more reactive than *o*-benzyloxyacetophenone.[58] This difference in reactivity is directly attributable to the nature of the lowest excited triplet of each ketone. Electron-donating substituents at any ring position lower π, π^* and raise n, π^* transition energies; in phenyl alkyl ketones they cause an inversion of triplets such that the unreactive π, π^* state is lowest in energy.[59] Careful analysis in our lab prompted the now widely accepted conclusion that in such cases hydrogen abstraction occurs from low equilibrium levels of the upper n, π^* triplet;[6] the observed reduced reactivities reflect the fractional population of that state. The two triplets also mix to a small extent, but this mixing does not affect reactivity significantly. 2-Alkoxy-3-alkylacetophenones, like *o*-benzyloxyacetophenone, have a π, π^* lowest triplet. Since n, π^* triplets are inherently more reactive than π, π^* triplets in hydrogen abstraction reactions, it is not surprising to find that 2-alkoxy-3-alkyl

Table 12. Kinetic Results on 2-Ethoxy-3-alkyl Acetophenones in Benzene at 25°C



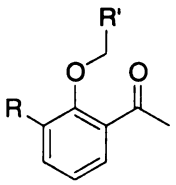
Ketone	R	$k_q\tau^a$, M^{-1}	τ^b, ns
10	CH_3	675.9	233.1
11	$CH(CH_3)_2$	511.8	176.5
12	$C(CH_3)_3$	304.7	105.1

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

[b]$k_q = 2.9 \times 10^9\ M^{-1}s^{-1}$.

acetophenones are less reactive than 2-alkoxy-3-alkylbenzophenones (Table 12, Table 13).

Table 13. k_H Values for 2-Alkoxy-3-alkyl Acetophenones in Benzene at 25°C



Ketone	R	R'	Φ[a]	τ^{-1} 10^6 s^{-1}	k_H[b] 10^6 s^{-1}	k_H[c] 10^6 s^{-1}
10	CH_3	CH_3	0.085	4.29	2.69	0.36
11	$CH(CH_3)_2$	CH_3	0.113	5.67	4.07	0.64
12	$C(CH_3)_3$	CH_3	0.036	9.51	7.91	0.34
13	CH_3	Ph	0.275			
14	$CH(CH_3)_2$	Ph	0.324			
15	$C(CH_3)_3$	Ph	0.272			

[a]Total quantum yield.

[b]Calculated from $1/\tau$, assuming $k_d = 1.6 \times 10^6$ s^{-1}.

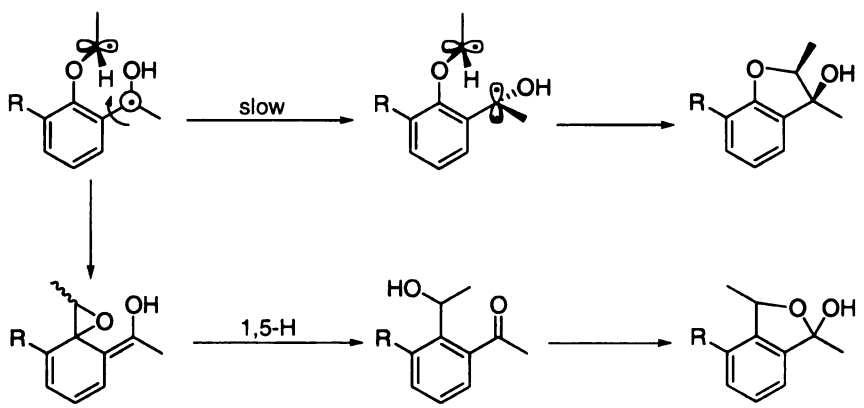
[c]Product of Φ and $1/\tau$.

Benzophenone **4** reacts in a 40-fold greater rate constant than acetophenone **10**, the same trend has also been observed for other benzophenones and their corresponding acetophenones, apparently because of much different rotational barriers and rates of intersystem crossing in the two 1,5-biradical intermediates.

10 photocyclizes to a single benzofuranol isomer, but its major products are two isomeric hemiketals; under the same photochemical condition, **11** also gives single benzofuranol and two hemiketals with benzofuranol as the major product; for **12**,

benzofuranol is the only observable product. Since the π, π^* lowest triplet of substituted acetophenones is less reactive than the n, π^* lowest of substituted benzophenones, the low quantum yield of acetophenones could be partially due to radiationless decay competing with δ-hydrogen abstraction. However, the triplet life time ratio for acetophenone/benzophenone is the same as the ratio of rate constants for γ-hydrogen abstraction for valerophenone/*o*-methoxyvalerophenone, models for n, π^* and π, π^* triplets undergoing the same internal reaction.[60] There δ-hydrogen abstraction is concluded to be the major mode for triplet decay for both acetophenones and benzophenones, and the lower quantum yields for acetophenones must involve competing reactions of the 1,5-biradical formed from the triplet.

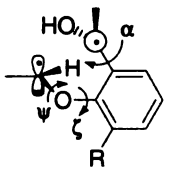
The formation of the hemiketals indicate that the 1,5-biradicals also cyclize at the ortho position of the benzene ring (Scheme 52). This competitive cyclization is minor with **11** but major with **10**.



Scheme 52. Proposed Mechanism for 2-Ethoxy-3-alkyl Acetophenones

The efficiency of benzofuranol formation apparently is directly related to the ease of rotation about the aryl-C_1 bond. The π-system of a substituted benzoyl group is conjugated in the triplet state, hydrogen abstraction produces a triplet 1,5-biradical with a

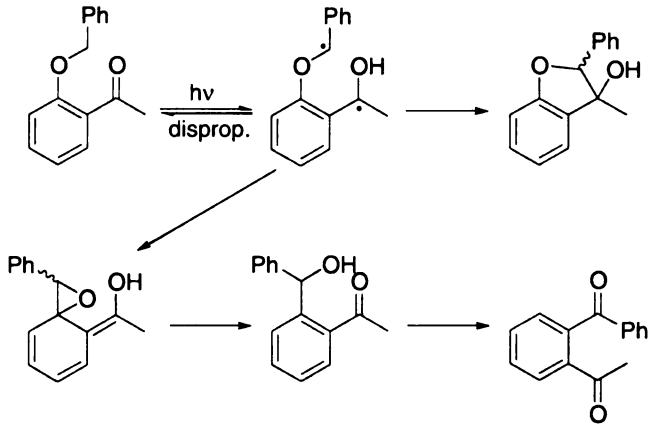
fully conjugated benzyl radical center. A rotation of approximately 90° is required before cyclization can occur. In the acetophenone-derived biradical, such a rotation reduces the benzylic conjugation and thus is slow. The competing spirocyclization does not require rotation about the benzyl bond. The biradical from **10** has more time to undergo this reaction, which thus predominates. Increasing the size of 3-alkyl substituent changes the triplet conformation equilibrium, making the (syn, syn) conformer more favored. The presence of an isopropyl or a t-butyl group *ortho* to the alkoxyl group makes the δ-hydrogens more available to the carbonyl oxygen, hence, the δ-hydrogen abstraction is more efficient for **11** and **12**. Scheme 53 outlined the preferred geometry of these 1,5-biradicals, as estimated by previous calculation on similar biradicals[61] and as suggested by the stereoselective cyclization of such biradicals. The rotation about α and ψ required for benzofuranol formation allows the two nearly orthogonal p orbitals to develop strong overlap. Rotation about ζ and ψ, as required for spirocyclization, allows one p orbital to develop weaker overlap with the partial spin density at a carbon *ortho* to the hemipinacol radical site. 3-Isoprpyl and 3-t-butyl groups inhibits the rotation about ψ, so the acetophenones can not assume the proper geometry for hemiketal formation. It is this barrier that apparently favors cyclization to benzofuranol for **11** and **12**.



Scheme 53. Biradical Geometry of 2-Ethoxy-3-alkyl Acetophenones

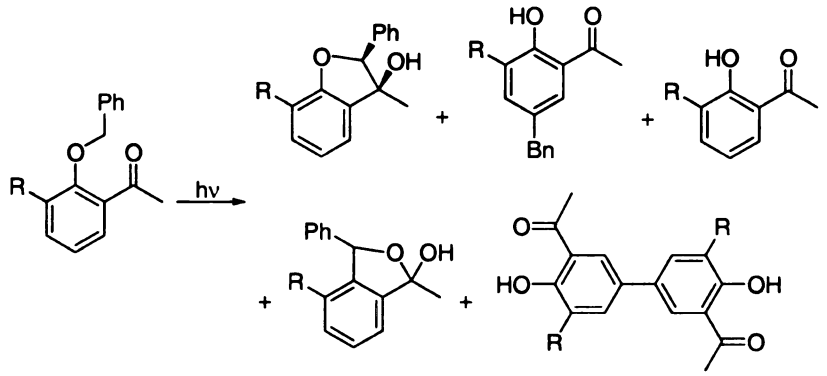
Wagner and coworkers have reported that photolysis of *o*-benzyloxyacetophenone produces the normal benzofuranol as well as 2-acetylbenzophenone.[23] The mechanism

described in Scheme 54 provides a plausible and rather attractive explanation for the formation of both products.



Scheme 54. Proposed Mechanism for *o*-Benzyloxyacetophenone

For 2-benzyloxy-3-alkylacetophenones, photolysis produces a complex mixture of products, which includes a single isomer of benzofuranol, two isomeric hemiketals, a benzyl transfer product, debenzylation product as well as its dimer (Scheme 55).

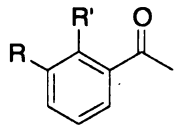


Scheme 55. Photochemistry of 2-Benzyloxy-3-alkyl Acetophenones

It has been known for some time that ^{13}C chemical shifts of carbonyl groups in phenyl ketones are strongly sensitive to the degree of coplanarity of the benzoyl group[62] and that the ^{13}C chemical shift of the methyl carbon in anisoles is sensitive to the geometry of the ring-methoxy bonding.[63] In both cases, twisting of the carbonyl or alkoxy group out of

planarity with the benzene ring increases δ. Table 14 lists some NMR chemical shifts of the CO and OCH_2Ph carbons in 2-benzyloxy-3-alkylacetophenones and in model compounds. 1,3-Disubstitution, both alkyl and acyl, that prevents the alkoxy group from lying in the plane of the benzene ring increases the chemical shift of the methylene carbon. All the 3-alkyl substituted acetophenones show δ values for the CH_2Ph carbom almost 7 to 8ppm larger than *o*-benzyloxyacetophenone, indicating a large degree of twisting out of plane. Substituted acetophenones show higher $\delta_{C=O}$ values than acetophenone but not nearly as high as 2,4-*tert*-butylacetophenone. We therefore concluded that the benzoyl groups in these compounds are twisted but not nearly perpendicular.

Table 14. ^{13}C Chemical Shifts for 2-Benzyloxy-3-alkyl Acetophenones[a]



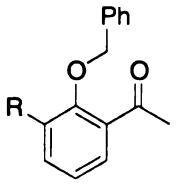
R	R'	$\delta_{O\text{-}CH_2\text{-}Ph}$, ppm	$\delta_{C=O}$, ppm
H	H		197.0
H	OCH_2Ph	70.6	199.8
CH_3	OCH_2Ph	76.7	201.4
$CH(CH_3)_2$	OCH_2Ph	78.1	201.9
$C(CH_3)_3$	OCH_2Ph	77.8	203.1

[a] In $CDCl_3$.

The quantum yields for various product formation of 2-benzyloxy-3-alkylacetophenones are listed in Table 15. The significantly lower $k_{\delta\text{-}H}$ value observed for

o-benzyloxyacetophenone reflects its π, π^* lowest triplet configuration. Further $^3 \pi, \pi^*$-stabilizing 3-alkyl substituents would lower rate constants so much that hydrogen abstraction would occur only in very low quantum yield; while the incorporation of these 3-alkyl groups also enhances abstraction rate constants because of the decreased loss of rotational entropy in the transition state. Hence, the overall rate constant for the formation of benzofuranol does not change very much a lot by the additional 3-alkyl substituents.

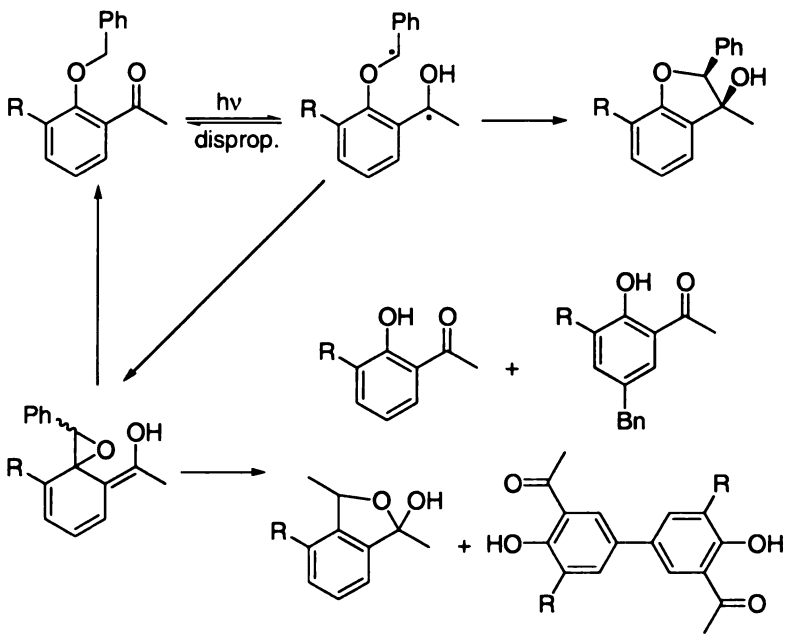
Table 15. Quantum Yields of 2-Benzyloxy-3-alkyl Acetophenones in Benzene at 25°C



R	$\Phi_{cyc.}$	$\Phi_{spiro.}$	$\Phi_{Bn\text{-}trans.}$	$\Phi_{coupl.}$	Φ_{deBn}
H	0.023				
CH_3	0.026	0.039	0.095	0.085	0.030
$CH(CH_3)_2$	0.031	0.059	0.11	0.10	0.024
$C(CH_3)_3$	0.045	0.064	0.086	0.047	0.030

The formation of benzofuranol and hemiketals are due to the normal cyclization as well as the spirocyclization of the 1,5-biradical intermediate. This competition represents another unique example of conformational restrictions on a reactive intermediate. Since π, π^* is the lowest triplet for these 2-benzyloxy-3-alkylacetophenones, the efficiency of reaction is normally much smaller because reaction takes place from low equilibrium populations of the reactive upper triplet. The benzyl transfer products, debenzylation

products and their dimers probably are secondary products arising from the spiroepoxides (Scheme 56).

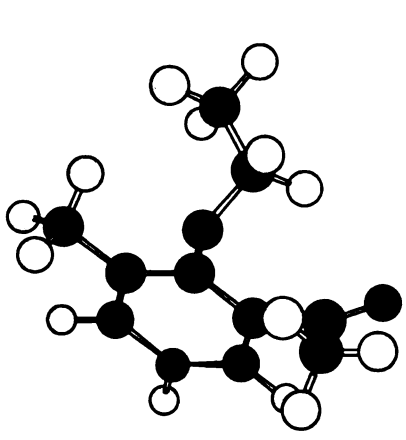


Scheme 56. Proposed Mechanism for 2-Benzyloxy-3-alkyl Acetophenones

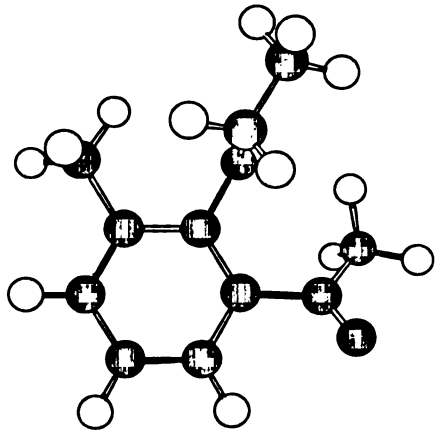
2-Ethoxy-3-methylacetophenone (10):

Semiempirical calculations at AM1 level were performed on **10**. The lowest energy geometry **A** has one methylene hydrogen at an abstractable distance (d= 2.64 Å, ω= 77°) from the carbonyl oxygen. Minimizations (semiempirical-AM1 level) were also performed with dihedral drivers (15° increments) for rotations around the benzene-acyl bond and the benzene-ether oxygen bond. The calculations reveal three other minima within 0.4 kcal/mol of each other. **B** is 0.26 kcal/mol higher in energy than the global minimum. In this geometry, however, the methylene hydrogens are too far to be abstracted. Another minimum **C** (0.32 kcal/mol higher than global minimum) has the closest methylene hydrogen 2.28 Å (ω= 38°) away from the carbonyl oxygen. Minimum **D** (0.37 kcal/mol higher in energy than global minimum) has an abstractable hydrogen

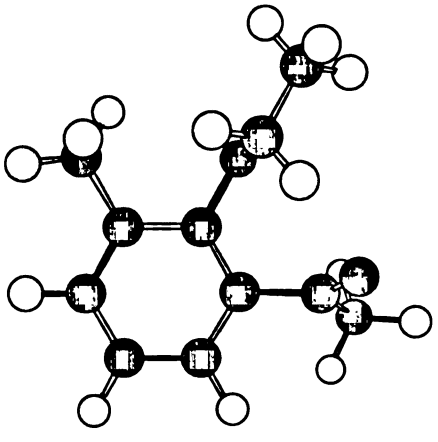
2.56 Å (ω= 38°) away from the carbonyl oxygen. **A** is in a pro-*cis* geometry, **C** and **D** are in the pro-*trans* geometry.



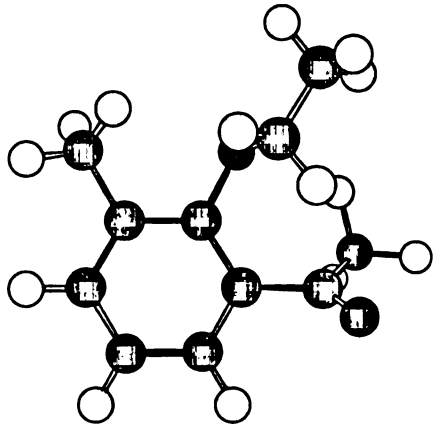
A



B



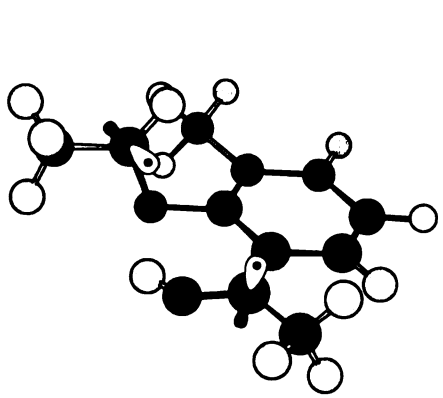
C



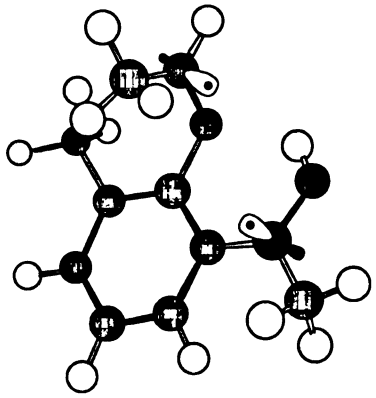
D

Global minimizations on the hydroxybiradical from **10** reveal the presence of 2 minima within 0.5 kcal/mol of each other. Global minimum **a** is in a pro-*cis* geometry, while conformer **b** (0.47 kcal/mol higher in energy than **a**) is in a pro-*trans* geometry. Given the short biradical lifetimes and the strong preference for a single benzofuranol isomer as product, it is tempting to speculate that the biradicals may be too short-lived to rotate out of their nascent geometries. It was thought that ground state control might be operative.

However, analysis of the lowest energy rotational path for the interconversion of the two biradical conformers did not reveal significant barriers (5 kcal/mol). Thus, biradical minima can interconvert and ground state control can not be operative. An extra feature of the photobehavior of **10** is the formation of hemiketal. The calculations reveal that neither cyclization mode can occur from the minimum energy conformation. Hemiketal formation requires that ψ twist to 90°, which the calculations suggest costs 4.4 kcal/mol. Benzfuranol formation requires a significant increase in α, a 60° twist costs about 4 kcal/mol. Since the rotational barriers for both cyclization modes are quite similar, there should be no significant differences in product ratio, which is in good agreement with the experimental results.



a

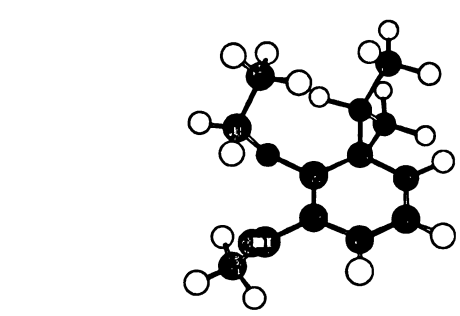


b

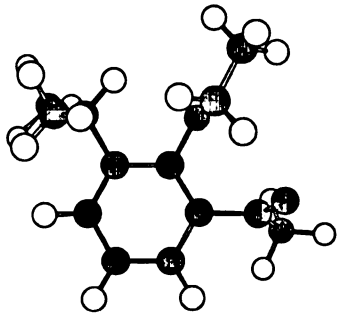
2-Ethoxy-3-isopropylacetophenone (11):

Molecular mechanics and semiempirical calculations were performed on **11**. In its lowest energy geometry **A**, one of the methylene hydrogens is close enough (d= 2.63 Å, ω= 79°) for abstraction. Global minimizations with dihedral drivers (15° increments) around benzene-acyl bond and benzene-ether oxygen bond reveal 4 other minima within 0.3 kcal/mol of each other: **B**, which is 0.1 kcal/mol higher in energy than **A**, has one

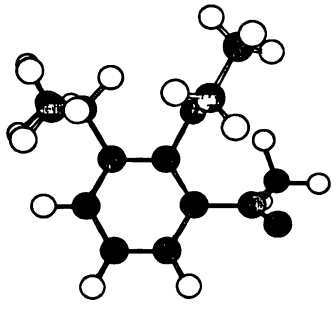
abstractable hydrogen (d= 2.27 Å, ω= 39°); conformer **C** (0.14 kcal/mol higher than global minimum) has one methylene hydrogen close enough for abstraction (d= 2.89 Å, ω= 74°); in conformer **D** (0.26 kcal/mol higher than **A**), no hydrogens are close enough for abstraction; the other minimum **E** (0.27 kcal/mol higher in energy than global minimum) has one methylene hydrogen 2.52 Å (ω= 40°)away from the carbonyl oxygen. **B**, **C** and **E** are all in pro-*trans* geometries, while global minimum **A** is in a pro-*cis* geometry. The rotational energy map for interconversion of **A** to **E** does not indicate any significant barrier, the interconversion of biradical conformers can compete with cyclization. Thus, rotational control must be operative.



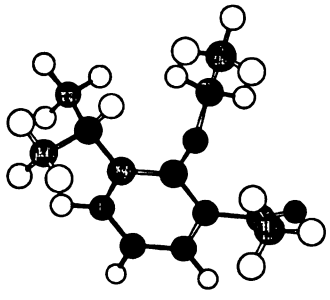
A



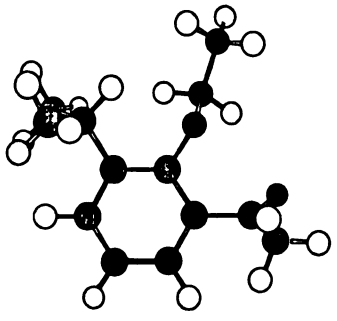
B



C



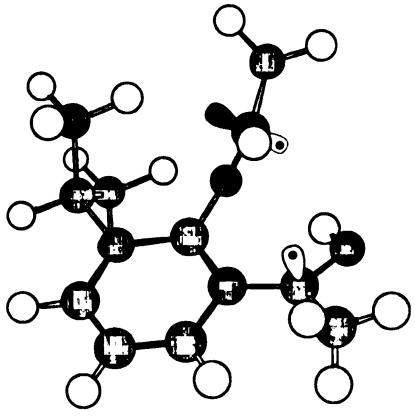
D



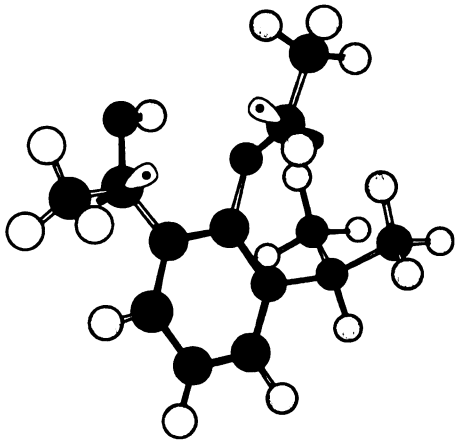
E

Global minimizations on the biradical from **11** reveal the presence of 4 minima within 0.35 kcal/mol of each other, and all of them are in pro-*cis* geometries. None of the biradicals can cyclize directly, calculations suggest that it costs 5.8 kcal/mol for ψ to

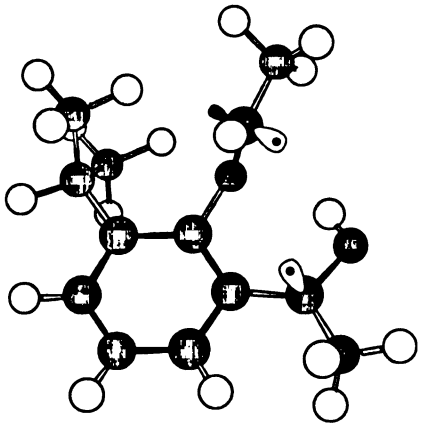
twist to 90°, a 50° twist of α costs 2.5 kcal/mol. Different product partitioning, which clearly reflects different barriers to rotation around bonds α and ψ, indicates that additional differentiation must occur.



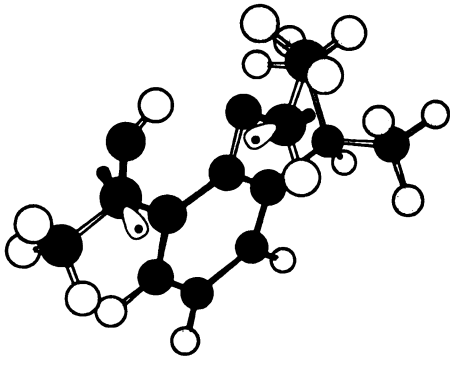
a



b



c

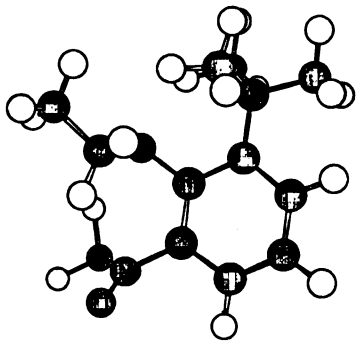


d

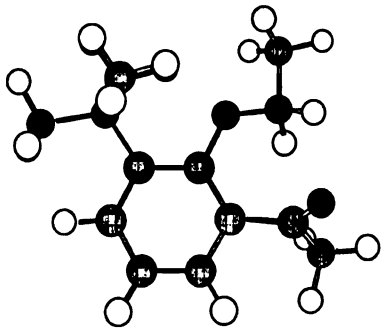
3-t-Butyl-2-ethoxyacetophenone (12):

In the lowest geometry of **12**, the closest methylene hydrogen is 2.58 Å away from and makes a dihedral angle of 82° with the carbonyl σ plane. Another geometry, **B**, lies 1.82 kcal/mol above the global minimum. In this geometry the closest hydrogen is 2.36 Å from the carbonyl oxygen and makes a dihedral angle of 78° with the carbonyl nodal

plane.

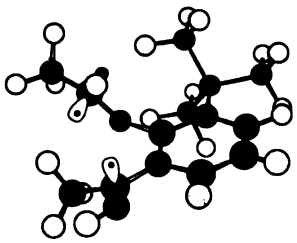


A

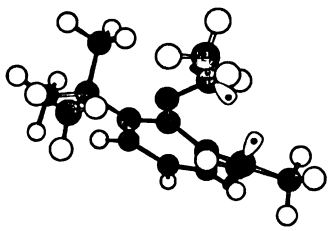


B

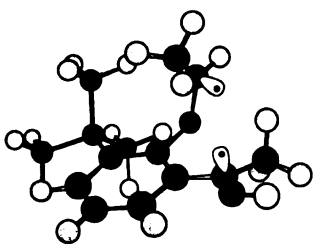
Semiempirical minimizations on the biradical of **12** show the presence of four minima within 1.6 kcal/mol of each other. Global minimum is in a pro-*trans* geometry, the other three minima **b** (0.07 kcal/mol higher than **a**), **c** (0.70 kcal/mol above the global minimum) and **d** (1.59 kcal/mol less stable than **a**) are all in pro-*cis* geometries.



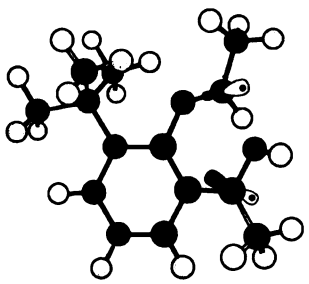
a



b



c



d

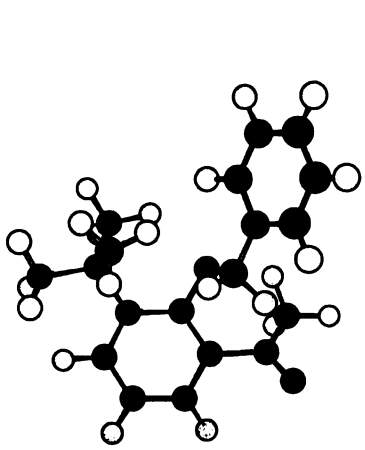
At room temperature, photolysis of **12** results in the formation of only *cis*-benzfuranol.

This high diastereoselectivity can not be ground state controlled, because 1) analysis of the lowest energy rotational path for the interconversion of the two biradical conformers **a** and **d** did not reveal significant barriers (5 kcal/mol) and 2) lowest energy ground state ketone is in a pro-*trans* geometry, while the pro-*cis* conformer **B** is 1.82 kcal/mol higher than **A** and will not contribute much to the overall yield of *cis*-benzfuranol if ground state control is operative. The efficiency of benzfuranol formation is directly related to the ease of rotation about the benzene-acyl bond. For biradical from **12**, semiempirical calculations strongly suggest that the t-butyl group forces the biradical into a geometry in which one radical center is pointed directly at the other radical site, thus inviting cyclization. Spirocyclization, on the other hand, requires bond rotation which may be impeded by the t-butyl group. The minimized geometries of **12** lead to the minimum energy biradical geometries, which favor cyclization, as just noted.

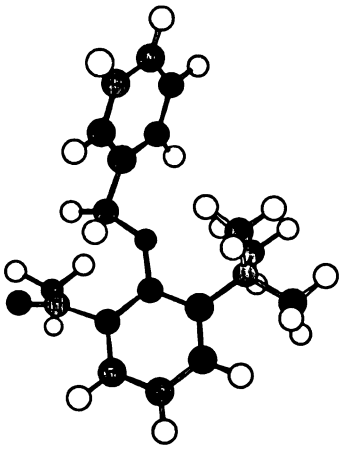
2-Benzyloxy-3-t-butylacetophenone (15):

Wagner reported a sharp contrast in the photobehavior of *o*-alkoxyacetophenones and benzophenones. Irradiation of benzophenones results in efficient formation of benzfuranols while that of acetophenones results mainly in diketones. Rotation of the 1,5-biradical produced by δ-hydrogen abstraction in these phenyl ketones is necessary for cyclization but destroy the benzylic conjugation. π-Conjugation is more important in excited states than in ground state. In the benzophenone derivatives, the benzylic radical center of the biradical can remain conjugated with the unsubstituted phenyl ring while the *o*-alkoxyphenyl ring rotates. The absence of the second phenyl ring in the acetophenone derivatives causes a retarded rotation. Thus, the difference in behavior was attributed to the retarded rotation of the benzylic center of the biradical which slows down the

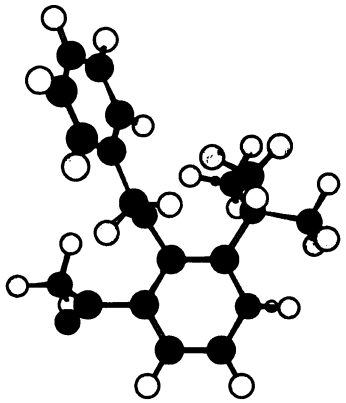
benzfuranol formation and allows the biradical to undergo a less favored reaction, namely spirocyclization.



A



B

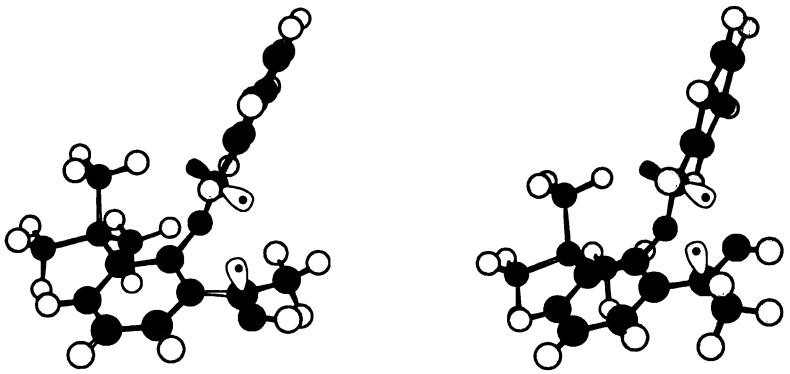


C

The decrease in the quantum efficiencies of benzfuranol formation in the 2-benzyloxy-3-alkylacetophenones as compared to 2-ethoxy-3-alkylacetophenones can be attributed to increasingly more efficient side reactions as the size of the 2-alkoxy group increases (which impedes cyclization due to increased strain during cyclization).

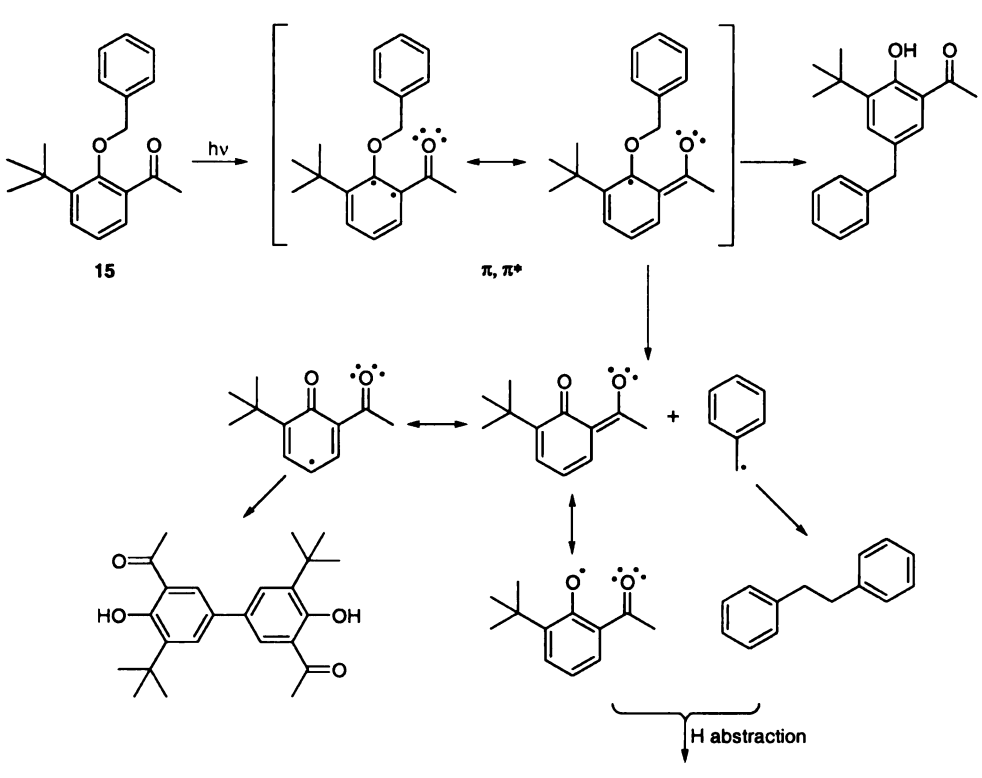
The conformational factors involved in hydrogen abstraction of 2-benzyloxy-3-alkylacetophenones might be expected to be similar to those of 2-ethoxyacetophenones.

Ground state global minimizations indicate the presence of three reactive geometries, a low energy **A** in a pro-*trans* geometry with an abstractable methylene hydrogen 2.57 Å (ω= 81°) away from the carbonyl oxygen. **B** is 0.5 kcal/mol higher in energy (d_1= 2.87 Å, ω_1= 80°; d_2= 2.91 Å, ω_2= 62°) and **C** (0.92 kcal/mol higher than **A**) is also in a pro-*trans* geometry with one methylene hydrogen 2.71 Å (ω= 74°) away from the carbonyl oxygen.



a **b**

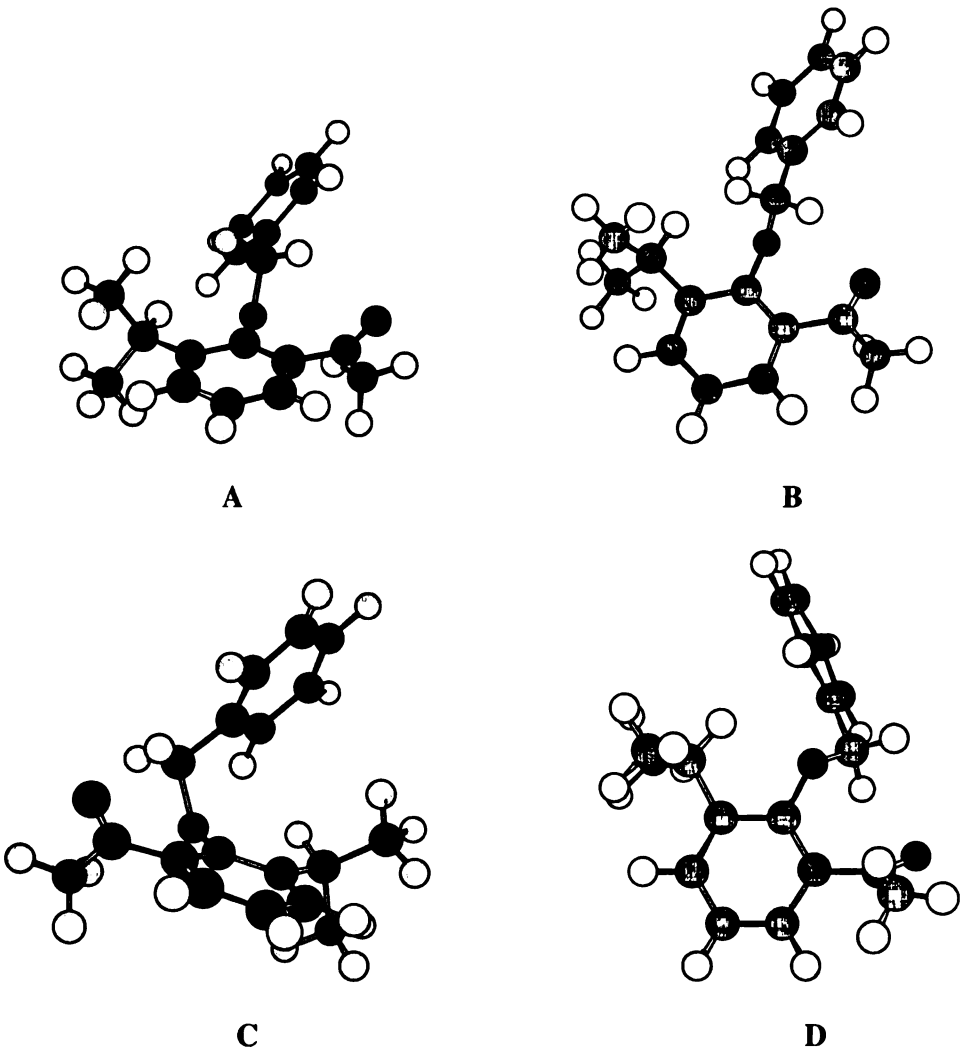
Semiempirical calculations have been performed on the conformational distribution of the hydroxybiradical from **15**. There are only two minima within 0.9 kcal/mol of each other. Global minimum has a pro-*trans* geometry, the other conformer, which lies 0.90 kcal/mol above the global minimum, is in a pro-*cis* geometry. Analysis of the lowest energy rotational path for the interconversion of the two biradical conformers did not reveal significant barriers (4~5 kcal/mol). Thus, biradical minima can interconvert and ground state control can not be operative. It is believed that the formation of only the *cis*-benzfuranol is rotationally controlled, the pro-*cis* biraidcal cyclizes more efficiently. Both normal cyclization and spirocyclization require additional bond rotation: a 30° twist of α costs 1.3 kcal/mol and 50° twist costs 2.4 kcal/mol; while a 75° twist of ψ costs about 8 kcal/mol.



Scheme 57. Photochemistry of 15

15 also undergoes benzyl transfer, debenzylation as well as dimerization. Scheme 57 depicts the postulated mechanisms. Given its π, π* lowest triplet, we suspect some form of biradical process. There has been long-standing interest in the extent to which steric congestion drives radical cleavage reactions.[64] These reactions obviously demand steric congestion. As for benzyl transfer reaction, the driving force for actual bonding of the benzyl group to oxygen is attributed to increased steric congestion; such bonding pulls the benzyl group away from the center of congestion. For the other two reactions, cleavage of the benzylic carbon-ether oxygen bond forms a fully conjugated benzyl radical, which is also a compromise to relieve a good deal of built-in steric strain.

2-Benzyloxy-3-isopropylacetophenone (14):



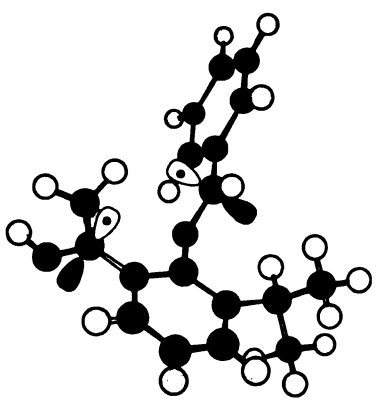
A **B**

C **D**

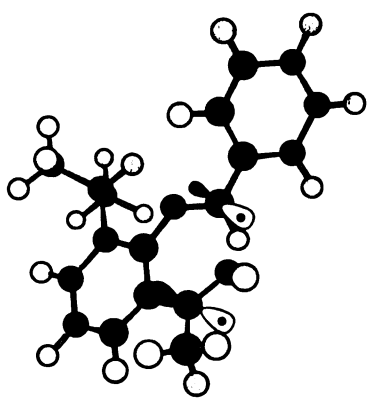
Given that this ketone appears to be so sterically congested that bond rotations are relatively slow, we calculated various energy-minimized conformations of **14**. Dihedral drivers were used for rotation about two key bonds: the benzene-acyl bond and the benzene-ether oxygen bond. Semiempirical (AM1 level) calculations show that in the lowest energy geometry (**A**) of ground state **14** has one of the methylene hydrogen (d= 2.88 Å, ω= 75°) close enough for abstraction, and it is in a pro-*trans* geometry. Global minimizations reveal three minima; in all, methylene hydrogens are abstractable. These

conformers are 0.03, 0.08 and 0.11 kcal/mol higher in energy than the global minimum. The lower energy conformer **B** (d= 2.25 Å, ω= 41°) is in a pro-*trans* geometry; the middle energy conformer **C** has one methylene hydrogen 2.65 Å (ω= 73°) away from the carbonyl oxygen and is in a pro-*cis* geometry; while in the higher energy conformer **D**, both methylene hydrogens are close enough for abstraction (d_1= 2.32 Å, ω_1= 28°; d_2= 2.76 Å, ω_2= 70°).

The lowest energy biradical conformer **a** is in a pro-*trans* geometry, global minimization reveals another local minimum **b** 1.8 kcal/mol higher in energy than **a** and it is in a pro-*cis* geometry. As mentioned before, benzofuranol formation requires a significant increase in α. For **b**, rotation of 30° costs only 1.6 kcal/mol, but rotation to 60° results in a 5 kcal/mol energy increase. It is this barrier that apparently inhibits cyclization to benzofuranol. Twisting of ψ to 90° which is required for spiroepoxide formation costs 10-13 kcal/mol, so few molecules can assume the proper geometry and the observed rate for spirocyclization is low.



a



b

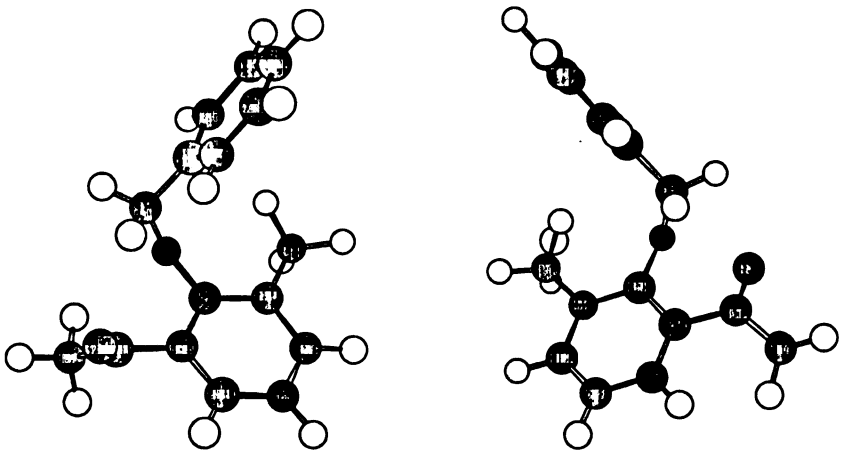
As described above, these 2-benzyloxy-3-alkylacetophenones undergo five reactions in varying proportions: cyclization to benzofuranol, spirocyclization to hemiketals, benzyl

transfer reaction, debenzylation and dimerization. **14** undergoes all these reactions competitively. The cyclization and spirocyclization are known to proceed by triplet-state δ-hydrogen abstraction that generates 1,5-biraidcal. **14** has π, π* and n, π* lowest triplets, respectively, but it undergoes hydrogen abstraction only from its n, π* triplet. The other three reactions involve triplet-state bond cleavage. In the absence of trapping agent, normal radical coupling and rearrangement products are formed. No mechanism has been postulated for these reactions; we suggest that it is initiated by π, π* lowest triplet, a reaction that we believe is common to acetophenones with electron-donating substituents.

2-Benzyloxy-3-methylacetophenone (13):

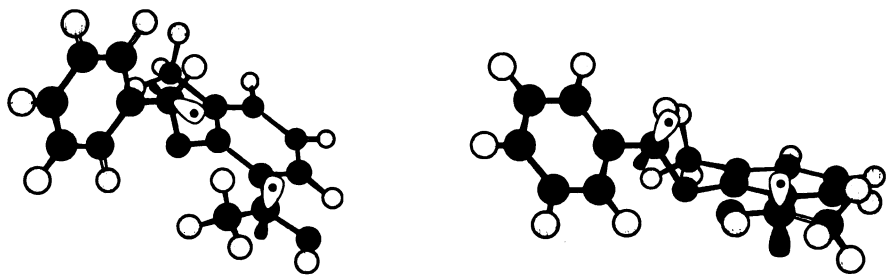
Semiempirical calculations at AM1 level were performed on **13**. The lowest energy geometry was calculated to be the one (**A**) with one methylene hydrogen at an abstractable distance from the carbonyl oxygen (d= 2.63 Å, ω= 75°). Minimizations (semiempirical-AM1 level) were also performed with dihedral drivers (15° increments) for rotation around benzene-acyl bond and benzene-ether oxygen bond to detect other conformations with methylene hydrogens aligned for abstraction. The calculations reveal another minimum 0.25 kcal/mol higher in energy than the global minimum. In this conformation (**B**), both methylene hydrogens are close enough for abstraction (d_1= 2.26 Å, ω_1= 30°; d_2= 2.93 Å, ω_2= 69°).

Experimental results show the *cis*-benzofuranol to be the only cyclization product. Ground state global minimizations indicate the presence of two reactive geometries with the lower energy one in a pro-*cis* geometry. Furthermore, semiempirical minimizations on the biradical of 2-BnO-3-MeAP show the presence of two minima within 2.0 kcal/mol of each other. Lowest energy biradical conformer **a** is in a pro-*trans* geometry, the



A B

other local minimum **b** is 1.9 kcal/mol higher in energy than **a** and is in a pro-*cis* geometry. The rotational energy map for interconversion between **a** and **b** indicates 4-6 kcal/mol barrier. None of the minima can cyclize directly, both of them require additional rotation about α and ψ. For **b** a twist of α to 30° requires 1.3 kcal/mol of energy, a 50° twist costs 3 kcal/mol, while the twist of ψ to 90° costs 5-9 kcal/mol.



a **b**

II. Photoinduced Carbon-Halogen Bond Cleavage

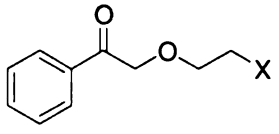
A. Substituted Acetophenones

Irradiation of α-(bromoethoxy)acetophenone (**17**) produced a yellow solution, α-(iodoethoxy)acetophenone (**18**) a red solution, while α-(chloroethoxy)acetophenone (**16**) remained water-white. The colors produced suggest the presence of the respective molecular halogen. What is unexpected is why loss of HX from parent haloketone did not generate terminal olefin.

For δ-halovalerophenones, pyridine was added to trap any HX produced during irradiation. The quantum yield of β-elimination was maximized by 0.005-0.01 M pyridine. This corresponds to roughly the amount of HX that could be produced since conversion of the parent ketone (0.05 M) was limited to $\leq$ 10%. Pyridine has been previously shown to maximize type II quantum yields by solvation of the biradical intermediate, thus preventing reverse hydrogen abstraction to give the ground state parent ketone.[50] However, the concentration of pyridine necessary to maximize type II quantum yields by the solvation mechanism is typically 0.5-1.0 M. The maximization of elimination quantum yield at such low concentration of pyridine is consistent with the pyridine acting essentially as an HX trap, rather than by any biradical solvation mechanism. Sample of **17** and **18** containing pyridine gave white precipitates upon irradiation, presumably the pyridinium hydrohalide salt. No precipitate was formed with **16** under identical conditions. The solutions of the α-haloethoxyacetophenones remained water-white when irradiated in the presence of pyridine. The presence of pyridine did not affect the photochemical behavior of **16**; while for **17** and **18**, the major product became α-vinyloxyacetophenone (**58**). Table 16 lists the quantum yields for product formation of α-(haloethoxy)acetophenones in various solvents.

The quantum yields of α-(haloethoxy)acetophenones in benzene are quite high as

Table 16. Quantum Yields of α-(Haloethoxy)acetophenones at 25°C



Ketone	X	Φ_{II}	$\Phi_{eli.}$	$\Phi_{cyc.}$	$\Phi_{2\text{-OHAP}}$
16[a]	Cl	0.46		0.43	
17[a]	Br	0.041			0.49
18[a]	I				0.29
16[b]	Cl	0.45		0.43	
17[b]	Br	0.039	0.97		
18[b]	I		0.71		
16[c]	Cl	0.56			

[a] Degassed benzene solutions containing 0.1 M ketone irradiated at 313 nm

[b] In the presence of 0.1 M pyridine.

[c] In CH_3CN.

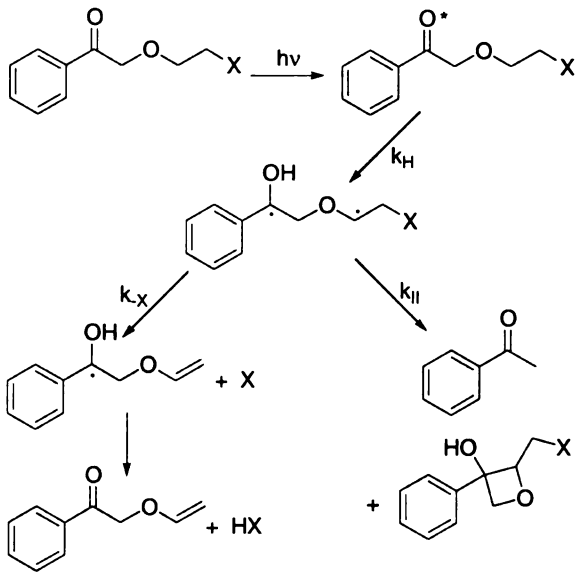
opposed to values of δ-halovalerophenones.[32] High quantum yields are consistent with totally efficient biradical formation. Also, biradical reaction must be faster than reversal to starting ketone. Another intriguing aspect of the results in Table 16 is the decrease in total quantum yield in polar solvent. We believe the solvent effect on quantum yield is due to increased efficiency of return of the biradical intermediate to starting ketone in polar solvents. Wagner has suggested that hydrogen bonding of the biradical hydroxyl proton in polar solvents should impede back-transfer to the γ-carbon and thus decrease k_{-r} relative to k_{II} and k_{cyc}.[9] Hydrogen bonding is more complicated for the α-

(haloethoxy)acetophenones due to the presence of the internal ether oxygen. In nonpolar solvents the hydroxyl proton is internally hydrogen bonded to the ether oxygen, thus preventing back transfer to the γ-carbon. Intramolecular hydrogen bonding in vicinal hydroxy ethers is moderately strong as long as geometrical restrictions do not prevent coplanarity. In polar solvents, intermolecular hydrogen bonding would compete with the intramolecular bonding to the ether oxygen as well as tie up hydroxyl protons and could thus occur with unpredictable results so that a different biradical solvent effect is not surprising.

For δ-halovalerophenones type II elimination and β-elimination predominate, cyclobutanol formation only accounts for 12% of the biradical products. This determination of cyclobutanol yields together with the results in Table 10 clearly shows a relatively slow cyclization rate constant which could be due to steric considerations. In benzene, **16** preferentially forms the *trans*-cyclization product which indicates steric requirements are significant for cyclization. A small solvent effect resulting in less cyclization in polar solvents is observed: in methanol-d_4, only trace amount of cyclization products were detected, while in acetonitrile acetophenone was the only detectable product. Also in methanol cyclization becomes less selective with a *cis*:*trans* ratio for the 3-oxetanols being 1.3:1. Both results are consistent with the interpretation that increased solvation or hydrogen bonding to the biradical makes cyclization more difficult because of steric factors.

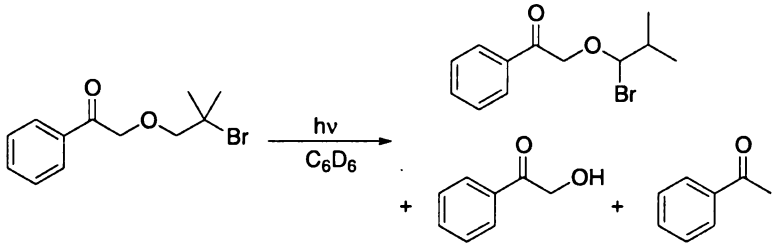
Previous experiment indicates that the carbon-halogen bonds are not broken by direct interaction with the excited triplet ketone.[65] The best mechanism for product formation

involves competitive reactions of the biradicals formed by triplet state γ-hydrogen abstraction (Scheme 58).



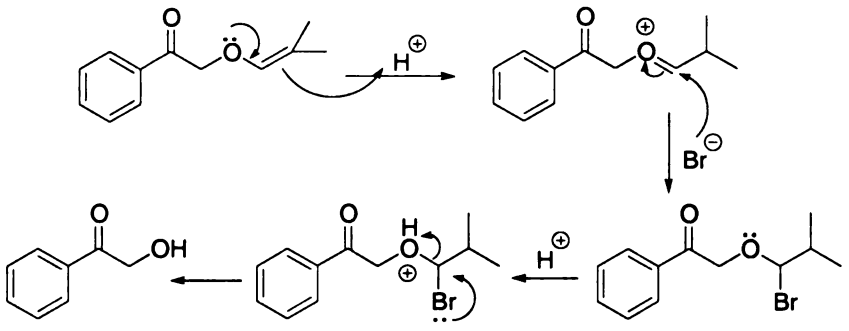
Scheme 58. Proposed Mechanism for α-(Haloethoxy)acetophenones

The formation of 2-hydroxyacetophenone (**57**) without pyridine is not totally unexpected since HX is capable of adding to olefins. In order to explore whether the addition process is an ionic or a free radical mechanism, we synthesized *gem*-dimethyl analog of α-(bromoethoxy)acetophenone. The irridiation of α-(2-bromo-2-methylpropoxy)acetophenone (**19**) in benzene gave three detectable products (Scheme 59). With the presence of pyridine, photolysis gave the normal β-elimination product as well as acetophenone.



Scheme 59. Photochemistry of 19 in Benzene Without Additive

We proposed an ionic addition mechanism for the formation of both 2-hydroxyacetophenone (**57**) and α-(1-bromo-2-methylpropoxy)acetophenone (**60**) (Scheme 60):

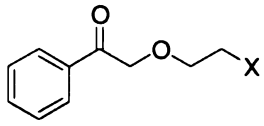


Scheme 60. Proposed Mechanism for 19

Triplet lifetimes were measured by a Stern-Volmer treatment using 2,5-dimethyl-2,4-hexadiene as a quencher for product formation. In the presence of 0.1 M pyridine the Stern-Volmer plots for α-(haloethoxy)acetophenones were linear (Table 17). It is well known that β-haloalkyl radicals eliminate halogen atoms readily.[66] The relative rates of halogen cleavage from the biradical is apparent from the product distribution (type II products *vs.* halogen elimination products) and are in the expected order I>Br>Cl. Table 11 lists relative k_X values for these ketones. Since carbon-halogen bonds do not quench the relatively long-lived triplet butyrophenone,[67] it must be concluded that the $1/\tau$ values represent the rate of γ-hydrogen abstraction (k_H, Table 17). The hydrogen abstraction rate constants for α-(haloethoxy)acetophenones are much faster than those for δ-halovalerophenones. A plausible explanation is that the ether oxygen lowers the entropy requirements for the formation of the six-membered ring transition state necessary for hydrogen abstraction. The substantial inductive effect of γ-substituents on k_H values has been shown to follow a linear free energy relationship. The chlorine decreases k_H to 1/29

its value in α-ethoxyacetophenone ($8.4 \times 10^9 s^{-1}$). The σ_I values for I and Br are slightly lower than for Cl, so that the k_H values for **17** and **18** should be respectively 15.5% and 90.4% greater than that for **16** if only inductive effects are important. The actual k_H values suggest that β-bromo and iodo groups can participate in γ-hydrogen abstraction (Scheme 61). This anchimeric assistance is known to be substantial for hydrogen abstraction by bromine atom, but minor for the more reactive alkoxy radical. The calculated rate enhancements, corrected for inductive effects are 146% and 122% for bromine and iodine respectively. As usual the n, π^* mimics the behavior of alkoxy radicals and provides quantitative information not readily accessible from studies of radical reactions.

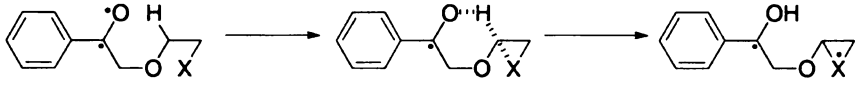
Table 17. Kinetic Results of α-(Haloethoxy)acetophenones in Benzene with Pyridine at 25°C



Ketone	X	$k_q\tau$[a], M^{-1}	τ[b], ns	k_H, 10^7 s^{-1}	k_X/k_{Br}	σ_I
16	Cl	17.2	3.44	29.1	<0.001	0.47
17	Br	10.2	2.04	49.0	1	0.45
18	I	7.4	1.48	67.6	>30	0.38

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

[b]$k_q = 5 \times 10^9 M^{-1}s^{-1}$.

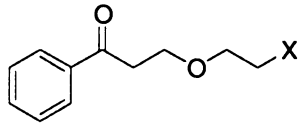


Scheme 61. Anchimeric Assistance

B. Substituted Propiophenones

Opposing to their α-(haloethoxy)acetophenone analogues, the photochemical behavior of β-(haloethoxy)propiophenones looks quite simple: in benzene with the presence of pyridine, photolysis of β-(haloethoxy)propiophenones gives a single β-elimination product. Table 18 lists steady state kinetic data for these ketones.

Table 18. Kinetic Results of β-(Haloethoxy)propiophenones in Benzene with Pyridine at 25°C



Ketone	X	$\Phi_{eli.}$	$k_q\tau$[a], M^{-1}	τ[b], ns	k_H[c], 10^7 s^{-1}	σ_I
20	Cl	0.27	604.8	121.0	0.83	0.47
21	Br	0.26	450.8	90.2	1.11	0.45
22	I	0.26	85.4	17.1	5.85	0.38

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

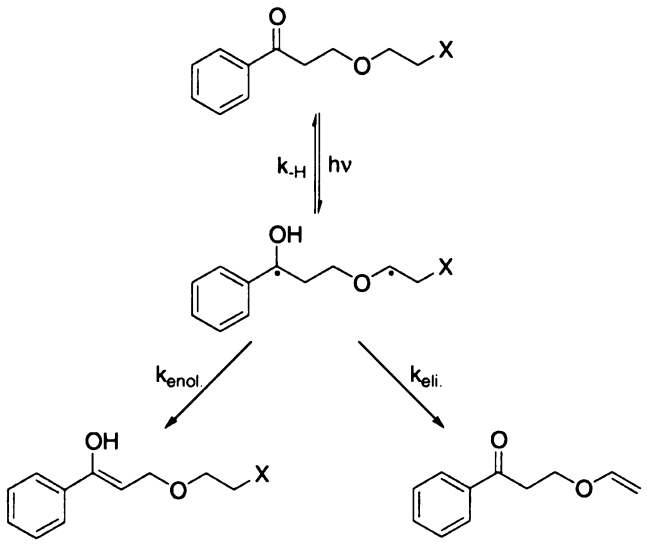
[b]$k_q = 5 \times 10^9$ $M^{-1}s^{-1}$.

[c]$k_H = 1/\tau$.

The reciprocal triplet lifetime of β-ethoxypropiophenone, presumably the rate constant for δ-hydrogen abstraction by its n, π^* lowest triplet, is 2×10^7 s^{-1}.[11] This value is large enough that no physical decay processes compete. Electron-withdrawing ε-substituents such as halogen atoms should lower the observed rate constant sufficiently. We observed that a ε-Cl deactivates δ-hydrogens by an order of magnitude. The effects of Br and I on triplet reactivity do not correlate well with their σ_I values. We have suggested that they

provide anchimeric assistance to hydrogen abstraction, as is well known for the halogen atoms in free radical hydrogen abstraction.

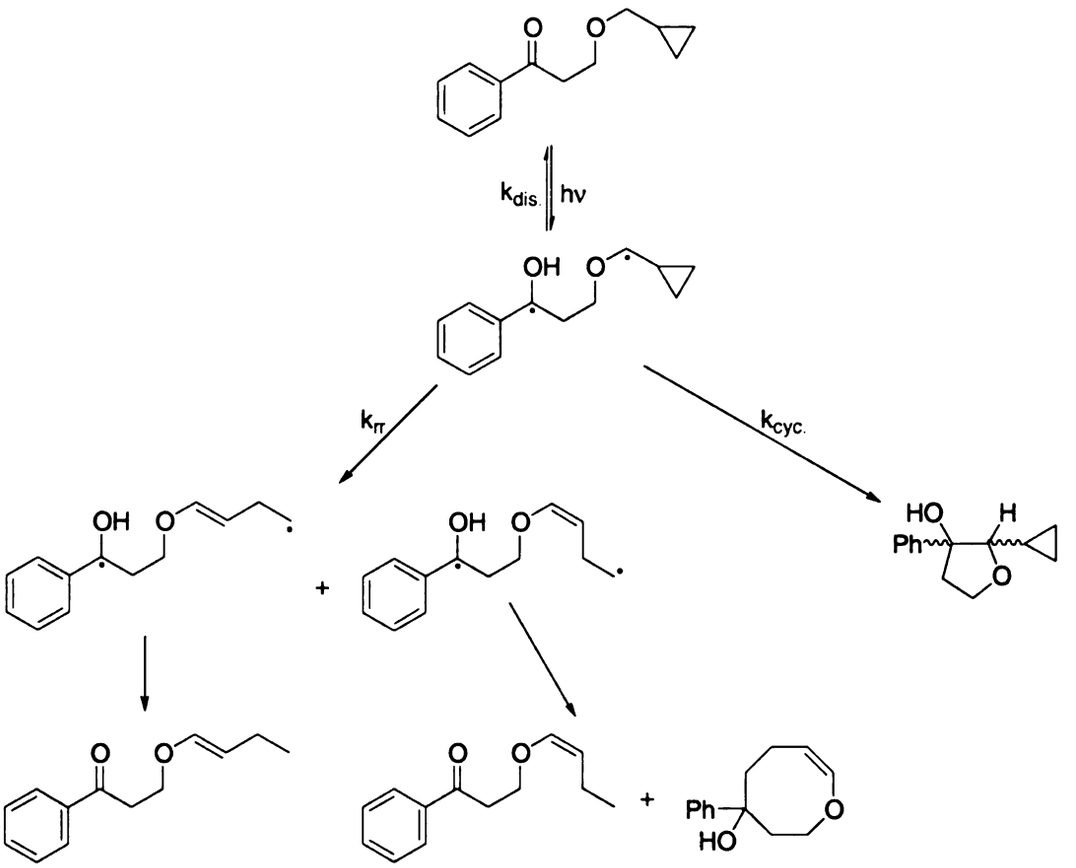
Comparing the data in Table 17 and Table 18, it can be seen clearly that δ-hydrogen abstractions have relatively low rate constants, which can be explained in terms of the well-known preference for 1,5-hydrogen transfers in radical chemistry. Our early studies indicated that 1,5-biradical efficiently disproportionates to form the enol of starting ketone, which rapidly tautomerizes; hydrogen bonding by the hydroxy group to solvent suppresses disproportionation to ketone but cannot suppress enolization. The low quantum yield of product formation for β-(haloethoxy)propiophenones also are caused by substantial 1,5-biradical disproportionation to enol of starting ketone (Scheme 62). Fortunately this competing enolization lowers only the quantum yield, not the chemical yield; the enols reketonize rapidly.



Scheme 62. Proposed Mechanism for β-(Haloethoxy)propiophenones

III. Triplet Biradical Behavior

1,5-Biradical cyclization is a 'non-ionic' process for five-membered ring formation, but the relatively large number of competitive reactions need to be taken into consideration from a synthetic standpoint. In order to determine the potential utility of photoinduced intramolecular hydrogen transfer for the synthesis of five-membered rings, we devised following experiment in which competitive reaction is used to determine the rate constant of 1,5-biradical cyclization.



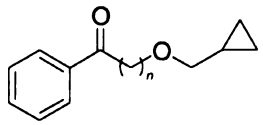
Scheme 63. Photochemistry of 69

Varsha Govardhan studied the reactivity of β-(cyclopropylmethoxy)propiophenone (**69**),[68] irradiation at low temperature provided both the cyclization and ring-opening products (Scheme 63), which indicated that normal cyclization and rearrangement were competitive. If k_{rr} at 20°C is ~7 x 10^7 s^{-1} as in the α-cyclopropylethyl radical,[69] then the life time of this 1,5-biradical is much longer than that of the 1,4-biradicals formed from

α-alkoxyacetophenones, as expected if the oxygen's effect is mainly as a heavy atom rather than as a minimizer of eclipsing interactions.

It might be expected that the oxygen in this 1,5-biradical, which is conjugated to the δ radical site, would lower the k_{rr} value from that for cyclopropylethyl radical, as is the case for α-cyclopropylbenzyl radicals.[70] Rate constant of 1,5-biradical cyclization can then be deduced from the observed product ratios and the rate constant for the cyclopropylmethoxy radical rearrangement. The measurement of rate constant for opening of cyclopropylmethoxy radical has been done in photolysis of α-cyclopropylmethoxyacetophenone (**23**) and based on the assumption that the rearrangement has identical rate constant in both β-(cyclopropylmethoxy)propiophenone (**69**) and α-cyclopropylmethoxyacetophenone (**23**). Table 19 lists the quantum yield of product formation for these two ketones.

Table 19. Quantum Yields of Product Formation for 69 and 23 at 25°C



Ketone	n	Φ_{II}	$\Phi_{cyc.}$	Φ_{rr}
69[a]	2		0.41	0.09
23[b]	1	0.15	0.31	0.03
23[c]	1	0.28	0.43	

[a] In toluene. [b] In methanol. [c] In benzene.

Irradiation of **23** in benzene provided only the type II and cyclization products. No ring-opening product could be detected. Further work in methanol produced mainly

acetophenone and oxetanols, the normal 1,4-biradical reactions, and very little ring-opening, indicating that k_{rr} is much slower than the 1,4-biradical decay rate ($>10^8$ s^{-1}). The lifetime of such a 1,4-biradical in methanol is 3 ns,[71] which indicates a decay rate of 1,4-biradical to be 3.3×10^8 s^{-1}. The rearrangement/(type II + cyclization) ratio is 1:15.3. Taking these numbers and the quantum yield of 0.49, i.e., 51% of the biradicals disproportionate to the starting ketone, the rate constant of cyclopropylmethoxy radical rearrangement is calculated to be 9.9×10^6 s^{-1}. For **69** we assume the rearrangement rate constant is the same as in **23**. Given the assumption that 50% quantum yield reflects 50% biradical disproportionation, the product ratios indicate a 1,5-biradical cyclization rate constant to be 4.5×10^7 s^{-1}.

Solvent effect has also been studied for this 1,4-biradical, results are shown in Table 20. Several issues are of our interest. First, the cyclization/elimination ratio decreases with the increase of solvent polarity. In benzene the ratio is 1.8:1, while in acetonitrile it becomes 1.1:1. Hydrogen bonding seems to play an important role. It is possible that in non-polar solvents the hydroxyl proton is internally hydrogen bonded to the ether oxygen. Intramolecular hydrogen bonding in vicinal hydroxyl ethers is moderately strong as long as geometrical restrictions do not prevent coplanarity. Such an intermediate could accout for the relatively high ratio of cyclization products. In polar solvents, intermolecular hydrogen bonding would compete with the intramolecualr bonding to the ether oxygen, in this case the biradical prefers to exist in the stretched *anti*-conformation and give the observed result.[72] Another important feature is the diastereoselectivity of cyclization. The *cis/trans* ratio depends on solvent polarity, showing little selectivity in polar solvents but favoring the isomer with the phenyl trans to the cyclopropyl group in

hydrocarbon solvents. Hydrogen bonding of the OH in 1,4-biradicals to solvent molecules increases the effective bulk of OH group, thus lowering the diastereoselectivity in cyclization.

Table 20. Product Ratio for Photolysis of 23

Solvent	***cis*-63**	***trans*-63**	**55**
Toluene	3.85	1	3.9
Benzene	3.57	1	2.57
Acetonitrile	2.19	1	2.85
t-Butanol	1.78	1	1.59

Another important feature of cyclization is the diastereoselectivity displayed when the prochiral carbonyl carbon becomes tetrahedral. Lewis reported years ago that two different types of selectivity arise,[73] as demonstrated by valerophenone and α-methylbutyrophenone. They both form 1-phenyl-2-methylcyclobutanol; but the former gives a 3.5:1 *cis/trans* ratio while the latter gives only the *cis*-isomer. In α-methylbutyrophenone, the methyl and the phenyl groups assume *anti* orientations in the biradical before it cyclizes. Such steric preferences can involve several kcal/mol. In valerophenone, nonbonding interactions between methyl and phenyl are developed only as the two ends of the biradical begin to bond and obviously produce an energy differential of less than 1 kcal. Wagner and coworkers pointed out other examples of what may be a general rule, namely that pre-existing conformational preferences can be much larger than those developed only during cyclization. It seems to be the case for **23**, the interaction between the phenyl and the cyclopropyl groups should be small until the

1,4 bond is almost completely formed, so at room temperature the photochemical cyclization of **23** shows a diastereoselectivity of 3.8:1, almost the same as that of valerophenone.

Table 21. Temperature Effect on Cyclization Stereoselectivity of 23 in Toluene

Temperature, °C	***cis*-63**	***trans*-63**
-70	9.09	1
-15	5.30	1
25	3.85	1
80	2.81	1
E_{trans}-E_{cis} (kcal/mol)	1.11	
A_{trans}/A_{cis}	1.73	

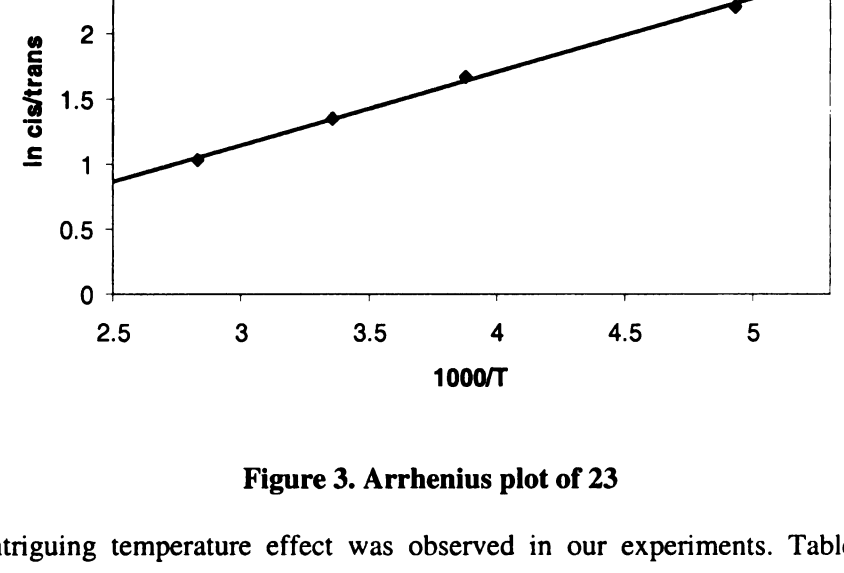
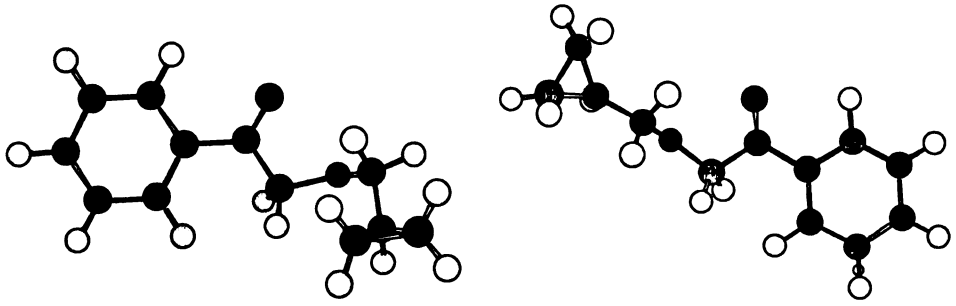


Figure 3. Arrhenius plot of 23

An intriguing temperature effect was observed in our experiments. Table 21 lists product ratios in toluene as a function of temperature for **23**. The corresponding

Arrhenius plot is shown in Figure 3, with the activation parameter differences listed in Table 21.

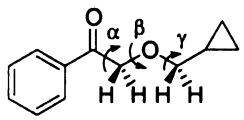
Chandra's group reported an investigation of the intramolecular γ-hydrogen abstraction process in photoexcited alkyl ketones and diketones from their lowest n, π* triplet states.[45] In order to achieve hydrogen abstraction, the abstractable hydrogen atom must approach the oxygen atom of the carbonyl group to form a six-membered ring. Scheffer has reported several examples of ketones that undergo efficient intramolecular γ-hydrogen abstraction in the crystalline phase.[16] He suggestes that, since the sum of the H and O van der Waals' radii is 2.7 Å, unless the abstractable hydrogen atom approaches to within 2.7 Å of the carbonyl oxygen, reaction can not occur. Several ketones with separation distances between the H and O atoms of more than 2.7 Å are found to be unreactive. The Norrish type II reactions generate 1,4-biradicals as intermediates which cyclize to oxetanols from alkoxy ketones.



A **B**

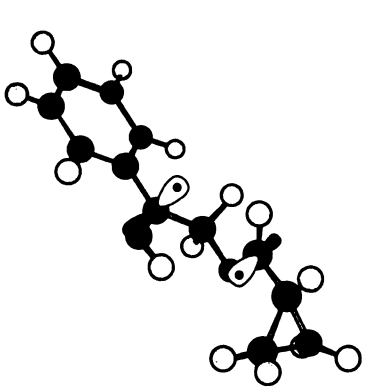
23 can exist in a number of conformations defined by the dihedral angles α, β and γ as shown in Scheme 64. Molecular mechanics and semiempirical calculations at AM1 level were performed on **23**. The lowest energy geometry **A** was calculated to be the one with one γ-hydrogen at an abstractable distance from the carbonyl oxygen (d= 2.32 Å, α= 164°, β= 75°, γ= 70°). Minimizations (semiempirical-AM1 level) were also performed with a

dihedral driver (15° increments) for rotation around β bond. The calculations revealed another minimum 1.49 kcal/mol higher in energy than the global minimum. In this conformation **B**, still only one of the methylene hydrogens is close enough for abstraction (d= 2.30 Å, ω= 18°).

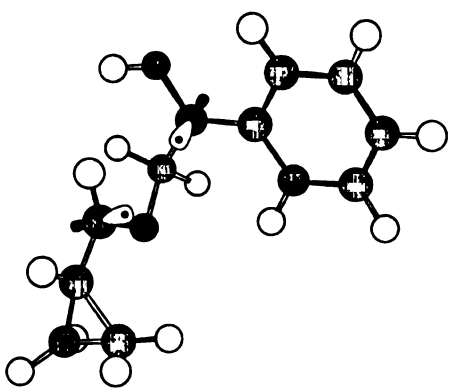


Scheme 64. Dihedral Angles of 23

Experimental results show the *cis*-oxetanol to be the major cyclization product under all conditions. Ground state global minimizations indicate the presence of two reactive geometries, a low energy in a pro-*trans* and a pro-*cis* 1.49 kcal/mol higher in energy. Furthermore, semiempirical minimizations on the biradical of **23** show the presence of two minima within 3.3 kcal/mol of each other. The global minimum **a** is in a pro-*cis* geometry; **b** is higher in energy than **a** by 3.3 kcal/mol and in a pro-*trans* geometry.



a



b

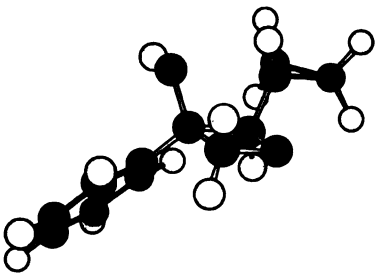
Cyclization processes, with their potential for ring strain, steric crowding and a loss of rotational entropy, are expected to produce barriers. The difference in A factors can be attributed to a faster cyclization rate of the pro-*trans* precursor, due to its higher energy

which in turn means a lower activation energy for cyclization. Therefore, the photocyclization of **23** is believed to be conformationally controlled which means that the triplet biradical lives long enough to allow equilibration. Furthermore, the difference in the A factors indicates that there needs to be an activation energy for cyclization. In their computational study of α-methoxyacetone, Chandra and coworkers found that in the nascent triplet biradical the two p orbitals on the carbon atoms at the radical sites are almost perpendicular to each other.[45] This orientation is favorable for spin-orbit coupling, but the two-center spin-orbit coupling is enhanced as the distance between the radical sites decreases. This occurs as the cyclization process progresses. The height of the barrier for the cyclization process is estimaterd to be 53 kJ/mol.

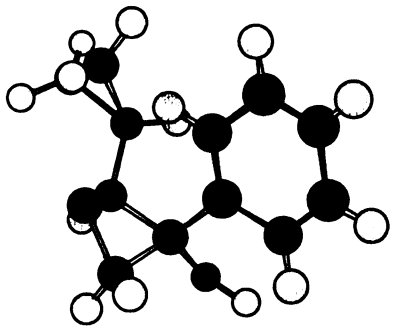
Another explanation for the observed diastereoselectivity is that ground state control is operative but the pro-*trans* biradical cyclizes less efficiently than the pro-*cis* biradical. This could be the case since the cyclization of the pro-*trans* biradical suffers from larger steric/non-bonded interactions during the closure than the pro-*cis*.

Wagner pointed out that cleavage of 1,4-biradical can occur efficiently only in a conformation (anti) in which the two p orbitals are parallel to the C-C bond being broken.[74] Hoffman's calculations indicate such a conformation optimizes the mixing of π and σ levels which promotes cleavage.[75] Our considerations of steric and conformational effects in type II reactions suggests that the initial conformation of the biradical has the γ p orbital almost parallel to the benzylic p orbital perpendicular to the β C-C bond. In order for the biradical to attain anti conformation, it must rotate about both the α and β bonds. Lewis has pointed out that cyclization of 1,4-biradical most likely produces a puckered cyclobutane ring,[76] for which not as much bond rotation is necessary as for

cleavage. However, as mentioned above, the cyclization process suffers from the activation energy barrier, so for dialkyl and aryl alkyl ketones elimination is the predominant reaction. 3-oxetanol formation accounts for as much as 61% of the biradical products from α-alkoxyacetophenones, because the unfavorable eclipsing interaction in cyclobutane can be reduced with an oxygen in the skeleton. Actually, both Chandra[45] and our calculation results reveal that 3-oxetanol is almost a planar four-membered ring.



***cis*-oxetanol**



***trans*-oxetanol**

The preferential formation of *cis*-oxetanol in nonpolar solvents should be reconciled from the transition state structure for its formation, which should have less steric repulsion owing to the anti relationship between the sterically bulky phenyl and cyclopropyl groups at the 1,4 positions; since singlet biradicals are known to retain conformational memory of their precursor triplet biradicals before collapsing to the products, the low energy biradical **a** is pertinent for the observed trend.

IV. Singlet *vs.* Triplet Behavior

A. β-Cyclopropylmethoxybutanone (25)

The main goal of this project was to determine the similarities and differences in

reactivity and selectivity of 1,5-singlet and triplet biradicals. From a mechanistic point of view, the difference in the reactivity of the singlet and triplet 1,5-biradicals and the role of environmental and conformational factors in determining the overall efficiency and chemical yield of tetrahydrofuranol formation must be addressed.

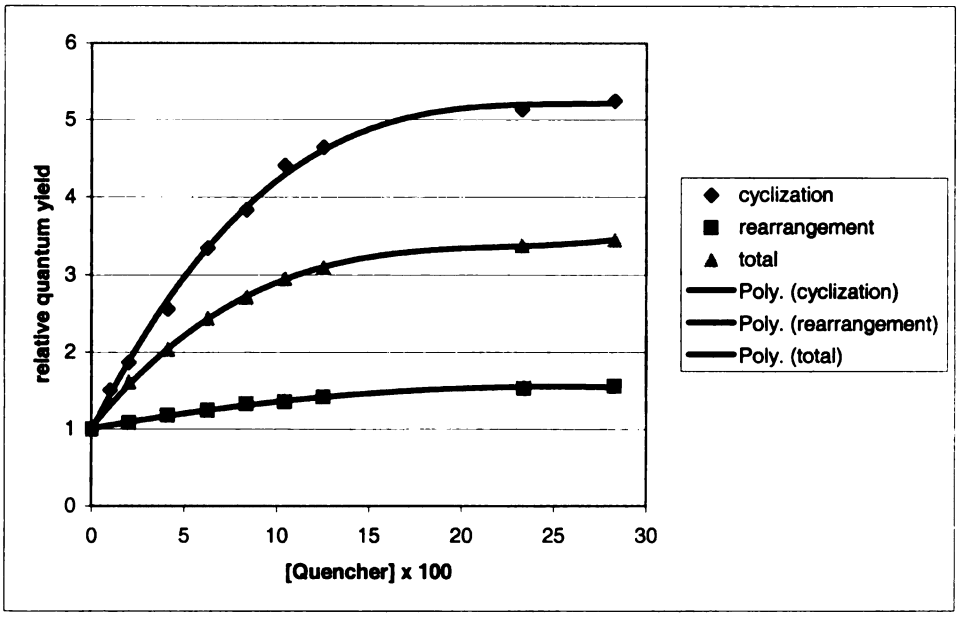


Figure 4. Stern-Volmer Quenching Plot of 25

As mentioned earlier, the reactive excited states for aliphatic ketones are both singlet and triplet states.[35,36] Thus, the excited states responsible for the observed photoreaction in **25**, namely δ-hydrogen abstraction, have to be determined. Our study indicates that in benzene both cyclization and rearrangement can occur. Figure 4 shows plots of Φ_0/Φ against the concentration of 2,5-dimethyl-2,4-hexadiene for the ketone. The simple Stern-Volmer relationship is obviously not followed in either case. Relatively low concentrations of quencher do a good deal of quenching, but at higher concentrations the quantum yields for both reactions level off to constant values. The most obvious interpretation of the results is that both reactions arise from both excited singlet and

triplet. If we take the quantum yield in 0.3 M quencher as a measure of the amount of singlet reaction, the mechanism is dissected as shown in Table 22. The overall quantum efficiency is low because of the well known highly efficient radiationless decay that accompanies singlet state hydrogen transfers. We have considered the possibility of enol formation for β-cycloprpopylmethoxybutanone. In our investigation, however, we were unable to detect any. The enol is expected to be much less stable with respect to ketone and if formed apparently is too short-lived to detect.

Table 22. Quantum Yields for Product Formation of 25 at 25°C

Ketone	$\Phi_{cyc.}$[c]	$\Phi_{cyc.-s}$[d]	$\Phi_{cyc.-t}$[e]	Φ_{rr}	Φ_{rr-s}[d]	Φ_{rr-t}[e]
25[a]	0.054	0.010	0.044	0.032	0.021	0.011
25[b]	0.068					

[a] [Ketone] = 0.2 M in benzene. [b] In methanol. [c] Quantum yield with no added quencher. [d] Quantum yield in 0.3 M 2,5-dimethyl-2,4-hexadiene. [e] $\Phi_t = \Phi - \Phi_s$.

The initial slope of the curve in Figure 4 should be equal to k_q/k_H, where k_H is the rate constant of δ-hydrogen abstraction quenched by 2,5-dimethyl-2,4-hexadiene. The value is 25 M^{-1}. We expect that energy transfer should be diffusion controlled, this would place the value of k_q at about 5×10^9 $M^{-1}s^{-1}$. We therefore estimate the value of k_H as 2×10^8 s^{-1} for **25**. The result was quite reasonable. The reactivity of excited singlet and triplet of unconjugated carbonyl compounds should be qualitatively similar since both states have the n, π^* configuration.

Quenching of the formation of tetrahydrofuranols demonstrates that cyclization occurs dominantly from the triplet state. The T_1-spinisomer forms a long-lived triplet biradical which leads to low diastereoselectivity in cyclization (*cis/trans* = 2.9:1, Table 23).

The formation of rearrangement products is weakly quenched by 2,5-dimethyl-2,4-hexadiene, this result is consistent with the postulate that T_1 does not lead to significant amounts of ***E*-67** and ***Z*-67**, i.e., rearrangement occurs mainly from S_1. The model 1-cyclopropylethyl radical opens to a 2.3:1 *E/Z* ratio of 2-penten-5-yl.[77] However, photochemical rearrangement product is a 1:1 mixture of both E- and Z-alkenes (Table 17). There has been tendency to attribute 'biradical' character solely to triplet states.[78] Our result indicates that singlet rearrangement could proceed concertedly. Consideration of bond energies indicates that the ring-opening is highly exothermic, so that the system has enough energy for the concerted formation of singlet alkenes. The absence of rearrangement products in methanol is another intriguing phenomenon. Since it is the singlet excited state that is mainly responsible for the ring-opening process and the following reaction rate constant may not be large enough that quenching by impurities or solvent would become competitive.

Table 23. Product Ratio for Photolysis of 25[a]

Solvent	***cis*-68**	***trans*-68**	***E*-67**	***Z*-67**
Benzene	2.9	1	1.1	1.1
Methanol	1.1	1		

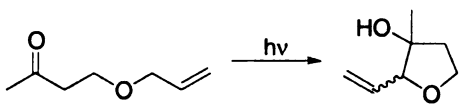
[a] Product ratio without quencher.

As mentioned before, the calculated triplet state δ-hydrogen abstraction rate constant of **25** is about 2 x $10^8 s^{-1}$, which is comparable to the triplet δ-hydrogen abstraction rate constant of β-ethoxypropiophenone (2 x $10^7 s^{-1}$).[11] It is interesting that substitution of an oxygen atom for the γ-methylene does not enhance the rate of δ-hydrogen abstraction. One might have expected the lone pairs on oxygen to cause less torsional strain than C-H

bonds in the seven-membered ring transition state. But the presence of the ether oxygen does increase the percent cyclization as compared to simple alkyl ketones, which could be explained in terms of relief of strain energy due to the eclipsed conformation of vicinal hydrogens in a five-membered ring system.

The *cis/trans* product ratio depends strongly on solvent (Table 23), as expected with hydroxybiradicals; but polar solvent only slightly raised the cyclization quantum efficiency. Combining this result with previous study on β-ethoxypropiophenone,[79] we speculated that in the 1,5-biradicals a 1,4-hydrogen transfer might provide an alternative mode of internal disproportionation, one not affected by hydrogen bonding involving the OH group, although the resulting enol could not be detected.

Studies of type II photocyclization reactions of dialkyl ketones are less common. The vast majority focus on the formation of cyclobutanols. Indeed, unless the 1,5-hydrogen abstraction pathway is blocked, it will be the predominant one. A limited study of five-membered ring formation was made by Descotes.[80] His studies, which dealt largely with carbohydrate systems, showed that such cyclizations generally afforded stereoisomeric mixtures of tetrahydrofuranols. Additionally, Carless and coworkers noted the following cyclization with rather low stereoselectivity (Scheme 65).[81]



Scheme 65. Photochemistry of β-Allyloxybutanone

The concerns of this investigation are both synthetic and mechanistic. At the synthetic level, we address the relationship of the structure to the yield of tetrahydrofuran products, as well as the possible means available to manipulate reaction conditions to enhance the

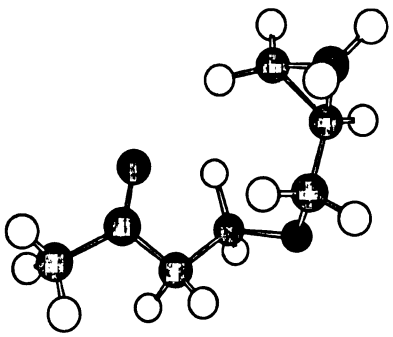
yield of THFs. At the mechanistic level, we identify the excited state responsible for THF formation, the role of conformational factors and environmental factors in determining the overall efficiency of THF formation.

The rate constant of triplet δ-hydrogen abstraction for **25** has been estimated to be ca. 2 x 10^8 s^{-1}. Since for triplet 2-pentanone k_H is 0.16 x 10^8 s^{-1} and for singlet 2-pentanone is 1.8 x 10^8 s^{-1},[82] we can estimate the rate constant of δ-hydrogen abstraction given a rate for the triplet decay. By applying this factor to the rate constant for triplet δ-hydrogen abstraction for **25**, we estimate the rate constant of singlet δ-hydrogen abstraction for **25** to be ca. 2.2 x 10^9 s^{-1}. This value is large enough to compete with intersystem crossing but not so fast as to completely dominate singlet deactivation, i.e., some intersystem crossing to produce a triplet that undergoes hydrogen abstraction is expected.

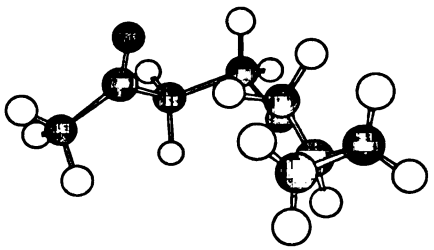
For δ-hydrogen transfer, rotation about the β, γ C-C bond is also required. Since δ-hydrogen abstraction involves twice as many frozen rotation in its cyclic transition state as does γ-hydrogen abstraction, part of the rate difference must reflect the differing entropy losses for the two processes.

Global minimizations (semiempirical-AM1 level) with dihedral drivers around β and γ bonds have shown that the lowest energy geometry (**A**) of **25** has one of the δ-hydrogens close enough for abstraction (d= 2.63 Å, ω= 36°). Geometries **B** and **C** exist as local minima 1.45 kcal/mol and 1.60 kcal/mol higher than global minimum, respectively. In both **B** (d= 2.38 Å, ω= 66°) and **C** (d= 2.52 Å, ω= 50°), one of the methylene protons is abstractable.

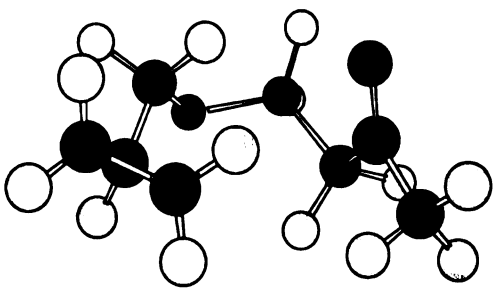
The observed diastereoselectivity in benzene demands 0.6 kcal/mol energy differential



A



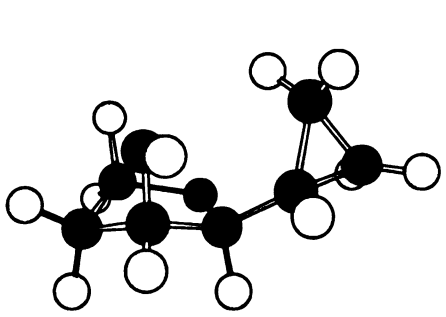
B

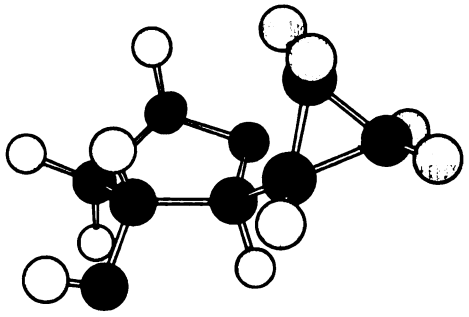


C

between the *cis* and *trans* modes of cyclization. As Lewis' work first showed,[73] the nonbonded interactions that cause such selectivity can either pre-exist in the biradicals or be created during cyclization as the methyl and cyclopropyl groups on the biradical ends approach each other. In the latter case, the energy differences between the two isomeric products would have to be even greater than the differential transition state energies for cyclization. The thermodynamic energy difference between the *cis* and *trans* products is not known, but molecular mechanics calculations suggest that puckering of the five-membered ring reduces the difference to near zero. Therefore the discrimination between the two modes of cyclization probably reflects pre-existing energy differences that persist during cyclization.

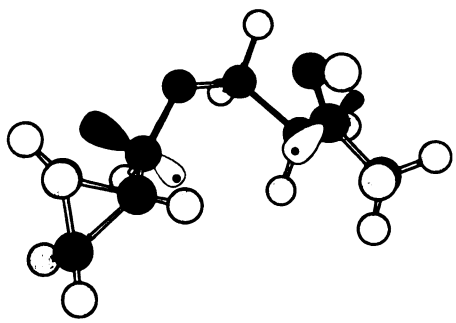
We have tested this idea by performing MM2 calculations on the triplet biradical from **25**. After minimization with respect to rotation about all acyclic C-C bonds, the two

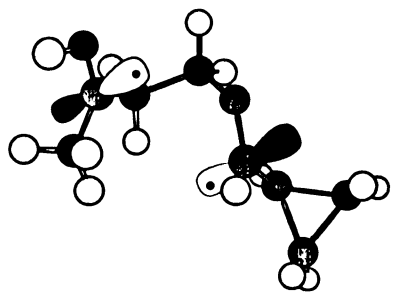




cis-**68** *trans*-**68**

minimum energy geometries were calculated to differ in energy by 0.64 kcal/mol. If the two biradical rotamers indeed differ by 0.64 kcal/mol, most of the observed selectivity simply reflects conformational equilibrium in the biradical before cyclization, provided that cyclization of both rotamers involves the same motion. This assumption seems reasonable here, since a simple disrotation around the two ortho C-C bonds is all that is required for coupling. When the OH group is solvated by hydrogen bonding in methanol, it is comparable in size to the methyl group, such that the two rotamers are nearly equal in energy and selectivity is lost.





a **b**

Scaiano postulated that the product composition from triplet biradicals is determined by variations in intersystem crossing rates of various biradical conformers.[72] In short biradcials, ISC is mainly driven by spin-orbit coupling, which is known to be very much dependent upon the distance between radical centers. This means that ISC occurs most

fast when the biradical ends are proximate, which is most likely to be at the moment of biradical coupling.

Wagner has proposed the notion of coupled ISC and reaction.[11] Both the singlet and triplet surfaces rise in energy with movement along the reaction coordinate, but the singlet surface is soon stabilized by the developing bond, such that the two surfaces cross at points that represent very low activation energy. The singlet biradical is then trapped in a conformational well that leads to reaction. The concept of reaction induced ISC has also been implied by Griesbeck's explanation on stereoslectivity in [2+2] photocycloaddition of benzaldehyde to cyclic alkenes.[83,84] He suggested that the observed stereoselectivity is caused by relative energy difference of two different conformers, which he interpreted as transient points through which stable 1,4-biradicals have to pass in order to invert spin and to overcome the spin barrier for bond formation. It is consistent with Wagner' proposal in that ISC and product formation are induced by molecular motion along reaction coordinate. Our current results provide another example of the same phenomenon.

As mentioned earlier, oxygen is said to have an effect on the 1,5-biradical, wherein the eclipsing effect is reduced when the carbon atom is replaced with oxygen, which facilitates bringing the two ends of the biradical together. This phenomenon has also been used to explain the high cyclization efficiency of the β-alkoxypropiophenones. On the other hand, it might be expected that an oxygen which is conjugated to the δ radical center, would lower the k_{rr} value from that for cyclopropylethyl radical, as is the case for α-cyclopropylbenzyl radicals. Our study on **25** in benzene produced both the cyclization

and rearrangement products, indicating that cyclization and ring-opening were competitive.

B. α-Cyclopropylmethoxyacetone (24)

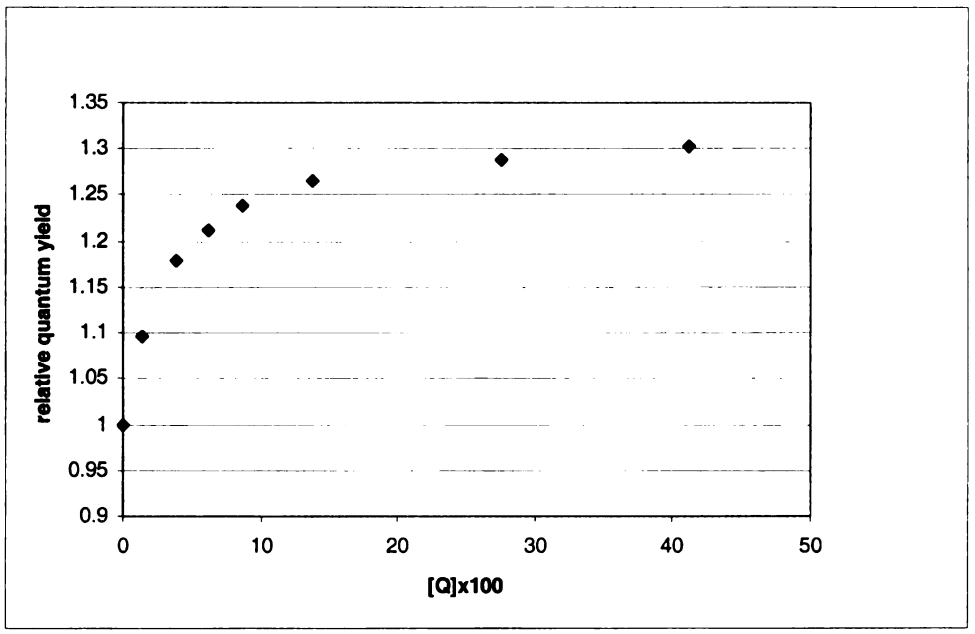
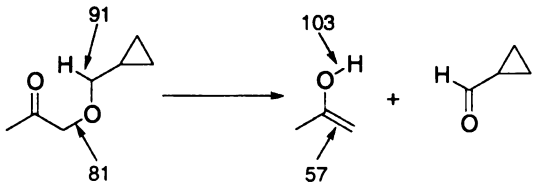


Figure 5. Stern-Volmer Quenching Plot of 24

The lowest energy excited state for aliphatic ketones is n, π^* state, both singlet and triplet n, π^* states undergo the Norrish type II photoreaction. Figure 3 shows plot of Φ_0/Φ for **24** disappearance against quencher concentrations. The amount of nonquenchable reaction may reasonably be attributed to reaction through the excited singlet state with the remainder of the photochemical reaction occurring through the excited triplet state. The initial slope in Figure 5 can be equated to k_q/k_r (k_r = sum of rate constants for reactions quenched). Our value of 4.4 indicates a k_r value of 1.1 x $10^9 s^{-1}$ for **24**. Calculation done by Chandra and coworkers showed that the ether oxygen in the β-position has no activating influence on the carbonyl oxygen for hydrogen abstraction.[45]

The increased rate constant of α-alkoxy acetone relative to aliphatic ketones may be due to a decrease in the bond dissociation energy of C-H homolysis in ethers relative to alkanes. It may be explained by the fact that the back lobe of the σ^* orbital of the C-H bond overlaps with one of the two lone pair orbitals on the ether oxygen leading to a flow of electrons to the antibonding σ^* orbital. This should cause a decrease in the C-H bond order of the bond containing the abstractable hydrogen.

Irradiation of **24** in benzene resulted in the formation of both acetone and a single isomeric 3-oxetanol, identification of the excited state responsible for these reactions is of considerable interest. From the slight quenching of type II product formation, we conclude that excited singlet was primarily responsible for the photoelimination. This result does not, of course, establish the intermediacy of a biradical. One might expect that excited singlet could undergo the elimination reaction by a completely concerted mechanism.[38] Consideration of bond energies suggests a ΔH = 12 kcal/mol for type II elimination of α-CPMOA (Scheme 66).[85] E_{S1} of aliphatic ketones at room temperature in benzene is about 80.6 kcal/mol.[86] Therefore, the type II reaction from singlet is 69 kcal/mol exothermic, not enough to produce aldehyde in its singlet state.



91 + 81 - 103 - 57 = 12

Scheme 66. Norrish Type II Reaction of 24

On the other hand, the formation of 3-oxetanol is almost unquenchable, which indicates that cyclization also occurs from the excited singlet, the formation of a single stereoisomer seems to confirm that: if triplet state is responsible for cyclization, then the

resulting triplet biradical would have enough time to equilibrate and a relatively low stereoselectivity would have been observed; when the cyclization occurs from singlet state, either the process is concerted, or the resulting singlet biradical is too short-lived to allow equilibration. The heteroatom reduces the distance between the biradical termini and reduces steric hindrance to the close approach of the termini because the number of H-H eclipsing interactions is reduced. Lifetime of this singlet biradical is short enough that bond rotation will not occur; that is, singlet biradical decay has to occur from a semi-frozen conformation.

The cyclization process is observed in α-alkoxy acetophenones leading to the formation of 3-oxetanols. Experimental results have not been reported for α-alkoxy acetones. However, Chandra's analysis shows that the singlet 1,4-biradical derived from α-methoxy acetone can cyclize readily to form 3-oxetanol.[45] In the nascent triplet biradical, the distance between the radical sites is 3.0 Å and the two p orbitals on the carbon atoms at the radical sites are almost perpendicular to each other.

The mechanism suggested above is consistent with the solvent effect: in methanol photolysis of **24** gave only the type II elimination product. It is widely recognized that the effect is the result of the engagement of the OH group (from the ketyl center) in H-bonding,[9] thus increasing the steric hindrance in cyclization. The model presented here provides a simple explanation: H-bonding solvent changes the conformational distribution, since singlet biradical will now be formed in somewhat different conformations the cyclization/fragmentation ratio can be expected to change.

Our results indicate that the biradical intermediate from **24** undergoes cyclization and type II elimination before the cyclopropyl ring opening, so does the absence of

rearrangement product. In fact, it has been known that benzylic stabilization perturbs the equilibrium of the cyclopropylcarbinyl radical rearrangement and that the conjugation of oxygen lowers the rate even further down.[70] The ring-opening rate of cyclopropylmethoxy radical is determined to be 9.9 x 10^6 from previous experiment.

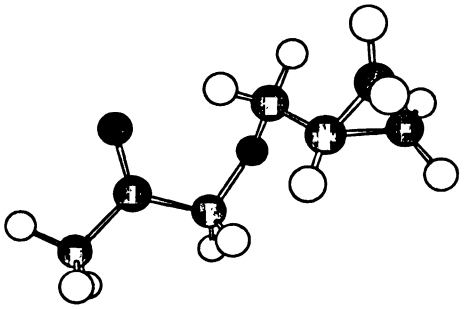
Table 24. Quantum Yields for Ketone Disappearence and Product Formation of 24 in Benzene at 25°C

Ketone	$\Phi_{dis.}$ [a]	$\Phi_{dis.-s}$ [b]	$\Phi_{dis.-t}$ [c]	Φ_{II} [a]	Φ_{II-s} [b]	Φ_{II-t} [c]	$\Phi_{cyc.}$ [a]
24	0.29	0.22	0.07	0.25	0.19	0.06	0.034

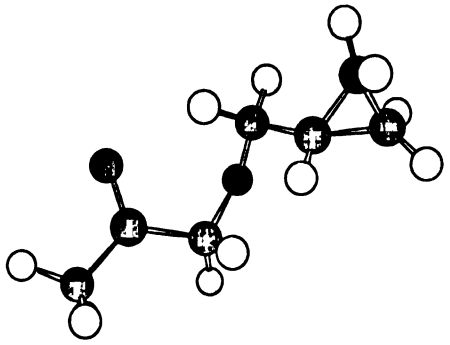
[a] Quantum yield without quencher. [b] Quantum yield in 0.4 M quencher. [c] $\Phi_t = \Phi - \Phi_s$.

The high yield of acetone would support Wagner's suggestion that cyclization reactions have large barriers (due to loss of rotational freedom, ring strain and steric crowding around the forming bond) even on the singlet surface.[87]

Our calculations reveal that **24** has a similar conformation in the lowest n, π^* singlet and triplet states. Both of these states have a favorable conformation for hydrogen abstraction: lowest energy conformer on singlet surface has one methylene hydrogen close enough for abstraction (d= 2.17 Å, α= 156°, β= 75°, γ= 72°); the lowest energy triplet state ketone also has only one of the γ hydrogens abstractable (d= 2.15 Å, α= 145°, β= 75°, γ= 72°). It has been postulated that for γ-hydrogen abstraction, once the reactive ketone conformer is reached, a further barrier is required to transfer the abstractable hydrogen to the carbonyl oxygen. Chandra's computational study on α-alkoxyacetones confirmed the presence of such a barrier: for α-alkoxyacetone containing secondary C-H bonds in γ-position, the barrier of γ-hydrogen abstraction in the lowest triplet state is about 20 kJ/mol.[45]



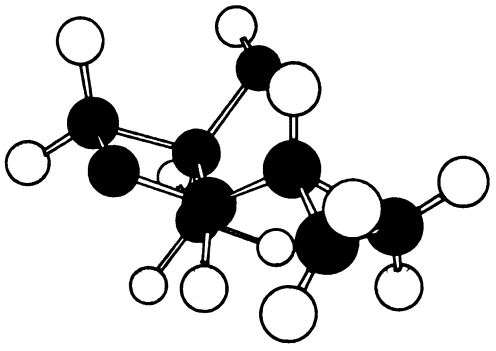
Lowest energy singlet conformer



Lowest energy triplet conformer

Dialkyl ketones are known to undergo γ-hydrogen abstraction in both T_1 and S_1.[36,37] Although studies of comparative processes are relatively few in number, in some cases the rate of γ-hydrogen abstraction from S_1 is much higher than from T_1. For *t*-butyl alkyl ketones it was found that γ-hydrogen abstraction arises predominantly from a singlet excited state. A more rapid rate for hydrogen abstraction from the singlet state may be rationalized on the basis of the higher energy of S_1 and appear to the common relationship between rate and exothermicity in radical reactions. We conclude that an inherently faster rate of γ-hydrogen abstraction in S_1 leads to the selectivity observed.

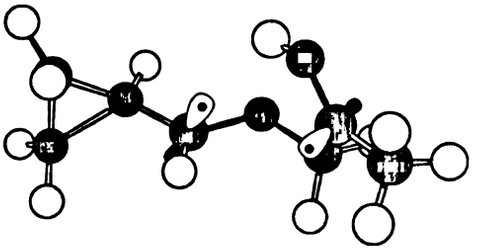
We now take the issue of an excited-state precursor of the products as settled and consider briefly some further mechanistic aspects of the results, particularly the effect of conformation on the chemical yield of products.



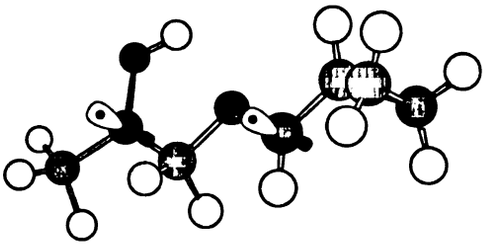
***cis*-oxetanol**

Singlet state type II reactions differ in many respects from the triplet reaction: cyclization/elimination ratio is smaller; radiationless decay/reaction ratio is higher; no polar solvent effect on singlet state quantum yield. In Table 18, we note that the quantum yield for cyclization is rather low as compared to that of **24**. The act of hydrogen abstraction may produce a surface crossing along the singlet reaction surface that serves as a special 'chemically assisted' internal conversion.[1,36,37,38,82,88] This type of inefficiency is well documented and accepted in the case of singlet 1,4-biradicals from the experimental results of Wagner[38] and Yang[82] on the Norrish type II reaction and from the theoretical models of Salem[89] and Michl.[90] Based on these pioneering efforts, we interpret the inefficiency as resulting from a γ-hydrogen-excited carbonyl interaction which either induces internal conversion or leads to formation of a singlet 1,4-biradical which efficiently disproportionates to the starting ketone. Since analogous triplet 1,4-biradical produced from **23** cyclizes efficiently to oxetanols, it is difficult to understand why the singlet 1,4-biradical produced from **24** would not cyclize efficiently.

The singlet biradicals have very short lifetimes and the ground state control might be assumed to control their reactivity. However, our experimental result shows *cis*-oxetanol to be the only cyclization product. Global minimization on singlet excited state ketone indicates the presence of one reactive conformer which is in a pro-*trans* geometry. While semiempirical calculation on the singlet biraidcal shows the presence of two minima within 1.3 kcal/mol of each other. The global minimum **a** is in a pro-*cis* geometry, **b** is 1.21 kcal/mol higher in energy than **a** and is not in a good geometry to cyclize. Our results seem to indicate conformational control of reactivity in photocyclization of singlet biradicals.



a



b

Experimental Section

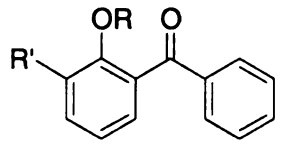
I. General Procedures

^{1}H and ^{13}C NMR spectra were obtained using either a 300 MHz Varian Gemini, a 300 MHz Varian UnityPlus, a 300 MHz Inova or a 500 MHz Varian UnityPlus instrument. IR spectra were recorded using solutions in CCl_4 on a Nicolet IR-42 Fourier Transform IR spectrometer. Compounds with low solubility in carbon tetrachloride were prepared as thin films on a NaCl plate by dissolving in an appropriate solvent then pipetting the solution on the salt plate. The solvent was allowed to evaporate and the cycle repeated until an acceptable film was achieved. UV spectra were recorded on a Shimadzu UV-160 spectrometer. Low resolution mass spectra were recorded on a Hewlett-Packard 5890 GC/MS Trio-1. The electron impact (EI) and direct probe methods were used.

Gas chromatographic analysis were performed on a Varian 3400 machine with flame ionization detector, splitless capillary injector and a Megabore DB-210 capillary column. The GC was connected to a Hewlett-Packard 3393A integrating recorder. HPLC analyses were performed on a Rainin system equipped with Dynamax UV-D absorbance detector using a silica column. For the preparative TLC, Analtech Uniplate silica gel plates (20 x 20 cm, 1000 micron) were used.

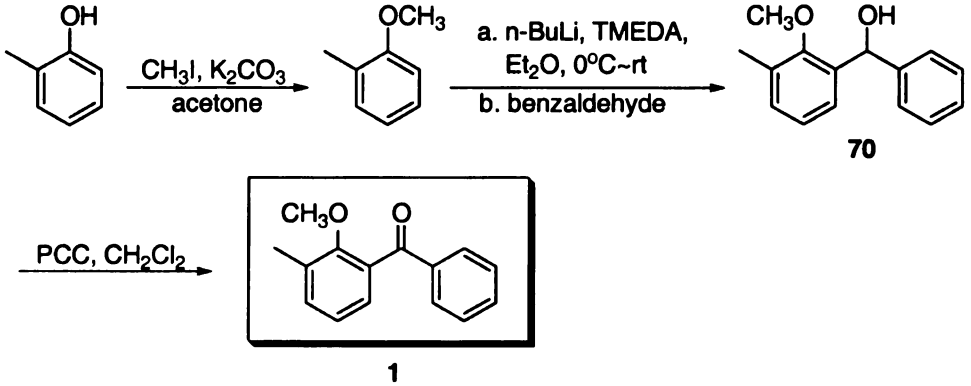
I. Synthesis: Preparation of Starting Ketones

ı. Substituted 2-Alkoxy-3-alkyl Benzophenones



Ketone	R	R'
1	CH_3	CH_3
2	CH_3	$CH(CH_3)_2$
3	CH_3	$C(CH_3)_3$
4	CH_3CH_2	CH_3
5	CH_3CH_2	$CH(CH_3)_2$
6	CH_3CH_2	$C(CH_3)_3$
7	$PhCH_2$	CH_3
8	$PhCH_2$	$CH(CH_3)_2$
9	$PhCH_2$	$C(CH_3)_3$

. *2-Methoxy-3-methylbenzophenone* (1)



Scheme 67. Synthesis of 1

2-methylanisole[91]

To a 250 mL round-bottom flask were placed 2-cresol (8.7 g, 8.4 mL, 80 mmol) and 80 mL of acetone. Potassium carbonate (11.1 g, 80 mmol) was added followed by methyl iodide (28.4 g, 12.5 mL, 200 mmol). The mixture was allowed to reflux for about 12 hours and then cooled to room temperature. The white solid was filtered off, the filtrate was evaporated under reduced pressure. The residue was purified by SiO_2 column chromatography with pure hexanes as the eluent to provide 2-methylanisole (5.8 g, 59% yield) as a colorless liquid.

2-methoxy-3-methylbenzhydrol (**70**)

To a vigorously stirred solution of 2-methylanisole (3.2 g, 26.2 mmol) and tetramethylethylenediamine (3.0 g, 26.2 mmol, 3.9 mL) in 80 mL of diethyl ether, was added n-butyl lithium (16.4 mL, 1.6 M in hexanes, 26.2 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and benzaldehyde (2.8 g, 26.2 mmol, 2.7 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 10:1) to give **70** (3.9 g, 65% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 2.28 (s, 3H), 3.51 (s, 3H), 3.84 (s, 1H), 6.03 (s, 1H), 7.01 (t, *J*= 7.5 Hz, 1H), 7.14 (dd, *J*= 7.8, 13.5 Hz, 2H), 7.34 (m, 5H).

2-methoxy-3-methylbenzophenone (**1**)[92]

Pyridinium chlorochromate (5.5 g, 16.4 mmol) was suspended in 60 mL of anhydrous CH_2Cl_2. **70** (2.5 g, 11.0 mmol) in 10 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 30 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotoevaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 50:1) to give **1** (1.7 g, 69% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 2.32 (s, 3H), 3.60 (s, 3H), 7.07 (t, *J*= 7.5 Hz, 1H), 7.17 (dd, *J*= 1.8, 7.5 Hz, 1H), 7.31 (dd, *J*= 0.9, 7.5 Hz, 1H), 7.45 (t, *J*= 7.8 Hz, 2H), 7.55 (tt, *J*= 1.5, 7.5 Hz, 1H), 7.81 (dt, *J*= 1.5, 7.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 16.02, 61.81, 123.44, 127.21, 128.30, 129.94, 131.71, 132.87, 133.15, 133.47, 137.47, 156.45, 196.84.

IR (neat, cm^{-1}): 2941.82 (w), 1668.64 (s), 1597.26 (m), 1466.09 (m), 1317.55 (m), 1288.61 (m), 1226.88 (m), 1006.97 (m), 966.46 (w).

MS, m/z: 226.1 (100.0%), 208.4 (100.0%), 181.1 (100.0%), 148.8 (100.0%), 134.5 (98.9%), 104.9 (100.0%), 76.9 (100.0%).

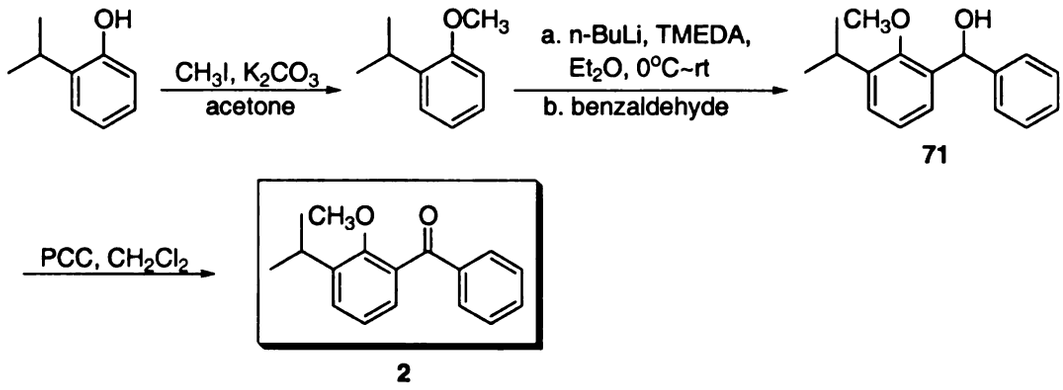
Anal. Calcd $C_{15}H_{14}O_2$: C, 79.65; H, 6.19.

Found: C, 79.84; H, 6.15.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 282 (3,019), 313 (449).

2. ***3-Isopropyl-2-methoxybenzophenone*** **(2)**

2-isopropylanisole[91]



Scheme 68. Synthesis of 2

To a 250 mL round-bottom flask were placed 2-isopropylphenol (8.2 g, 8.1 mL, 60 mmol) and 60 mL of acetone. Potassium carbonate (8.3 g, 60 mmol) was added followed by methyl iodide (17.0 g, 7.5 mL, 120 mmol). The mixture was allowed to reflux for about 12 hours and then cooled to room temperature. The white solid was filtered off, the filtrate was evaporated under reduced pressure. The residue was purified by SiO_2 column chromatography with pure hexanes as the eluent to provide 2-isopropylanisole (5.6 g, 62% yield) as a colorless liquid.

3-isopropyl-2-methoxybenzhydrol (**71**)

To a vigorously stirred solution of 2-isopropylanisole (4.4 g, 29.0 mmol) and tetramethylethylenediamine (3.5 g, 29.0 mmol, 4.5 mL) in 80 mL of diethyl ether, was added n-butyl lithium (18.2 mL, 1.6 M in hexanes, 29.0 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and benzaldehyde (2.8 g, 26.0 mmol, 2.7 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated to yield crude product which was purified by column chromatography

(hexanes: ethyl acetate 10:1) followed by recrystallization from hexanes to give **71** (4.0 g, 60% yield) as a white crystalline solid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.20 (d, *J*= 6.9 Hz, 3H), 1.22 (d, *J*= 6.9 Hz, 3H), 2.89 (s, broad, 1H), 3.29 (heptet, *J*= 6.9 Hz, 1H), 3.56 (s, 3H), 6.07 (s, 1H), 7.11 (m, 2H), 7.23 (m, 2H), 7.32 (tt, *J*= 1.2, 7.5 Hz, 2H), 7.39 (dd, *J*= 1.8, 7.5 Hz, 2H).

m.p.: 75.3~76.5°C

3-isopropyl-2-methoxybenzophenone (**2**)[92]

Pyridinium chlorochromate (7.5 g, 22.0 mmol) was suspended in 80 mL of anhydrous CH_2Cl_2. **71** (3.8 g, 15.0 mmol) in 15 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 4 hours 40 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotoevaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 50:1) to give **2** (3.6 g, 96% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.25 (d, *J*= 6.9 Hz, 6H), 3.36 (heptet, *J*= 6.9 Hz, 1H), 3.60 (s, 3H), 7.17 (m, 2H), 7.43 (m, 3H), 7.56 (tt, *J*= 1.5, 7.2 Hz, 1H), 7.83 (dd, *J*= 1.2, 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 23.61, 26.33, 62.90, 123.76, 127.13, 128.31, 129.10, 129.98, 132.76, 133.19, 137.42, 142.32, 155.50, 197.00.

IR (neat, cm^{-1}): 2964.97 (m), 1670.57 (s), 1597.26 (w), 1290.54 (s), 1006.97 (m).

MS, m/z: 253.9 (37.7%), 238.8 (19.4%), 195.1 (20.2%), 177.0 (50.6%), 161.0 (43.5%),

105.0 (100.0%), 91.0 (100.0%), 76.8 (100.0%).

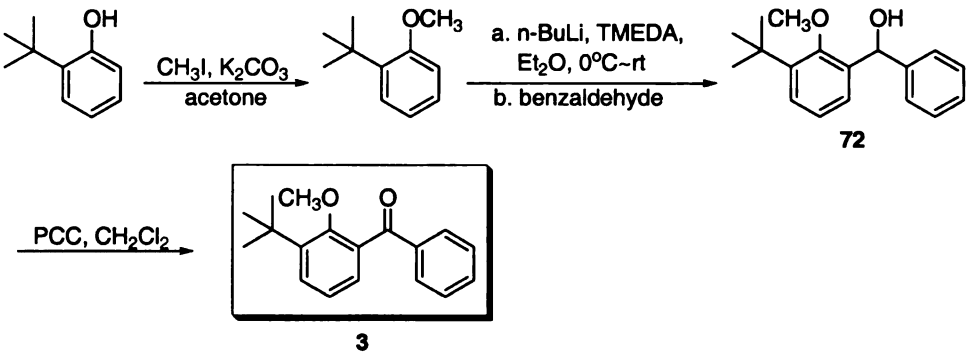
Anal. Calcd $C_{17}H_{18}O_2$: C, 80.31; H, 7.09.

Found: C, 80.21; H, 7.13.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 281 (3,289), 313 (497).

m.p.: 69.6~70.3°C

3. ***3-t-Butyl-2-methoxybenzophenone*** **(3)**



Scheme 69. Synthesis of 3

2-t-butylanisole[91]

To a 250 mL round-bottom flask were placed 2-t-butylphenol (9.0 g, 9.2 mL, 60 mmol) and 60 mL of acetone. Potassium carbonate (8.3 g, 60 mmol) was added followed by methyl iodide (17.0 g, 7.5 mL, 120 mmol). The mixture was allowed to reflux for about 12 hours and then cooled to room temperature. The white solid was filtered off, the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography with pure hexanes as the eluent to provide 2-t-butylanisole (6.0 g, 61% yield) as a colorless liquid.

3-t-butyl-2-methoxybenzhydrol (**72**)

To a vigorously stirred solution of 2-t-butylanisole (5.3 g, 32.0 mmol) and tetramethylethylenediamine (3.7 g, 32.0 mmol, 4.8 mL) in 80 mL of diethyl ether, was added n-butyl lithium (20.0 mL, 1.6 M in hexanes, 32.0 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and benzaldehyde (3.4 g, 32.0 mmol, 3.3 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 15:1) followed by recrystallization from hexanes to give **72** (5.4 g, 63% yield) as a white crystalline solid.

^1H NMR ($CDCl_3$, 300MHz), δ ppm: 1.38 (s, 9H), 2.58 (s, broad, 1H), 3.57 (s, 3H), 6.06 (s, 1H), 7.01 (t, *J*= 7.5 Hz, 1H), 7.18 (dd, *J*= 1.8, 7.5 Hz, 1H), 7.41 (m, 2H), 7.52 (tt, *J*= 1.5, 7.5 Hz, 2H), 7.80 (dd, *J*= 1.8, 7.8 Hz, 2H).

m.p.: 78.2~79.1°C.

3-t-butyl-2-methoxybenzophenone (**3**)[92]

Pyridinium chlorochromate (10.1 g, 30.0 mmol) was suspended in 100 mL of anhydrous CH_2Cl_2. **72** (5.4 g, 20.0 mmol) in 15 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 40 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotoevaporation. The crude product was purified by column chromatography (hexanes:

ethyl acetate 50:1) to give **3** (5.4 g, 100% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.39 (s, 9H), 3.55 (s, 3H), 7.07 (t, *J*= 7.8 Hz, 1H), 7.22 (dd, *J*= 2.1, 7.8 Hz, 1H), 7.44 (m, 3H), 7.56 (tt, *J*= 1.2, 7.5 Hz, 1H), 7.84 (dd, *J*= 1.8, 8.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 30.47, 35.10, 62.10, 122.71, 128.33, 128.43, 129.44, 130.03, 132.37, 133.23, 137.16, 142.75, 158.39, 197.26.

IR (neat, cm^{-1}): 2959.18 (m), 1684.78 (s), 1583.70 (w), 1412.07 (m), 1290.54 (m), 1230.74 (m), 1008.90 (w).

MS, m/z: 268.8 (26.7%), 267.9 (26.7%), 252.9 (42.0%), 235.2 (30.6%), 175.0 (21.4%), 105.0 (100.0%), 91.0 (100.0%), 76.9 (100.0%).

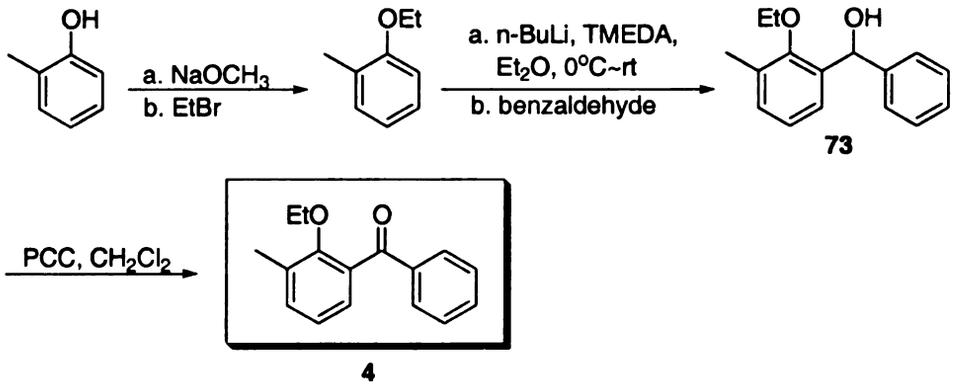
Anal. Calcd $C_{18}H_{20}O_2$: C, 80.60; H, 7.46.

Found: C, 80.63; H, 7.33.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 280 (3,662), 313 (803).

m.p.: 54.0~54.8°C

4. ***2-Ethoxy-3-methylbenzophenone*** **(4)**



Scheme 70. Synthesis of 4

2-ethoxytoluene[23]

2-Cresol (8.6 g, 8.2 mL, 80.0 mmol) was added to sodium methoxide (4.3 g, 80.0 mmol) in 60 mL of methanol and stirred under nitrogen for about 1 hour. Ethyl bromide (21.8 g, 14.9 mL, 200.0 mmol) in 15 mL of methanol was added dropwise; the solution was refluxed overnight. The methanol was removed on a rotary evaporator and residue taken up into 80 mL of diethyl ether. The ether was washed with saturated sodium bicarbonate. The aqueous layers were combined and washed with ether. The ether extracts were combined, washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford a yellow oil. This oil was purified by column chromatography (hexanes) to give 2-ethoxytoluene (6.6 g, 61% yield) as a colorless liquid.

2-ethoxy-3-methylbenzhydrol (**73**)

To a vigorously stirred solution of 2-ethoxytoluene (4.8 g, 35.0 mmol) and tetramethylethylenediamine (4.1 g, 35.0 mmol, 5.3 mL) in 80 mL of diethyl ether, was added n-butyl lithium (22.0 mL, 1.6 M in hexanes, 35.0 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and benzaldehyde (3.4 g, 32.0 mmol, 3.3 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 20:1) to afford **73** (6.4 g, 83% yield) as a pale yellow oil.

^1H NMR ($CDCl_3$, 300MHz), δ ppm: 1.29 (t, *J*= 7.2 Hz, 3H), 2.27 (s, 3H), 2.96 (s, broad, 1H), 3.61 (dq, *J*= 7.2, 9.3 Hz, 1H), 3.74 (dq, *J*= 7.2, 9.3 Hz, 1H), 6.05 (s, 1H), 6.99 (dd,

J= 6.9, 8.1 Hz, 1H), 7.10 (d, *J*= 7.5 Hz, 2H), 7.34 (stack, 5H).

2-ethoxy-3-methylbenzophenone (**4**)

Pyridinium chlorochromate (13.3 g, 40.0 mmol) was suspended in 80 mL of anhydrous CH_2Cl_2. **73** (6.4 g, 26.4 mmol) in 15 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotoevaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 50:1, then hexanes: dichloromethane 2:1) to afford **4** (3.6 g, 56% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.06 (t, *J*= 7.2 Hz, 3H), 2.31 (s, 3H), 3.75 (q, *J*= 7.2 Hz, 2H), 7.06 (t, *J*= 7.5 Hz, 1H), 7.21 (dd, *J*= 1.8, 7.5 Hz, 1H), 7.32 (dd, *J*= 1.8, 7.5 Hz, 1H), 7.42 (tt, *J*= 1.8, 7.8 Hz, 2H), 7.54 (tt, *J*= 2.1, 7.2 Hz, 1H), 7.82 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 15.27, 16.21, 70.37, 123.32, 127.39, 128.23, 129.93, 131.91, 133.00, 133.02, 133.46, 137.58, 155.56, 197.02.

IR (neat, cm^{-1}): 3067.21 (w), 2978.47 (w), 2924.46 (w), 1670.57 (s), 1597.26 (m), 1448.73 (m), 1317.55 (m), 1288.61 (m), 1219.17 (m), 1087.99 (w), 1032.05 (m), 966.46 (w), 848.79 (w).

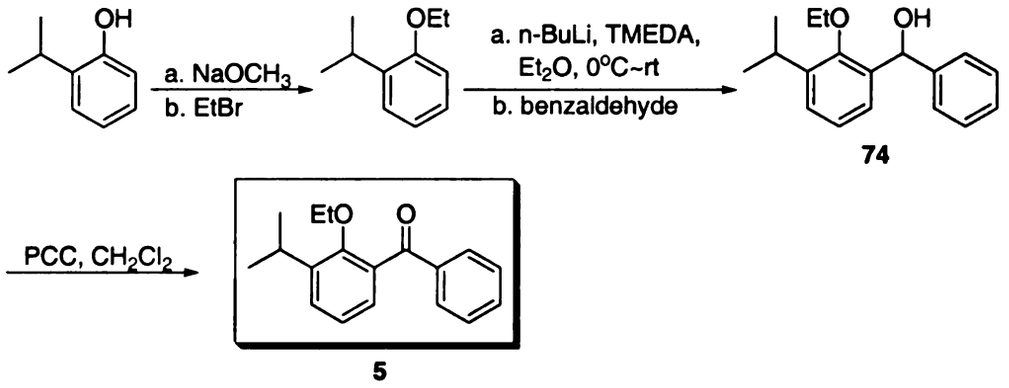
MS, m/z: 240.2 (12.4%), 210.9 (26.7%), 134.6 (100.0%), 104.5 (27.9%), 76.9 (91.6%), 50.8 (41.6%).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67.

Found: C, 79.82; H, 6.37.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 281 (3,212), 313 (529).

5. ***2-Ethoxy-3-isopropylbenzophenone* (5)**



Scheme 71. Synthesis of 5

2-ethoxycumene[23]

2-Isopropylphenol (8.2 g, 8.1 mL, 60.0 mmol) was added to sodium methoxide (3.3 g, 60.0 mmol) in 60 mL of methanol and stirred under nitrogen for about 1 hour. Ethyl bromide (13.1 g, 9.0 mL, 120.0 mmol) in 15 mL of methanol was added dropwise; the solution was refluxed overnight. The methanol was removed on a rotary evaporator and residue taken up into 80 mL of diethyl ether. The ether was washed with saturated sodium bicarbonate. The aqueous layers were combined and washed with ether. The ether extracts were combined, washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford a yellow oil. This oil was purified by column chromatography (hexanes) to give 2-ethoxycumene (6.3 g, 64% yield) as a colorless liquid.

2-ethoxy-3-isopropylbenzhydrol (**74**)

To a vigorously stirred solution of 2-ethoxycumene (3.2 g, 20.0 mmol) and tetramethylethylenediamine (2.3 g, 20.0 mmol, 3.0 mL) in 60 mL of diethyl ether, was added n-butyl lithium (12.5 mL, 1.6 M in hexanes, 20.0 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and benzaldehyde (1.9 g, 18.0 mmol, 1.9 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated off to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 20:1) to afford **74** (4.1 g, 84% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.20 (d, *J*= 6.9 Hz, 3H), 1.22 (d, *J*= 6.9 Hz, 3H), 1.34 (t, *J*= 6.9 Hz, 3H), 2.99 (s, broad, 1H), 3.26 (heptet, *J*= 6.9 Hz, 1H), 3.46 (q, *J*= 6.9 Hz, 2H), 3.68 (stack, 2H), 6.08 (s, 1H), 7.06 (stack, 2H), 7.22 (stack, 2H), 7.32 (t, *J*= 7.8 Hz, 2H), 7.40 (dd, *J*= 1.2, 9.0 Hz, 2H).

2-ethoxy-3-isopropylbenzophenone (**5**)

Pyridinium chlorochromate (7.7 g, 23.0 mmol) was suspended in 60 mL of anhydrous CH_2Cl_2. **74** (4.1 g, 15.2 mmol) in 15 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotaevaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 60:1) to afford **5** (3.5 g, 85% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.05 (t, *J*= 7.2 Hz, 3H), 1.24 (d, *J*= 6.9 Hz, 6H), 3.72 (heptet, *J*= 6.9 Hz, 1H), 3.74 (q, *J*= 7.2 Hz, 2H), 7.13 (dt, *J*= 0.3, 7.5 Hz, 1H), 7.20 (dd, *J*= 2.1, 7.5 Hz, 1H), 7.42 (stack, 3H), 7.57 (tt, *J*= 1.5, 7.5 Hz, 1H), 7.82 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 15.29, 23.69, 26.22, 71.43, 123.67, 127.23, 128.24, 129.09, 129.98, 132.95, 133.02, 137.50, 142.52, 154.43, 197.15.

IR (neat, cm^{-1}): 3065.28 (w), 2964.97 (m), 2930.24 (w), 2870.44 (w), 1672.50 (s), 1597.26 (w). 1446.80 (m), 1388.92 (w), 1288.61 (m), 1217.24 (m), 1030.12 (w).

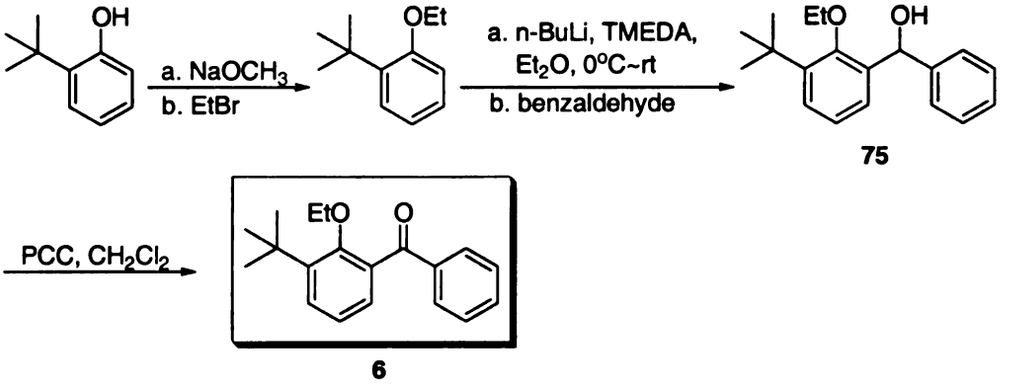
MS, m/z: 268.2 (23.4%), 238.8 (14.3%), 224.8 (7.9%), 163.4 (53.0%), 147.0 (29.8%), 105.0 (100.0%), 77.0 (84.0%).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46.

Found: C, 80.71; H, 7.35.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 280 (3,637), 313 (545).

6. ***3-t-Butyl-2-ethoxybenzophenone* (6)**



Scheme 72. Synthesis of 6

2-t-butylethoxybenzene[23]

2-t-Butylphenol (9.0 g, 9.2 mL, 60.0 mmol) was added to sodium methoxide (3.3 g, 60.0 mmol) in 60 mL of methanol and stirred under nitrogen for about 1 hour. Ethyl

bromide (16.4 g, 11.2 mL, 150.0 mmol) in 15 mL of methanol was added dropwise; the solution was refluxed overnight. The methanol was removed on a rotary evaporator and residue taken up into 80 mL of diethyl ether. The ether was washed with saturated sodium bicarbonate. The aqueous layers were combined and washed with ether. The ether extracts were combined, washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford a yellow oil. This oil was purified by column chromatography (hexanes) to give 2-t-butylethoxybenzene (7.2 g, 67% yield) as a colorless liquid.

3-t-butyl-2-ethoxybenzhydrol (**75**)

To a vigorously stirred solution of 2-t-butylethoxybenzene (4.6 g, 26.0 mmol) and tetramethylethylenediamine (3.0 g, 26.0 mmol, 3.9 mL) in 60 mL of diethyl ether, was added n-butyl lithium (16.3 mL, 1.6 M in hexanes, 26.0 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and benzaldehyde (2.5 g, 24.0 mmol, 2.4 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated off to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 20:1) to afford **75** (4.7 g, 69% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.47 (t, *J*= 7.8 Hz, 3H), 1.47 (s, 9H), 2.74 (s, 1H), 3.91 (dq, *J*= 6.9, 9.3 Hz, 1H), 4.04 (dq, *J*= 6.9, 9.3 Hz, 1H), 6.25 (s, 1H), 7.06 (t, *J*= 7.5 Hz, 1H), 7.12 (dd, *J*= 2.1, 7.5 Hz, 1H), 7.43 (stack, 4H), 7.47 (dd, *J*= 1.5, 7.5 Hz, 2H).

3-t-butyl-2-ethoxybenzophenone (**6**)

Pyridinium chlorochromate (8.3 g, 25.0 mmol) was suspended in 70 mL of anhydrous CH_2Cl_2. **75** (4.7 g, 16.5 mmol) in 15 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3.5 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 60:1) to afford **6** (2.9 g, 62% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 0.96 (t, *J*= 6.9 Hz, 3H), 1.40 (s, 9H), 3.73 (q, *J*= 6.9 Hz, 2H), 7.06, (t, *J*= 7.8Hz, 1H), 7.23 (dd, *J*= 1.8, 7.8 Hz, 1H), 7.42 (tt, *J*= 1.8, 7.5 Hz, 2H), 7.46 (dd, *J*= 2.1, 7.8 Hz, 1H), 7.54 (tt, *J*= 1.2, 7.5 Hz, 1H), 7.82 (dd, *J*= 2.1, 7.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 14.98, 30.48, 35.08, 70.76, 122.67, 128.19, 128.46, 129.46, 130.07, 132.70, 133.03, 137.11, 142.79, 157.05, 197.32.

IR (neat, cm^{-1}): 2963.04 (m), 2876.23 (w), 1666.71 (s), 1583.76 (m), 1429.43 (s), 1387.00 (m), 1317.55 (m), 1290.54 (s), 1265.46 (m), 1224.95 (s), 1033.98 (m), 964.53 (m), 912.45 (w).

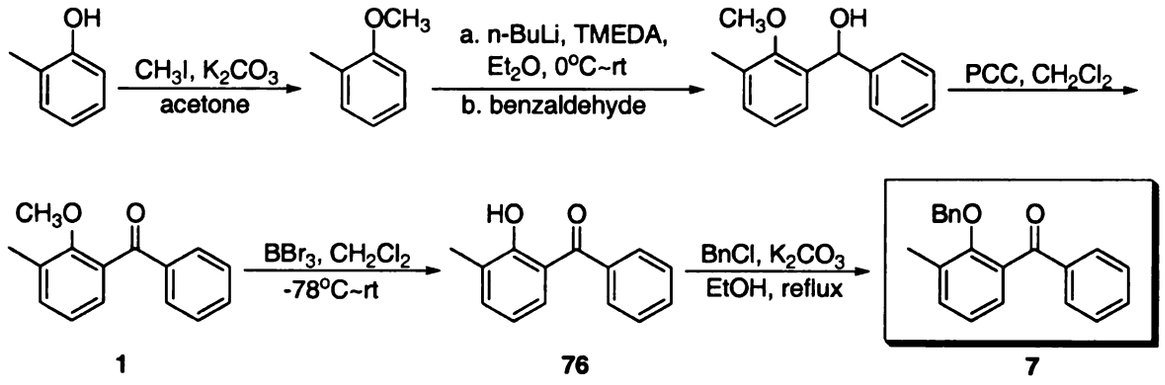
MS, m/z: 282.0 (65.5%), 267.0 (63.5%), 249.0 (53.7%), 238.9 (48.2%), 177.0 (100.0%), 161.0 (100.0%), 132.9 (69.0%), 104.9 (100.0%), 76.8 (100.0%).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80.

Found: C, 80.87; H, 7.77.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 281 (3,375), 313 (818).

7. ***2-Benzyloxy-3-methylbenzophenone*** **(7)**



Scheme 73. Synthesis of 7

2-hydroxy-3-methylbenzophenone (**76**)[94,95]

A solution of **1** (2.6 g, 11.5 mmol) in 40 mL of dichloromethane cooled to -78°C was treated with boron tribromide (23 mL, 1 M in CH_2Cl_2, 23.0 mmol). After 30 mins the reaction was warmed to -10°C, where stirring was continued for another 2 hours. The reaction was quenched at -10°C by the addition of 10 mL of ether. The reaction mixture was warmed to room temperature and was stirred an additional 30 mins followed by addition of water. Isolation of the product by dichloromethane extraction gave a dark red liquid, which was chromatographed (hexanes: ethyl acetate 30:1) to afford **76** (2.1 g, 87% yield) as a yellow liquid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 2.31 (s, 3H), 6.76 (t, *J*= 7.5 Hz, 1H), 7.44 (stack, 3H), 7.56 (tt, *J*= 1.8, 7.5 Hz, 1H), 7.66 (dd, *J*= 1.5, 7.8 Hz, 2H), 12.32 (s, 1H).

2-benzyloxy-3-methylbenzophenone (**7**)[23]

To a 250 mL round-bottom flask were added **76** (2.1 g, 10.0 mmol), benzyl chloride (1.3 g, 10.0 mmol, 1.2 mL), potassium carbonate (0.7 g, 5.0 mmol) and 30 mL of absolute ethanol. The mixture was refluxed overnight then cooled to room temperature.

Vacuum filtration gave a clear pale yellow solution, which was concentrated under reduced pressure. The residue was partitioned between diethyl ether and water. Aqueous phase was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (hexanes: ethyl acetate 60:1) to afford **7** (2.7 g, 90% yield) as a pale yellow oil.

^1H NMR ($CDCl_3$, 300MHz), δ ppm: 2.36 (s, 3H), 4.80 (s, 2H), 7.19 (stack, 3H), 7.29 (stack, 4H), 7.39 (dd, *J*= 1.2, 7.5 Hz, 1H), 7.46 (tt, *J*= 1.5, 7.2 Hz, 2H), 7.61 (tt, *J*= 1.2, 7.2 Hz, 1H), 7.90 (dd, *J*= 1.5, 7.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 16.33, 76.45, 123.76, 127.62, 127.94, 127.97, 128.26, 128.29, 130.12, 132.15, 133.12, 133.24, 133.64, 136.74, 137.54, 155.06, 196.78.

IR (neat, cm^{-1}): 3063.35 (w), 2922.53 (w), 1666.71(s), 1597.26 (m), 1448.73 (m), 1317.55 (m), 1215.31 (m), 1087.99 (w).

MS, m/z: 302.2 (7.8%), 134.8 (21.6%), 91.0 (100.0%), 76.9 (34.5%), 65.0 (26.3%).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96.

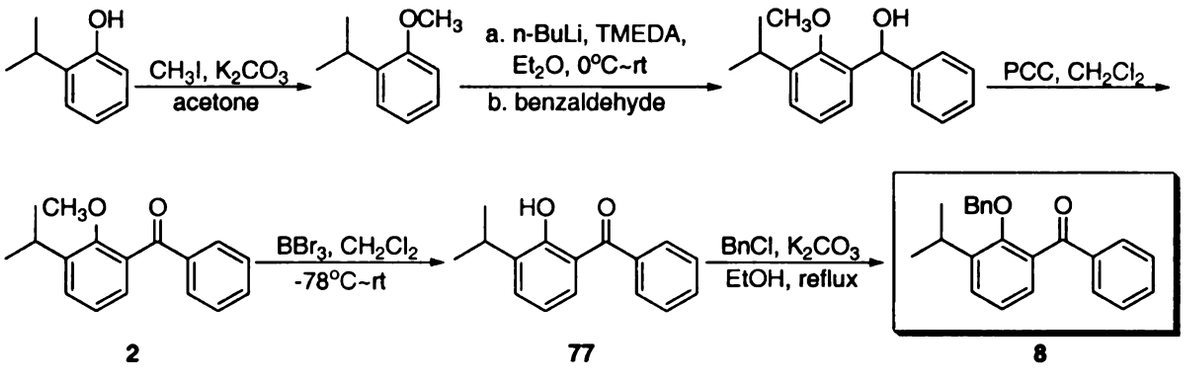
Found: C, 83.32; H, 6.00.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 280 (3,547), 313 (525).

8. ***2-Benzyloxy-3-isopropylbenzophenone*** **(8)**

2-hydroxy-3-isopropylbenzophenone (**77**)[94,95]

A solution of **2** (3.3 g, 13.0 mmol) in 40 mL of dichloromethane cooled to -78°C was treated with boron tribromide (26 mL, 1 M in CH_2Cl_2, 26.0 mmol). After 30 mins the reaction was warmed to -10°C, where stirring was continued for another 2 hours. The reaction was quenched at -10°C by the addition of 10 mL of ether. The reaction mixture



Scheme 74. Synthesis of 8

was warmed to room temperature and was stirred an additional 30 mins followed by addition of water. Isolation of the product by dichloromethane extraction gave a dark red liquid, which was chromatographed (hexanes: ethyl acetate 35:1) to afford **77** (2.7 g, 87% yield) as a yellow liquid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.27 (d, *J*= 7.2 Hz, 6H), 3.44 (heptet, *J*= 7.2 Hz, 1H), 6.82 (t, *J*= 7.5 Hz, 1H), 7.46 (stack, 4H), 7.56 (tt, *J*= 1.8, 7.5 Hz, 1H), 7.64 (dd, *J*= 1.5, 7.8 Hz, 2H), 12.20 (s, 1H).

2-benzyloxy-3-isopropylbenzophenone (**8**)[23]

To a 250 mL round-bottom flask were added **77** (2.7 g, 11.3 mmol), benzyl chloride (1.4 g, 11.3 mmol, 1.3 mL), potassium carbonate (0.8 g, 6.0 mmol) and 30 mL of absolute ethanol. The mixture was refluxed overnight then cooled to room temperature. Vacuum filtration gave clear pale yellow solution which was concentrated under reduced pressure. The residue was partitioned between diethyl ether and water. Aqueous phase was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (hexanes: ethyl acetate 60:1) to afford **8** (3.2 g, 87% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.28 (d, *J*= 6.9 Hz, 6H), 3.45 (heptet, *J*= 6.9 Hz, 1H), 4.80 (s, 2H), 7.13 (stack, 2H), 7.27 (stack, 5H), 7.47 (stack, 3H), 7.63 (tt, *J*= 1.5, 7.5 Hz, 1H), 7.93 (dd, *J*= 1.5, 7.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 23.69, 26.22, 77.50, 124.15, 127.39, 127.84, 127.91, 128.24, 128.29, 129.26, 130.14, 133.13, 133.18, 136.70, 137.47, 142.75, 153.83, 196.95.

IR (neat, cm^{-1}): 3065.28 (w), 2946.97 (s), 2868.51 (m), 1662.85 (s), 1597.26 (m), 1439.68 (s), 1298.54 (s), 1253.89 (m), 1213.38 (s), 1163.22 (m), 1093.78 (w).

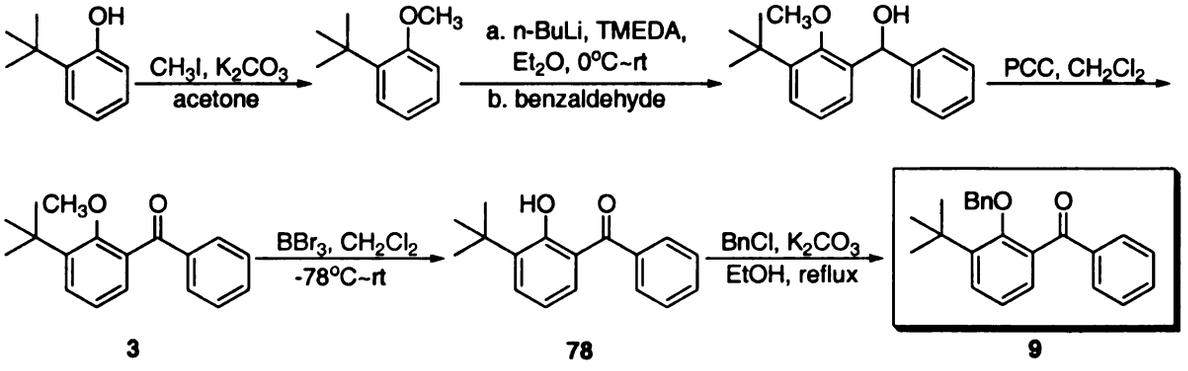
MS, m/z: 330.4 (20.4%), 239.3 (100.0%), 225.3 (28.6%), 162.8 (40.8%), 104.9 (100.0%), 90.8 (100.0%), 76.9 (100.0%), 65.0 (100.0%).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.64; H, 6.67.

Found: C, 83.69; H, 6.66.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 280 (3,580), 313 (555).

9. ***2-Benzyloxy-3-t-butylbenzophenone*** **(9)**



Scheme 75. Synthesis of 9

3-t-butyl-2-hydroxybenzophenone **(78)**[94,95]

A solution of **3** (4.7 g, 17.5 mmol) in 40 mL of dichloromethane cooled to -78°C was treated with boron tribromide (35 mL, 1 M in CH_2Cl_2, 35.0 mmol). After 30 mins the

reaction was warmed to -10°C, where stirring was continued for another 2 hours. The reaction was quenched at -10°C by the addition of 10 mL of ether. The reaction mixture was warmed to room temperature and was stirred an additional 30 mins followed by addition of water. Isolation of the product by dichloromethane extraction gave a dark red liquid, which was chromatographed (hexanes: ethyl acetate 20:1) to afford **78** (3.0 g, 67% yield) as a yellow liquid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.45 (s, 9H), 6.77 (t, *J*= 7.5 Hz, 1H), 7.51 (stack, 5H), 7.65 (dd, *J*= 1.5, 8.4 Hz, 2H).

2-benzyloxy-3-t-butylbenzophenone (**9**)[23]

To a 250 mL round-bottom flask were added **78** (2.7 g, 11.3 mmol), benzyl chloride (1.4 g, 11.3 mmol, 1.3 mL), potassium carbonate (0.8 g, 6.0 mmol) and 30 mL of absolute ethanol. The mixture was refluxed overnight then cooled to room temperature. Vacuum filtration gave a clear pale yellow solution, which was concentrated under reduced pressure. The residue was partitioned between diethyl ether and water. Aqueous phase was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (hexanes: ethyl acetate 60:1) to afford **9** (3.2 g, 87% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.37 (s, 9H), 4.75 (s, 2H), 6.89 (stack, 2H), 7.16 (stack, 4H), 7.32 (dd, *J*= 1.8, 7.5 Hz, 1H), 7.40 (tt, *J*= 1.5, 7.8 Hz, 2H), 7.51(dd, *J*= 1.8, 7.8 Hz, 1H), 7.56 (tt, *J*= 2.1, 7.2 Hz, 1H), 7.84 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 30.51, 35.13, 76.72, 123.36, 127.01, 127.54, 128.06, 128.30, 128.54, 129.83, 130.19, 133.09, 133.16, 136.59, 137.15, 143.17, 156.50, 197.18.

IR (neat, cm^{-1}): 2961.11 (m), 1660.92 (s), 1583.76 (m), 1427.51 (s), 1375.42 (s), 1288.61 (s), 1219.17 (s), 964.53 (m).

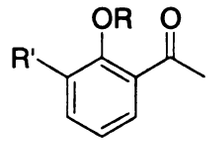
MS, m/z: 344.1 (24.5%), 329.1 (7.9%), 239.3 (15.2%), 177.3 (24.4%), 105.0 (98.4%), 90.9 (100.0%), 77.0 (69.8%), 65.0 (31.8%).

Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.72; H, 6.98.

Found: C, 83.68; H, 7.22.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 281 (3,545), 313 (770).

B. Substituted 2-Alkoxy-3-alkyl Acetophenones

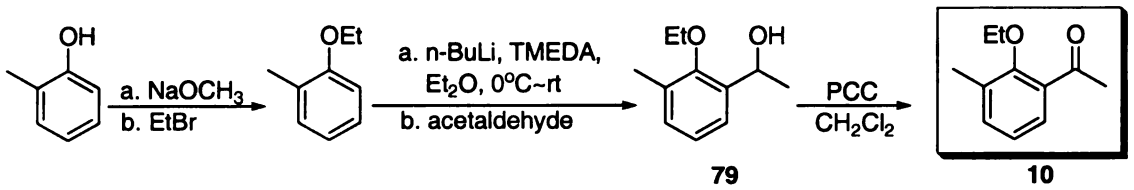


Ketone	R	R'
10	CH_3CH_2	CH_3
11	CH_3CH_2	$CH(CH_3)_2$
12	CH_3CH_2	$C(CH_3)_3$
13	$PhCH_2$	CH_3
14	$PhCH_2$	$CH(CH_3)_2$
15	$PhCH_2$	$C(CH_3)_3$

1. ***2-Ethoxy-3-methylacetophenone*** **(10)**

1-(2-ethoxy-3-methyl)phenylethanol **(79)**

To a vigorously stirred solution of 2-ethoxytoluene (6.6 g, 48.5 mmol) and tetramethylethylenediamine (5.6 g, 48.5 mmol, 7.3 mL) in 80 mL of diethyl ether, was



Scheme 76. Synthesis of 10

added n-butyl lithium (30.3 mL, 1.6 M in hexanes, 48.5 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and acetaldehyde (1.9 g, 44.0 mmol, 1.9 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 60:1~8:1) to afford **79** (3.3 g, 42% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.42 (t, *J*= 6.9 Hz, 3H), 1.48 (d, *J*= 6.3 Hz, 3H), 3.86 (stack, 2H), 5.18 (q, *J*= 6.3 Hz, 1H), 7.01 (t, *J*= 7.5 Hz, 1H), 7.08 (dd, *J*= 2.1, 7.5 Hz, 1H), 7.24 (dd, *J*= 2.1, 7.5 Hz, 1H).

2-ethoxy-3-methylacetophenone (**10**)

Pyridinium chlorochromate (7.4 g, 22.0 mmol) was suspended in 60 mL of anhydrous CH_2Cl_2. **79** (3.3 g, 18.3 mmol) in 10 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (hexanes: ethyl

acetate 60:1~30:1) to afford **10** (2.8 g, 85% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.37 (t, *J*= 7.2 Hz, 3H), 2.28 (s, 3H), 2.60 (s, 3H), 3.83 (q, *J*= 7.2 Hz, 2H), 7.02 (t, *J*= 7.8 Hz, 1H), 7.28 (dd, *J*= 1.5, 7.8 Hz, 1H), 7.37 (dd, *J*= 1.5, 7.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 15.56, 16.07, 30.42, 70.63, 123.79, 127.24, 132.29, 133.99, 134.69, 156.36, 197.45.

IR (neat, cm^{-1}): 2980.40 (w), 2926.39 (w), 1687.93 (s), 1587.62 (w), 1462.23 (w), 1387.00 (w), 1356.13 (w), 1277.04 (s), 1213.38 (m), 1032.05 (m), 906.66 (w).

MS, m/z: 178.1 (20.4%), 163.1 (39.6%), 135.0 (100.0%), 77.0 (60.8%), 50.7 (30.2%), 43.0 (54.5%).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87.

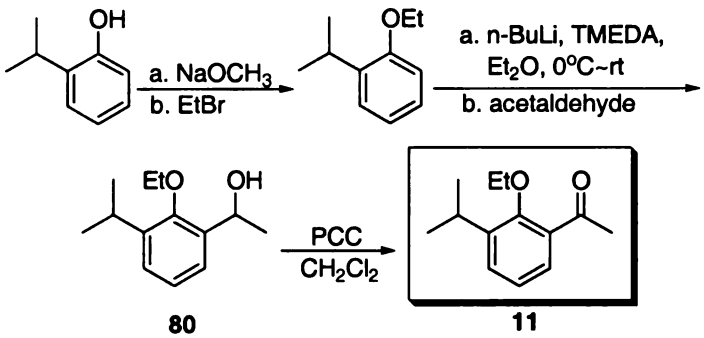
Found: C, 74.22; H, 8.01.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 290 (1,338), 313 (433).

2. ***2-Ethoxy-3-isopropylacetophenone*** **(11)**

1-(2-ethoxy-3-isopropyl)phenylethanol **(80)**

To a vigorously stirred solution of 2-ethoxycumene (4.7 g, 28.7 mmol) and tetramethylethylenediamine (3.3 g, 28.7 mmol, 4.3 mL) in 60 mL of diethyl ether, was added n-butyl lithium (17.9 mL, 1.6 M in hexanes, 28.7 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and acetaldehyde (1.3 g, 28.7 mmol, 1.2 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was



Scheme 77. Synthesis of 11

evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 10:1~5:1) to afford **80** (3.1 g, 52% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.12 (d, *J*= 7.2 Hz, 6H), 1.42 (t, *J*= 6.9 Hz, 3H), 1.50 (d, *J*= 6.6 Hz, 3H), 3.22 (heptet, *J*= 7.2 Hz, 1H), 3.84 (dq, *J*= 1.5, 7.5 Hz, 1H), 3.96 (dq, *J*= 1.5, 7.5 Hz, 1H), 5.20 (q, *J*= 6.9 Hz, 1H), 7.04 (t, *J*= 7.5 Hz, 1H), 7.24 (dd, *J*= 1.5, 7.5 Hz, 1H), 7.28 (dd, *J*= 1.5, 7.5 Hz, 1H).

2-ethoxy-3-isopropylacetophenone (**11**)

Pyridinium chlorochromate (6.0 g, 18.0 mmol) was suspended in 50 mL of anhydrous CH_2Cl_2. **80** (3.1 g, 15.0 mmol) in 10 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 60:1~30:1) to afford **11** (2.1 g, 68% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.12 (d, *J*= 6.9 Hz, 6H), 1.29 (t, *J*= 7.2 Hz, 3H), 2.51

(s, 3H), 3.26 (heptet, *J*= 6.9 Hz, 1H), 3.72 (q, *J*= 7.2 Hz, 2H), 7.02 (t, *J*= 7.8 Hz, 1H), 7.25 (dd, *J*= 1.5, 7.5 Hz, 1H), 7.30 (dd, *J*= 1.5, 7.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 15.64, 23.78, 26.08, 30.30, 72.05, 124.15, 126.90, 130.26, 134.22, 142.96, 155.04, 186.36.

IR (neat, cm^{-1}): 2966.90 (m), 2932.17 (w), 2872.37 (w), 1686.00 (s), 1585.69 (w), 1441.01 (m), 1356.13 (m), 1261.61 (m), 1209.52 (m), 1030.12 (w), 912.45 (w).

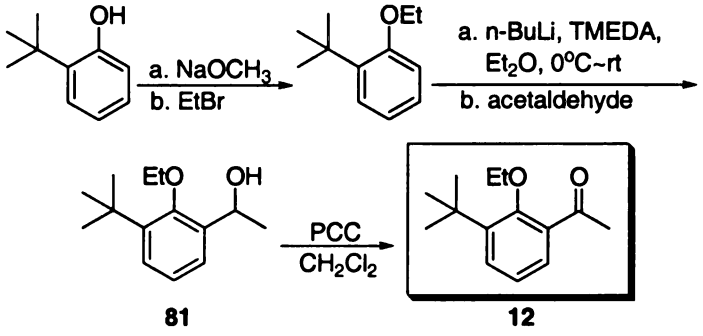
MS, m/z: 206.3 (100.0%), 191.3 (100.0%), 177.3 (100.0%), 163.3 (99.6%), 135.0 (62.0%), 121.0 (45.5%), 91.1 (100.0%), 77.0 (72.1%), 65.3 (44.7%).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74.

Found: C, 76.03; H, 8.98.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 288 (1,501), 313 (351).

3. ***3-t-Butyl-2-ethoxyacetophenone*** **(12)**



Scheme 78. Synthesis of 12

1-(3-t-butyl-2-ethoxy)phenylethanol **(81)**

To a vigorously stirred solution of 2-ethoxycumene (4.7 g, 28.7 mmol) and tetramethylethylenediamine (3.3 g, 28.7 mmol, 4.3 mL) in 60 mL of diethyl ether, was added n-butyl lithium (17.9 mL, 1.6 M in hexanes, 28.7 mmol) slowly at 0°C under

nitrogen.[92] The lithiation mixture was stirred overnight and acetaldehyde (1.3 g, 28.7 mmol, 1.2 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 10:1~5:1) to afford **81** (3.1 g, 52% yield) as a colorless oil.

^1H NMR ($CDCl_3$, 300MHz), δ ppm: 1.38 (s, 9H), 1.44 (t, *J*= 7.2 Hz, 3H), 1.51 (d, *J*= 6.6 Hz, 3H), 2.10 (s, 1H), 3.85 (dq, *J*= 7.2, 9.0 Hz, 1H), 3.96 (dq, *J*= 7.2, 9.0 Hz, 1H), 5.22 (q, *J*= 6.6 Hz, 1H), 7.06 (t, *J*= 7.5 Hz, 1H), 7.26 (dd, *J*= 1.5, 7.5 Hz, 1H), 7.34 (dd, *J*= 1.5, 7.5 Hz, 1H).

3-t-butyl-2-ethoxyacetophenone (**12**)

Pyridinium chlorochromate (2.4 g, 7.2 mmol) was suspended in 40 mL of anhydrous CH_2Cl_2. **81** (1.5 g, 6.5 mmol) in 10 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 50:1) to afford **12** (1.0 g, 69% yield) as a colorless oil.

^1H NMR ($CDCl_3$, 300MHz), δ ppm: 1.38 (s, 9H), 1.41 (t, *J*= 7.2 Hz, 3H), 2.59 (s, 3H), 3.77 (q, *J*= 7.2 Hz, 2H), 7.01 (t, *J*= 7.8 Hz, 1H), 7.26 (dd, *J*= 1.5, 7.5 Hz, 1H), 7.41 (dd, *J*= 1.5, 7.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 15.52, 29.68, 30.60, 35.10, 72.10, 123.18, 127.37, 130.33, 135.40, 143.25, 164.10, 198.56.

IR (neat, cm^{-1}): 2963.04 (m), 1689.86 (s), 1581.83 (w), 1427.51 (m), 1387.00 (m), 1356.13 (w), 1282.83 (w), 1263.54 (m), 1221.10 (m), 1032.05 (w).

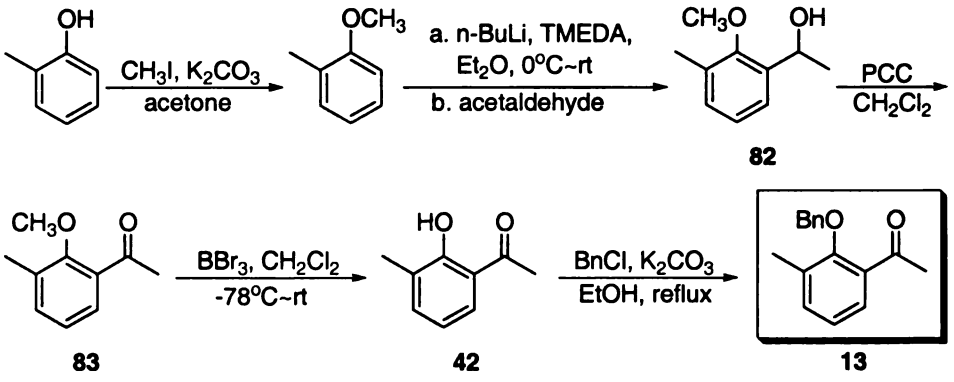
MS, m/z: 220.2 (19.1%), 205.1 (50.0%), 187.1 (33.8%), 177.1 (41.3%), 158.9 (46.3%), 148.9 (28.8%), 130.9 (37.9%), 114.9 (26.7%), 90.9 (31.3%), 77.1 (20.3%), 43.0 (100.0%).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09.

Found: C, 76.55; H, 9.02.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 289 (1.430), 313 (463).

4. ***2-Benzyloxy-3-methylacetophenone*** **(13)**



Scheme 79. Synthesis of 13

1-(2-methoxy-3-methyl)phenylethanol **(82)**

To a vigorously stirred solution of 2-methylanisole (7.9 g, 65.0 mmol) and tetramethylethylenediamine (7.5 g, 65.0 mmol, 9.7 mL) in 100 mL of diethyl ether, was added n-butyl lithium (40.6 mL, 1.6 M in hexanes, 65.0 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and acetaldehyde (2.6 g, 60.0

mmol, 2.5 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 10:1) to afford **82** (4.5 g, 45% yield) as a pale yellow oil.

^1H NMR ($CDCl_3$, 300MHz), δ ppm: 1.49 (d, *J*= 6.3 Hz, 3H), 2.03 (s, 1H), 2.29 (s, 3H), 3.78 (s, 3H), 5.17 (q, *J*= 6.3 Hz, 1H), 7.03 (t, *J*= 7.8 Hz, 1H), 7.10 (dd, *J*= 2.1, 7.8 Hz, 1H), 7.24 (dd, *J*= 2.1, 7.8 Hz, 1H).

2-methoxy-3-methylacetophenone (**83**)

Pyridinium chlorochromate (10.0 g, 30.0 mmol) was suspended in 60 mL of anhydrous CH_2Cl_2. **82** (4.5 g, 27.0 mmol) in 10 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 50:1~30:1) to afford **83** (2.6 g, 57% yield) as a colorless oil.

^1H NMR ($CDCl_3$, 300MHz), δ ppm: 2.30 (s, 3H), 2.61 (s, 3H), 3.74 (s, 3H), 7.04 (t, *J*= 7.5 Hz, 1H), 7.31 (dd, *J*= 1.8, 7.5 Hz, 1H), 7.42 (dd, *J*= 1.8, 7.5 Hz, 1H).

2-hydroxy-3-methylacetophenone (**42**)

A solution of **83** (2.5 g, 15.0 mmol) in 50 mL of dichloromethane cooled to -78°C was

treated with boron tribromide (18 mL, 1 M in CH_2Cl_2, 18.0 mmol).[94,95] After 30 mins the reaction was warmed to -10°C, where stirring was continued for another 2 hours. The reaction was quenched at -10°C by the addition of 10 mL of ether. The reaction mixture was warmed to room temperature and was stirred an additional 30 mins followed by addition of water. Isolation of the product by dichloromethane extraction gave a dark red liquid, which was chromatographed (hexanes: ethyl acetate 100:1) to afford **42** (2.0 g, 90% yield) as a yellow liquid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 2.24 (s, 3H), 2.61 (s, 3H), 6.78 (t, *J*= 7.8 Hz, 1H), 7.33 (dd, *J*= 1.2, 7.8 Hz, 1H), 7.57 (dd, *J*= 1.2, 7.8 Hz, 1H), 11.9 (s, 1H).

2-benzyloxy-3-methylacetophenone (**13**)

To a 100 mL round-bottom flask were added **42** (2.0 g, 13.3 mmol), benzyl chloride (1.7 g, 13.3 mmol, 1.5 mL), potassium carbonate (0.9 g, 6.7 mmol) and 40 mL of absolute ethanol.[23] The mixture was refluxed overnight then cooled to room temperature. Vacuum filtration gave a clear pale yellow solution, which was concentrated under reduced pressure. The residue was partitioned between diethyl ether and water. Aqueous phase was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (hexanes: ethyl acetate 80:1~60:1) to afford **13** (2.5 g, 78% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 2.31 (s, 3H), 2.57 (s, 3H), 4.83 (s, 2H), 7.08 (t, *J*= 7.5 Hz, 1H), 7.38 (stack, 7H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 16.25, 30.60, 76.71, 124.14, 127.33, 128.04, 128.27, 128.57, 132.43, 134.22, 134.79, 136.63, 155.84, 201.42.

IR (neat, cm^{-1}): 3032.48 (w), 2924.46 (w), 1684.07 (s), 1587.62 (m), 1456.44 (m), 1373.49 (m), 1356.13 (m), 1275.11 (s), 1203.73 (s), 1086.06 (w), 972.25 (w).

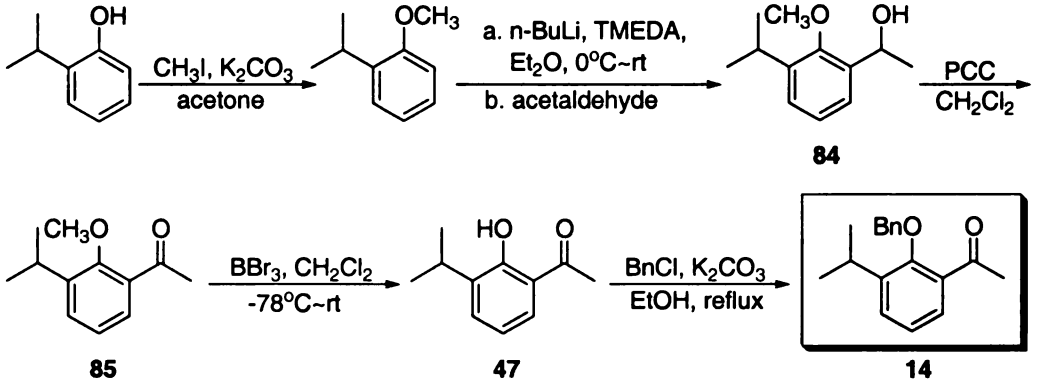
MS, m/z: 240.0 (1.9%), 222.0 (2.6%), 197.0 (9.8%), 134.9 (10.4%), 91.0 (100.0%), 64.9 (16.5%).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67.

Found: C, 79.84; H, 6.90.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 289 (1,526), 313 (401).

5. ***2-Benzyloxy-3-isopropylacetophenone*** **(14)**



Scheme 80. Synthesis of 14

1-(3-isopropyl-2-methoxy)phenylethanol **(84)**

To a vigorously stirred solution of 2-isopropylanisole (6.8 g, 45.0 mmol) and tetramethylethylenediamine (5.3 g, 45.0 mmol, 6.8 mL) in 80 mL of diethyl ether, was added n-butyl lithium (28.1 mL, 1.6 M in hexanes, 45.0 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and acetaldehyde (1.8 g, 41.0 mmol, 2.3 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was

evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 16:1) to afford **84** (5.1 g, 58% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.21 (d, *J*= 7.2 Hz, 3H), 1.23 (d, *J*= 7.2 Hz, 3H), 1.50 (d, *J*= 6.3 Hz, 3H), 2.16 (s, 1H), 3.30 (heptet, *J*= 6.9 Hz, 1H), 3.78 (s, 3H), 5.19 (q, *J*= 6.6 Hz, 1H), 7.12 (t, *J*= 7.5 Hz, 1H), 7.19 (dd, *J*= 1.8, 7.8 Hz, 1H), 7.26 (dd, *J*= 1.8, 7.5 Hz, 1H).

3-isopropyl-2-methoxyacetophenone (**85**)

Pyridinium chlorochromate (9.7 g, 29.0 mmol) was suspended in 60 mL of anhydrous CH_2Cl_2. **84** (5.1 g, 26.3 mmol) in 10 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 50:1) to afford **85** (3.8 g, 75% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.22 (d, *J*= 7.2 Hz, 6H), 2.62 (s, 3H), 3.59 (heptet, *J*= 7.2 Hz, 1H), 3.73 (s, 3H), 7.12 (t, *J*= 7.5 Hz, 1H), 7.38 (d, *J*= 7.5 Hz, 2H).

2-hydroxy-3-isopropylacetophenone (**47**)

A solution of **85** (3.7 g, 19.3 mmol) in 50 mL of dichloromethane cooled to -78°C was treated with boron tribromide (28.9 mL, 1 M in CH_2Cl_2, 28.9 mmol).[94,95] After 30 mins the reaction was warmed to -10°C, where stirring was continued for another 2 hours. The

reaction was quenched at -10°C by the addition of 10 mL of ether. The reaction mixture was warmed to room temperature and was stirred an additional 30 mins followed by addition of water. Isolation of the product by dichloromethane extraction gave a dark red liquid, which was chromatographed (hexanes: ethyl acetate 100:1~60:1) to afford **47** (2.9 g, 85% yield) as a yellow liquid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.22 (d, *J*= 6.6 Hz, 6H), 2.62 (s, 3H), 3.37 (heptet, *J*= 6.9 Hz, 1H), 6.85 (t, *J*= 7.8 Hz, 1H), 7.40 (dd, *J*= 1.5, 7.8 Hz, 1H), 7.57 (dd, *J*= 1.5, 7.8 Hz, 1H), 11.8 (s, 1H).

2-benzyloxy-3-isopropylacetophenone (**14**)

To a 100 mL round-bottom flask were added **47** (2.9 g, 16.3 mmol), benzyl chloride (2.1 g, 16.3 mmol, 1.9 mL), potassium carbonate (1.1 g, 8.2 mmol) and 40 mL of absolute ethanol.[23] The mixture was refluxed overnight then cooled to room temperature. Vacuum filtration gave clear pale yellow solution which was concentrated under reduced pressure. The residue was partitioned between diethyl ether and water. Aqueous phase was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (hexanes: ethyl acetate 80:1~50:1) to afford **14** (3.4 g, 78% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.20 (d, *J*= 6.9 Hz, 6H), 2.58 (s, 3H), 3.39 (heptet, *J*= 6.9 Hz, 1H), 4.82 (s, 2H), 7.16 (t, *J*= 7.5 Hz, 1H), 7.40 (stack, 7H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 23.73, 26.17, 30.54, 78.08, 124.53, 127.04, 127.87, 128.25, 128.59, 130.35, 134.44, 136.66, 143.11, 154.52, 201.85.

IR (neat, cm^{-1}): 3065.28 (w), 2964.97 (m), 2870.44 (w), 1688.00 (s), 1585.69 (m),

1437.15 (m), 1356.13 (m), 1286.68 (m), 1261.61 (m), 1203.73 (m), 1095.71 (w), 1014.69 (w).

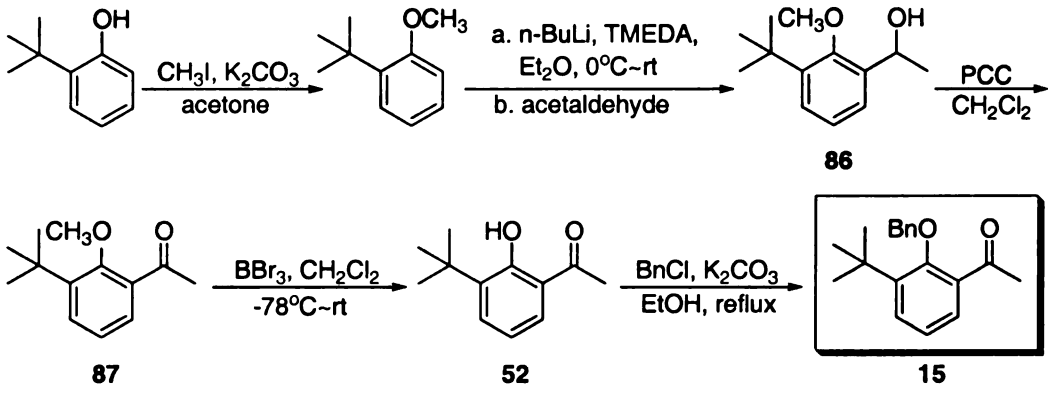
MS, m/z: 268.1 (2.4%), 224.9 (13.3%), 176.9 (21.1%), 162.9 (16.0%), 92.1 (45.9%), 90.9 (100.0%), 65.0 (47.5%), 43.0 (37.7%).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46.

Found: C, 80.59; H, 7.72.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 289 (1,569), 313 (399).

6. ***2-Benzyloxy-3-t-butylacetophenone*** **(15)**



Scheme 81. Synthesis of 15

1-(3-t-butyl-2-methoxy)phenylethanol **(86)**

To a vigorously stirred solution of 2-t-butylanisole (8.0 g, 48.8 mmol) and tetramethylethylenediamine (5.7 g, 48.8 mmol, 7.3 mL) in 80 mL of diethyl ether, was added n-butyl lithium (30.5 mL, 1.6 M in hexanes, 48.8 mmol) slowly at 0°C under nitrogen.[92] The lithiation mixture was stirred overnight and acetaldehyde (2.2 g, 48.8 mmol, 2.1 mL) was added to this solution. The reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0°C. Water layer was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Solvent was

evaporated to yield crude product which was purified by column chromatography (hexanes: ethyl acetate 12:1~5:1) to afford **86** (6.3 g, 62% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.38 (s, 9H), 1.52 (d, *J*= 6.3 Hz, 3H), 1.88 (s, 1H), 3.81 (s, 3H), 5.28 (q, *J*= 6.3 Hz, 1H), 7.07 (t, *J*= 7.8 Hz, 1H), 7.25 (dd, *J*= 1.5, 7.8 Hz, 1H), 7.35 (dd, *J*= 1.5, 7.8 Hz, 1H).

m.p.: 86.2~87.5°C

3-t-butyl-2-methoxyacetophenone (**87**)

Pyridinium chlorochromate (10.0 g, 29.8 mmol) was suspended in 80 mL of anhydrous CH_2Cl_2. **86** (6.2 g, 29.8 mmol) in 10 mL of CH_2Cl_2 was added in one portion to the magnetically stirred solution.[93] After 3 hours 50 mL of dry ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with anhydrous ether whereupon it became a black granular solid. The combined organic layer was passed through a short pad of silica gel, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (hexanes: ethyl acetate 40:1~20:1) to afford **87** (4.8 g, 77% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.38 (s, 9H), 2.61 (s, 3H), 3.71 (s, 3H), 7.03 (t, *J*= 7.8 Hz, 1H), 7.29 (dd, *J*= 1.5, 7.8 Hz, 1H), 7.41 (dd, *J*= 1.5, 7.8 Hz, 1H).

3-t-butyl-2-hydroxyacetophenone (**52**)

A solution of **87**(4.8 g, 23.3 mmol) in 60 mL of dichloromethane cooled to -78°C was treated with boron tribromide (23.3 mL, 1 M in CH_2Cl_2, 23.3 mmol).[94,95] After 30 mins the reaction was warmed to -10°C, where stirring was continued for another 2 hours. The

reaction was quenched at -10°C by the addition of 10 mL of ether. The reaction mixture was warmed to room temperature and was stirred an additional 30 mins followed by addition of water. Isolation of the product by dichloromethane extraction gave a dark red liquid, which was chromatographed (hexanes: ethyl acetate 70:1~40:1) to afford **52** (2.0 g, 44% yield) as a yellow liquid.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.40 (s, 9H), 2.62 (s, 3H), 6.80 (t, *J*= 7.8 Hz, 1H), 7.46 (dd, *J*= 1.5, 7.8 Hz, 1H), 7.60 (dd, *J*= 1.5, 7.8 Hz, 1H), 12.1 (s, 1H).

2-benzyloxy-3-t-butylacetophenone (**15**)

To a 100 mL round-bottom flask were added **52** (1.9 g, 9.9 mmol), benzyl chloride (1.3 g, 9.9 mmol, 1.2 mL), potassium carbonate (0.7 g, 5.0 mmol) and 30 mL of absolute ethanol.[23] The mixture was refluxed overnight then cooled to room temperature. Vacuum filtration gave a clear pale yellow solution, which was concentrated under reduced pressure. The residue was partitioned between diethyl ether and water. Aqueous phase was extracted with ether, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (hexanes: ethyl acetate 50:1~30:1) to afford **15** (1.8 g, 64% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300MHz), δ ppm: 1.41 (s, 9H), 2.56 (s, 3H), 4.85 (s, 2H), 7.09 (t, *J*= 7.8 Hz, 1H), 7.41 (stack, 7H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 30.20, 30.71, 35.23, 77.84, 123.68, 126.72, 127.55, 127.89, 128.54, 130.47, 135.63, 136.83, 143.51, 157.09, 203.06.

IR (neat, cm^{-1}): 2961.11 (m), 2872.37 (w), 1687.93 (s), 1579.90 (m), 1425.58 (s), 1375.42 (m), 1263.54 (m), 1215.31 (s), 1014.69 (m).

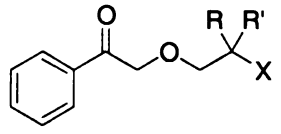
MS, m/z: 282.1 (4.9%), 267.1 (3.8%), 239.1 (9.4%), 177.0 (12.7%), 92.1 (31.8%), 90.9 (100.0%), 65.0 (24.4%), 43.0 (28.6%).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80.

Found: C, 81.01; H, 8.06.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 290 (1,460), 313 (449).

C. α-(Haloethoxy)acetophenones

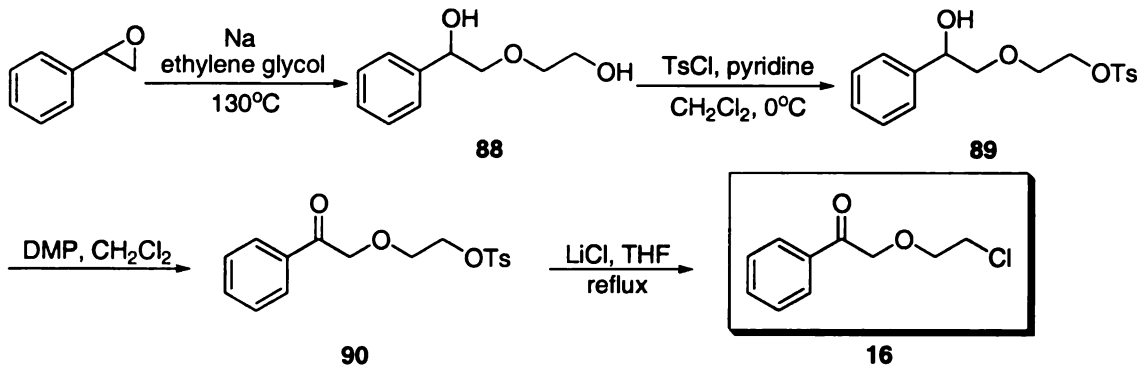


Ketone	X	R	R'
16	Cl	H	H
17	Br	H	H
18	I	H	H
19	Br	CH_3	CH_3

1. ***α-(Chloroethoxy)acetophenone* (16)**

1-phenyl-3-oxa-1,5-pentanediol (**88**)[96]

Styrene oxide (19.7 g, 164.2 mmol, 18.7 mL) was slowly added to a stirred solution of sodium (1.8 g, 80.0 mmol) dissolved in 180 mL of ethylene glycol at 130°C under nitrogen atmosphere. This mixture was stirred at 130°C for 24 hours and the excess ethylene glycol was distilled under vacuum. The residue was thoroughly mixed with 100 mL of ethyl acetate, 50 g of ice and 100 mL of cold 10% aqueous sulfuric acid. The organic phase was separated and washed successively with water, saturated aqueous



Scheme 82. Synthesis of 16

sodium bicarbonate solution and saturated brine. The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Purification by flash chromatography (hexanes: ethyl acetate 1:1) gave **88** (13.5 g, 74.0 mmol, 45% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.52 (m, 6H), 4.68 (s, broad, 1H), 4.90 (dd, *J*= 3.0, 9.0 Hz, 1H), 7.23 (m, 5H).

toluene-4-sulfonic acid 2-(2-hydroxy-2-phenyl-ethoxy)-ethyl ester (**89**)

To a 100 mL round-bottom flask were added **88** (2.0 g, 11.0 mmol), pyridine (3.5 g, 44.3 mmol, 3.6 mL) and 30 mL of CH_2Cl_2. *p*-Toluenesulfonyl chloride (2.3 g, 12.0 mmol) was added in portions at 0°C.[97] The reaction mixture was allowed to warm to room temperature and stirred for additional 10 hours. Water was added to this mixture, organic phase was separated and aqueous layer was extracted with CH_2Cl_2 . Combined organic phase was washed with saturated brine and dried over anhydrous sodium sulfate. Solvent was removed under vacuum, column chromatography (hexanes: ethyl acetate 4:1) gave **89** (3.4 g, 10.1 mmol, 92% yield) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 2.43 (s, 3H), 2.71 (s, 1H), 3.40 (t, *J*= 9.6 Hz, 1H),

3.54 (dd, *J*= 3.3, 9.6 Hz, 1H), 3.70 (m, 2H), 4.18 (t, *J*= 5.1 Hz, 2H), 4.79 (dd, *J*= 3.0, 9.0 Hz, 1H), 7.31 (m, 7H), 7.80 (d, *J*= 8.4 Hz, 2H).

toluene-4-sulfonic acid 2-(2-oxo-2-phenyl-ethoxy)-ethyl ester (**90**)

A solution of **89** (8.9 g, 26.5 mmol) in 10 mL of methylene chloride was added to a solution of Dess-Martin periodinane (12.4 g, 29.2 mmol) in 50 mL of methylene chloride with stirring.[98] After 2 hours the homogeneous reaction mixture was diluted with 20 mL of methylene chloride and 30 mL of 1 M NaOH aqueous solution. After the mixture was stirred for 30 mins, organic phase was separated and water layer was extracted with methylene chloride. Combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and flash chromatography (hexanes: ethyl acetate 3:1) gave **90** (7.3 g, 21.9 mmol, 82% yield) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 2.41 (s, 3H), 3.82 (t, *J*= 4.5 Hz, 2H), 4.22 (t, *J*= 4.5 Hz, 2H), 4.73 (s, 2H), 7.30 (d, *J*= 8.1 Hz, 2H), 7.45 (t, *J*= 7.8 Hz, 2H), 7.58 (t, *J*= 7.5 Hz, 1H), 7.77 (d, *J*= 8.1 Hz, 2H), 7.85 (d, *J*= 7.5 Hz, 2H).

m.p.: 58.1~59.0°C

α-(chloroethoxy)acetophenone (16)

A solution of **90** (0.9 g, 2.7 mmol) and lithium chloride (0.46 g, 10.8 mmol) in 30 mL of tetrahydrofuran was refluxed for 14 hours.[99] The reaction mixture was cooled to room temperature and water was added. Water layer was extracted with ether. Combined organic layer was washed with saturated brine, dried over anhydrous Na_2SO_4 and

concentrated under reduced pressure. Purification by flash chromatography (hexanes: ethyl acetate 30:1) gave **16** (0.45 g, 2.3 mmol, 85% yield) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.70 (t, *J*= 5.7 Hz, 2H), 3.87 (t, *J*= 5.7 Hz, 2H), 4.84 (s, 2H), 7.46 (t, *J*= 7.8 Hz, 2H), 7.58 (t, *J*= 7.5 Hz, 1H), 7.90 (d, *J*= 7.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 42.78, 71.67, 74.04, 127.86, 128.77, 133.72, 134.61, 195.96.

IR ($CHCl_3$, cm^{-1}): 3063.35 (w), 2872.37 (w), 1701.43 (s), 1597.26 (w), 1448.73 (w), 1228.81 (m), 1145.86 (s), 968.39 (w).

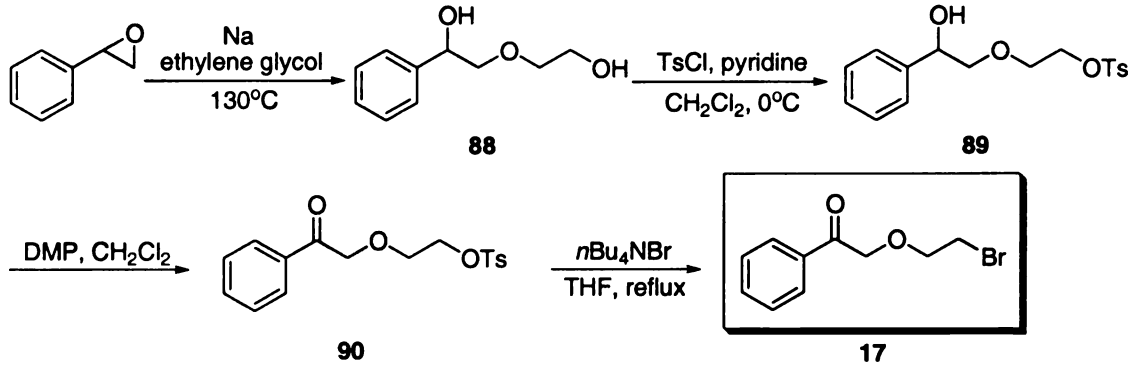
MS, m/z: 162.0 (27.4%), 105.0 (100.0%), 76.9 (66.2%), 50.7 (31.0%).

Anal. Calcd for $C_{10}H_{11}ClO_2$: C, 60.45; H, 5.54.

Found: C, 60.52; H, 5.59.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 282 (944), 313 (47).

2. ***α-(Bromoethoxy)acetophenone*** **(17)**



Scheme 83. Synthesis of 17

α-(bromoethoxy)acetophenone **(17)**

A solution of **90** (3.0 g, 9.0 mmol) and nBu$_4$NBr (4.3 g, 13.5 mmol) in 50 mL of dry THF was heated to reflux under N_2.[99] After 24 hours, the reaction mixture was cooled,

diluted with 10 mL of ether, and washed with water and brine. The organic layer was dried with Na_2SO_4 and concentrated under vacuum. Purification by flash chromatography (hexanes: ethyl acetate 40:1) gave **17** (1.8 g, 7.4 mmol, 82% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.53 (t, *J*= 6.0 Hz, 2H), 3.92 (t, *J*= 6.0 Hz, 2H), 4.83 (s, 2H), 7.46 (t, *J*= 7.5 Hz, 2H), 7.58 (t, *J*= 7.5 Hz, 1H), 7.90 (d, *J*= 7.2 Hz, 2H);

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 30.14, 71.53, 73.93, 127.88, 128.79, 133.74, 134.61, 195.94;

IR ($CHCl_3$, cm^{-1}): 3063.35 (w), 2872.37 (w), 1699.50 (s), 1597.26 (m), 1448.73 (m), 1282.83 (w), 1226.88 (m), 1140.08 (s), 966.46 (w);

MS, m/z: 162.0 (27.5%), 105.0 (100.0%), 76.9 (67.6%), 50.7 (32.0%).

Anal. Calcd for $C_{10}H_{11}BrO_2$: C, 49.38; H, 4.53.

Found: C, 49.47; H, 4.53.

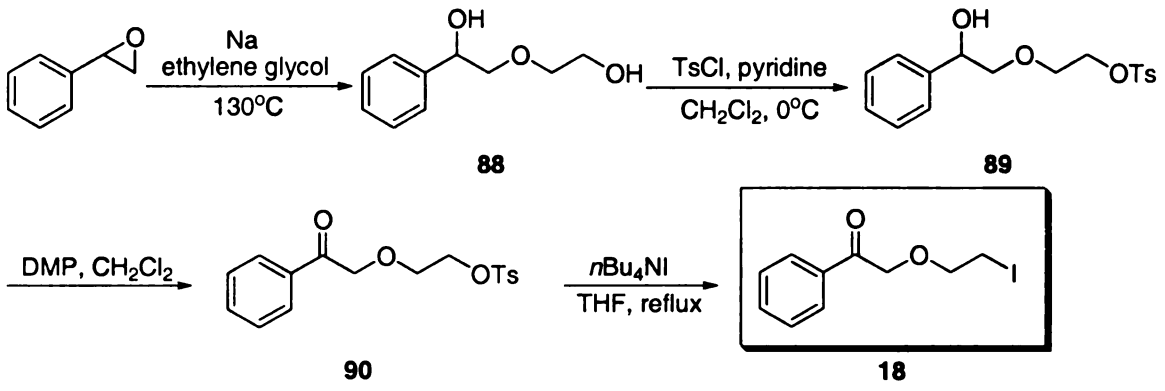
UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 282 (937), 313 (48.4).

3. ***α-(Iodoethoxy)acetophenone* (18)**

α-(iodoethoxy)acetophenone (**18**)

A solution of **90** (3.0 g, 9.0 mmol) and *n*Bu_4NI (5.0 g, 13.5 mmol) in 50 mL of dry THF was heated to reflux under N_2.[99] After 24 hours, the reaction mixture was cooled, diluted with 10 mL of ether, and washed with water and brine. The organic layer was dried with Na_2SO_4 and concentrated under vacuum. Purification by flash chromatography (hexanes: ethyl acetate 30:1) gave **18** (2.3 g, 7.9 mmol, 88% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.32 (t, *J*= 6.9 Hz, 2H), 3.87 (t, *J*= 6.9 Hz, 2H), 4.82 (s, 2H), 7.46 (t, *J*= 7.8 Hz, 2H), 7.58 (t, *J*= 7.5 Hz, 1H), 7.91 (d, *J*= 7.8 Hz, 2H);



Scheme 84. Synthesis of 18

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 2.19, 72.28, 73.62, 127.90, 128.77, 133.72, 134.61, 195.93;

IR ($CHCl_3$, cm^{-1}): 2918.67 (w), 2868.51 (w), 1699.50 (s), 1597.26 (w), 1448.73 (w), 1228.81 (m), 1124.64 (m), 974.18 (w);

MS, m/z: 162.0 (27.5 %), 105.0 (100.0%), 76.9 (69.8%), 50.7 (36.0%).

Anal. Calcd for $C_{10}H_{11}IO_2$: C, 41.38; H, 3.79.

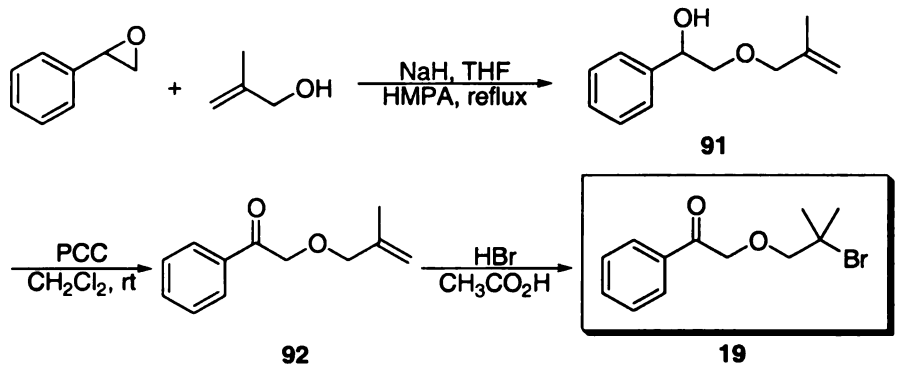
Found: C, 41.26; H, 3.78.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 282 (1,057), 313 (140.4).

4. ***α-(2-Bromo-2-methylpropoxy)acetophenone*** **(19)**

2-(2-methylallyloxy)-1-phenylethanol **(91)**

To a 250 mL three–neck round-bottom flask, equipped with a condenser, were added NaH (1.0 g, 25.0 mmol, 60% dispersion in mineral oil), 40 mL of THF and 20 mL of HMPA.[100] 2-Methyl-2-propen-1-ol (1.8 g, 25.0 mmol) was added dropwise over a 20 mins period under dry nitrogen. The resulting yellowish solution was refluxed for 30 mins and cooled to room temperature, and styrene oxide (3.0 g, 25.0 mmol) was added dropwise over 15 mins. After 30 mins of stirring at room temperature, the mixture was



Scheme 85. Synthesis of 19

boiled under reflux for 4 hours. The cooled reaction mixture was quenched with H_2O, acidified with aqueous 3 M HCl, and extracted with ether. The extracts were combined, washed with water, aqueous $NaHCO_3$ and saturated aqueous NaCl solution, and finally dried over Na_2SO_4. The solvent was removed under vacuum, purification of the crude product by column chromatography (hexanes: ethyl acetate 10:1) afforded **91** (3.6 g, 18.8 mmol, 75% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 1.73 (s, 3H), 2.76 (s, broad, 1H), 3.41 (dd, *J*= 9.3, 9.9 Hz, 1H), 3.56 (dd, *J*= 3.3, 9.9 Hz, 1H), 3.96 (s, 2H), 4.91 (stack, 3H), 7.34 (stack, 5H).

α-(2-methylallyloxy)acetophenone (**92**)

PCC (5.2 g, 21.8 mmol) was dispersed in 50 mL of CH_2Cl_2, **91** (2.6 g, 13.3 mmol) was added dropwise to this solution at 0°C and the reaction mixture was allowed to warm to room temperature.[93] After 6 hours of stirring at room temperature, sticky solid was filtered off and organic phase was washed with saturated brine, dried over Na_2SO_4. Solvent was removed under reduced pressure, the residue was purified by column chromatography (hexanes: ethyl acetate 20:1) to give **92** (1.8 g, 9.5 mmol, 71% yield) as

a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 1.75 (s, 3H), 4.04 (s, 2H), 4.70 (s, 2H), 4.93 (d, *J*= 1.2 Hz, 1H), 4.99 (d, *J*= 1.2 Hz, 1H), 7.47 (t, *J*= 7.8 Hz, 2H), 7.57 (t, *J*=8.7 Hz, 1H), 7.92 (d, *J*= 7.8 Hz, 2H).

α-(2-bromo-2-methylpropoxy)acetophenone (**19**)

92 (1.6 g, 8.4 mmol) was dissolved in 20 mL of acetic acid, dry HBr gas was bubbled into this solution.[101] Water was added to quench the reaction, this reaction mixture was neutralized by saturated $NaHCO_3$ aqueous solution. Organic layer was then washed with brine and dried over Na_2SO_4. Concentration of solvent under vacuum followed by column chromatography (hexanes: ethyl acetate 40:1) gave **19** (1.0 g, 3.7 mmol, 44% yield) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 1.77 (s, 6H), 3.67 (s, 2H), 4.85 (s, 2H), 7.45 (t, *J*= 7.5 Hz, 2H), 7.56 (t, *J*= 7.2 Hz, 1H), 7.91 (d, *J*= 7.2 Hz, 2H);

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 30.85, 63.37, 74.41, 81.42, 127.95, 128.72, 133.63, 134.73, 196.43;

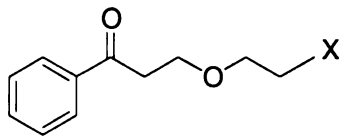
IR ($CHCl_3$, cm^{-1}): 2972.68 (w), 2926.39 (w), 1703.36 (s), 1599.19 (w), 1450.65 (w), 1228.81 (s), 1128.50 (s), 993.47 (w);

MS, m/z: 190.1 (2.2%), 105.0 (100.0%), 85.0 (10.3%), 76.9 (51.1%), 57.0 (28.0%), 50.8 (30.2%).

Anal. Calcd for $C_{12}H_{15}BrO_2$: C, 53.14; H, 5.54.

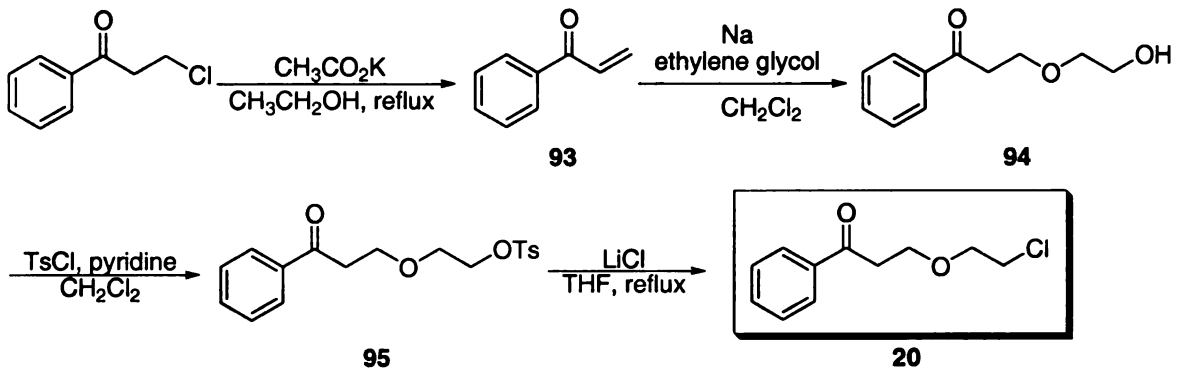
Found: C, 53.32; H, 5.77.

D. β-(Haloethoxy)propiophenones



Ketone	R
20	Cl
21	Br
22	I

1. *β-(Chloroethoxy)propiophenone* (20)



Scheme 86. Synthesis of 20

phenyl vinyl ketone (**93**)[102]

3-Chloropropiophenone (8.4 g, 50.0 mmol) was dissolved in 30 mL of absolute ethanol. The solution was heated and potassium acetate (5.0 g, 51.0 mmol) was added slowly with vigorous stirring. The solution was filtered, 50 mL of chloroform was added, the alcohol was then removed by washing with water. The chloroform was removed on a rotary evaporator and the residue was distilled under vacuum to give **93** (4.8 g, 36.4 mmol, 73% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 5.92 (dd, *J*= 1.5, 10.5 Hz, 1H), 6.42 (dd,*J*= 1.5, 17.1

Hz, 1H), 7.18 (dd, *J*= 10.5, 17.1 Hz, 1H), 7.47, (t, *J*= 7.5 Hz, 2H), 7.55 (d, *J*= 6.9 Hz, 1H), 7.92 (d, *J*= 6.9 Hz, 2H).

β-(2-hydroxy)ethoxypropiophenone (**94**)

Sodium (0.9 g, 37.8 mmol) was dissolved in 2.7 mL of ethylene glycol, this solution was then introduced to the methylene chloride solution of **93** (1.0 g, 7.6 mmol) in 10 mins at 0°C.[103] This mixture was allowed to warm to room temperature and stirred for another 4 hours. Water was added to quench the reaction, and the solution was acidified by addition of 3 M hydrochloric acid. Aqueous layer was extracted with methylene chloride. Organic layer was combined, washed with saturated brine and dried over Na_2SO_4. Solvent was removed under vacuum and flash chromatography (hexanes: ethyl acetate 3:1) gave **94** (0.8 g, 4.1 mmol, 54% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.26 (t, *J*= 6.0 Hz, 2H), 3.60 (t, *J*=5.1Hz, 2H), 3.72 (t, *J*=5.1 Hz, 2H), 3.92 (t, *J*= 6.0 Hz, 2H), 7.45 (t, *J*= 7.8 Hz, 2H), 7.55 (t, *J*= 7.8 Hz, 1H), 7.96 (d, *J*= 8.4 Hz, 2H).

toluene-4-sulfonic acid 2-(3-oxo-3-phenyl-propoxy)-ethyl ester (**95**)

94 (0.8 g, 3.9 mmol) and pyridine (1.3 mL, 15.5 mmol) were dissolved in 20 mL of CH_2Cl_2.[97] At 0°C, *p*-toluenesulfonyl chloride (0.8 g, 4.3 mmol) was added in portions to this solution. The mixture was allowed to warm to room temperature and stirred for another 5 hours. Water was added and the solution was acidified to pH 6-7. Aqueous layer was extracted with CH_2Cl_2. Combined organic layer was washed with brine and dried over Na_2SO_4. Removal of solvent under reduced pressure and flash chromatography

(hexanes: ethyl acetate 3:1) gave **95** (1.2 g, 3.5 mmol, 89% yield) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 2.39 (s, 3H), 3.17 (t, *J*= 6.6 Hz, 2H), 3.66 (t, *J*= 4.8 Hz, 2H), 3.82 (t, *J*= 6.6 Hz, 2H), 4.13 (t, *J*= 4.8 Hz, 2H), 7.27 (d, *J*= 8.4 Hz, 2H), 7.45 (t, *J*= 7.5 Hz, 2H), 7.56 (tt, *J*= 1.5, 7.5 Hz, 1H), 7.76 (d, *J*= 8.4 Hz, 2H), 7.91 (d, *J*= 7.5 Hz, 2H).

m.p.: 65.0~65.9°C

β-(chloroethoxy)propiophenone (**20**)

A solution of **95** (1.4 g, 4.0 mmol) and lithium chloride (0.7 g, 16.0 mmol) in 30 mL of tetrahydrofuran was refluxed for 24 hours.[99] The reaction mixture was cooled to room temperature and water was added. Water layer was extracted with ether. Combined organic layer was washed with saturated brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (hexanes: ethyl acetate 30:1) gave **20** (0.8 g, 3.7 mmol, 92% yield) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.27 (t, *J*= 6.6 Hz, 2H), 3.60 (t, *J*= 6.0 Hz, 2H), 3.74 (t, *J*= 6.0 Hz, 2H), 3.93 (t, *J*= 6.6 Hz, 2H), 7.45 (t, *J*= 7.8 Hz, 2H), 7.55 (t, *J*= 7.2 Hz, 1H), 7.95 (d, *J*= 7.8 Hz, 2H);

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 38.69, 42.72, 66.38, 71.23, 128.10, 128.62, 133.23, 136.89, 198.10;

IR ($CHCl_3$, cm^{-1}): 2876.23 (w), 1684.07 (s), 1597.26 (w), 1448.73 (m), 1369.63 (m), 1215.31 (m), 1122.71 (s), 748.48 (w);

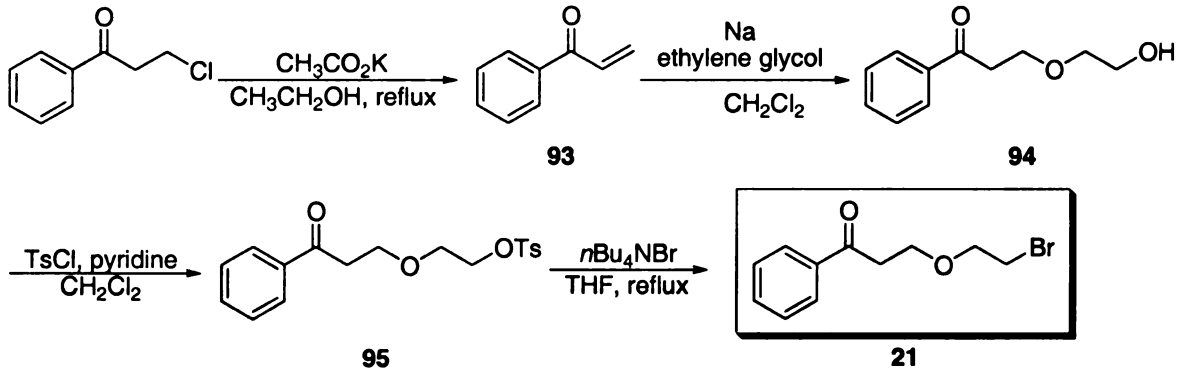
MS, m/z: 214.2 (0.8%), 212.1 (2.7%), 149.0 (12.1%), 132.0 (15.6%), 105.0 (100.0%), 77.0 (100.0%), 50.6 (63.1%).

Anal. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.12.

Found: C, 62.16; H, 6.16.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 282 (680), 313 (45.8).

2. ***β-(Bromoethoxy)propiophenone*** **(21)**



Scheme 87. Synthesis of 21

β-(bromoethoxy)propiophenone (**21**)

A solution of **95** (1.4 g, 4.0 mmol) and nBu$_4$NBr (1.9 g, 6.0 mmol) in 35 mL of dry THF was heated to reflux under N_2.[99] After 6 hours, the reaction mixture was cooled, diluted with 10 mL of ether, and washed with water and brine. The organic layer was dried with Na_2SO_4 and concentrated under vacuum. Purification by flash chromatography (hexanes: ethyl acetate 20:1) gave **21** (0.9 g, 3.6 mmol, 89% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.27 (t, J= 6.6 Hz, 2H), 3.44 (t, J= 6.0 Hz, 2H), 3.80 (t, J= 6.0 Hz, 2H), 3.93 (t, J= 6.6 Hz, 2H), 7.45 (t, J= 7.5 Hz, 2H), 7.56 (t, J= 6.9 Hz, 1H), 7.95 (d, J= 6.9 Hz, 2H);

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 30.33, 38.68, 66.24, 71.05, 128.12, 128.63, 133.26, 136.87, 171.83;

IR (neat, cm^{-1}): 2874.30 (w), 1682.14 (s), 1597.26 (w), 1448.73 (m), 1367.70 (w),

1215.31 (m), 1120.78 (s), 748.48 (m);

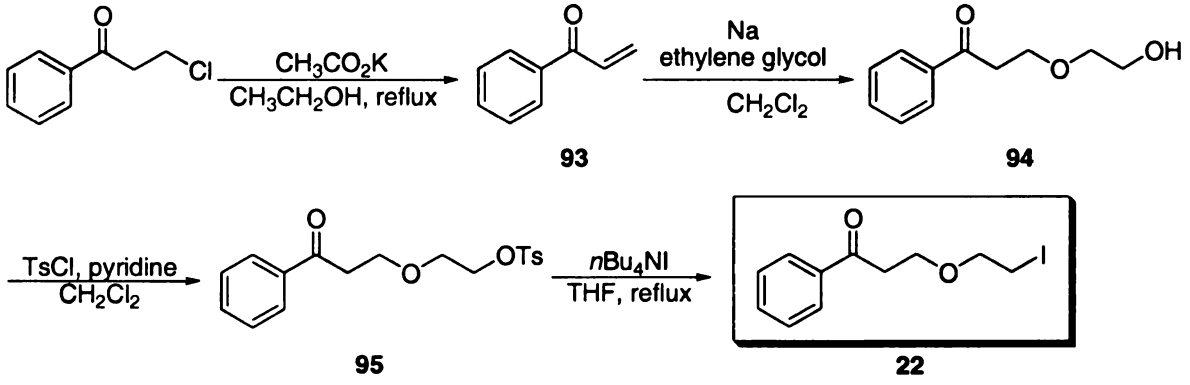
MS, m/z: 258.2 (0.3%), 256.2 (0.3%), 149.0 (6.8%), 133.2 (7.7%), 105.0 (100.0%), 77.0 (52.1%), 50.8 (29.6%).

Anal. Calcd for $C_{11}H_{13}BrO_2$: C, 51.36; H, 5.06.

Found: C, 51.63; H, 5.14.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 281 (1,099), 313 (69.7).

3. ***β-(Iodoethoxy)propiophenone* (22)**



Scheme 88. Synthesis of 22

β-(iodoethoxy)propiophenone (**22**)

A solution of **95** (1.4 g, 4.0 mmol) and nBu$_4$NI (2.2 g, 6.0 mmol) in 35 mL of dry THF was heated to reflux under N_2.[99] After 4 hours, the reaction mixture was cooled, diluted with 10 mL of ether, and washed with water and brine. The organic layer was dried with Na_2SO_4 and concentrated under vacuum. Purification by flash chromatography (hexanes: ethyl acetate 20:1) gave **22** (1.1 g, 3.6 mmol, 90% yield) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.23 (t, J= 6.6 Hz, 2H), 3.26 (t, J= 6.6 Hz, 2H), 3.73 (t, J= 6.6 Hz, 2H), 3.92 (t, J= 6.6 Hz, 2H), 7.45 (t, J= 7.5 Hz, 2H), 7.55 (t, J= 7.2 Hz,

1H), 7.96 (d, *J*= 7.2 Hz, 2H);

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 2.91, 38.65, 65.91, 71.70, 128.10, 128.60, 133.22, 136.84, 198.11;

IR ($CHCl_3$, cm^{-1}): 2874.54 (w), 1684.87 (s), 1448.73 (w), 1367.70 (w), 1209.52 (w), 1105.35 (s), 746.55 (m);

MS, m/z: 304.1 (0.3%), 154.8 (11.9%), 133.0 (34.9%), 105.0 (100.0%), 77.0 (84.7%), 50.8 (43.5%), 42.7 (10.8%).

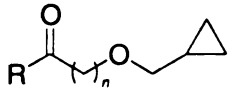
Anal. Calcd for $C_{11}H_{13}IO_2$: C, 43.42; H, 4.28.

Found: C, 43.68; H, 4.53.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 281 (1,048), 313 (55.3).

m.p.: 36.5~37.2°C

E. α/β-Cyclopropylmethoxy Ketones

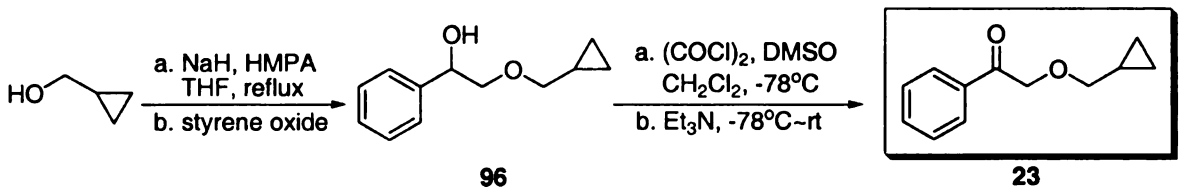


Ketone	R	*n*
23	Ph	1
24	CH_3	1
25	CH_3	2

1. ***α-(Cyclopropylmethoxy)acetophenone* (23)**

2-(cyclopropylmethoxy)-1-phenylethanol (**96**)

Sodium hydride (3.2 g, 80.0 mmol, 60% dispersion in mineral oil) was added to a dry three-neck round-bottom flask, 80 mL of THF and 40 mL of HMPA were then



Scheme 89. Synthesis of 23

introduced.[100] Cyclopropylmethanol (5.8 g, 80.0 mmol, 6.5 mL) was added dropwise during a 20 mins period under dry argon. The resulting solution was refluxed for 1 hour and then cooled to room temperature. Styrene oxide (9.6 g, 80.0 mmol, 9.1 mL) was then added to the reaction mixture. After 30 mins of stirring at room temperature, the mixture was refluxed for 2 hours and cooled to room temperature. The reaction mixture was quenched with water, acidified with 3 M HCl, and then extracted with ether. The extracts were combined, washed with water, aqueous $NaHCO_3$ solution and brine, and finally dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, crude product was purified by column chromatography (hexanes: ethyl acetate 6:1) to afford **96** (9.9 g, 64% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 0.19 (m, 2H), 0.54 (m, 2H), 1.08 (m, 1H), 2.69 (s, broad, 1H), 3.37 (stack, 3H), 3.61 (dd, *J*= 3.0, 9.9 Hz, 1H), 4.89 (dd, *J*= 3.0, 9.3 Hz, 1H), 7.33 (stack, 5H).

α-(cyclopropylmethoxy)acetophenone (**23**)

A solution of oxalyl chloride (1.5 g, 12.0 mmol, 1.0 mL) in 50 mL of dichloromethane was added to a 100 mL round-bottom flask. DMSO (1.9 g, 24.1 mmol, 1.7 mL) was dissolved in dichloromethane and then added dropwise to the reaction mixture at -78°C.[104] After 5 mins stirring, **96** (2.1 g, 10.9 mmol) was added. 15 mins later,

triethylamine was introduced and the reaction mixture was allowed to warm to room temperature. Water was used to quenched reaction, aqueous layer was extracted with dichloromethane, combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent afforded an orange oil, the crude product was purified by column chromatography (hexanes: ethyl acetate 15:1) to afford **23** (1.6 g, 79% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 0.22 (m, 2H), 0.54 (m, 2H), 1.12 (m, 1H), 3.43 (d, *J*= 8.4 Hz, 2H), 4.76 (s, 2H), 7.45 (tt, *J*= 1.8, 7.8 Hz, 2H), 7.56 (dt, *J*= 1.8, 7.5 Hz, 1H), 7.94 (dd, *J*= 1.8, 7.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 2.96 (2 lines), 10.42, 72.05, 73.86, 127.72, 128.67, 133.55, 134.64, 195.87.

IR ($CHCl_3$, cm^{-1}): 3082.64 (w), 3007.41 (w), 2866.59 (w), 1701.43 (s), 1599.19 (w), 1448.73 (w), 1226.88 (m), 1132.36 (m), 756.19 (w).

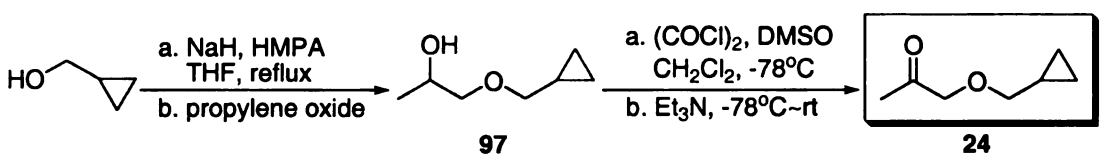
MS, m/z: 189.5 (5.0%), 121.6 (5.0%), 119.8 (100.0%), 105.1 (100.0%), 90.8 (21.6%), 77.8 (95.3%), 65.2 (14.5%), 55.4 (100.0%), 51.5 (49.4%), 50.4 (32.6%).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37.

Found: C, 75.91; H, 7.21.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 274 (927), 313 (54.5).

2. ***α-(Cyclopropylmethoxy)acetone* (24)**



Scheme 90. Synthesis of 24

1-(cyclopropylmethoxy)-2-propanol (**97**)

To a 500 mL three-neck round-bottom flask were added NaH (10.0 g, 253.0 mmol), 70 mL of THF and 35 mL of HMPA.[100] Then cyclopropylmethanol (18.3 g, 253.0 mmol, 20.0 mL) was added dropwise to this solution at such a rate that mild refluxing is maintained. Upon completion of the addition, the reaction mixture was refluxed additional 30 mins and then cooled to room temperature. At this point, propylene oxide (14.8 g, 253.0 mmol, 17.6 mL) was added dropwise to the solution, the mixture was then allowed to stir overnight at approximately 30~40°C. After about 2 days' reaction, water was added and the solution was acidified to pH~7 by addition of 1 M HCl at 0°C, water layer was extracted with ether, combined organic layer was washed with water, saturated $NaHCO_3$ solution, brine and then dried over anhydrous Na_2SO_4. Vaccum distillation afforded **97** (13.0 g, 40% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 0.19 (m, 2H), 0.51 (m, 2H), 1.07 (m, 1H), 1.12 (d, *J*= 7.8 Hz, 3H), 2.27 (s, broad, 1H), 3.22 (t, *J*= 9.9 Hz, 1H), 3.28 (d, *J*= 6.9 Hz, 2H), 3.44 (dd, *J*= 3.0, 9.9 Hz, 1H), 3.95 (m, 1H).

α-(cyclopropylmethoxy)acetone (**24**)

Dess-Martin Periodinane (45.2 g, 1.1 mol) was dissolved in 80 mL of dichloromethane, at room temperature a solution of **97** (9.2 g, 708.0 mmol) in dichoromethane was added dropwise to this oxidant.[98] Upon completion of the addition, the reaction mixture was allowed to stir at room temperature. After 48 hours' reaction, water and 2.5 M NaOH solution were added and the mixture was stirred for additional 30 mins. Water layer was extracted with dichloromethane, combined organic layer was

washed with brine and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure, vacuum distillation gave **24** (7.0 g, 77% yield) as a colorless liquid.

^1H NMR (300 MHz, $CDCl_3$), δ ppm: 0.20 (m, 2H), 0.54 (m, 2H), 1.06 (m, 1H), 2.14 (s, 3H), 3.31 (d, *J*= 7.2 Hz, 2H), 4.05 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 2.99 (2 lines), 10.31, 26.31, 75.88, 76.23, 207.26.

IR (neat, cm^{-1}): 3084.57 (m), 3007.41 (m), 2872.37 (s), 1720.72 (s), 1415.93 (m), 1356.13 (m), 1122.71 (s), 1020.47 (m), 831.43 (w).

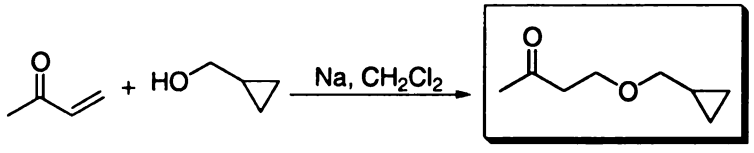
MS, m/z: 127.1, 96.0, 82.9, 71.0, 58.0, 55.0, 43.0.

Anal. Calcd for $C_7H_{12}O_2$: C, 65.63; H, 9.38.

Found: C, 65.58; H, 9.27.

UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 284 (20.6), 313 (7.7).

3. ***β-(Cyclopropylmethoxy)butanone* (25)**



25

Scheme 91. Synthesis of 25

β-(cyclopropylmethoxy)butanone (**25**)

Sodium (0.3 g, 13.0 mmol) was dissolved in cyclopropylmethanol (14.4 g, 200.0 mmol, 16.2 mL), this solution was then added to a solution of methyl vinyl ketone (17.5 g, 250.0 mmol, 20.8 mL) in dichloromethane at 0°C.[103] After 2 hours, water was added to quench the reaction, the mixture was acidified to pH 6~7 by adding 1 M HCl. Organic phase was rinsed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent followed by vacuum distillation afforded **25** (12.5 g, 44% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 0.16 (m, 2H), 0.51 (m, 2H), 1.01 (m, 1H), 2.16 (s, 3H), 2.68 (t, *J*= 6.6 Hz, 2H), 3.23 (d, *J*= 6.9 Hz, 2H), 3.67 (t, *J*= 6.6 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 2.92 (2 lines), 10.45, 30.44, 43.78, 65.32, 75.84, 207.40.

IR (neat, cm^{-1}): 3082.64 (m), 3005.48 (s), 2868.51 (s), 1713.01 (s), 1369.99 (m), 1169.01 (m), 1107.28 (s), 1020.47 (m), 933.67 (w).

MS, m/z: 141.0, 112.0, 85.0, 70.9, 57.1, 43.0.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.61; H, 9.86.

Found: C, 67.57; H, 10.03.

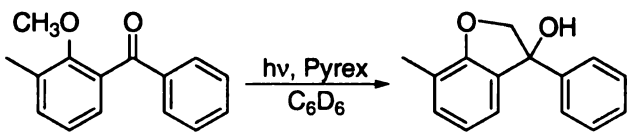
UV (path= 1cm, λ_{max} nm (ε_{max} M^{-1})): Benzene, 277 (183), 313 (3.8).

III. Identification of Photoproducts

Preparative photochemistry was carried out in either a Rayonet reactor equipped with 300 nm lamps or a Pyrex, water-cooled immersion well with a 450 W medium pressure mercury arc light source. The temperature in the Rayonet reactor averaged 35°C. Submerging the immersion well in deionized water in a mirrored dewar maintained the temperature between 17~23°C, which fluctuated with the temperature of the cooling water. The immersion well was fitted with a Pyrex (>290 nm) sleeve. Quantum yields and Stern-Volmer quenching studies were measured with filtered light at 313 nm. The 313 nm band was isolated from a medium pressure 450 W Hanovia mercury arc lamp using a solution of alkaline potassium chromate (0.002 M K_2CrO_4 in 1% aqueous potassium carbonate).

All samples were degassed by purging with argon for twenty minutes prior to irradiation with a continuous stream of oxygen free argon. The outlet needle was then be removed to maintain a positive pressure. After removal of the argon source the septum was wrapped several times with Teflon tape to ensure an air tight seal. If irradiation took longer than 24 hours, the samples were degassed at each 24 hour interval in case oxygen had leaked in through the speta.

Products from 2-methoxy-3-methylbenzophenone **(1)**



1 **26**

Scheme 92. Photoproduct from 1

NMR experiment

A 0.75 mL benzene-d_6 solution of **1** (8.1 mg, 0.036 mmol, 0.048 M) was degassed and irradiated in a NMR tube. Irradiation gave only one product. The reaction was monitored by ^{1}H NMR and was complete (100% conversion) after 20 minutes of irradiation with Pyrex filtered light (medium pressure mercury arc lamp). The ^{1}H NMR spectra showed the disappearence of the 2-methoxy group (singlet at 3.36ppm) with the simultaneous growth of two doublets at 4.27ppm (J= 10.2 Hz) and 4.42ppm (J= 9.9 Hz). The product was identified as **26**.

Preparative experiment

A preparative scale reaction was carried out in 60 mL of benzene with **1** (650 mg, 2.9 mmol, 0.048 M). The reaction was complete after 16 hours of irradiation in a Rayonet reactor equipped with 300 nm lamps. The benzene was removed by rotoevaporation and the residue was purified by column chromatography (hexanes: ethyl acetate 20:1) to afford a single product.

3-hydroxy-7-methyl-3-phenyl-2,3-dihydrobenzofuranol **(26)**

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.74 (s, 1H), 2.26 (s, 3H), 4.27 (d, J= 10.0 Hz, 1H), 4.42 (d, J= 10.0 Hz, 1H), 6.68 (t, J= 7.5 Hz, 1H), 6.75 (d, J= 6.5 Hz, 1H), 6.92 (d, J= 7.0 Hz, 1H), 7.04 (t, J= 7.0 Hz, 1H), 7.09 (t, J= 7.5 Hz, 2H), 7.41 (d, J= 7.0 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 15.18, 82.84, 86.27, 120.84, 121.46, 122.17, 126.42, 127.40, 128.27, 131.55, 132.34, 143.78, 159.67.

IR (neat, cm^{-1}): 3418.30 (s, broad), 3059.49 (w), 3028.63 (w), 2945.68 (w), 1599.19 (s),

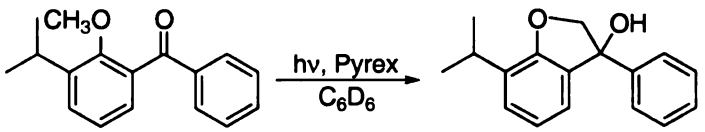
1448.73 (s), 1313.69 (m), 1190.23 (s), 1068.70 (s), 987.68 (m).

MS, m/z: 208.3 (100.0%), 207.4 (72.6%), 178.3 (44.7%), 165.2 (47.5%), 152.2 (13.0%), 89.4 (52.9%), 76.2 (20.2%).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19.

Found: C, 79.79; H, 6.09.

Product from 3-isopropyl-2-methoxybenzophenone **(2)**



2 **27**

Scheme 93. Photoproduct from 2

NMR experiment

A 0.75 mL benzene-d_6 solution of **2** (7.3 mg, 0.029 mmol) was degassed in a NMR tube. Within 20 minutes of irradiation through Pyrex with a mercury arc lamp, most of the **2** had disappeared with the formation of only one photostable product. The product possessed a ^{1}H NMR spectrum consistent with **27**.

Preparative experiment

A preparative reaction was carried out with **2** (500 mg, 2.0 mmol, 0.033 M) in 60 mL of benzene. The preparatory scale reaction gave an identical result as the NMR scale reaction. Silica gel column chromatography with hexanes gave a single product.

3-hydroxy-7-isopropyl-3-phenyl-2,3-dihydrobenzofuranol **(27)**

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 1.32 (d, *J*= 6.6 Hz, 3H), 1.33 (d, *J*= 6.9 Hz, 3H), 1.69

(s, 1H), 3.32 (heptet, *J*= 6.9 Hz, 1H), 4.29 (d, *J*= 10.2 Hz, 1H), 4.38 (d, *J*= 10.2 Hz, 1H), 6.76 (dd, *J*= 0.6, 4.5 Hz, 2H), 7.08 (stack, 4H), 7.40 (dt, *J*= 1.8, 6.9 Hz, 2H).

^{13}C NMR (75 MHz, C_6D_6), δ ppm: 22.43, 22.57, 28.79, 82.70, 86.24, 121.75, 122.18, 126.45, 127.39, 127.49, 128.26, 131.75, 132.71, 143.81, 158.78.

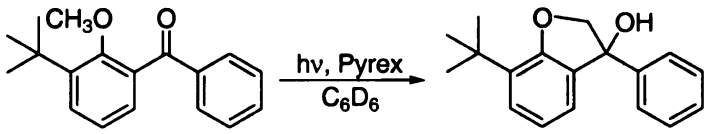
IR (neat, cm^{-1}): 3418.30 (m), 2961.11 (s), 1672.50 (m), 1595.33 (m), 1441.01 (s), 1302.12 (w), 1186.37 (m), 1066.77 (w), 964.53 (w).

MS, m/z: 236.4 (100.0%), 221.4 (100.0%), 177.8 (42.0%), 164.8 (42.4%), 114.7 (20.8%), 94.7 (24.0%).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.31; H, 7.09.

Found: C, 80.30; H, 7.01.

Product from 3-t-butyl-2-methoxybenzophenone **(3)**



3 **28**

Scheme 94. Photoproduct from 3

NMR experiment

A 0.75 mL benzene-d_6 solution of **3** (7.8 mg, 0.029 mmol, 0.039 M) was degassed in a NMR tube. Within 15 minutes of irradiation through Pyrex with a mercury arc lamp all of the **3** had disappeared, with the formation of only one product. The photostable product possessed a ^1H NMR spectrum consistent with **28**.

Preparative experiment

A preparative scale reaction was carried out in 60 mL of benzene with **3** (800 mg, 3.0 mmol, 0.050 M). The reaction was complete after 6 hours of irradiation in a Rayonet reactor equipped with 300 nm lamps. The benzene was removed by rotoevaporation and the residue was purified by column chromatography (hexanes: ethyl acetate 20:1) to afford a single product.

7-t-butyl-3-hydroxy-3-phenyl-2,3-dihydrobenzofuranol **(28)**

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 1.50 (s, 9H), 1.66 (s, 1H), 4.28 (d, *J*= 10.2 Hz, 1H), 4.44 (d, *J*= 10.2 Hz, 1H), 6.78 (stack, 2H), 7.08 (stack, 3H), 7.17 (dd, *J*= 2.4, 6.9 Hz, 1H), 7.41 (dd, *J*= 1.8, 7.8 Hz, 2H).

^{13}C NMR (75 MHz, C_6D_6), δ ppm: 29.57, 34.42, 82.25, 85.88, 121.58, 122.60, 126.46, 127.22, 127.37, 128.25, 133.59, 134.10, 143.90, 159.13.

IR (neat, cm^{-1}): 3414.44 (m, broad), 2957.25 (s), 1589.55 (w), 1429.43 (s), 1207.59 (w), 1068.70 (w).

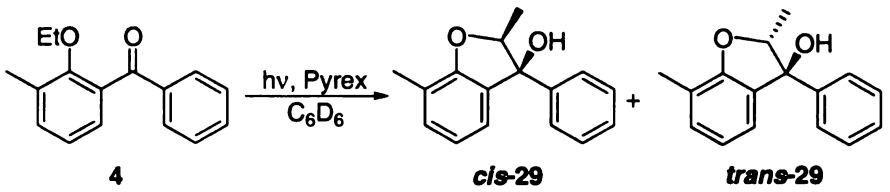
MS, m/z: 250.3 (44.6%), 235.3 (100.0%), 207.2 (33.8%), 165.0 (34.1%), 103.3 (38.3%), 76.5 (16.6%).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46.

Found: C, 80.81; H, 7.28.

Products from 2-ethoxy-3-methylbenzophenone **(4)**

4 (7.5 mg, 0.030 mmol) in 0.75 mL of deuterated toluene was irradiated until no trace of starting material could be observed by NMR. The signals for two isomeric benzofuranols (***cis*-29** and ***trans*-29**) were detected upon analysis of the NMR spectrum of



Scheme 95. Photoproducts from 4

the photolysis mixture. In our investigation, photochemistry was conducted at various temperatures to ascertain the effect of temperature on product ratios. The diastereometric ratio of benzofuranols was determined by NMR integration of the methine quartet signals corresponding to each isomer. In order to separate the two benzofuranols, large scale irradiation using **4** (0.9 g, 3.8 mmol) in 80 mL of benzene was performed. Solvent was evaporated to leave a yellow oil which was chromatographed by column using 2% ethyl acetate in hexanes solution. The *cis*-isomer was the first compound eluted.

cis-3-hydroxy-2,7-dimethyl-3-phenyl-2,3-dihydrobenzofuranol **(*cis*-29)**

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.28 (s, 1H), 1.31 (d, *J*= 7.0 Hz, 3H), 2.29 (s, 3H), 4.44 (q, *J*= 6.5 Hz, 1H), 6.70 (t, *J*= 7.5 Hz, 1H), 6.75 (d, *J*= 6.5 Hz, 1H), 6.93 (d, *J*= 7.5 Hz, 1H), 7.06 (dt, *J*= 1.5, 7.5 Hz, 1H), 7.12 (t, *J*= 7.5 Hz, 2H), 7.45 (d, *J*= 7.0 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 12.03, 15.31, 82.76, 90.64, 120.65, 121.40, 122.62, 126.90, 127.40, 127.95, 131.57, 133.23, 143.33, 159.40.

IR (neat, cm^{-1}): 3547.54 (m, broad), 3028.63 (w), 2934.10 (w), 1599.19 (s), 1446.73 (s), 1381.21 (m), 1213.36 (s), 1064.84 (m), 1022.40 (w).

MS, m/z: 239.9 (62.8%), 222.1 (91.4%), 221.0 (60.8%), 177.9 (49.0%), 134.9 (100.0%), 104.9 (38.0%), 76.3 (58.0%).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67.

Found: C, 80.04; H, 6.48.

m.p.: 75.0~75.8°C

trans-3-hydroxy-2,7-dimethyl-3-phenyl-2,3-dihydrobenzofuranol (***trans*-29**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 0.82 (d, *J*= 7.0 Hz, 3H), 1.72 (s, 1H), 2.28 (s, 3H), 4.60 (q, *J*= 7.0 Hz, 1H), 6.75 (t, *J*= 7.5 Hz, 1H), 6.82 (d, *J*= 6.5 Hz, 1H), 6.96 (dd, *J*= 1.0, 7.5 Hz, 1H), 7.02 (tt, *J*= 1.5, 7.5 Hz, 1H), 7.08 (t, *J*= 6.5 Hz, 2H), 7.31 (d, *J*= 6.5 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 15.22, 17.61, 85.48, 90.85, 121.38, 122.65, 127.30, 127.51, 127.96, 128.04, 131.54, 132.28, 141.72, 159.02.

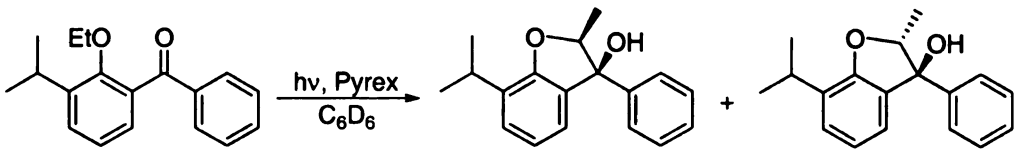
IR (neat, cm^{-1}): 3418.30 (s, broad), 2980.40 (m), 2932.17 (w), 1599.19 (s), 1458.85 (m), 1379.28 (w), 1192.18 (m), 1055.30 (m).

MS, m/z: 239.9 (0.3%), 222.2 (93.3%), 221.1 (100.0%), 179.1 (29.8%), 177.9 (99.2%), 144.9 (52.9%), 114.9 (30.6%), 95.9 (27.5%).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67.

Found: C, 79.79; H, 6.57.

Products from 2-ethoxy-3-isopropylbenzophenone (**5**)



Scheme 96. Photoproducts from 5

5 (7.5 mg, 0.028 mmol) in 0.75 mL of deuterated benzene was irradiated until starting material could not be observed by NMR. The signals corresponding to two isomeric

benzofuranols (***cis*-30** and ***trans*-30**) were detected in the NMR spectrum of the mixture. The effect of temperature on product ratios was investigated by conducting the photochemistry in acetone-dry ice, NaCl-ice, ice water and silicon oil (66°C) baths. Solid state irradiation was performed by packing a melting point capillary tube with the compound and irradiating it through Pyrex-filtered UV light for 30 minutes. The diastereomeric ration of the products was determined by NMR integration of the methine quartet peaks corresponding to each isomer. Large scale irradiation using **5** (0.45 g, 1.7 mmol) in 60 mL of benzene was performed until 100% conversion (GC). Solvent was removed to leave a yellow oil which was separated by column chromatography (hexanes: ethyl acetate 40:1). The *cis*-isomer was eluted before the *trans*-isomer. The products were recovered as oils.

cis-3-hydroxy-7-isopropyl-2-methyl-3-phenyl-2,3-dihydrobenzofuranol **(*cis*-30)**

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.29 (s, 1H), 1.32 (d, *J*= 11.5 Hz, 6H), 1.33 (d, *J*= 11.0 Hz, 3H), 3.37 (heptet, *J*= 11.5 Hz, 1H), 4.48 (q, *J*= 11.0 Hz, 1H), 6.77 (d, *J*= 6.0 Hz, 1H), 6.78 (d, *J*= 9.0 Hz, 1H), 7.11 (stack, 4H), 7.44 (dd, *J*= 2.5, 11.0 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 12.12, 22.62, 28.60, 82.63, 90.61, 121.71, 122.64, 126.91, 127.37, 127.42, 128.17, 131.56, 133.57, 143.40, 158.47.

IR (neat, cm^{-1}): 3549.47 (m, broad), 2961.11 (s), 1597.26 (m), 1442.94 (s), 1383.14 (w), 1201.81 (w), 1064.84 (m).

MS, m/z: 268.0 (38.0%), 250.0 (12.9%), 235.0 (16.8%), 163.0 (100.0%), 104.9 (47.8%), 76.9 (36.9%).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46.

Found: C, 80.60; H, 7.34.

trans-3-hydroxy-7-isopropyl-2-methyl-3-phenyl-2,3-dihydrobenzofuranol (***trans*-30**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 0.82 (d, *J*= 11.0 Hz, 3H), 1.33 (d, *J*= 11.5 Hz, 6H), 1.72 (s, 1H), 3.33 (heptet, *J*= 11.5 Hz, 1H), 4.62 (q, *J*= 11.0 Hz, 1H), 6.84 (stack, 2H), 7.09 (stack, 4H), 7.31 (dd, *J*= 2.5, 11.5 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 17.61, 22.49, 28.69, 85.34, 90.77, 121.63, 122.66, 127.32, 127.36, 127.50, 131.72, 132.54, 137.89, 141.70, 158.12.

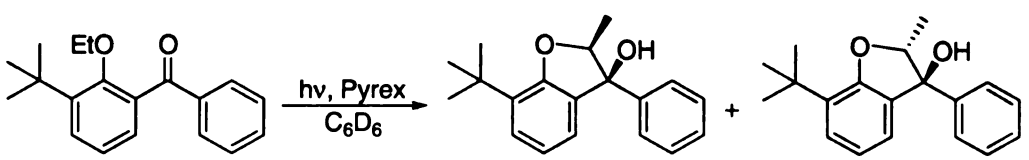
IR (neat, cm^{-1}): 3426.01 (m), 2963.04 (m), 1445.66 (s), 1190.23 (m), 1059.05 (s), 939.45 (w).

MS, m/z: 250.0 (100.0%), 234.9 (100.0%), 206.9 (25.9%), 191.0 (25.9%), 188.9 (24.7%), 177.9 (36.5%), 164.9 (33.7%), 114.9 (28.6%), 102.8 (34.9%), 90.9 (22.1%), 77.0 (18.0%), 43.0 (24.7%).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46.

Found: C, 80.81; H, 7.26.

Products from 3-t-butyl-2-ethoxybenzophenone (**6**)



6 *cis*-**31** *trans*-**31**

Scheme 97. Photoproducts from 6

6 (8.0 mg, 0.028 mmol) in 0.75 mL of deuterated benzene was irradiated until starting material could not be observed by NMR. The signals corresponding to two isomeric

benzofuranols (***cis*-31** and ***trans*-31**) were detected in the NMR spectrum of the mixture. The effect of temperature on product ratios was investigated by conducting photochemistry in acetone-dry ice, NaCl-ice, ice water and silicon oil (66°C) baths. The diastereometric ratio of benzofuranols was determined by NMR integration of the methine quartet signals corresponding to each isomer. Large scale irradiation using **6** (0.6 g, 2.1 mmol) in 60 mL of benzene was performed until 100% conversion by NMR. The products were separated by column chromatography (hexanes: ethyl acetate 50:1~35:1) and characterized.

cis-7-t-butyl-3-hydroxy-2-methyl-3-phenyl-2,3-dihydrobenzofuranol **(*cis*-31)**

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.29 (s, 1H), 1.32 (d, *J*= 10.5 Hz, 3H), 1.52 (s, 9H), 4.47 (q, *J*= 10.5 Hz, 1H), 6.78 (stack, 2H), 7.11 (stack, 3H), 7.20 (dd, *J*= 4.5, 10.5 hz, 1H), 7.43 (dt, *J*= 3.0, 11.0 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 12.16, 29.62, 34.48, 82.18, 90.24, 121.52, 123.08, 126.93, 127.21, 127.35, 128.16, 133.88, 134.46, 143.51, 158.88.

IR (neat, cm^{-1}): 3456.88 (m), 2957.25 (m), 1591.48 (w), 1431.36 (s), 1072.56 (m), 885.44 (m).

MS, m/z: 282.0 (56.1%), 267.0 (40.8%), 249.0 (51.4%), 177.0 (100.0%), 161.0 (33.3%), 132.9 (32.6%), 104.9 (88.6%), 90.9 (24.6%), 76.8 (62.8%), 57.0 (28.6%).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80.

Found: C, 80.80; H, 7.99.

trans-7-t-butyl-3-hydroxy-2-methyl-3-phenyl-2,3-dihydrobenzofuranol **(*trans*-31)**

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 0.81 (d, *J*= 11.5 Hz, 3H), 1.50 (s, 9H), 1.71 (s, 1H), 4.60 (q, *J*= 11.0 Hz, 1H), 6.81 (t, *J*= 12.0 Hz, 1H), 6.87 (dd, *J*= 3.0, 12.5 Hz, 1H), 7.06 (stack, 3H), 7.21 (dd, *J*= 3.0, 12.5 Hz, 1H), 7.32 (dt, *J*= 2.5, 11.5 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 17.55, 29.53, 34.39, 84.89, 90.41, 121.44, 123.07, 127.09, 127.35, 127.49, 127.85, 133.34, 134.07, 141.67, 158.51.

IR (neat, cm^{-1}): 3383. 57 (m, broad), 2959.18 (m), 1591.48 (w), 1431.38 (s), 1213.38 (w), 1057.13 (m).

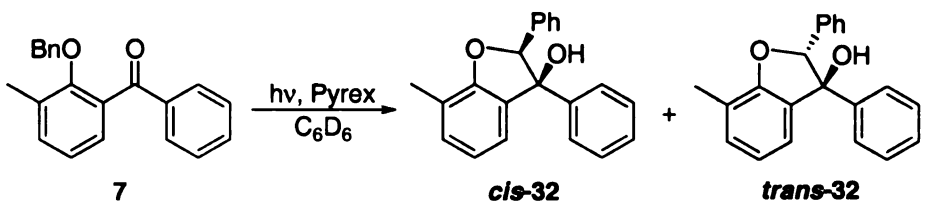
MS, m/z: 264.0 (100.0%), 250.3 (35.7%), 249.0 (100.0%), 221.1 (65.5%), 178.0 (44.7%), 164.9 (31.4%), 110.0 (60.8%), 102.9 (33.7%), 77.1 (14.6%).

Anal. Calcd for $C_{19}H_{22}IO_2$: C, 80.85; H, 7.80.

Found: C, 80.81; H, 7.71.

m.p.: 74.8~75.5°C

Products from 2-benzyloxy-3-methylbenzophenone (**7**)



7 ***cis*-32** ***trans*-32**

Scheme 98. Photoproducts from 7

NMR experiment

A 0.75 mL benzene-d_6 solution of **7** (8.2 mg, 0.027 mmol) was degassed in a NMR tube. The reaction was monitored by ^{1}H NMR and was complete (100% conversion) after 10 minutes of irradiation with Pyrex filtered light (medium pressure mercury arc lamp). The ^{1}H NMR spectra showed the disappearence of the methylene group (singlet at

4.80ppm) with the simultaneous growth of two singlets at 5.57ppm and 5.61ppm corresponding to two isomeric benzofuranols (***cis*-32** and ***trans*-32**). The effect of temperature on product ratios was investigated by conducting photochemistry in acetone-dry ice, NaCl-ice, ice water and silicon oil (66°C) baths. The diastereometric ratio of benzofuranols was determined by NMR integration of the methine singlet signals corresponding to each isomer.

Preparative experiment

A preparative reaction was carried out with **7** (800 mg, 2.7 mmol) in 60 mL of benzene. The preparatory scale reaction gave a identical results as the NMR scale reaction. Silica gel column chromatography (hexanes: ethyl acetate 30:1~20:1) gave two products.

cis-3-hydroxy-7-methyl-2,3-diphenyl-2,3-dihydrobenzofuranol **(*cis*-32)**

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.53 (s, 1H), 2.36 (s, 3H), 5.57 (s, 1H), 6.74 (t, *J*= 7.0 Hz, 1H), 6.83 (d, *J*= 7.0 Hz, 1H), 6.98 (d, *J*= 7.5 Hz, 1H), 7.13 (stack, 8H), 7.34 (dd, *J*= 1.5, 7.0 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 15.30, 83.57, 95.57, 120.80, 121.94, 123.14, 127.15, 127.42, 127.48, 128.22, 128.25, 128.41, 131.60, 132.92, 134.80, 143.55, 159.15.

IR (neat, cm^{-1}): 3545.61 (m), 3030.56 (m), 2918.67 (w), 1599.19 (s), 1446.73 (s), 1207.59 (s), 1064.84 (m), 947.17 (m).

MS, m/z: 284.1 (100.0%), 268.4 (13.5%), 255.3 (17.8%), 239.3 (22.1%), 140.9 (34.5%), 134.4 (42.0%), 119.8 (35.3%), 113.2 (19.3%).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96.

Found: C, 83.10; H, 5.79.

m.p.: 89.0~89.6°C

trans-3-hydroxy-7-methyl-2,3-diphenyl-2,3-dihydrobenzofuranol (***trans*-32**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 2.00 (s, 1H), 2.36 (s, 3H), 5.61 (s, 1H), 6.84 (stack, 8H), 7.03 (stack, 5H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 15.22, 87.32, 96.44, 121.94, 122.80, 123.43, 126.54, 127.11, 127.40, 127.45, 127.55, 127.77, 131.68, 132.35, 137.68, 141.38, 159.45.

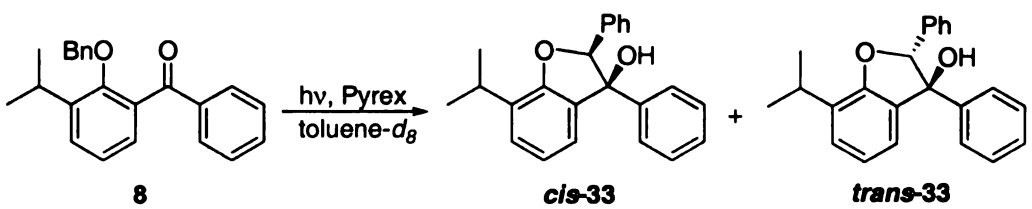
IR (neat, cm^{-1}): 3424.08 (m, broad), 3032.48 (m), 1597.26 (s), 1446.76 (s), 1263.54 (m), 1005.01 (s), 956.81 (m).

MS, m/z: 284.2 (100.0%), 255.2 (27.1%), 239.2 (29.8%), 140.5 (38.0%), 119.4 (42.4%), 76.8 (20.6%).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96.

Found: C, 83.57; H, 5.79.

Products from 2-benzyloxy-3-isopropylbenzophenone (**8**)



8 ***cis*-33** ***trans*-33**

Scheme 99. Photoproducts from 8

NMR experiment

A 0.75 mL toluene-d_8 solution of **8** (7.7 mg, 0.023 mmol) was prepared in an NMR

tube. The ketone was irradiated through Pyrex. The reaction was monitored by ^{1}H NMR analysis. The two products had ^{1}H NMR spectra consistent with ***cis*-33** and ***trans*-33**. The effect of temperature on product ratios was investigated by conducting photochemistry in acetone-dry ice, NaCl-ice, ice water and silicon oil (66°C) baths. The diastereometric ratio of two benzofuranols was determined by NMR integration of the methine singlet signals corresponding to each isomer.

Preparative experiment

The preparative photolysis of **8** was carried out in 25 mm x 250 mm pyrex tube irradiated in a Rayonet reactor equipped with 300 nm lamps. **8** (0.85 g, 2.6 mmol) was dissolved in 60 mL of benzene and degassed. The tube was irradiated for 12 hours and the solvent removed. TLC analysis (SiO_2, hexanes: ethyl acetate 40:1) revealed two major products. The photoproducts were isolated using column chromatography (hexanes: ethyl acetate 40:1). The first compound eluted had spectral data consistent with ***cis*-33**. The second compound eluted had spectral data consistent with ***trans*-33**.

cis-3-hydroxy-7-isopropyl-2,3-diphenyl-2,3-dihydrobenzofuranol **(*cis*-33)**

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.38 (d, *J*= 7.0 Hz, 3H), 1.40 (d, *J*= 7.0 Hz, 3H), 1.53 (s, 1H), 3.39 (septet, *J*= 7.0 Hz, 1H), 5.61 (s, 1H), 6.81 (t, *J*= 7.5 Hz, 1H), 6.84 (dd, *J*= 2.0, 7.5 Hz, 1H), 7.10 (stack, 7H), 7.17 (m, 2H), 7.34 (dt, *J*= 2.0, 8.0 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 22.50, 22.68, 29.04, 83.44, 95.55, 122.21, 123.21, 127.17, 127.37, 127.46, 127.56, 128.22, 128.29, 128.41, 131.65, 133.18, 134.99, 143.67, 158.24.

IR (neat, cm^{-1}): 3545.61 (m, broad), 3063.35 (w), 2963.04 (m), 1444.37 (s), 1197.95 (m), 1010.83 (m), 952.96 (m), 860.36 (w).

MS, m/z: 330.4 (11.0%), 239.3 (35.7%), 163.2 (56.5%), 105.1 (53.7%), 91.0 (100.0%), 77.0 (34.1%).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.64; H, 6.67.

Found: C, 83.58; H, 6.62.

trans-3-hydroxy-7-isopropyl-2,3-diphenyl-2,3-dihydrobenzofuranol (***trans*-33**)

^1H NMR (500 MHz, C_6D_6), δ ppm: 1.38 (d, *J*= 7.0 Hz, 3H), 1.40 (d, *J*= 7.0 Hz, 3H), 1.96 (s, 1H), 3.38 (septet, *J*= 7.0 Hz, 1H), 5.62 (s, 1H), 6.83 (stack, 8H), 7.04 (stack, 4H), 7.14 (m, 1H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 22.47, 22.61, 29.06, 87.15, 96.40, 122.21, 122.85, 126.52, 127.08, 127.39, 127.45, 127.54, 127.68, 127.79, 131.58, 132.62, 137.85, 141.44, 158.59.

IR (neat, cm^{-1}): 3406.72 (m, broad), 3034.41 (w), 2961.11 (m), 1595.33 (w), 1448.80 (s), 1005.04 (m), 837.21 (w).

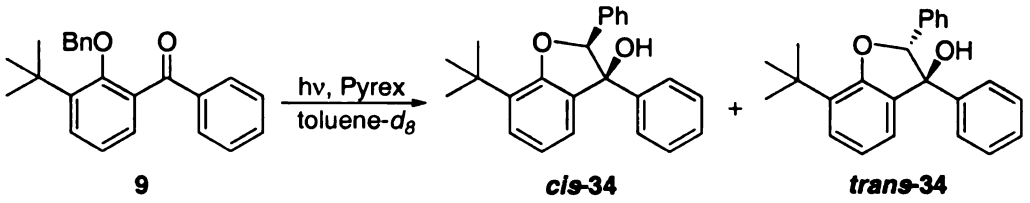
MS, m/z: 312.0 (100.0%), 297.4 (72.9%), 296.5 (40.8%), 269.3 (16.1%), 239.3 (16.9%), 191.3 (21.4%), 165.2 (25.1%), 141.2 (23.4%), 105.0 (28.2%), 91.2 (14.3%), 77.2 (20.7%).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.64; H, 6.67.

Found: C, 83.48; H, 6.37.

m.p.: 84.1~84.5°C

Products from 2-benzyloxy-3-t-butylbenzophenone (9)



9 ***cis*-34** ***trans*-34**

Scheme 100. Photoproducts from 9

NMR experiment

A 0.75 mL toluene-d_8 solution of **9** (8.2 mg, 0.024 mmol) was degassed in a NMR tube. The reaction was monitored by ^{1}H NMR and was complete (100% conversion) after 10 minutes of irradiation with Pyrex filtered light (medium pressure mercury arc lamp). The ^{1}H NMR spectra showed the disappearence of the methylene group (singlet at 4.67ppm) with the simultaneous growth of two singlets at 5.53ppm and 5.59ppm corresponding to two isomeric benzofuranols (**34**). The effect of temperature on product ratios was investigated by conducting photochemistry in acetone-dry ice, NaCl-ice, ice water and silicon oil (66°C) baths. The diastereometric ratio of benzofuranols was determined by NMR integration of the methine singlet signals corresponding to each isomer.

Preparative experiment

A preparative reaction was carried out with **7** (750 mg, 2.2 mmol) in 60 mL of benzene. The preparatory scale reaction gave a identical results as the NMR scale reaction. Silica gel column chromatography (hexanes: ethyl acetate 30:1~20:1) gave two products.

cis-7-t-butyl-3-hydroxy-2,3-diphenyl-2,3-dihydrobenzofuranol (***cis*-34**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.56 (s, 10H), 5.63 (s, 1H), 6.80 (t, *J*= 7.5 Hz, 1H), 6.86 (dd, *J*= 1.5, 7.5 Hz, 1H), 7.10 (stack, 6H), 7.19 (dd, *J*= 2.0, 7.5 Hz, 2H), 7.22 (dd, *J*= 1.5, 8.0 Hz, 1H), 7.35 (dd, *J*= 1.5, 8.5 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 29.70, 34.50, 83.02, 95.32, 122.04, 123.62, 127.20, 127.27, 127.32, 127.45, 128.22, 128.34, 128.40, 133.97, 134.03, 135.09, 143.75, 158.56.

IR (neat, cm^{-1}): 3547.54 (m), 2959.18 (m), 1431.30 (s), 1361.92 (w), 1010.83 (m), 949.10 (w).

MS, m/z: 344.1, 329.1, 239.4, 177.0, 165.0, 133.0, 118.4, 91.0, 76.9, 57.1.

Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.72; H, 6.98.

Found: C, 83.50; H, 6.77.

m.p.: 81.9~82.5°C

trans-7-t-butyl-3-hydroxy-2,3-diphenyl-2,3-dihydrobenzofuranol (***trans*-34**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.57 (s, 9H), 1.86 (s, 1H), 5.60 (s, 1H), 6.84 (stack, 8H), 7.07 (stack, 4H), 7.26 (dd, *J*= 2.0, 7.0 Hz, 1H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 29.65, 34.47, 86.66, 96.14, 122.03, 123.20, 126.52, 127.06, 127.29, 127.33, 127.46, 127.54, 127.81, 133.49, 133.93, 137.83, 141.57, 158.84.

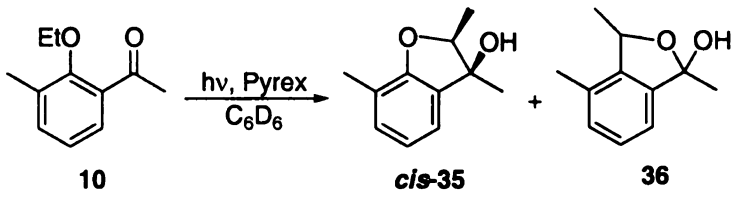
IR (neat, cm^{-1}): 3399.01 (m, broad), 3065.28 (w), 2961.11 (m), 1591.48 (m), 1431.38 (s), 1228.81 (m), 1006.97 (m), 960.67 (m).

MS, m/z: 326.2 (100.0%), 311.0 (100.0%), 283.4 (36.1%), 282.5 (35.3%), 165.0 (34.9%), 141.3 (100.0%), 134.2 (55.7%), 126.1 (47.5%), 119.5 (37.7%), 76.8 (29.4%).

Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.72; H, 6.98.

Found: C, 84.08; H, 6.75.

Products from 2-ethoxy-3-methylacetophenone **(10)**



10 ***cis*-35** **36**

Scheme 101. Photoproducts from 10

10 (4.4 mg, 0.025 mmol) in 0.75 mL of deuterated benzene was irradiated. The signals for three products were detected in the NMR spectrum of the mixture. Two of these products, the hemiketals (**36**), disappear as the irradiation time (percent conversion) increases. The signal for one product was detected at 100% conversion in the NMR spectrum of the photolysis mixture. This product was a benzofuranol (***cis*-35**). The hemiketal/benzofuranol ratio was determined by NMR integration of the methine quartet signal of the hemiketals and the methine quartet signal of the benzofuranol. Large scale irradiation using **10** (0.5 g, 2.8 mmol) in 60 mL of benzene was performed until 40% conversion (GC). Solvent was removed to leave a yellow oil which was chromatographed by deactivated silica gel (hexanes: ethyl acetate 20:1) to separate the products. The starting ketone was the first fraction eluted followed by benzofuranol and the two hemiketals. The two hemiketals were obtained as a 1:1 mixture. The structural assignment of the benzofuranol was accomplished by performing nOe experiment: irradiation of the methine signal caused an enhancement of the methyl signal (singlet at 1.26ppm). This suggests that the benzofuranol has a *cis*-stereochemistry.

cis-3-hydroxy-2,3,7-trimethyl-2,3-dihydrobenzofuranol (***cis*-35**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.01 (s, 1H), 1.26 (s, 3H), 1.28 (d, *J*= 6.5 Hz, 3H), 2.24 (s, 3H), 4.03 (q, *J*= 6.5 Hz, 1H), 6.77 (t, *J*= 7.5 Hz, 1H), 6.92 (dd, *J*= 1.5, 7.5 Hz, 1H), 6.98 (d, *J*= 7.0 Hz, 1H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 13.22, 15.24, 23.96, 77.45, 87.65, 120.58, 120.93, 121.02, 131.25, 132.72, 158.25.

IR (neat, cm^{-1}): 3404.79 (m, broad), 2976.54 (m), 1601.12 (m), 1442.94 (m), 1217.24 (s), 1059.05 (s).

MS, m/z: 177.9 (16.5%), 163.2 ((49.7%), 145.1 (26.7%), 135.2 (100.0%), 119.0 (26.1%), 91.1 (38.0%), 77.1 (33.2%).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87.

Found: C, 74.30; H, 7.80.

1,3-dihydro-1,3,4-trimethylisobenzofuran-1-ol (**36**)

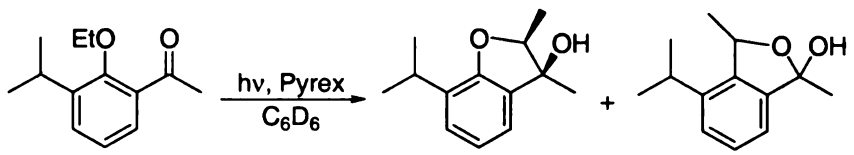
^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.30 (d, 6.5 Hz, 3H), 1.37 (d, *J*= 6.5 Hz, 3H), 1.70 (s, 3H), 1.77 (s, 3H), 1.89 (s, 3H), 1.92 (s, 3H), 2.26 (s, 1H), 2.35 (s, 1H), 5.06 (q, *J*= 6.5 Hz, 1H), 5.18 (q, *J*= 6.5 Hz, 1H), 6.85 (d, *J*= 7.5 Hz, 2H), 7.02 (dt, *J*= 3.0, 7.5 Hz, 2H), 7.07 (d, *J*= 7.5 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 18.18, 18.48, 21.31, 22.90, 27.60, 28.56, 77.49, 78.02, 106.90, 107.04, 119.86, 119.92, 128.33, 128.37, 130.17. 130.26, 131.26, 131.33, 142.02, 142.39, 142.93, 143.38.

IR (neat, cm^{-1}): 3416.37 (m, broad), 2988.12 (m), 2937.96 (m), 1787.02 (s), 1699.50 (m), 1684.07 (m), 1479.59 (w), 1437.15 (w), 1275.11 (m), 1096.71 (m), 1057.13 (m).

MS, m/z: 176.3 (1.0%), 161.2 (100.0%), 105.1 (49.1%), 77.2 (16.6%), 43.2 (47.1%).

Products from 2-ethoxy-3-isopropylacetophenone **(11)**



11 ***cis*-37** **38**

Scheme 102. Photoproducts from 11

11 (3.7 mg, 0.018 mmol) in 0.75 mL of deuterated benzene was irradiated. The signals for three products were detected in the NMR spectrum of the mixture. Two of these products, the hemiketals (**38**), disappear as the irradiation time (percent conversion) increases. The signal for one product was detected at 100% conversion in the NMR spectrum of the photolysis mixture. This product was a benzofuranol (***cis*-37**). The structural assignment of the benzofuranol was accomplished by performing nOe experiment: irradiation of the methine signal (quartet at 4.05ppm, J= 7.0 Hz) caused an enhancement of the methyl signal (singlet at 1.26ppm). This suggests that the benzofuranol has a *cis*-stereochemistry. The hemiketal/benzofuranol ratio was determined by NMR integration of the methine quartet signal of the hemiketals and the methine quartet signal of the benzofuranol. The hemiketals were difficult to isolate because of a rapid decomposition on silica gel. The spectroscopic data given are from the NMR mixture of photoproducts in benzene. The large scale irradiation using 0.5 g (2.4 mmol) of **11** in 60 mL of benzene was performed until 100% conversion (GC). Solvent was removed to leave a yellow oil which was chromatographed by column chromatography (hexanes: ethyl acetate 15:1~10:1) to separate the product.

cis-3-hydroxy-7-isopropyl-2,3-dimethyl-2,3-dihydrobenzofuranol (**cis-37**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 0.96 (s, 1H), 1.26 (s, 3H), 1.29 (d, *J*= 7.0 Hz, 6H), 1.31 (d, *J*= 7.0 Hz, 3H), 3.30 (septet, *J*= 7.0 Hz, 1H), 4.05 (q, *J*= 7.0 Hz, 1H), 6.84 (t, *J*= 7.5 Hz, 1H), 7.01 (dd, *J*= 1.5, 7.5 Hz, 1H), 7.06 (dd, *J*= 1.5, 7.5 Hz, 1H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 13.30, 22.53, 22.63, 24.07, 28.58, 77.30, 87.61, 121.04, 121.24, 127.11, 131.49, 133.04, 157.30.

IR (neat, cm^{-1}): 3391.29 (m, broad), 2964.97 (s), 1559.19 (w), 1442.94 (s), 1209.52 (m), 1062.91 (m).

MS, m/z: 188.0 (100.0%), 173.1 (100.0%), 158.0 (29.0%), 145.1 (52.6%), 127.7 (76.1%), 115.1 (55.7%), 105.2 (20.1%), 91.1 (30.2%), 79.1 (38.4%), 43.2 (100.0%).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74.

Found: C, 76.07; H, 8.76.

m.p.: 35.2~35.8°C

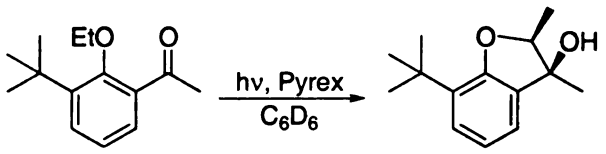
1,3-dihydro-4-isopropyl-1,3-dimethylisobenzofuran-1-ol (**38**)

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 1.36 (d, *J*= 6.3 Hz, 3H), 1.43 (d, *J*= 6.6 Hz, 3H), 1.70 (s, 3H), 1.77 (s, 3H), 2.63 (septet, *J*= 6.6 Hz, 2H), 5.22 (q, *J*= 6.6 Hz, 1H), 5.34 (q, *J*= 6.6 Hz, 1H).

Product from 3-t-butyl-2-ethoxyacetophenone (**12**)

NMR experiment

Irradiation of **12** (4.1 mg, 0.019 mmol) in 0.75 mL of benzene-d_6 gave only one product. The reaction was monitored by ^{1}H NMR analysis periodically. The quartet at



12 *cis*-39

Scheme 103. Photoproduct from 12

3.52ppm for the methylene group disappeared at the same rate as the growth of a quartet at 4.04ppm in benzene-d_6. The product was determined to be *cis*-7-t-butyl-3-hydroxy-2,3-dimethyl-2,3-dihydrobenzofuranol (***cis*-39**) based on its ^{1}H and ^{13}C NMR spectra.

Preparative experiment

A preparative reaction was carried out with 0.5 g (2.3 mmol) of **12** in 60 mL of benzene. The preparatory scale reaction gave an identical results as the NMR scale reaction. Silica gel column chromatography (hexanes: ethyl acetate 20:1) gave a single product.

cis-7-t-butyl-3-hydroxy-2,3-dimethyl-2,3-dihydrobenzofuranol **(*cis*-39)**

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 0.89 (s, 1H), 1.19 (s, 3H), 1.22 (d, *J*= 6.6 Hz, 3H), 1.42 (s, 9H), 3.98 (q, *J*=6.6 Hz. 1H), 6.78 (t, *J*= 7.5 Hz, 1H), 6.97 (dd, *J*= 1.5, 7.5 Hz, 1H), 7.11 (dd, *J*= 1.5, 7.5 Hz, 1H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 13.29, 24.15, 29.56, 34.39, 76.84, 87.27, 121.05, 121.44, 126.85, 133.78, 133.87, 157.72.

IR (neat, cm^{-1}): 3379.72 (m, broad), 2959.18 (s), 1595.33 (w), 1431.36 (s), 1209.52 (m), 1062.91 (m), 893.16 (m).

MS, m/z: 202.0 (100.0%), 188.5 (26.7%), 187.0 (100.0%), 159.3 (54.5%), 158.6 (55.7%),

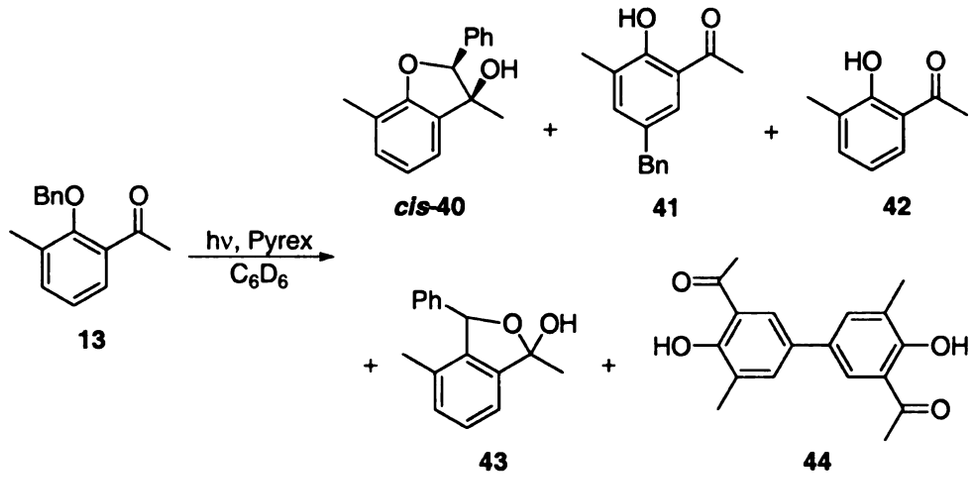
127.7 (72.9%), 114.9 (52.2%), 90.9 (39.2%), 79.0 (43.5%), 71.5 (45.9%), 42.9 (73.7%).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09.

Found: C, 76.51; H, 9.20.

m.p.: 32.5~32.9°C

Products from 2-benzyloxy-3-methylacetophenone **(13)**



Scheme 104. Photoproducts from 13

Irradiation of a 0.019 M benzene-d_6 solution of **13** gave a complex mixture of products. The NMR tube was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp. The progress of the reaction was monitored by ^{1}H NMR analysis. The reaction was approximately 50% complete after 10 hours.

The preparative reaction sample was prepared using the same technique that was applied to the NMR scale sample except with 0.38 g (1.58 mmol) of **13**. The solvent was removed by rotoevaporation and a yellow oil remained. The crude product was purified by column chromatography (hexanes: ethyl acetate 30:1~15:1): the first fraction eluted had the spectral data consistent with **42**; the second fraction was recrystallized from hexanes to afford a yellow crystal which was determined by ^{1}H and ^{13}C NMR to be **41**;

the third compound eluted was recovered starting material; the fourth fraction was purified again by crystallization from hexanes to give yellow powder, this compound was determined to be **44** based on spectral data; the last fraction was purified again by column chromatography (hexanes: ethyl acetate 30:1~20:1), it was assigned to be ***cis*-40** based on spectral data. The two hemiketals (**43**) were unable to isolate due to quick decomposition on silica gel, NMR spectrum of the photoproducts mixture shows two singlets at 5.84ppm and 5.96ppm corresponding to the methine protons of the two hemiketals.

5-benzyl-2-hydroxy-3-methylacetophenone (**41**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 1.88 (s, 3H), 2.16 (s, 3H), 3.62 (s, 2H), 6.90 (d, *J*= 1.5 Hz, 1H), 6.97 (d, *J*= 1.5 Hz, 1H), 7.05 (stack, 3H), 7.15 (stack, 2H), 13.11 (1H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 15.59, 26.00, 41.19, 119.10, 126.53, 127.91, 128.25, 128.82, 128.99, 130.51, 138.19, 141.50, 160.17, 204.52.

IR (neat, cm^{-1}): 2920.60 (w), 1633.91 (s), 1429.43 (m), 1369.63 (m), 1292.47 (m), 1128.50 (w).

MS, m/z: 240.2 (88.3%), 225.2 (100.0%), 197.1 (70.7%), 178.0 (31.8%), 165.0 (24.5 %), 151.8 (33.9%), 91.0 (54.8%), 43.1 (77.4%).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67.

Found: C, 80.05; H, 6.59.

m.p.: 89.1~89.7°C

1-(3'-acetyl-4,4'-dihydroxy-5,5'-dimethyl-biphenyl-3-yl)-ethanone (**44**)

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 2.32 (s, 3H), 2.69 (s, 3H), 7.50 (d, *J*=2.1 Hz, 1H), 7.65 (d, *J*= 2.1 Hz, 1H), 12.56 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 15.69, 26.92, 119.03, 126.10, 128.14, 130.75, 135.83, 160.21, 204.72.

IR (neat, cm^{-1}): 2933.53 (w), 1637.77 (m), 1425.58 (s), 1278.97 (s), 1207.59 (s), 1174.80 (m).

MS, m/z: 281.1 (23.0%), 207.1 (100.0%), 187.2 (17.2%), 147.1 (19.9%), 135.1 (26.1%), 73.1 (56.0%).

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04.

Found: C, 72.55; H, 5.98.

m.p.: 240.5~241.3°C

cis-3-hydroxy-3,7-dimethyl-2-phenyl-2,3-dihydrobenzofuranol (***cis*-40**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 0.96 (s, 1H), 1.39 (s, 3H), 2.30 (s, 3H), 5.00 (s, 1H), 6.83 (t, *J*= 8.0 Hz, 1H), 6.97 (d, *J*= 8.0 Hz, 1H), 7.08 (d, *J*= 7.5 Hz, 1H), 7.14 (stack, 3H), 7.25 (dd, *J*= 2.0, 8.5 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 15.24, 25.11, 78.44, 92.93, 120.73, 121.44, 121.50, 127.56, 127.91, 128.39, 131.32, 132.15, 135.91, 158.27.

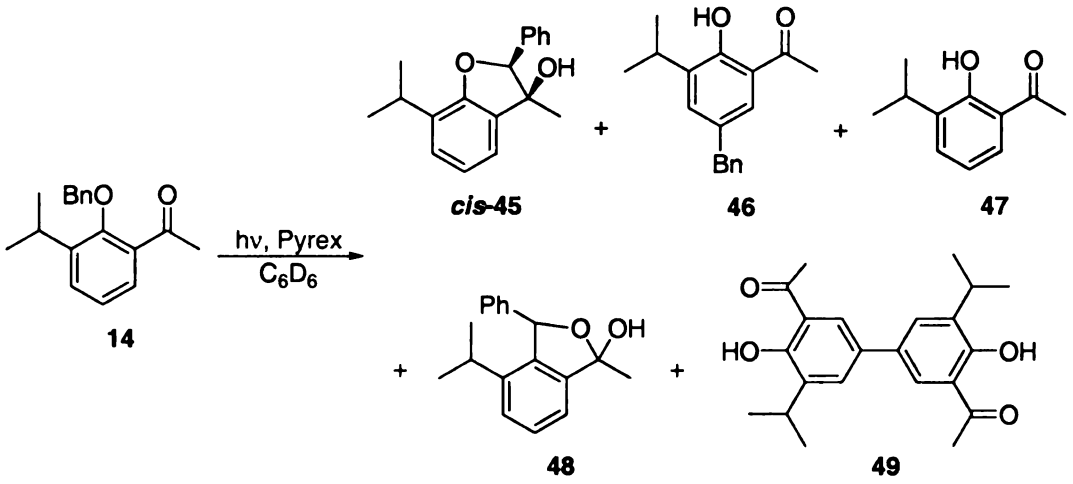
IR (neat, cm^{-1}): 3439.52 (m, broad), 2924.46 (w), 1599.19 (m), 1454.51 (s), 1207.59 (s), 1093.78 (w).

MS, m/z: 222.4 (100.0%), 178.1 (43.4%), 145.1 (32.1%), 115.0 (31.3%), 76.9 (31.3%).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67.

Found: C, 80.06; H, 6.85.

Products from 2-benzyloxy-3-isopropylacetophenone **(14)**



Scheme 105. Photoproducts from 14

Irradiation of a 0.020 M benzene-d_6 solution of **14** gave a complex mixture of products. The NMR tube was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp. The progress of the reaction was monitored by ^{1}H NMR analysis. The reaction was approximately 60% complete after 12 hours.

The preparative reaction sample was prepared using the same technique that was applied to the NMR scale sample except with 0.90 g (3.36 mmol) of **14**. The solvent was removed by rotoevaporation and a yellow oil remained. The crude product was purified by column chromatography (hexanes: ethyl acetate 30:1~15:1): the first fraction eluted had the spectral data consistent with **47**; the second fraction was recrystallized from hexanes to afford a yellow crystal which was determined by ^{1}H and ^{13}C NMR to be **46**; the third compound eluted was recovered starting material; the fourth fraction was purified again by crystallization from hexanes to give yellow powder, this compound was determined to be **49** based on spectral data; the last fraction was purified again by column chromatography (hexanes: ethyl acetate 30:1~20:1), it was assigned to be ***cis*-45** based on spectral data. The two hemiketals (**48**) were unable to isolate due to quick

decomposition on silica gel, NMR spectrum of the photoproducts mixture shows two singlets at 5.92ppm and 6.05ppm corresponding to the methine protons of the two hemiketals.

5-benzyl-2-hydroxy-3-isopropylacetophenone **(46)**

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 1.28 (d, *J*= 6.9 Hz, 6H), 1.97 (s, 3H), 3.60 (septet, *J*= 6.9 Hz, 1H), 3.76 (s, 2H), 7.07 (d, *J*= 2.1 Hz, 1H), 7.13 (stack, 3H), 7.24 (stack, 3H), 13.32 (1H).

^{13}C NMR (75 MHz, C_6D_6), δ ppm: 22.38, 26.10, 27.04, 41.39, 119.36, 126.53, 128.23, 128.82, 128.96, 130.72, 133.96, 138.03, 141.48, 159.43, 204.73.

IR (neat, cm^{-1}): 3026.70 (w), 2963.04 (m), 1635.84 (s), 1454.51 (s), 1389.63 (m), 1250.03 (m), 1167.08 (m), 979.96 (w).

MS, m/z: 268.2 (45.5%), 253.2 (52.9%), 165.1 (13.0%), 115.0 (14.1%), 91.1 (100.0%), 76.5 (27.1%), 43.0 (87.5 %).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46.

Found: C, 80.72; H, 7.15.

1-(3'-acetyl-4,4'-dihydroxy-5,5'-diisopropyl-biphenyl-3-yl)-ethanone **(49)**

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 1.33 (d, *J*= 6.9 Hz, 6H), 2.03 (s, 3H), 3.63 (septet, *J*= 6.9 Hz, 1H), 7.40 (d, *J*= 2.4 Hz, 1H), 7.61 (d, *J*= 2.1 Hz, 1H), 13.37 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 22.40, 26.18, 27.41, 119.62, 126.56, 131.78, 131.92, 138.53, 160.27, 204.84.

IR (neat, cm^{-1}): 2963.04 (w), 1633.91 (s), 1433.29 (m), 1317.55 (s), 1236.53 (m),

1169.01 (w), 979.96 (w).

MS, m/z: 354.2 (60.2%), 339.1 (16.1%), 297.1 (6.6%), 165.0 (6.8%), 43.3 (100.0%).

Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.58; H, 7.34.

Found: C, 74.53; H, 7.19.

m.p.: 182.8~183.5°C

cis-3-hydroxy-7-isopropyl-3-methyl-2-phenyl-2,3-dihydrobenzofuranol (***cis*-45**)

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 1.02 (s, 1H), 1.32 (d, *J*= 6.9 Hz, 3H), 1.34 (d, *J*= 6.9Hz, 3H), 1.38 (s, 3H), 3.31 (septet, *J*= 6.9 Hz, 1H), 5.04 (s, 1H), 6.88 (t, *J*= 7.5 Hz, 1H), 7.12 (stack, 5H), 7.27 (dd, *J*= 1.8, 7.5 Hz, 2H).

^{13}C NMR (75 MHz, C_6D_6), δ ppm: 22.48, 22.57, 25.27, 28.96, 78.28, 92.88, 121.58, 121.70, 127.27, 127.47, 128.32, 128.38, 131.55, 132.39, 136.10, 157.32.

IR (neat, cm^{-1}): 3437.59 (m, broad), 3032.48 (w), 2963.04 (m), 1597.26 (w), 1442.94 (s), 1203.73 (m), 1080.27 (w), 993.47 (m).

MS, m/z: 250.4 (100.0%), 249.1 (65.5%), 234.8 (36.9%), 207.2 (49.0%), 177.9 (33.3%), 173.1 (52.2%), 157.2 (34.5%), 151.5 (21.3%), 114.9 (60.8%), 91.0 (56.5%).

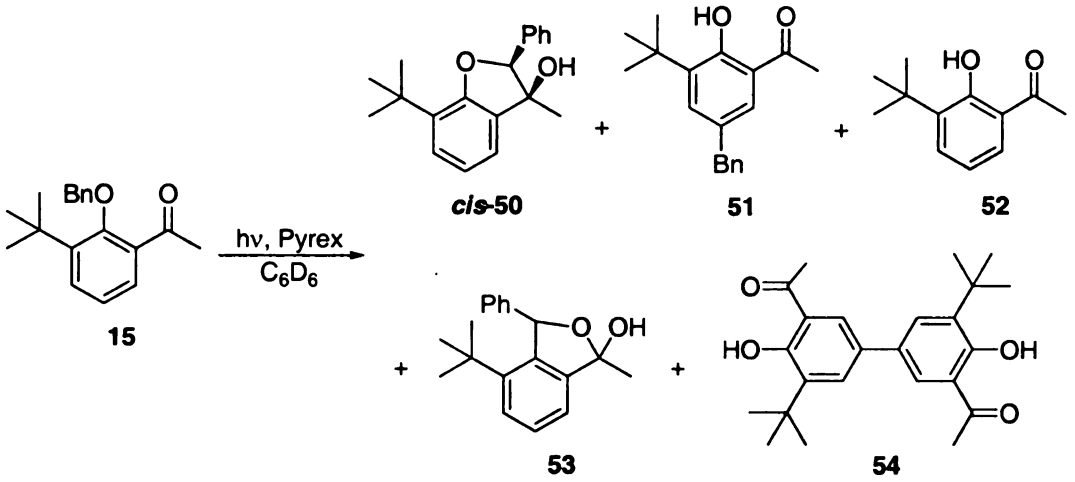
Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46.

Found: C, 80.68; H, 7.68.

Products from 2-benzyloxy-3-t-butylacetophenone (**15**)

Irradiation of a 0.018 M benzene-d_6 solution of **15** gave a complex mixture of products. The NMR tube was irradiated with Pyrex filtered light from a medium pressure mercury arc lamp. The progress of the reaction was monitored by ^{1}H NMR analysis. The

reaction was approximately 90% complete after 10 hours.



Scheme 106. Photoproducts from 15

The preparative reaction sample was prepared using the same technique that was applied to the NMR scale sample except with 0.30 g (1.06 mmol) of **15**. The solvent was removed by rotoevaporation and a yellow oil remained. The crude product was purified by column chromatography (hexanes: ethyl acetate 30:1~10:1): the first fraction eluted had the spectral data consistent with **52**; the second fraction was purified again by column chromatography (hexanes: ethyl acetate 80:1) to afford a yellow solid which was determined by ^{1}H and ^{13}C NMR to be **51**; the third compound eluted was recovered starting material; the fourth fraction was purified again by crystallization from hexanes to give yellow powder, this compound was determined to be **54** based on spectral data; the last fraction was purified again by crystallization from hexanes, it was assigned to be ***cis*-50** based on spectral data. The two hemiketals (**53**) were unable to isolate due to quick decomposition on silica gel, NMR spectrum of the photoproducts mixture shows two singlets at 5.85ppm and 5.98ppm corresponding to the methine protons of the two hemiketals.

5-benzyl-3-t-butyl-2-hydroxyacetophenone **(51)**

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 1.43 (s, 9H), 1.83 (s, 3H), 3.65 (s, 2H), 7.01 (stack, 4H), 7.10 (stack, 2H), 7.28 (d, *J*= 2.1 Hz, 1H), 13.46 (1H).

^{13}C NMR (75 MHz, C_6D_6), δ ppm: 26.30, 29.47, 35.13, 41.51, 119.74, 126.54, 128.68, 128.85, 128.99, 130.28, 134.54, 139.03, 141.43, 161.24, 205.05.

IR (neat, cm^{-1}): 2959.19 (m), 1631.99 (s), 1433.29 (s), 1363.85 (m), 1331.05 (m), 1238.46 (s), 1105.35 (w).

MS, m/z: 282.3 (51.3%), 267.3 (100.0%), 266.5 (38.4%), 178.0 (8.2%), 91.0 (73.7%), 43.0 (61.0%).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80.

Found: C, 80.69; H, 7.46.

1-(3'-acetyl-5,5'-di-t-butyl-4,4'-dihydroxy-biphenyl-3-yl)-ethanone **(54)**

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 1.46 (s, 9H), 2.70 (s, 3H), 7.58 (d, *J*= 2.1 Hz, 1H), 7.67 (d, *J*= 2.1 Hz, 1H), 13.11 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 27.21, 29.27, 35.11, 119.50, 126.69, 131.00, 132.59, 139.36, 161.46, 205.18.

IR (neat, cm^{-1}): 2951.46 (m), 1630.06 (s), 1427.51 (s), 1361.92 (m), 1319.48 (m), 1205.66 (m), 1103.42 (w).

MS, m/z: 382.8 (87.1%), 381.7 (68.2%), 367.8 (47.1%), 366.7 (41.6%), 176.0 (25.1%), 165.0 (14.4%), 130.6 (34.9%), 57.3 (49.4%), 43.0 (100.0%).

Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.39; H, 7.85.

Found: C, 75.34; H, 7.84.

m.p.: 219.5~219.8°C

cis-7-t-butyl-3-hydroxy-2,3-dimethyl-2,3-dihydrobenzofuranol (***cis*-50**)

^{1}H NMR (500 MHz, C_6D_6), δ ppm: 0.94 (s, 1H), 1.38 (s, 3H), 1.50 (s, 9H), 5.06 (s, 1H), 6.88 (t, *J*= 7.5 Hz, 1H), 7.14 (stack, 4H), 7.21 (dd, *J*= 1.0, 7.5 Hz, 1H), 7.29 (dd, *J*= 1.5, 7.5 Hz, 2H).

^{13}C NMR (125 MHz, C_6D_6), δ ppm: 25.28, 29.62, 34.40, 77.83, 92.70, 121.55, 121.96, 126.97, 127.41, 127.77, 128.46, 133.13, 133.93, 136.21, 157.69.

IR (neat, cm^{-1}): 3433.73 (m, broad), 2959.18 (s), 1593.40 (w), 1431.38 (s), 1361.92 (w), 1205.66 (m), 1066.77 (w).

MS, m/z: 264.3 (100.0%), 249.2 (100.0%), 221.2 (67.1%), 178.0 (45.5%), 110.2 (94.9%), 102.6 (24.2%), 76.7 (66.7%).

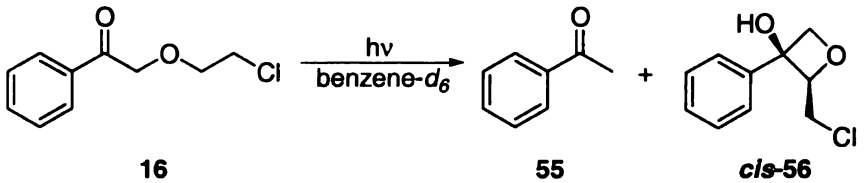
Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80.

Found: C, 80.84; H, 7.62.

m.p.: 112.2~112.9°C

Products from α-(chloroethoxy)acetophenone (**16**)

NMR experiment in benzene-d_6



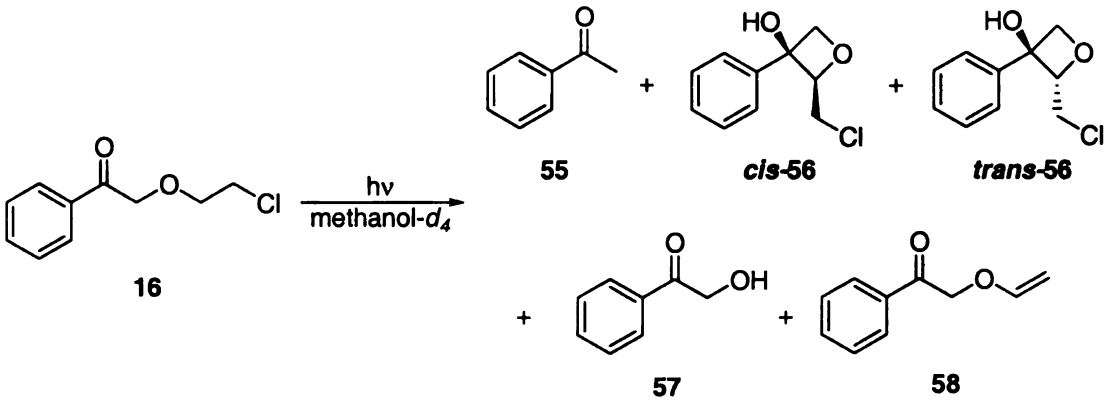
16 **55** ***cis*-56**

Scheme 107. Photoproducts from 16 in Benzene

A 0.75 mL of benzene-d_6 solution of **16** (7.1 mg, 0.036 mmol, 0.048 M) was degassed in a NMR tube. Irradiation gave two major products. The reaction was monitored by ^{1}H

NMR and was nearly complete after 30 minutes of irradiation with Pyrex filtered light (medium pressure mercury arc lamp). One of the products had a ^{1}H NMR spectrum consistent with acetophenone (**55**). The NMR solution was also injected into the gas chromatograph and had a peak with an identical retention time as **55**. The other product was determined to be ***cis*-56** based on its ^{1}H and ^{13}C NMR spectra. This reaction was repeated with the presence of pyridine which gave identical result as the one without pyridine.

NMR experiment in methanol-d_4



Scheme 108. Photoproducts from 16 in Methanol

A 0.75 mL methanol-d_4 solution of **16** (8.1 mg, 0.041 mmol, 0.055 M) was degassed. The sample was irradiated with Pyrex filtered light. After 30 minutes of irradiation, a mixture of several products including two isomeric oxetanols, acetophenone, 2-hydroxyacetophenone and a trace amount of α-vinyloxyacetophenone were detected, by their signals, upon analysis of the NMR spectrum of the photolysis mixture. The reaction was complete (100% conversion) after 1.5 hours of irradiation, ^{1}H NMR spectrum showed the disappearence of a doublet of doublet at 6.54ppm corresponding to the vinylidene proton of α-vinyloxyacetophenone (**58**).

Preparative experiment

A preparative reaction was carried out with 0.2 g (1.01 mmol, 0.025 M) of **16** in 40 mL of benzene. The preparatory scale reaction gave identical results as the NMR scale reaction. Silica gel column chromatography (hexanes: ethyl acetate 40:1~20:1) gave two major products: the first fraction eluted had the spectral data consistent with **55**, the second fraction eluted was the cyclization product ***cis*-56**. The structural assignment of the oxetanol was accomplished by performing nOe experiment: irradiation of the methine signal (octet at 5.05ppm) caused an enhancement of one of the aryl proton signals (dt at 7.53ppm). This suggests that the oxetanol has a *cis*-stereochemistry.

cis-2-chloromethyl-3-phenyl-oxetan-3-ol **(*cis*-56)**

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 2.51 (s, broad, 1H), 3.77 (dd, *J*= 5.0, 11.0 Hz, 1H), 4.10 (dd, *J*= 8.0, 11.0 Hz, 1H), 4.77 (dd, *J*= 1.0, 7.0 Hz, 1H), 4.87 (d, *J*= 7.0 Hz, 1H), 5.05 (ddd, *J*= 1.0, 5.0, 8.0 Hz, 1H), 7.34 (tt, *J*= 1.0, 7.5 Hz, 1H), 7.43 (tt, *J*= 2.0, 7.5 Hz, 2H), 7.53 (dt, *J*= 1.0, 7.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 41.67, 76.15, 82.48, 89.16, 124.90, 128.27, 128.83, 142.25.

IR (neat, cm^{-1}): 3375.86 (s, broad), 2966.90 (w), 1448.73 (m), 1176.73 (m), 1057.13 (m), 984.53 (s), 850.72 (m).

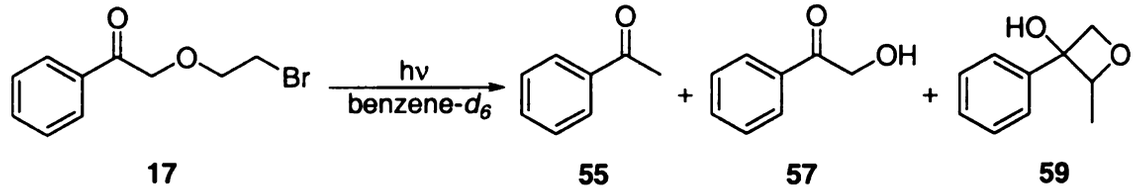
MS, m/z: 162.0 (100.0%), 147.0 (51.9%), 105.0 (96.1%), 89.1 (71.2%), 77.0 (41.7%), 51.1 (17.5%).

Anal. Calcd for $C_{10}H_{11}ClO_2$: C, 60.45; H, 5.54.

Found: C, 60.47; H, 5.56.

Products from α-(bromoethoxy)acetophenone **(17)**

NMR experiment in benzene-d_6 (without pyridine)

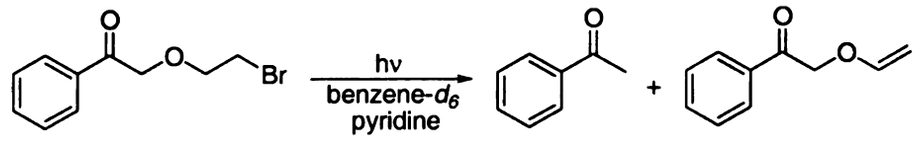


17 **55** **57** **59**

Scheme 109. Photoproducts from 17 in Benzene

A 0.75 mL benzene-d_6 solution of **17** (7.1 mg, 0.029 mmol, 0.039 M) was degassed in a NMR sample tube. The sample was irradiated with Pyrex filtered light in an immersion well setup. The well was submerged in deionized water and the reaction temperature was maintained between 17~20°C during the reaction period. The reaction was continued for 30 minutes, the starting ketone had been completely consumed and the solution had turned yellow. The ^{1}H NMR spectrum showed a mixture of **55**, **57** and trace amount of 2-methyl-3-phenyl-oxetan-3-ol (**59**).

NMR experiment in benzene-d_6 (with pyridine)



17 **55** **58**

Scheme 110. Photoproducts from 17 in Benzene With Pyridine

A 0.75 mL benzene-d_6 solution of **17** (6.7 mg, 0.027 mmol, 0.037 M) and a drop of pyridine was degassed and irradiated in an immersion well setup. The sample gave white precipitates upon irradiation, presumably the pyridinium bromide salt. After 20 minutes of reaction, 40% of the starting ketone had been consumed, the ^{1}H NMR spectrum showed the formation of two products: **55** and **58**.

NMR experiment in toluene-d_8

A solution of **17** (8.5 mg, 0.035 mmol, 0.047 M) in 0.75 mL of toluene-d_8 was degassed in a NMR tube. The sample was irradiated with Pyrex filtered light in a acetone-dry ice bath. 50% of the starting ketone had been consumed after 40 minutes of irradiation and the solution had turned yellow. ^{1}H NMR spectrum showed the formation of **55**, **57** and **59**.

NMR experiment in methanol-d_4

A solution of **17** (7.4 mg, 0.032 mmol, 0.045 M) in 0.70 mL of methanol-d_4 was degassed and irradiated. The reaction was complete after 30 minutes of irradiation. The NMR spectrum of the crude reaction sample was virtually uninterpretable due to overlapping peaks. No attempt was made to isolate the products.

Preparative experiment (without pyridine)

A preparative reaction was carried out with 0.40 g (1.65 mmol, 0.027 M) of **17** in 60 mL of benzene. The preparatory scale reaction gave an identical result as the NMR scale reaction. Silica gel column chromatography (hexanes: ethyl acetate 8:1) gave two major products: the first fraction eluted had the spectral data consistent with **55**, the second fraction eluted was **57** based on ^{1}H and ^{13}C NMR spectral data as well as the comparison with authentic sample of **57** purchased from Aldrich.

2-hydroxyacetophenone **(57)**

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 3.47 (t, *J*= 5.0 Hz, 1H), 4.86 (d, *J*= 5.0 Hz, 2H),

7.49 (t, *J*= 7.5 Hz, 2H), 7.61 (tt, *J*= 1.0, 7.5 Hz, 1H), 7.91 (dd, *J*= 1.0, 7.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 65.46, 127.69, 128.98, 133.43, 134.28, 198.39.

Preparative experiment (with pyridine)

A preparative reaction was carried out with 0.60 g (2.47 mmol, 0.031 M) of **17** and 0.39 g (5.0 mmol, 0.062 M) of pyridine in 80 mL of benzene. The reaction was nearly complete after 6 hours of irradiation. The white precipitate was filtered and solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexanes: ethyl acetate 20:1) to afford 0.1 g of **58** as white solid.

α-vinyloxyacetophenone **(58)**

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 4.13 (dd, *J*= 3.0, 6.9 Hz, 1H), 4.25 (dd, *J*= 3.0, 14.4 Hz, 1H), 4.97 (s, 2H), 6.54 (dd, *J*= 6.9, 14.4 Hz, 1H), 7.47 (t, *J*= 7.5 Hz, 2H), 7.59 (t, *J*= 7.5 Hz, 1H), 7.93 (d, *J*= 7.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 70.24, 88.02, 127.99, 128.80, 133.81, 134.58, 150.94, 194.14.

IR (neat, cm^{-1}): 1693.72 (s), 1599.19 (m), 1450.65 (m), 1230.74 (m), 1095.71 (m).

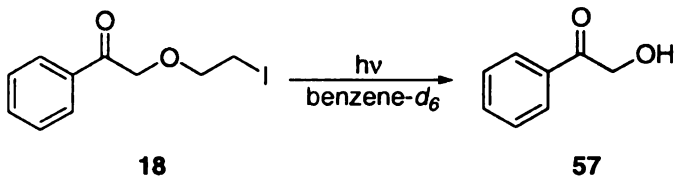
MS, m/z: 105.0 (100.0%), 77.1 (71.4%), 51.2 (15.5%).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.07; H, 6.17.

Found: C, 73.97; H, 6.31.

Products from α-(iodoethoxy)acetophenone **(18)**

NMR experiment (without pyridine)

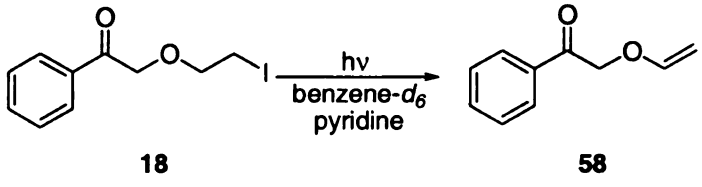


18 57

Scheme 111. Photoproduct from 18 in Benzene

A 0.75 mL benzene-d_6 solution of **18** (9.0 mg, 0.031 mmol, 0.041 M) was degassed. The sample was irradiated with Pyrex filtered light in an immersion well setup. The well was submerged in deionized water and the reaction temperature was maintained between 17~20°C during the reaction period. After 50 minutes of irradiation the sample had become dark red in color. The major product had ^{1}H NMR consistent with **57**.

NMR experiment (with pyridine)



18 58

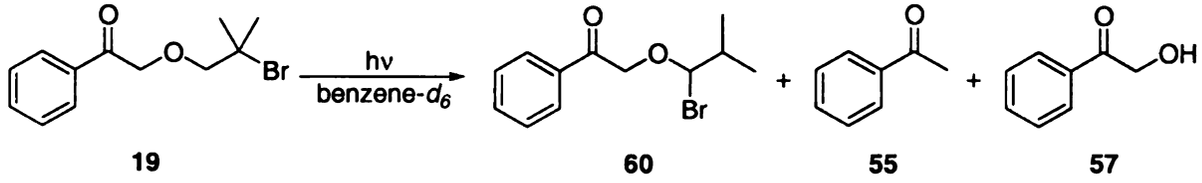
Scheme 112. Photoproduct from 18 in Benzene With Pyridine

A solution of **18** (8.4 mg, 0.029 mmol, 0.039 M) and a drop of pyridine in 0.75 mL of benzene-d_6 was degassed and irradiated. The reaction was complete after 5 hours of irradiation and gave one major product although the reaction solution gave white precipitates. The product had a ^{1}H NMR spectrum consistent with **58**.

Products from α-(2-bromo-2-methylpropoxy)acetophenone **(19)**

NMR experiment in benzene-d_6

A solution of **19** (7.6 mg, 0.028 mmol, 0.038 M) in 0.75 mL of deuterated benzene was degassed in a NMR tube. The sample was irradiated with Pyrex filtered light in an



19 60 55 57

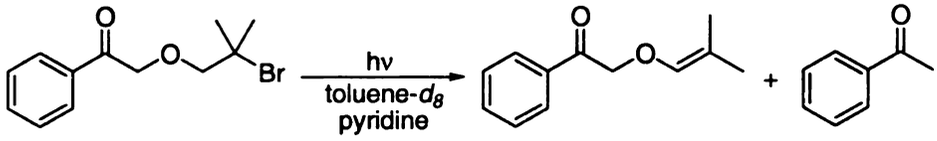
Scheme 113. Photoproducts from 19 in Benzene

immersion well setup. The reaction gave three major products: **55**, **57** and the third product had the ^{1}H NMR spectrum consistent with α-(1-bromo-2-methylpropoxy)acetophenone (**60**). No attempt was made to isolate the products. The spectroscopic data given are from the NMR mixture of photoproducts in benzene.

α-*(1-bromo-2-methylpropoxy)acetophenone* **(60)**

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 1.07 (d, *J*= 6.6 Hz, 3H), 1.13 (d, *J*= 6.6 Hz, 3H), 2.20 (ds, *J*= 3.3, 6.6 Hz, 1H), 4.53 (d, *J*= 16.0 Hz, 1H), 4.54 (d, *J*= 16.0 Hz, 1H), 5.83 (d, *J*= 3.6 Hz, 1H), can't identify aryl protons due to the peak overlap.

NMR experiment in toluene-d_8 (with pyridine)



19 61 55

Scheme 114. Photoproducts from 19 in Benzene With Pyridine

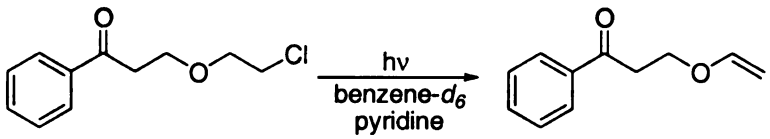
A solution of **19** (8.0 mg, 0.030 mmol, 0.040 M) and a drop of pyridine in 0.75 mL of toluene-d_8 was degassed and irradiated. The sample gave white precipitates upon irradiation. After 2 hours of irradiation the ^{1}H NMR showed the formation of two major products: **55** and **61**. No attempt was made to isolate the products. The spectroscopic data given are from the NMR mixture of photoproducts in toluene.

α-(2-methyl-1-propenoxy)acetophenone **(61)**

^{1}H NMR (300 MHz, toluene-d_8), δ ppm: 1.45 (s, 3H), 1.71 (s, 3H), 4.35 (s, 2H), 5.66 (t, *J*= 1.5 Hz, 1H), can't identify aryl protons due to the peak overlap.

Products from β-(chloroethoxy)propiophenone **(20)**

NMR experiment in benzene-d_6 (with pyridine)



20 **62**

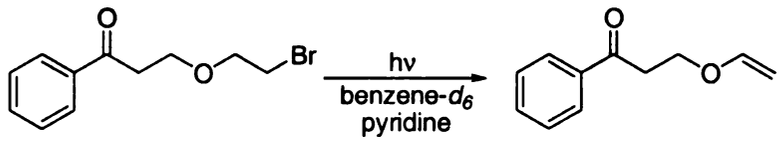
Scheme 115. Photoproduct from 20

A 0.75 mL benzene-d_6 solution of **20** (6.9 mg, 0.032 mmol, 0.043 M) and a drop of pyridine was degassed and irradiated. The reaction was monitored by ^{1}H NMR analysis periodically. The reaction was nearly complete after 2 hours of irradiation. The product was determined to be β-vinyloxypropiophenone (**62**) based on its ^{1}H and ^{13}C NMR spectra. The formation of **62** was independent of the light source employed. **62** was formed by irradiation with a medium pressure mercury arc lamp (Pyrex filtered) and 300 nm lamps in a Rayonet reactor. Each reactor gave identical results.

NMR experiment in methanol-d_4 (with pyridine)

A 0.75 mL methanol-d_4 solution of **20** (7.0 mg, 0.033 mmol, 0.044 M) and a drop of pyridine was degassed and irradiated. After 30 minutes of irradiation ^{1}H NMR spectrum showed the formation of one major product: **62**. After one hour of irradiation, the NMR spectrum of the crude reaction sample was virtually uninterpretable due to overlapping peaks.

Products from β-(bromoethoxy)propiophenone **(21)**



21 **62**

Scheme 116. Photoproduct from 21

NMR experiment (with pyridine)

A 0.75 mL benzene-d_6 solution of **21** (6.8 mg, 0.026 mmol, 0.035 M) and a drop of pyridine was degassed and irradiated. The reaction was monitored by ^{1}H NMR analysis periodically. The reaction was nearly complete after 2 hours of irradiation. The product was determined to be β-vinyloxypropiophenone (**62**) based on its ^{1}H and ^{13}C NMR spectra.

Preparative experiment (with pyridine)

A preparative reaction was carried out with 0.50 g (1.95 mmol, 0.039 M) of **21** and 0.15 g (1.90 mmol, 0.038 M) of pyridine in 50 mL of benzene. The reaction was nearly complete after 5 hours of irradiation. The white precipitate was filtered and solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexanes: ethyl acetate 30:1~20:1) to afford **62**.

β-vinyloxypropiophenone **(62)**

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.33 (t, *J*= 6.6 Hz, 2H), 4.02 (dd, *J*= 2.1, 6.9 Hz, 1H), 4.13, (t, *J*= 6.6 Hz, 2H), 4.24 (dd, *J*= 2.1, 14.4 Hz, 1H), 6.45 (dd, *J*= 6.9, 14.4 Hz, 1H), 7.46 (t, *J*= 7.8 Hz, 2H), 7.56 (t, *J*= 7.2 Hz, 1H), 7.97 (d, *J*= 7.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 37.83, 63.18, 86.96, 128.09, 128.64, 133.31,

136.78, 151.53;

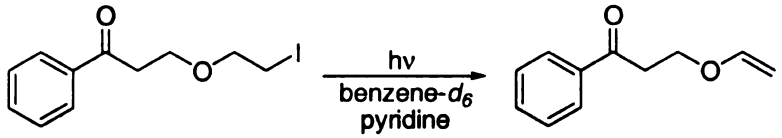
IR (film, cm^{-1}): 3067.21 (w), 2926.39 (w), 2853.08 (w), 1674.43 (s), 1616.55 (w), 1448.73 (w), 1196.02 (m), 817.92 (w).

MS, m/z: 176.2 (3.4%), 133.2 (22.6%), 105.0 (100.0%), 76.9 (72.7%), 50.8 (38.3%).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.82.

Found: C, 75.21; H, 7.01.

Products from β-(iodoethoxy)propiophenone **(22)**



22 **62**

Scheme 117. Photoproduct from 22

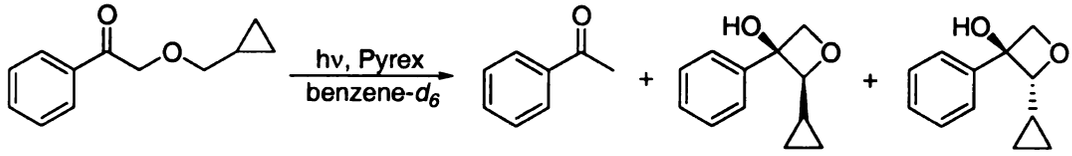
NMR experiment (with pyridine)

A 0.75 mL benzene-d_6 solution of **22** (8.1 mg, 0.027 mmol, 0.036 M) and a drop of pyridine was degassed and irradiated. The reaction was monitored by ^1H NMR analysis periodically. The reaction was nearly complete after 2 hours of irradiation. The product was determined to be β-vinyloxypropiophenone (**62**) based on its ^1H and ^{13}C NMR spectra.

Products from α-cyclopropylmethoxyacetophenone **(23)**

NMR experiment in benzene-d_6

A 0.8 mL benzene-d_6 solution of **23** (6.6 mg, 0.035 mmol, 0.043 M) was irradiated until starting material could not be observed by NMR. The signals for three products were detected in the NMR spectrum of the mixture. These products included two



23 55 *cis*-63 *trans*-63

Scheme 118. Photoproducts from 23 in Benzene

isomeric oxetanols (**cis-63** and ***trans*-63**) and **55**. The effect of temperature on product ratios was also investigated by conducting the photochemistry in ice water and silicon oil (60°C) baths. The product ratios were determined by NMR integration of the methine doublet signals of the oxetanols and the methyl singlet signal of acetophenone. The structural assignments of the oxetanols was accomplished by performing nOe experiments. Irradiation of the methine doublet at 4.08ppm in the minor isomer caused an enhancement of the OH signal, irradiation of the methine doublet at 4.30ppm in the major isomer caused an enhancement of one of the aryl proton signals. These data strongly suggest that the minor isomer has a *trans*-stereochemistry.

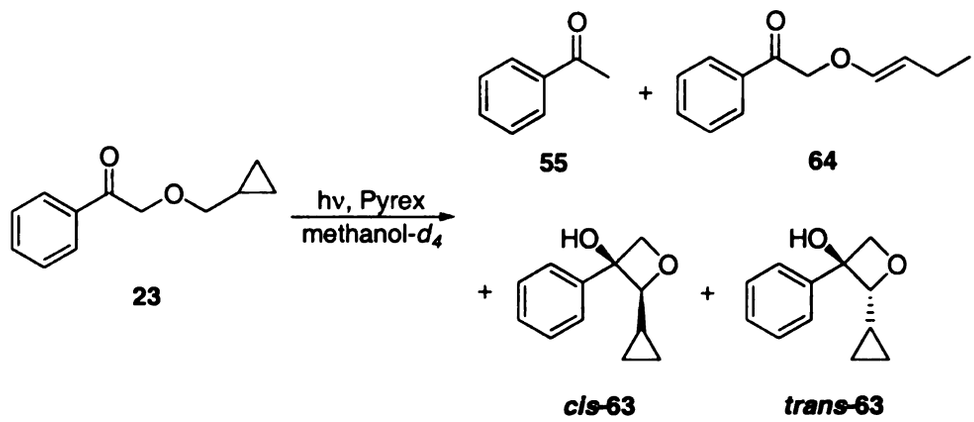
NMR experiment in toluene-d_8

23 (6.8 mg, 0.036 mmol, 0.048 M) in 0.75 mL of deuterated toluene was irradiated through Pyrex filter until no trace of starting material could be observed by NMR. The signals of two isomeric oxetanols (**63**) and acetophenone were detected upon analysis of the NMR spectrum of the photolysis mixture. In our investigation, photochemistry was conducted at various temperature to acertain the effect of temperature on product ratios. The diastereomeric ratio of oxetanols was determined by NMR integration of the methine doublet signals corresponding to each isomer.

NMR experiment in acetonitrile-d_3

A solution of **23** (7.0 mg, 0.037 mmol, 0.046 M) in 0.8 mL of acetonitrile-d_3 was degassed in an NMR tube. The sample was irradiated with Pyrex filtered light. The reaction was complete after 2 hours of irradiation and gave three major products including two isomeric oxetanols (**63**) and acetophenone. The diastereomeric ratio of oxetanols was determined by NMR integration of the methine doublet signals corresponding to each isomer.

NMR experiment in methanol-d_4



Scheme 119. Photoproducts from 23 in Methanol

23 (7.6 mg, 0.040 mmol, 0.053 M) in 0.75 mL of deuterated methanol was degassed and irradiated until no starting ketone could be observed by NMR analysis. The signals for two isomeric oxetanols (**63**), **55** and **64** were detected upon analysis of the NMR spectrum of the photolysis mixture. The diastereomeric ratio of oxetanols was determined by NMR integration of the methine doublet signals corresponding to each isomer.

Preparative experiment in t-butanol

0.5 g (2.6 mmol, 0.044 M) of **23** was dissolved in 60 mL of *t*-butanol, degassed and irradiated with Pyrex filtered light. The reaction was complete after 1.5 hours of irradiation and a pale yellow color persisted. The solvent from a small fraction of the reaction solution was removed by rotary evaporation; the residue was dissolved in $CDCl_3$ and the ^1H NMR analysis revealed a mixture of two isomeric oxetanols and acetophenone. The crude reaction mixture was separated by deactivated silica gel column chromatography (CH_2Cl_2: ethyl acetate 10:1). The first fraction eluted had the spectral data consistent with acetophenone, its NMR solution was also injected into the gas chromatograph and had a peak with an identical retention time as acetophenone, the NMR solution was also spiked with authentic acetophenone and reinjected into the gas chromatograph, only one peak was visible in the chromatogram. The ^1H NMR spectrum of the second product was consistent with the structure of ***cis*-63**; the last fraction eluted was determined to be ***trans*-63** based on spectral data.

cis-2-cyclopropyl-3-phenyl-oxetan-3-ol (***cis*-63**)

^1H NMR (500 MHz, $CDCl_3$), δ ppm: 0.25 (m, 1H), 0.52 (m, 1H), 0.62 (m, 1H), 0.74 (m, 1H), 1.40 (m, 1H), 2.79 (s, 1H), 4.30 (d, *J*= 7.5 Hz, 1H), 4.64 (dd, *J*= 1.0, 7.0 Hz, 1H), 4.84 (d, *J*= 7.0 Hz, 1H), 7.30 (tt, *J*= 1.5, 7.0 Hz, 1H), 7.40 (m, 2H), 7.55 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 0.83, 2.28, 10.30, 48.70, 82.82, 96.16, 124.60, 127.76, 128.62, 142.91.

IR (film, cm^{-1}): 3383.57 (s, broad), 2920.60 (w), 1495.02 (w), 1448.73 (w), 1170.94 (m), 1026.26 (w), 962.60 (m).

MS, m/z: 190.4 (0.3%), 172.3 (0.2%), 136.3 (7.0%), 105.2 (100.0%), 91.3 (11.2%), 77.3

(35.3%), 54.3 (60.3%).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37.

Found: C, 75.68; H, 7.39.

trans-2-cyclopropyl-3-phenyl-oxetan-3-ol (***trans*-63**)

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 0.21 (stack, 2H), 0.32 (m, 1H), 0.46 (m, 2H), 2.21 (s, 1H), 4.09 (d, *J*= 8.5 Hz, 1H), 4.68 (d, *J*= 7.5 Hz, 1H), 4.99 (dd, *J*= 1.0, 7.0 Hz, 1H), 7.34 (m, 1H), 7.42 (m, 2H), 7.59 (m, 2H).

^{1}H NMR (500 MHz, CD_3OD), δ ppm: 0.18 (m, 2H), 0.26 (m, 1H), 0.43 (m, 1H), 0.47 (m, 1H), 4.08 (d, *J*= 9.5 Hz, 1H), 4.64 (dd, *J*= 0.5, 7.0 Hz, 1H), 4.95 (dd, *J*= 1.0, 7.0 Hz, 1H), 7.30 (tt, *J*= 1.5, 7.0 Hz, 1H), 7.40 (m 2H), 7.61 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 1.41, 3.15, 12.25, 78.94, 79.69, 98.81, 126.00, 127.98, 128.41, 139.69.

IR (film, cm^{-1}): 3383.57 (s, broad), 3086.50 (w), 2882.02 (m), 1448.73 (w), 1153.58 (m), 1074.49 (m), 1026.26 (m), 954.89 (s).

MS, m/z: 172.3 (7.3%), 128.0 (7.3%), 105.3 (100.0%), 77.3 (77.6%), 51.1 (47.3%).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37.

Found: C, 75.78; H, 7.29.

Preparative experiment in methanol

A preparative reaction was carried out with 0.55 g (2.89 mmol, 0.048 M) of **23** in 60 mL of methanol. The preparatory scale reaction gave an identical result as the NMR scale reaction. Deactivated silica gel column chromatograph (dichloromethane: ethyl acetate

10:1) gave four products: **55**, **64** and two isomeric oxetanols (**63**).

α-(1-butenoxy)acetophenone **(64)**

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 0.95 (t, *J*= 7.5 Hz, 3H), 1.93 (dq, *J*= 1.5, 7.5 Hz, 2H), 4.89 (stack, 3H), 6.31 (dt, *J*= 1.5, 12.5 Hz, 1H), 7.46 (t, *J*= 8.0 Hz, 2H), 7.57 (tt, *J*= 1.5, 7.0 Hz, 1H), 7.92 (d, *J*= 7.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 14.99, 20.90, 71.42, 107.72, 128.02, 128.73, 133.65, 134.75, 144.75, 194.79.

IR (film, cm^{-1}): 2970.75 (w), 1689.86 (s), 1452.58 (w), 1290.54 (m), 1101.49 (w), 975.25 (w).

MS, m/z: 188.3 (5.9%), 160.3 (13.4%), 105.3 (94.6%), 83.3 (65.8%), 77.3 (88.7%), 55.4 (100.0%), 50.4 (32.4%).

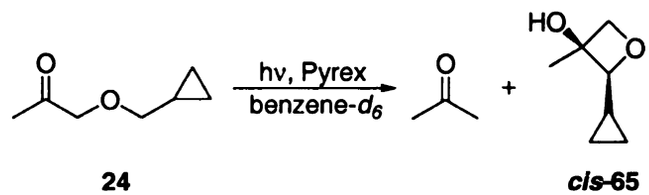
Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37.

Found: C, 75.62; H, 7.19.

Products from α-cyclopropylmethoxyacetone **(24)**

NMR experiment in benzene-d_6

A 0.6 mL benzene-d_6 solution of **24** (3.7 mg, 0.029 mmol, 0.048 M) was degassed and irradiated through Pyrex with a 450 W medium pressure mercury arc lamp. The sample

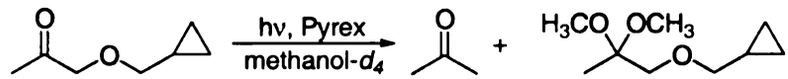


24 ***cis*-65**

Scheme 120. Photoproducts from 24 in Benzene

was hung outside the immersion well setup. The progress of the reaction was monitored by ^{1}H NMR and was complete after 12 hours. The ^{1}H NMR of the photolysis mixture showed two major products: acetone and oxetanol (***cis*-65**). The product ratio was determined by NMR integration of the methine doublet signal of the oxetanol and the methyl singlet signal of acetone. The structural assignments of the oxetanol was accomplished by performing nOe experiments. Irradiation of the methine doublet at 3.89ppm caused an enhancement of the methyl signal, this suggests that this oxetanol has a *cis*-stereochemistry.

NMR experiment in methanol-d_4



24 **66**

Scheme 121. Photoproducts from 24 in Methanol

A solution of **24** (4.4 mg, 0.034 mmol, 0.046 M) in 0.75 mL of deuterated methanol was degassed in an NMR tube. The sample was irradiated with Pyrex filtered light and the reaction was monitored by NMR analysis. After 13 hours of irradiation 50% of the starting ketone had been consumed, the ^{1}H NMR showed the formation of two major products. One of them has the ^{1}H NMR spectrum consistent with acetone, the other one was determined to be the acetal (**66**) of the starting ketone based on its ^{1}H and ^{13}C NMR spectral data.

NMR experiment in acetonitrile-d_3

A solution of **24** (5.2 mg, 0.041 mmol, 0.054 M) in 0.75 mL of acetonitrile-d_3 was

degassed and irradiated with Pyrex filtered light. After 84 hours of irradiation ^{1}H NMR spectrum showed the formation of acetone and oxetanol (**65**). However, it took almost 10 days for the starting ketone to be completely consumed.

Preparative experiment in benzene

A preparative reaction was carried out with 0.34 g (2.66 mmol, 0.044 M) of **24** in 60 mL of benzene. The preparatory scale reaction gave an identical result as the NMR scale reaction. Solvent was removed under reduced pressure, the residue was purified by column chromatography (hexanes: ethyl acetate 5:1). The first fraction eluted was recovered starting material, the second fraction eluted had the ^{1}H and ^{13}C NMR spectra consistent with oxetanol (***cis*-65**).

cis-2-cyclopropyl-3-methyl-oxetan-3-ol (***cis*-65**)

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 0.21 (m, 1H), 0.42 (m, 1H), 0.61 (stack, 2H), 1.19 (m, 1H), 1.46 (s, 3H), 2.61 (s, broad, 1H), 3.89 (d, *J*= 7.5 Hz, 1H), 4.35 (d, *J*= 10.5 Hz, 1H), 4.39 (d, *J*= 10.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 0.48, 1.78, 10.11, 25.44, 73.38, 82.60, 95.80.

IR (film, cm^{-1}): 3410.58 (s, broad), 2966.90 (s), 2876.23 (s), 1377.35 (m), 1221.10 (m), 1116.93 (m), 1026.26 (m), 964.53 (s).

MS, m/z: 128.5 (0.1%), 111.4 (0.1%), 101.3 (4.1%), 87.3 (17.7%), 57.3 (45.4%), 55.4 (100.0%), 41.4 (15.4%).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.63; H, 9.38.

Found: C, 65.62; H, 9.11.

Preparative experiment in methanol

A preparative reaction was carried out with 0.60 g (4.69 mmol, 0.059 M) of **24** in 80 mL of methanol. The sample was degassed and irradiated in a Rayonet reactor equipped with 300 nm lamps. Periodically a small aliquot of the reaction solution was taken out and analyzed by GC. The chromatogram gave a peak (~87%) with a retention time of 2.74 minutes after 20 hours of irradiation, the peak grew to ~90% of total area after 54 hours of irradiation. This compound had been isolated by column chromatography (hexanes: ethyl acetate 10:1), it was determined to be the acetal (**66**) of the starting ketone based on its ^{1}H NMR spectral data.

(2,2-dimethoxy-propoxymethyl)-cyclopropane **(66)**

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 0.17 (m, 2H), 0.49 (m, 2H), 1.03 (m, 1H), 1.33 (s, 3H), 3.20 (s, 6H), 3.31 (d, *J*= 7.0 Hz, 2H), 3.41 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 100.24, 76.06, 71.46, 48.21, 20.18, 10.31, 2.97.

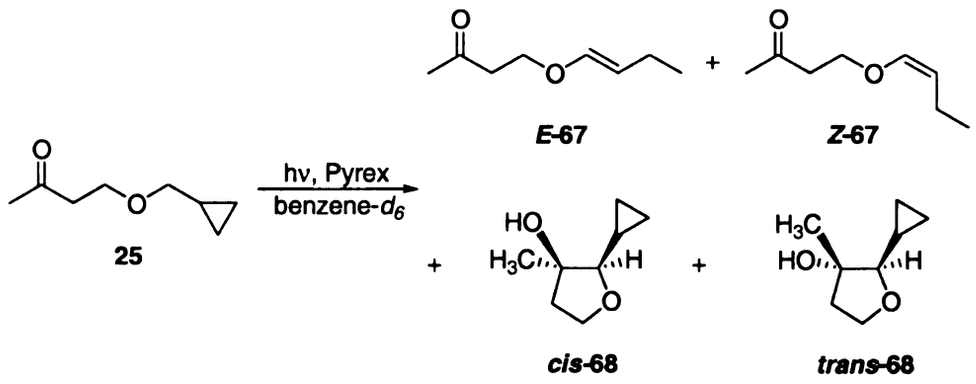
IR (film, cm^{-1}): 2943.75 (m), 2868.51 (m), 1462.23 (w), 1375.42 (m), 1251.96 (m), 1120.78 (s), 1055.20 (s).

MS, m/z: 142.0 (8.1%), 87.0 (23.3%), 71.9 (27.1%), 59.0 (36.4%), 55.1 (100.0%), 42.9 (36.4%).

Products from β-cyclopropylmethoxybutanone **(25)**

NMR experiment in benzene-d_6

A 0.75 mL benzene-d_6 solution of **25** (4.0 mg, 0.028 mmol, 0.038 M) was degassed. Irradiation was conducted with a Pyrex filtered light from a mercury arc lamp. Progress



Scheme 122. Photoproducts from 25 in Benzene

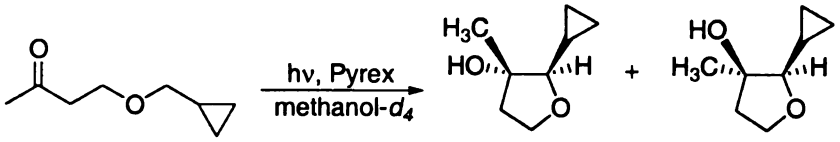
of the reaction was followed by ^{1}H NMR. The reaction was approximately 50% complete after 30 hours. Four products were detected in the NMR spectrum of the mixture and were identified as two 4-butenyloxybutanones (***E*-67** and ***Z*-67**) and two isomeric tetrahydrofurans (***cis*-68** and ***trans*-68**). Product ratio was determined by NMR integration of the vinyl proton signals of the 4-butenyloxybutanones and the methine signals (doublet) of the tetrahydrofurans.

NMR experiment in toluene-d_8

A solution of **25** (6.5 mg, 0.046 mmol, 0.057 M) in 0.8 mL of toluene-d_8 was irradiated with Pyrex filtered light at room temperature. The progress of the reaction was monitored by ^{1}H NMR analysis. After 100 hours of irradiation 70% of the starting ketone had been consumed. Four products were detected in the NMR spectrum of the photolysis mixture and were identified as ***E*-67**, ***Z*-67**, ***cis*-68** and ***trans*-68**. The effect of temperature on product ratios had also been investigated. However, at 0°C and -78°C irradiation of **25** in toluene did not give any product after 75 hours of irradiation.

NMR experiment in methanol-d_4

25 (6.6 mg, 0.046 mmol, 0.062 M) in 0.75 mL of deuterated methanol was degassed in



25 ***trans*-68** ***cis*-68**

Scheme 123. Photoproducts from 25 in Methanol

an NMR tube and irradiated with Pyrex filtered light from a medium pressure mercury arc lamp at room temperature. The reaction was monitored by ^{1}H NMR and it was approximately 50% complete after 48 hours of irradiation. Two products were detected in the NMR spectrum of the photolysis mixture and were identified as two isomeric tetrahydrofurans. The diastereomeric ratio of tetrahydrofurans was determined by NMR integration of the methine doublet signals corresponding to each isomer.

Preparative experiment

Large scale irradiation using 0.85 g (6.0 mmol, 0.060 M) of **25** in 100 mL of benzene was performed. Solvent was evaporated to leave a colorless liquid which was purified by column chromatography (hexanes: ethyl acetate 4:1). The first fraction eluted was a mixture of ***E*-67** and ***Z*-67** which could not be further separated. The stereochemistry of the double bonds was determined based on coupling constant of the vinyl protons. The second fraction eluted was recovered starting ketone. The third fraction was a mixture of two **THF**s, they were separated by column chromatography (chloroform: acetone 10:1). The structural assignments of the **THF**s was accomplished by performing nOe experiments. Irradiation of the methine doublet at 2.75ppm in the major isomer caused an enhancement of the methyl signal, irradiation of the methine signal at 2.94ppm in the

minor isomer caused an enhancement of the OH signal. These data suggest that the major isomer has a *cis*-stereochemistry and the minor isomer has a *trans*-stereochemistry.

cis-2-cyclopropyl-3-methyl-tetrahydrofuran-3-ol **(*cis*-68)**

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 0.27 (m, 1H), 0.35 (m, 1H), 0.56 (m, 2H), 0.95 (m, 1H), 1.35 (s, 3H), 1.85 (s, broad, 1H), 2.02 (stack, 2H), 2.75 (d, *J*= 8.5 Hz, 1H), 3.75 (dt, *J*= 4.5, 9.0 Hz, 1H), 3.96 (q, *J*= 8.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 1.23, 1.50, 8.32, 23.79, 41.32, 65.16, 78.36, 90.38.

IR (film, cm^{-1}): 3437.59 (s, broad), 2974.61 (s), 2880.09 (m), 1373.49 (w), 1124.64 (m), 1043.62 (s), 999.25 (m).

MS, m/z: 114.3 (5.9%), 72.5 (34.9%), 71.4 (54.1%), 57.4 (36.6%), 43.4 (100.0%).

trans-2-cyclopropyl-3-methyl-tetrahydrofuran-3-ol **(*trans*-68)**

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 0.30 (m, 2H), 0.52 (m, 2H), 0.70 (m, 1H), 1.43 (s, 3H), 1.70 (s, broad, 1H), 1.97 (stack, 2H), 2.94 (d, *J*= 8.5 Hz, 1H), 3.91 (stack, 2H).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 1.55, 2.21, 12.00, 23.08, 40.59, 65.52, 79.82, 91.91.

IR (film, cm^{-1}): 3416.37 (m, broad), 2922.53 (s), 2851.15 (s), 1462.23 (m), 1379.28 (m), 1099.56 (m), 1028.19 (m).

MS, m/z: 114.0 (4.0%), 72.2 (29.6%), 71.1 (46.4%), 57.1 (27.3%), 43.1 (100.0%).

E-4-but-1-enyloxy-2-butanone **(*E*-67)** and *Z-4-but-1-enyloxy-2-butanone* **(Z-67)**

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 0.93 (two triplets overlap, *J*= 7.5 Hz), 1.90 (qintet, *J*= 7.2 Hz), 2.01 (qintet, *J*= 7.5 Hz), 2.16 (s), 2.17 (s), 2.71 (two triplets overlap), 3.87 (t,

J= 6.3 Hz), 3.95 (t, *J*= 6.3 Hz), 4.34 (q, *J*= 6.9 Hz), 4.79 (sextet, *J*= 6.9, 12.6 Hz), 5.85 (dd, *J*= 1.5, 6.3 Hz), 6.17 (d, *J*= 12.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$), δ ppm: 14.36, 15.17, 17.31, 21.00, 30.42, 30.53, 43.02, 43.48, 63.81, 66.89, 106.70, 109.83, 143.88, 145.16, 206.49, 206.59.

IR (film, cm^{-1}): 2972.68 (w), 1710.88 (s), 1452.58 (m), 1290.54 (m), 1099.56 (w).

IV. Measurement of Quantum Yields

Solvents

Benzene- 3.5 L of reagent grade benzene was mixed with 500 mL concentrated sulfuric acid and the mixture was stirred for 2-3 days. The benzene layer was separated and was washed with 100 mL portions of concentrated sulfuric acid several times until the sulfuric acid layer did not turn yellow. The benzene was then washed with distilled water and saturated sodium bicarbonate solution. The benzene was separated, dried over magnesium sulfate and filtered into a 5 L round-bottom flask. Phosphorus pentoxide (100 g) was added and the solution was refluxed for 48 hours. After refluxing, the benzene was distilled through a one meter column packed with stainless steel helices. The first and last 10% were discarded. (b.p.: 78°C)

Benzene-d_6- The benzene-d_6 was purchased from Aldrich chemical in 5g quantities. The purity used was 99+ atom %D and was used without purification.

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

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

Internal standards

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

Methyl benzoate (**MB**)- Methyl benzoate was purified by fractional distillation.

n-Octyl benzoate (**OB**)- n-Octyl benzoate was purified by Dr. Peter J. Wagner and used without further purification.

Methyl 4-methoxybenzoate (**MMOB**)- Methyl 4-methoxybenzoate was prepared by methylation of methyl 4-hydroxybenzoate and purified by fractional distillation.

^{1}H NMR (300 MHz, $CDCl_3$), δ ppm: 3.84 (s, 3H), 3.86 (s, 3H), 6.89 (d, *J*= 9.0 Hz, 2H), 7.97 (d, *J*= 9.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ ppm: 166.82, 163.31, 131.55, 122.61, 113.56, 55.36, 51.78;

IR (film, cm^{-1}): 2968.83 (w), 1713.01 (s), 1610.77 (m), 1288.61 (s), 1107.28 (m), 1022.40 (m).

MS, m/z: 166.2 (100.0%), 135.2 (100.0%), 107.2 (44.3%), 92.2 (60.8%), 77.3 (100.0%), 70.3 (29.8%), 43.1 (100.0%).

Quencher

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

Actinometer

Valerophenone (**VP**)- Valerophenone (Aldrich Chemical) was purified by fractional distillation.

Glassware

All new glassware (syringes, volumetric flasks and pipettes) used in quantitative

measurements were rinsed with reagent grade acetone, deionized water and boiled in an Alconox (laboratory detergent) and deionized water solution for 24 hours. The glassware was rinsed and boiled in deionized water for 24 hours, this cycle was repeated 3 times. After the final rinse with deionized water, the glassware was dried at 140°C in a dedicated oven for photolysis glassware and cooled to room temperature prior to use. If the glassware was previously used, the glassware was rinsed thoroughly with HPLC grade acetone and oven dried, this cleaning (rinsing) procedure limits the inaccuracy due to glass degradation with constant Alconox washings.

Ampoules used for the irradiation were made from Alconox washed 13 x 100mm Pyrex culture tubes by flame heating approximately 2,5cm from the top with an oxygen-natural gas torch and drawing them to a uniform 15cm length.

The NMR sample tubes were prepared by the Michigan State University Glass Shop. High resolution model 535pp (pyrex, ID= 4.000mm ± ≤ 0.005'') from Wildmad Glass were fused to a 2 inch Pyrex extension and attached to a 10/30 ground glass joint. The tubes were cleaned by rinsing thoroughly with HPLC grade acetone and then oven dried. The tubes were recycled by scoring and breaking the Pyrex extension and reattaching the ground glass joint.

Preparation of samples

Solution Preparation

The solutions were prepared by weighing the desired material directly into a volumetric flask. Dilutions were made with the minimum number of transfers by volumetric pipettes. The ketone/internal standard solutions were divided equally into four

2.8 mL portions by a 5.0 mL Hamilton syringe with 20 gauge lure lock needle and placed into the pre-drawn ampoules.

In the case for NMR solutions, four 0.7 mL portions were syringed by a 1.0 mL Hamilton syringe with 20 gauge, 10 in. luer lock needle which limited the ketone solution beading to the wall of the NMR tube. In order to obtain accurate results we adapted our merry-go-round method, which was constructed for standardized test tubes.

Degassing Procedure

Previously filled irradiation ampoules were attached to a vacuum line that was evacuated for at least one hour. These tubes were arranged on a circular manifold equipped with twelve vacuum stopcocks each fitted with size 00 one hole rubber stoppers. The sample tubes were frozen in liquid nitrogen and evacuated for at least 20 minutes. The stopcocks were closed and the tubes were allowed to warm to room temperature. The freeze-pump-thaw cycle was conducted four times and the tubes sealed with an oxygen-natural gas torch while still under vacuum. In the degassing of NMR samples, it was necessary to facilitate the thawing procedure by rinsing the tubes with 95% ethanol from the top of the sample level to the bottom of the tubes. If this was not done the thawing solution would expand and crack the thin walled NMR sample tubes.

Photochemical Reaction Setup

The quantum yield measurements were conducted at 313 nm with filtered light. The 313 nm light was isolated using a solution of alkaline potassium chromate (0.002 M K_2CrO_4 in 1% aqueous potassium carbonate). Irradiation was conducted with the light

source mounted in the center of a merry-go-round setup. For NMR tubes, the 14 mm merry-go-round hole size was adapted with Teflon disk adapters (1 mm x 12 Teflon wafer with a 5 mm centered bore) to ensure the NMR tube fit snug inside of the standardized test tube. The portion of the NMR tube above the merry-go-round was wrapped with black electrical tape since the 0.7 mL volume was above this level and would have absorbed reflected light. The use of the Teflon adapter ensure the NMR sample tubes were equal distance from the light source which was mounted in the center.

Actinometry

The quantum yields for product formation were measured by irradiating ketone solutions parallel to valerophenone as an actinometer. The quantum yields were calculated using Equation 1,

Equation 1. $\Phi = [PP]/I$

where [PP] is the concentration of photoproduct and I is the intensity of light absorbed by the sample. The value of I was determined by parallel irridiation to valerophenone which forms acetophenone with a quantum yield of $\Phi_{AP} = 0.33$ at 313 nm. The acetophenone concentration was determined from Equation 2,

Equation 2. $[AP] = R_f * [IS] * A_{AP} / A_{IS}$

where,

[AP] is the concentration of acetophenone,

[IS] is the concentration of internal standard,

R_f is the instrument response factor,

A_{AP} is the integrated area of acetophenone,

A_{IS} is the integrated area of the internal standard.

The intensity of light, I, was determined from Equation 3 since [AP] is known.

Equation 3. $I = [AP]/ 0.33$

The concentration of photoproduct, [PP] was calculated from Equation 4.

Equation 4. $[PP] = R_{fPP} * [IS] * (A_{AP}/ A_{IS})$

where,

[PP] is the concentration of photoproduct,

[IS] is the concentration of internal standard,

R_{fPP} is the instrument response factor,

A_{PP} is the integrated area of product,

A_{IS} id the integrated area of the internal standard.

Quenching studies

Stern-Volmer quenching studies were performed with the appropriate triplet quencher. The Stern-Volmer expression (Equation 5) is:

Equation 5. $\Phi_0/\Phi = 1 + k_q[Q]\tau_0$

where,

Φ_0 is the quantum yield in the absence of quencher,

Φ is the quantum yield in the presence of quencher,

[Q] is the concentration of quencher,

k_q is the bimolecular rate constant for quenching,

τ_0 is the life time of the excited state being quenched.

There is a linear relation between Φ_0/Φ and the quencher concentration. When Φ_0/Φ is

plotted versus [Q], the slope is $k_q\tau_0$. The quenching is assumed to be diffusion controlled with a rate constant of 5×10^9 $M^{-1}s^{-1}$.

Quantum Yield Measurement for 2-Methoxy-3-methylbenzophenone in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 25. Product Quantum Yield of 2-Methoxy-3-methylbenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**26**	7003	53328	0.0008323	0.51
2	**26**	7797	54728	0.0009029	0.55
3	**26**	7388	51444	0.0009102	0.56
4	**26**	6122	52813	0.0007347	0.45
5	**26**	6353	53952	0.0007463	0.46
Average	**26**	6933	53253	0.0008253	0.51

ACT= VP, [VP]= 0.1008 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.004014 M; [ketone]= 0.01127 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.003986 M. Irradiation time 3 hours. Conversion= 7.3 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Methoxy-3-methylbenzophenone in Methanol

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 26. Product Quantum Yield of 2-Methoxy-3-methylbenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**26**	3938	17347	0.0006285	0.32
2	**26**	3319	15093	0.0006088	0.31
3	**26**	5105	17970	0.0007865	0.39
4	**26**	4620	17536	0.0007294	0.37
5	**26**	4242	17380	0.0006757	0.34
6	**26**	4201	16441	0.0007074	0.35
Average	**26**	4238	16961	0.0006894	0.35

ACT= VP, [VP]= 0.1002 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.003177 M; [ketone]= 0.01005 M, IS_{KET}= MB, [IS_{KET}]= 0.005324 M. Irradiation time 3 hours. Conversion= 6.9 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 3-Isopropyl-2-methoxybenzophenone in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 27. Product Quantum Yield of 3-Isopropyl-2-methoxybenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**27**	7365	55933	0.0008654	0.64
2	**27**	7198	54226	0.0008724	0.65
3	**27**	7069	54996	0.0008448	0.63
Average	**27**	7211	55052	0.0008609	0.64

ACT= VP, [VP]= 0.1008 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.004071 M; [ketone]= 0.01020 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.004057 M. Irradiation time 3.5 hours. Conversion= 8.4 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 3-Isopropyl-2-methoxybenzophenone in Methanol

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 28. Product Quantum Yield of 3-Isopropyl-2-methoxybenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**27**	6702	16695	0.0008955	0.45
2	**27**	6443	16764	0.0008674	0.44
3	**27**	7365	17266	0.0009516	0.48
4	**27**	7018	16365	0.0009567	0.48
5	**27**	6573	16245	0.0009026	0.45
Average	**27**	6820	16667	0.0009128	0.46

ACT= VP, [VP]= 0.1002 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.003177 M; [ketone]= 0.01014 M, IS_{KET}= MB, [IS_{KET}]= 0.005441 M. Irradiation time 3 hours. Conversion= 9.0 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 3-t-Butyl-2-methoxybenzophenone in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 29. Product Quantum Yield of 3-t-Butyl-2-methoxybenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**28**	12439	48878	0.001249	0.74
2	**28**	12823	47354	0.001308	0.78
3	**28**	11982	43425	0.001354	0.81
4	**28**	14383	48778	0.001447	0.86
5	**28**	12412	48787	0.001248	0.74
Average	**28**	12808	47444	0.001321	0.79

ACT= VP, [VP]= 0.1043 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.003887 M; [ketone]= 0.01021 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.003957 M. Irradiation time 2 hours. Conversion= 12.9 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 3-t-Butyl-2-methoxybenzophenone in Methanol

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 30. Product Quantum Yield of 3-t-Butyl-2-methoxybenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**28**	6492	14324	0.0009704	0.49
2	**28**	8415	16578	0.001087	0.55
3	**28**	7684	16143	0.001019	0.51
4	**28**	7425	15797	0.001006	0.50
Average	**28**	7504	15711	0.001021	0.51

ACT= VP, [VP]= 0.1002 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.003177 M; [ketone]= 0.01015 M, IS_{KET}= MB, [IS_{KET}]= 0.005353 M. Irradiation time 3 hours. Conversion= 10.1 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Ethoxy-3-methylbenzophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 97:3
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 31. Products Quantum Yield of 2-Ethoxy-3-methylbenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-29**	1654025	3069857	0.001503	0.39
2	***cis*-29**	1768669	3349770	0.001473	0.38
3	***cis*-29**	1867995	3265381	0.001596	0.41
4	***cis*-29**	1985509	3889244	0.001424	0.37
Average	***cis*-29**	1819050	3393563	0.001499	0.39

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-29**	270285	3069857	0.0002949	0.08
2	***trans*-29**	332009	3349770	0.0003320	0.09
3	***trans*-29**	360276	3265381	0.0003696	0.10
4	***trans*-29**	357911	3889244	0.0003083	0.08
Average	***trans*-29**	330120	3393563	0.0003117	0.08

ACT= VP, [VP]= 0.1003 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01051 M; [ketone]= 0.01145 M, IS_{KET}= OB, [IS_{KET}]= 0.01077 M. Irradiation time 3 hours. Conversion= 15.8 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Ethoxy-3-methylbenzophenone in Methanol

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 97:3
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 32. Products Quantum Yield of 2-Ethoxy-3-methylbenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-29**	2093021	15402006	0.0003586	0.11
2	***cis*-29**	1664169	15379874	0.0002856	0.09
3	***cis*-29**	1709047	15706222	0.0002872	0.09
4	***cis*-29**	1915236	15164859	0.0003333	0.10
5	***cis*-29**	1678344	15227359	0.0002909	0.09
Average	***cis*-29**	1811963	15376064	0.0003111	0.09

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-29**	4099983	15402006	0.0008436	0.25
2	***trans*-29**	3667472	15379874	0.0007557	0.23
3	***trans*-29**	4046209	15706222	0.0008164	0.24
4	***trans*-29**	4099182	15164859	0.0008566	0.26
5	***trans*-29**	3546696	15227359	0.0007381	0.22
Average	***trans*-29**	3891908	15376064	0.0008021	0.24

ACT= VP, [VP]= 0.1009 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01068 M; [ketone]= 0.01017 M, IS_{KET}= OB, [IS_{KET}]= 0.01019 M. Irradiation time 3 hours. Conversion= 10.9 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Ethoxy-3-isopropylbenzophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 97:3
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 33. Products Quantum Yield of 2-Ethoxy-3-isopropylbenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-30**	1375177	2884559	0.001250	0.43
2	***cis*-30**	1613032	3226327	0.001311	0.45
3	***cis*-30**	1486168	3209472	0.001215	0.42
Average	***cis*-30**	1491459	3106786	0.001259	0.43

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-30**	285140	2884559	0.0002880	0.10
2	***trans*-30**	331223	3226327	0.0002991	0.10
3	***trans*-30**	292018	3209472	0.0002651	0.09
Average	***trans*-30**	302794	3106786	0.0002841	0.10

ACT= VP, [VP]= 0.100 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01060 M; [ketone]= 0.01012 M, IS_{KET}= OB, [IS_{KET}]= 0.01075 M. Irradiation time 2.5 hours. Conversion= 15.2 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Ethoxy-3-isopropylbenzophenone in Methanol

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 97:3
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 34. Products Quantum Yield of 2-Ethoxy-3-isopropylbenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-30**	1583316	12108302	0.0003331	0.10
2	***cis*-30**	1664169	12260621	0.0003378	0.10
3	***cis*-30**	1625855	12261861	0.0003358	0.10
4	***cis*-30**	1597101	12083135	0.0003367	0.10
Average	***cis*-30**	1617610	12178480	0.0003359	0.10

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-30**	3859434	12108302	0.0009018	0.27
2	***trans*-30**	4040158	12260621	0.0009323	0.28
3	***trans*-30**	3992653	12261861	0.0009213	0.28
4	***trans*-30**	3940246	12083135	0.0009226	0.28
Average	***trans*-30**	3958123	12178480	0.0009195	0.28

ACT= VP, [VP]= 0.1009 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01068 M; [ketone]= 0.01016 M, IS_{KET}= OB, [IS_{KET}]= 0.01044 M. Irradiation time 3 hours. Conversion= 12.4 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 3-t-Butyl-2-ethoxybenzophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 97:3
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 35. Products Quantum Yield of 3-t-Butyl-2-ethoxybenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-31**	960284	2944582	0.0009005	0.53
2	***cis*-31**	970943	3006415	0.0008915	0.53
3	***cis*-31**	1084304	3087089	0.0009695	0.57
4	***cis*-31**	1001763	3202002	0.0008640	0.51
5	***cis*-31**	1140364	3486913	0.0000903	0.53
Average	***cis*-31**	1031532	3145400	0.0009055	0.53

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-31**	378139	2944582	0.0003713	0.22
2	***trans*-31**	383823	3006415	0.0003692	0.22
3	***trans*-31**	415431	3087089	0.0003891	0.23
4	***trans*-31**	389030	3202002	0.0003513	0.21
5	***trans*-31**	448683	3486913	0.0003721	0.22
Average	***trans*-31**	403021	3145400	0.0003706	0.22

ACT= VP, [VP]= 0.101 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01075 M; [ketone]= 0.009943 M, IS_{KET}= OB, [IS_{KET}]= 0.01087 M. Irradiation time 4.5 hours. Conversion= 12.9 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 3-t-Butyl-2-ethoxybenzophenone in Methanol

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 97:3
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 36. Products Quantum Yield of 3-t-Butyl-2-ethoxybenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-31**	1268137	11040178	0.0003011	0.09
2	***cis*-31**	1463886	11175273	0.0003433	0.10
3	***cis*-31**	1189772	10541632	0.0002959	0.09
4	***cis*-31**	1322986	11111558	0.0003121	0.09
5	***cis*-31**	1249445	10507371	0.0003117	0.09
Average	***cis*-31**	1298845	10875202	0.0003128	0.09

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-31**	4064690	11040178	0.001011	0.30
2	***trans*-31**	4741536	11175273	0.001165	0.35
3	***trans*-31**	3738846	10541632	0.0009736	0.29
4	***trans*-31**	4403951	11111558	0.001088	0.33
5	***trans*-31**	4084107	10507371	0.001067	0.32
Average	***trans*-31**	4206626	10875202	0.001061	0.32

ACT= VP, [VP]= 0.1009 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01068 M; [ketone]= 0.01010 M, IS_{KET}= OB, [IS_{KET}]= 0.01032 M. Irradiation time 3 hours. Conversion= 13.6 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-methylbenzophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 37. Products Quantum Yield of 2-Benzyloxy-3-methylbenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-32**	1749775	3005008	0.001736	0.58
2	***cis*-32**	1541765	2887493	0.001592	0.53
3	***cis*-32**	1851426	3020190	0.001828	0.61
4	***cis*-32**	1642339	2919449	0.001678	0.56
5	***cis*-32**	1638892	3007432	0.001625	0.54
Average	***cis*-32**	1684839	2967914	0.001692	0.56

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-32**	376496	3005008	0.0003732	0.12
2	***trans*-32**	349804	2887493	0.0003616	0.12
3	***trans*-32**	425434	3020190	0.0004201	0.14
4	***trans*-32**	359641	2910450	0.0003685	0.12
5	***trans*-32**	341804	3007432	0.0003389	0.11
Average	***trans*-32**	370636	2967914	0.0003725	0.12

ACT= VP, [VP]= 0.1006 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01258 M; [ketone]= 0.01036 M, IS_{KET}= OB, [IS_{KET}]= 0.01039 M. Irradiation time 2.5 hours. Conversion= 19.9 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-methylbenzophenone in Methanol

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 38. Products Quantum Yield of 2-Benzyloxy-3-methylbenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-32**	1152349	25940834	0.0003156	0.20
2	***cis*-32**	1225125	25273562	0.0003444	0.21
3	***cis*-32**	1316578	26460580	0.0003535	0.22
4	***cis*-32**	957385	23924716	0.0002843	0.18
5	***cis*-32**	1160469	25942198	0.0003178	0.20
Average	***cis*-32**	1162381	25508378	0.0003328	0.21

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-32**	2737374	25940834	0.0007495	0.46
2	***trans*-32**	2694473	25273562	0.0007575	0.47
3	***trans*-32**	2875658	26460580	0.0007720	0.48
4	***trans*-32**	2585594	23924716	0.0007675	0.48
5	***trans*-32**	2804635	25942198	0.0007680	0.48
Average	***trans*-32**	2739547	25508378	0.0007630	0.47

ACT= VP, [VP]= 0.1001 M; IS_{ACT}= OB, $[IS_{ACT}]$= 0.01017 M; [ketone]= 0.01032 M, IS_{KET}= MMOB, $[IS_{KET}]$= 0.001157 M. Irradiation time 3 hours. Conversion= 10.6 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-isopropylbenzophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 39. Products Quantum Yield of 2-Benzyloxy-3-isopropylbenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-33**	1131561	3449442	0.0009265	0.56
2	***cis*-33**	1081801	3175337	0.0009625	0.58
3	***cis*-33**	1088479	3216579	0.0009560	0.57
4	***cis*-33**	1086314	3228100	0.0009505	0.57
5	***cis*-33**	972562	2974809	0.0009255	0.56
Average	***cis*-33**	1072143	3208853	0.0009440	0.57

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-33**	338735	3449442	0.0002733	0.16
2	***trans*-33**	322351	3175337	0.0002825	0.17
3	***trans*-33**	321365	3216579	0.0002780	0.17
4	***trans*-33**	318791	3228100	0.0002748	0.17
5	***trans*-33**	266595	2974809	0.0002494	0.15
Average	***trans*-33**	313567	3208853	0.0002771	0.17

ACT= VP, [VP]= 0.1011 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01053 M; [ketone]= 0.01021 M, IS_{KET}= OB, [IS_{KET}]= 0.0105 M. Irradiation time 2 hours. Conversion= 12.0 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-isopropylbenzophenone in Methanol

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 40. Products Quantum Yield of 2-Benzyloxy-3-isopropylbenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-33**	1408113	26469996	0.0003834	0.24
2	***cis*-33**	1357258	26315792	0.0003717	0.23
3	***cis*-33**	1361312	27249610	0.0003600	0.22
4	***cis*-33**	1456114	28132438	0.0003730	0.23
Average	***cis*-33**	1395699	27041959	0.0003720	0.23

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-33**	2959210	26469996	0.0007975	0.49
2	***trans*-33**	2991773	26315792	0.0008110	0.50
3	***trans*-33**	3141865	27249610	0.0008225	0.51
4	***trans*-33**	3275875	28132438	0.0008305	0.51
Average	***trans*-33**	3092181	27041959	0.0008155	0.51

ACT= VP, [VP]= 0.1001 M; IS_{ACT}= OB, $[IS_{ACT}]$= 0.01017 M; [ketone]= 0.01057 M, IS_{KET}= MMOB, $[IS_{KET}]$= 0.001205 M. Irradiation time 3 hours. Conversion= 11.2 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-t-butylbenzophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 41. Products Quantum Yield of 2-Benzyloxy-3-t-butylbenzophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-34**	1099732	3438742	0.0008805	0.51
2	***cis*-34**	1151723	3305121	0.0009595	0.55
3	***cis*-34**	1040958	3145707	0.0009110	0.52
4	***cis*-34**	1027819	2844583	0.0009950	0.57
5	***cis*-34**	940908	2950084	0.0008780	0.51
Average	***cis*-34**	1052228	3136847	0.0009250	0.53

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-34**	737148	3438742	0.0005990	0.34
2	***trans*-34**	788226	3305121	0.0006665	0.38
3	***trans*-34**	715326	3145707	0.0006355	0.37
4	***trans*-34**	694686	2844583	0.0006825	0.39
5	***trans*-34**	620733	2950084	0.0005880	0.34
Average	***trans*-34**	711224	3136847	0.0006345	0.37

ACT= VP, [VP]= 0.1013 M; IS_{ACT}= OB, $[IS_{ACT}]$= 0.01044 M; [ketone]= 0.01076 M, IS_{KET}= OB, $[IS_{KET}]$= 0.01039 M. Irradiation time 1.5 hours. Conversion= 14.5 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-t-butylbenzophenone in Methanol

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 42. Products Quantum Yield of 2-Benzyloxy-3-t-butylbenzophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-34**	997494	28165682	0.0002750	0.17
2	***cis*-34**	1089359	29196418	0.0003040	0.19
3	***cis*-34**	1057382	29269584	0.0002944	0.18
4	***cis*-34**	927860	25673770	0.0002945	0.18
Average	***cis*-34**	1018024	28076364	0.0002918	0.18

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-34**	3058267	28165682	0.0008715	0.54
2	***trans*-34**	3363677	29196418	0.0009245	0.57
3	***trans*-34**	3278290	29269584	0.0008990	0.56
4	***trans*-34**	2852610	25673770	0.0008920	0.55
Average	***trans*-34**	3138211	28076364	0.0008970	0.56

ACT= VP, [VP]= 0.1001 M; IS_{ACT}= OB, $[IS_{ACT}]$= 0.01017 M; [ketone]= 0.01045 M, IS_{KET}= MMOB, $[IS_{KET}]$= 0.001349 M. Irradiation time 3 hours. Conversion= 11.4 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Ethoxy-3-methylacetophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 43. Product Quantum Yield of 2-Ethoxy-3-methylacetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-35**	1189901	11943471	0.0004312	0.040
2	***cis*-35**	1220458	11655668	0.0004531	0.042
3	***cis*-35**	1177504	12002069	0.0004245	0.039
4	***cis*-35**	1300661	12121396	0.0004644	0.043
5	***cis*-35**	1151178	11994237	0.0004154	0.038
Average	***cis*-35**	1207940	11943368	0.0004377	0.040

ACT= VP, [VP]= 0.1051 M; IS_{ACT}= OB, $[IS_{ACT}]$= 0.01115 M; [ketone]= 0.01045 M, IS_{KET}= MB, $[IS_{KET}]$= 0.01104 M. Irradiation time 14 hours. Conversion= 8.5 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Ethoxy-3-isopropylacetophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 44. Product Quantum Yield of 2-Ethoxy-3-isopropylacetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-37**	3179575	10646218	0.001067	0.084
2	***cis*-37**	3263724	10980159	0.001062	0.084
3	***cis*-37**	2866382	10478002	0.0009775	0.077
4	***cis*-37**	2789153	10899856	0.0009144	0.072
Average	***cis*-37**	3024709	10751059	0.001005	0.079

ACT= VP, [VP]= 0.0996 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01055 M; [ketone]= 0.01045 M, IS_{KET}= MB, [IS_{KET}]= 0.01021 M. Irradiation time 16.5 hours. Conversion= 14 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 3-t-Butyl-2-ethoxyacetophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 45. Product Quantum Yield of 3-t-Butyl-2-ethoxyacetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-39**	1192035	10805872	0.0003751	0.033
2	***cis*-39**	1390991	10511478	0.0004500	0.040
3	***cis*-39**	1292224	10158638	0.0004325	0.038
4	***cis*-39**	1084126	10231688	0.0003605	0.032
5	***cis*-39**	1192798	10301271	0.0003937	0.035
Average	***cis*-39**	1230435	10401789	0.0004024	0.036

ACT= VP, [VP]= 0.1002 M; IS_{ACT}= OB, [IS_{ACT}]= 0.01067 M; [ketone]= 0.01038 M, IS_{KET}= MB, [IS_{KET}]= 0.01003 M. Irradiation time 13 hours. Conversion= 4 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-methylacetophenone in Benzene

^{1}HNMR analysis: Varian Unity+_500
Relaxation time (d1)= 10 sec

Table 46. Products Quantum Yield of 2-Benzyloxy-3-methylacetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	***cis*-40**	0.31	100.00	2.995	0.027
2	***cis*-40**	0.27	100.00	2.602	0.023
3	***cis*-40**	0.26	100.00	2.504	0.022
4	***cis*-40**	0.29	100.00	2.848	0.025
5	***cis*-40**	0.30	100.00	2.946	0.026
Average	***cis*-40**	0.29	100.00	2.929	0.026

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	**43**	0.43	100.00	4.222	0.038
2	**43**	0.45	100.00	4.369	0.039
3	**43**	0.43	100.00	4.222	0.038
4	**43**	0.47	100.00	4.615	0.041
Average	**43**	0.45	100.00	4.357	0.039

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^3	Φ
1	**41**	2.14	100.00	1.048	0.094
2	**41**	2.09	100.00	1.024	0.091
3	**41**	2.12	100.00	1.039	0.093
4	**41**	2.33	100.00	1.144	0.10
Average	**41**	2.17	100.00	1.064	0.095

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	**44**	3.04	100.00	9.935	0.089
2	**44**	2.79	100.00	9.115	0.081
3	**44**	2.67	100.00	8.740	0.078
4	**44**	3.19	100.00	10.425	0.093
Average	**44**	2.92	100.00	9.554	0.085

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	**42**	0.78	100.00	2.537	0.023
2	**42**	0.92	100.00	2.995	0.027

3	**42**	1.15	100.00	3.764	0.033
4	**42**	1.06	100.00	3.469	0.031
Average	**42**	0.98	100.00	3.409	0.030

ACT= VP, [VP]= 0.1012 M; IS_{ACT}= MB, [IS_{ACT}]= 0.01147 M; [ketone]= 0.02067 M, IS_{KET}= TMS, [IS_{KET}]= 0.008182 M. Irradiation time 72 hours. Conversion= 14.9 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-isopropylacetophenone in Benzene

^{1}HNMR analysis: Varian Unity+_500
Relaxation time (d1)= 10 sec

Table 47. Products Quantum Yield of 2-Benzyloxy-3-isoprpopylacetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	***cis*-45**	0.46	100.00	3.475	0.031
2	***cis*-45**	0.42	100.00	3.208	0.029
3	***cis*-45**	0.46	100.00	3.475	0.031
4	***cis*-45**	0.51	100.00	3.895	0.035
Average	***cis*-45**	0.46	100.00	3.513	0.031

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	**48**	0.88	100.00	6.680	0.060
2	**48**	0.71	100.00	5.420	0.048
3	**48**	0.88	100.00	6.670	0.060
4	**48**	1.01	100.00	7.675	0.068
Average	**48**	0.87	100.00	6.610	0.059

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^3	Φ
1	**46**	3.22	100.00	1.230	0.11
2	**46**	2.70	100.00	1.029	0.092
3	**46**	3.24	100.00	1.237	0.11
4	**46**	3.53	100.00	1.346	0.12
Average	**46**	3.17	100.00	1.211	0.11

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^3	Φ
1	**49**	4.41	100.00	1.123	0.10
2	**49**	4.20	100.00	1.069	0.095
3	**49**	4.62	100.00	1.175	0.10
4	**49**	5.50	100.00	1.399	0.12
Average	**49**	4.41	100.00	1.122	0.10

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	**47**	0.90	100.00	2.279	0.020
2	**47**	1.24	100.00	3.157	0.028
3	**47**	1.00	100.00	2.533	0.023

4	**47**	1.15	100.00	2.915	0.026
Average	**47**	1.07	100.00	2.721	0.024

ACT= VP, [VP]= 0.1012 M; IS_{ACT}= MB, [IS_{ACT}]= 0.01147 M; [ketone]= 0.02037 M, IS_{KET}= TMS, [IS_{KET}]= 0.006364 M. Irradiation time 72 hours. Conversion= 17.8 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for 2-Benzyloxy-3-t-butylacetophenone in Benzene

^{1}HNMR analysis: Varian Unity+_500
Relaxation time (d1)= 10 sec

Table 48. Products Quantum Yield of 2-Benzyloxy-3-t-butylacetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	***cis*-50**	0.81	100.00	4.86	0.043
2	***cis*-50**	0.87	100.00	5.19	0.046
3	***cis*-50**	0.87	100.00	5.22	0.047
Average	***cis*-50**	0.85	100.00	5.09	**0.045**

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	**53**	1.17	100.00	6.990	0.062
2	**53**	1.27	100.00	7.590	0.068
3	**53**	1.16	100.00	6.960	0.062
Average	**53**	1.20	100.00	7.180	**0.064**

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^3	Φ
1	**51**	3.34	100.00	1.000	0.089
2	**51**	3.64	100.00	1.092	0.097
3	**51**	2.68	100.00	0.804	0.072
Average	**51**	3.22	100.00	0.966	**0.086**

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	**54**	2.72	100.00	5.440	0.049
2	**54**	2.95	100.00	5.900	0.053
3	**54**	2.20	100.00	4.400	0.039
Average	**54**	2.62	100.00	5.245	**0.047**

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]x10^4	Φ
1	**52**	1.50	100.00	3.000	0.027
2	**52**	1.68	100.00	3.350	0.030
3	**52**	1.87	100.00	3.730	0.033
Average	**52**	1.68	100.00	3.360	**0.030**

ACT= VP, [VP]= 0.1012 M; IS_{ACT}= MB, $[IS_{ACT}]$= 0.01147 M; [ketone]= 0.02028 M, IS_{KET}= TMS, $[IS_{KET}]$= 0.005 M. Irradiation time 72 hours. Conversion= 15.1 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for α-(Chloroethoxy)acetophenone in Benzene with Pyridine

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 49. Products Quantum Yield of α-(Chloroethoxy)acetophenone in Benzene with Pyridine

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**55**	8409	52070	0.001922	0.42
2	**55**	9975	51628	0.002300	0.50
3	**55**	8490	52033	0.001942	0.42
Average	**55**	8958	51910	0.002054	0.45

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-56**	8352	52070	0.002009	0.44
2	***cis*-56**	7731	51628	0.001876	0.41
3	***cis*-56**	8538	52033	0.002056	0.45
Average	***cis*-56**	8205	51910	0.001980	0.43

ACT= VP, [VP]= 0.1222 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.005191 M; [ketone]= 0.1227 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.005220 M; [Py]= 0.1246 M. Irradiation time 1.5 hours. Conversion= 3.3 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for α-(Chloroethoxy)acetophenone in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 50. Products Quantum Yield of α-(Chloroethoxy)acetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**55**	7248	52157	0.001578	0.48
2	**55**	6885	53322	0.001466	0.44
3	**55**	7840	52797	0.001686	0.51
4	**55**	6598	51039	0.001468	0.44
5	**55**	6698	52848	0.001439	0.43
6	**55**	7415	55856	0.001507	0.45
Average	**55**	7114	53003	0.001524	0.46

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-56**	5900	52157	0.001352	0.41
2	***cis*-56**	6148	53322	0.001378	0.42
3	***cis*-56**	6345	52797	0.001436	0.43
4	***cis*-56**	5823	51039	0.001363	0.41
5	***cis*-56**	5965	52848	0.001349	0.41
6	***cis*-56**	7005	55856	0.001499	0.45
Average	***cis*-56**	6198	53003	0.001396	0.43

ACT= VP, [VP]= 0.1165 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.004964 M; [ketone]= 0.1003 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.004979 M. Irradiation time 1.5 hours. Conversion= 2.9 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for α-(Chloroethoxy)acetophenone in Acetonitrile

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 51. Product Quantum Yield of α-(Chloroethoxy)acetophenone in Acetonitrile

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**55**	8965	22643	0.002180	0.51
2	**55**	10393	23053	0.002482	0.59
3	**55**	10828	24210	0.002462	0.58
Average	**55**	10062	23302	0.002375	0.56

ACT= VP, [VP]= 0.1002 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.005020 M; [ketone]= 0.09963 M, IS_{KET}= MB, [IS_{KET}]= 0.005735 M; [Py]= 0.1001M. Irradiation time 2 hours. Conversion= 2.4 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for α-(Bromoethoxy)acetophenone in Benzene with Pyridine

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 92:8
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 52. Products Quantum Yield of α-(Bromoethoxy)acetophenone in Benzene with Pyridine

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**58**	2845141	6599028	0.001969	0.98
2	**58**	2634157	6273533	0.001917	0.96
3	**58**	2818302	6623554	0.001943	0.97
4	**58**	2836361	6738881	0.001922	0.96
Average	**58**	2783490	6558749	0.001938	0.97

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**55**	88950	6599028	0.0000786	0.039
2	**55**	84609	6273533	0.0000786	0.039
3	**55**	88625	6623554	0.0000780	0.039
4	**55**	88321	6738881	0.0000764	0.038
Average	**55**	87673	6558749	0.0000779	0.039

ACT = VP, [VP]= 0.1003 M, IS_{ACT}= MB, [IS_{ACT}]= 0.02159 M, R_f (AP)= 0.270; [ketone]= 0.09988 M, IS_{KET}= MB, [IS_{KET}]= 0.02468 M, R_f (PP)= 0.185; [Py]= 0.09924 M. Irradiation time= 1.5 hours. Conversion= 2.0 %. Irradiation wavelength= 313nm.

Quantum Yield Measurement for α-(Bromoethoxy)acetophenone in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 53. Products Quantum Yield of α-(Bromoethoxy)acetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**55**	2039	56603	0.0003341	0.10
2	**55**	1661	52909	0.0002911	0.09
3	**55**	1719	54163	0.0002944	0.09
4	**55**	1665	59203	0.0002609	0.08
Average	**55**	1771	55720	0.0002951	0.09

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**57**	8200	56603	0.001567	0.48
2	**57**	8016	52909	0.001640	0.50
3	**57**	7825	54163	0.001564	0.48
4	**57**	8745	59203	0.001598	0.49
Average	**57**	8197	55720	0.001592	0.49

ACT= VP, [VP]= 0.1112 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.005065 M; [ketone]= 0.1118 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.004068 M. Irradiation time 2.5 hours. Conversion= 1.7 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for α-(Iodoethoxy)acetophenone in Benzene with Pyridine

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 92:8
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 54. Product Quantum Yield of α-(Iodoethoxy)acetophenone in Benzene with Pyridine

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**58**	2016267	6677598	0.001379	0.69
2	**58**	2037322	6575789	0.001415	0.71
3	**58**	2077216	6666886	0.001423	0.71
4	**58**	2141342	6701123	0.001459	0.73
Average	**58**	2068409	6655349	0.001419	0.71

ACT = VP, [VP]= 0.1003 M, IS_{ACT}= MB, [IS_{ACT}]= 0.02159 M, R_f (AP)= 0.270; [ketone]= 0.09888 M, IS_{KET}= MB, [IS_{KET}]= 0.02468 M, R_f (PP)= 0.185; [Py]= 0.09924 M. Irradiation time= 1.5 hours. Conversion= 1.4 %. Irradiation wavelength= 313nm.

Quantum Yield Measurement for α-(Iodoethoxy)acetophenone in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 55. Product Quantum Yield of α-(Iodoethoxy)acetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**57**	8116	59848	0.001888	0.30
2	**57**	6943	56753	0.001703	0.27
3	**57**	6750	56131	0.001674	0.26
4	**57**	8959	59235	0.002106	0.33
Average	**57**	7692	57992	0.001843	0.29

ACT= VP, [VP]= 0.1083 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.005050 M; [ketone]= 0.09956 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.005234 M. Irradiation time 2 hours. Conversion= 1.9 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for β-(Chloroethoxy)propiophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 92:8
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 56. Product Quantum Yield of β-(Chloroethoxy)propiophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**62**	8583762	6173298	0.005688	0.30
2	**62**	8148468	6506156	0.005123	0.27
3	**62**	8913927	8026826	0.004542	0.24
4	**62**	9423810	7709031	0.005000	0.26
Average	**62**	8767492	7103828	0.005088	0.27

ACT = VP, [VP]= 0.09990 M, IS_{ACT}= MB, [IS_{ACT}]= 0.02003 M, R_f (AP)= 0.270; [ketone]= 0.1006 M, IS_{KET}= MB, [IS_{KET}]= 0.02035 M, R_f (PP)= 0.201; [Py]= 0.09808 M. Irradiation time= 18 hours. Conversion=5.1 %. Irradiation wavelength= 313nm.

Quantum Yield Measurement for β-(Bromoethoxy)propiophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 57. Product Quantum Yield of β-(Bromoethoxy)propiophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**62**	3668457	7741138	0.002351	0.26
2	**62**	3549309	8071273	0.002181	0.25
3	**62**	4243011	8842783	0.002380	0.27
4	**62**	3645366	7640597	0.002367	0.27
Average	**62**	3776536	8073948	0.002366	0.26

ACT = VP, [VP]= 0.1003 M, IS_{ACT}= MB, [IS_{ACT}]= 0.02159 M, R_f (AP)= 0.270; [ketone]= 0.09888 M, IS_{KET}= MB, [IS_{KET}]= 0.02468 M, R_f (PP)= 0.201; [Py]= 0.09924 M. Irradiation time= 5 hours. Conversion= 2.4%. Irradiation wavelength= 313nm.

Quantum Yield Measurement for β-(Iodoethoxy)propiophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 58. Product Quantum Yield of β-(Iodoethoxy)propiophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**62**	6756031	6355221	0.003972	0.30
2	**62**	6024549	6610510	0.003405	0.26
3	**62**	4786325	6308394	0.002959	0.22
4	**62**	5578600	6781218	0.003074	0.23
5	**62**	5763102	6151670	0.003501	0.27
Average	**62**	5781721	6441403	0.003488	0.26

ACT = VP, [VP]= 0.09059 M, IS_{ACT}= MB, $[IS_{ACT}]$= 0.01909 M, R_f (AP)= 0.270; [ketone]= 0.08896 M, IS_{KET}= MB, $[IS_{KET}]$= 0.01859 M, R_f (PP)= 0.201; [Py]= 0.1002 M. Irradiation time= 8 hours. Conversion=3.9 %. Irradiation wavelength= 313nm.

Quantum Yield Measurement for α-Cyclopropylmethoxyacetophenone in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 59. Products Quantum Yield of α-Cyclopropylmethoxyacetophenone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**55**	1692273	6527340	0.001575	0.27
2	**55**	1819823	6503191	0.001700	0.29
3	**55**	1964772	6820565	0.001750	0.30
4	**55**	1627440	6179187	0.001600	0.27
Average	**55**	1773916	6507571	0.001656	0.28

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-63**	1889955	6527340	0.001954	0.33
2	***cis*-63**	1886644	6503191	0.001958	0.33
3	***cis*-63**	1867755	6820565	0.001848	0.31
4	***cis*-63**	1874811	6179187	0.002048	0.35
Average	***cis*-63**	1881893	6507571	0.001952	0.33

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-63**	579996	6527340	0.0005998	0.10
2	***trans*-63**	558407	6503191	0.0005796	0.10
3	***trans*-63**	590623	6820565	0.0005845	0.10
4	***trans*-63**	553421	6179187	0.0006045	0.10
Average	***trans*-63**	570834	6507571	0.0005921	0.10

ACT = VP, [VP]= 0.1050 M, IS_{ACT}= MB, [IS_{ACT}]= 0.02074 M; [ketone]= 0.09630 M, IS_{KET}= MB, [IS_{KET}]= 0.02250 M. Irradiation time= 4.5 hours. Conversion= 4.4 %. Irradiation wavelength= 313nm.

Quantum Yield Measurement for α-Cyclopropylmethoxyacetophenone in Methanol

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 60. Products Quantum Yield of α-Cyclopropylmethoxyacetophenone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**55**	1299578	6018519	0.001217	0.15
2	**55**	1440367	6221134	0.001305	0.16
3	**55**	1335558	6199573	0.001214	0.15
4	**55**	1246666	6058796	0.001160	0.14
Average	**55**	1329714	6124506	0.001224	0.15

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-63**	1705567	6018519	0.001775	0.22
2	***cis*-63**	1821082	6221134	0.001834	0.22
3	***cis*-63**	1765544	6199573	0.001784	0.22
4	***cis*-63**	1728459	6058796	0.001787	0.22
Average	***cis*-63**	1755222	6124506	0.001795	0.22

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-63**	708966	6018519	0.0007379	0.09
2	***trans*-63**	725663	6221134	0.0007307	0.09
3	***trans*-63**	719996	6199573	0.0007275	0.09
4	***trans*-63**	717209	6058796	0.0007415	0.09
Average	***trans*-63**	718046	6124506	0.0007344	0.09

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**64**	678886	6018519	0.0006595	0.08
2	**64**	692001	6221134	0.0006503	0.08
3	**64**	680024	6199573	0.0006413	0.08
4	**64**	684081	6058796	0.0006601	0.08
Average	**64**	683853	6124506	0.0006528	0.08

ACT = VP, [VP]= 0.1005 M, IS_{ACT}= MB, [IS_{ACT}]= 0.02046 M; [ketone]= 0.1027 M, IS_{KET}= MB, [IS_{KET}]= 0.02088 M. Irradiation time= 4 hours. Conversion= 4.3 %. Irradiation wavelength= 313nm.

Quantum Yield Measurement for α-Cyclopropylmethoxyacetone in Benzene

^{1}HNMR analysis: Varian Unity+_500
Relaxation time (d1)= 10 sec

Table 61. Products Quantum Yield of α-Cyclopropylmethoxyacetone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**Acetone**	302.97	100.00	0.06550	0.19
2	**Acetone**	422.62	100.00	0.09137	0.27
3	**Acetone**	378.02	100.00	0.08173	0.24
4	**Acetone**	413.18	100.00	0.08933	0.26
5	**Acetone**	368.86	100.00	0.07975	0.24
Average	**Acetone**	377.13	100.00	0.08555	0.25

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-65**	48.85	100.00	0.01056	0.031
2	***cis*-65**	58.40	100.00	0.01263	0.037
3	***cis*-65**	51.25	100.00	0.01108	0.033
4	***cis*-65**	59.26	100.00	0.01281	0.038
5	***cis*-65**	51.21	100.00	0.01107	0.033
Average	***cis*-65**	53.79	100.00	0.01163	0.034

ACT= VP, [VP]= 0.1057 M; IS_{ACT}= MB, $[IS_{ACT}]$= 0.02051 M; [ketone]= 0.624 M, IS_{KET}= MB, $[IS_{KET}]$= 0.02162 M. Irradiation time 353.3 hours. Conversion= 15.2 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for β-Cyclopropylmethoxybutanone in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 70°C
Hold time: 3min.
Final temperature: 220°C
Rate: 7°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 62. Products Quantum Yield of β-Cyclopropylmethoxybutanone in Benzene

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-68**	11159	36457	0.002193	0.042
2	***cis*-68**	8390	30202	0.001984	0.038
3	***cis*-68**	7410	26547	0.002000	0.038
4	***cis*-68**	9048	30063	0.002157	0.041
5	***cis*-68**	7980	26002	0.002200	0.042
6	***cis*-68**	8274	28450	0.002084	0.040
Average	***cis*-68**	8710	29620	0.002103	0.040

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-68**	3958	36457	0.0007833	0.015
2	***trans*-68**	3108	30202	0.0007400	0.014
3	***trans*-68**	2574	26547	0.0006995	0.013
4	***trans*-68**	2580	30063	0.0006192	0.012
5	***trans*-68**	2630	26002	0.0007297	0.014
6	***trans*-68**	2951	28450	0.0007483	0.014
Average	***trans*-68**	2967	29620	0.0007200	0.014

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	**67**	14787	36457	0.001682	0.032
2	**67**	11690	30202	0.001660	0.031
3	**67**	11522	26547	0.001800	0.034
4	**67**	11167	30063	0.001541	0.029
5	**67**	12227	26002	0.001950	0.037
6	**67**	10599	28450	0.001545	0.029
Average	**67**	11999	29620	0.001697	0.032

ACT= VP, [VP]= 0.1004 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.002780 M; [ketone]= 0.145 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.002454 M. Irradiation time 156 hours. Conversion= 3.1 %. Irradiation wavelength= 313 nm.

Quantum Yield Measurement for β-Cyclopropylmethoxybutanone in Methanol

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 70°C
Hold time: 3min.
Final temperature: 220°C
Rate: 7°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 63. Products Quantum Yield of β-Cyclopropylmethoxybutanone in Methanol

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***cis*-68**	18704	33583	0.004416	0.037
2	***cis*-68**	16752	34512	0.003849	0.032
3	***cis*-68**	16902	32057	0.004181	0.035
4	***cis*-68**	16885	29678	0.004511	0.038
5	***cis*-68**	18865	34119	0.004384	0.037
Average	***cis*-68**	17622	32790	0.004268	0.036

Sample #	Photoproduct (PP)	Area (PP)	Area (IS)	[PP]	Φ
1	***trans*-68**	15833	33583	0.003767	0.032
2	***trans*-68**	16542	34512	0.003830	0.032
3	***trans*-68**	15530	32057	0.003871	0.033
4	***trans*-68**	13912	29678	0.003746	0.032
5	***trans*-68**	16037	34119	0.003756	0.032
Average	***trans*-68**	15568	32790	0.003794	0.032

ACT= VP, [VP]= 0.1087 M; IS_{ACT}= C_{20}, [IS_{ACT}]= 0.005333 M; [ketone]= 0.2035 M, IS_{KET}= MB, [IS_{KET}]= 0.006147 M. Irradiation time 64 hours. Conversion= 4.0 %. Irradiation wavelength= 313 nm.

Quenching of the Product Formation in 2-Methoxy-3-methylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 64. Quenching of the Product Formation in 2-Methoxy-3-methylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.438	1.00
0.0010	0.261	1.68
0.0021	0.190	2.30
0.0031	0.149	2.95
0.0062	0.089	4.92

[ketone]= 0.01016 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.003965 M, R_f (PP)= 1.59; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 2.5 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 629.7\ M^{-1}$

Quenching of the Product Formation in 3-Isopropyl-2-methoxybenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 65. Quenching of the Product Formation in 3-Isopropyl-2-methoxybenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.471	1.00
0.0011	0.282	1.67
0.0022	0.194	2.43
0.0032	0.148	3.17
0.0077	0.076	6.16

[ketone]= 0.01009 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.003911 M, R_f (PP)= 1.62; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 2 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 673\ M^{-1}$

Quenching of the Product Formation in 3-t-Butyl-2-methoxybenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 66. Quenching of the Product Formation in 3-t-Butyl-2-methoxybenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.563	1.00
0.0012	0.396	1.42
0.0024	0.312	1.81
0.0036	0.256	2.21
0.0072	0.166	3.40

[ketone]= 0.01006 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.003972 M, R_f (PP)= 1.24; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 2 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 333.3\ M^{-1}$

Quenching of the Products Formation in 2-Ethoxy-3-methylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 67. Quenching of the Products Formation in 2-Ethoxy-3-methylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.125	1.00
0.0017	0.107	1.16
0.0033	0.097	1.28
0.0050	0.091	1.47
0.0096	0.067	1.87

[ketone]= 0.0102 M, IS_{KET}= OB, $[IS_{KET}]$= 0.01014 M, R_f(***cis*-29**)= 0.259, R_f(***trans*-29**)= 0.311; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 3 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 91.6\ M^{-1}$

Quenching of the Products Formation in 2-Ethoxy-3-isopropylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 68. Quenching of the Products Formation in 2-Ethoxy-3-isopropylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.192	1.00
0.0012	0.170	1.13
0.0023	0.156	1.23
0.0035	0.139	1.38
0.0092	0.097	1.97

[ketone]= 0.01006 M, IS_{KET}= OB, $[IS_{KET}]$= 0.01027 M, R_f (***cis*-30**)= 0.244, R_f (***trans*-30**)= 0.271; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 3 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 105.5\ M^{-1}$

Quenching of the Products Formation in 3-t-Butyl-2-ethoxybenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 69. Quenching of the Products Formation in 3-t-Butyl-2-ethoxybenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.766	1.00
0.00098	0.722	1.06
0.0020	0.676	1.13
0.0029	0.671	1.19
0.010	0.462	1.66

[ketone]= 0.01011 M, IS_{KET}= OB, $[IS_{KET}]$= 0.01049 M, R_f(***cis*-31**)= 0.254, R_f(***trans*-31**)= 0.266; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 7 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 65.7\ M^{-1}$

Quenching of the Products Formation in 2-Benzyloxy-3-methylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 70. Quenching of the Products Formation in 2-Benzyloxy-3-methylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.226	1.00
0.0057	0.203	1.12
0.0114	0.184	1.23
0.0171	0.171	1.33

[ketone]= 0.01025 M, IS_{KET}= OB, $[IS_{KET}]$= 0.0111 M, R_f(***cis*-32**)= 0.287, R_f(***trans*-32**)= 0.287; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 3 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 19.1\ M^{-1}$

Quenching of the Products Formation in 2-Benzyloxy-3-isopropylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 71. Quenching of the Products Formation in 2-Benzyloxy-3-isopropylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	Φ°/Φ
0.00	0.278	1.00
0.0020	0.248	1.12
0.0040	0.224	1.24
0.0060	0.204	1.36
0.010	0.174	1.60

[ketone]= 0.01015 M, IS_{KET}= OB, $[IS_{KET}]$= 0.01022 M, R_f (***cis*-33**)= 0.269, R_f (***trans*-33**)= 0.265; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 3 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 60\ M^{-1}$

Quenching of the Products Formation in 2-Benzyloxy-3-t-butylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 30:1
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 72. Quenching of the Products Formation in 2-Benzyloxy-3-t-butylbenzophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.199	1.00
0.0057	0.187	1.06
0.011	0.176	1.13
0.017	0.168	1.19

[ketone]= 0.01095 M, IS_{KET}= OB, $[IS_{KET}]$= 0.01046 M, R_f (***cis*-34**)= 0.265, R_f (***trans*-34**)= 0.269; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 2 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 11\ M^{-1}$

Quenching of the Products Formation in 2-Ethoxy-3-methylacetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 73. Quenching of the Products Formation in 2-Ethoxy-3-methylacetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	Φ°/Φ
0.00	0.076	1.00
0.0050	0.019	3.93
0.011	0.0090	8.41
0.020	0.0053	14.4

[ketone]= 0.01 M, IS_{KET}= MB, $[IS_{KET}]$= 0.01 M, R_f (***cis*-35**)= 0.392; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 40 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 675.9\ M^{-1}$

Quenching of the Products Formation in 2-Ethoxy-3-isopropylacetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 74. Quenching of the Products Formation in 2-Ethoxy-3-isopropylacetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.076	1.00
0.0060	0.018	4.36
0.012	0.011	7.26
0.024	0.0057	13.3

[ketone]= 0.01 M, IS_{KET}= MB, $[IS_{KET}]$= 0.01 M, R_f (***cis*-37**)= 0.35; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 18 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 511.8\ M^{-1}$

Quenching of the Products Formation in 3-t-Butyl-2-ethoxyacetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 95:5
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 75. Quenching of the Products Formation in 3-t-Butyl-2-ethoxyacetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.063	1.00
0.0059	0.024	2.63
0.012	0.015	4.27
0.024	0.0077	8.19

[ketone]= 0.01 M, IS_{KET}= MB, $[IS_{KET}]$= 0.01 M, R_f (***cis*-39**)= 0.339; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 21 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 304.7\ M^{-1}$

Quenching of the Products Formation in α-(Chloroethoxy)acetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 80°C
Hold time: 1min.
Final temperature: 220°C
Rate: 8°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 76. Quenching of the Products Formation in α-(Chloroethoxy)acetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$		$\Phi°/\Phi$	
	#1	#2	#1	#2
0.00	0.166	0.144	1.00	1.00
0.0050	0.153	0.137	1.08	1.05
0.010	0.142	0.125	1.17	1.15
0.015	0.130	0.116	1.28	1.24

[ketone]= 0.05 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.004 M, R_f (**55**)= 2.28, R_f(***cis*-56**)= 2.40; [Py]= 0.10 M. Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 3 hours. Irradiation wavelength= 313 nm.

#1 = acetophenone (**55**)
#2 = *cis*-2-chloromethyl-3-phenyl-oxetan-3-ol (***cis*-56**)

$k_q\tau_1$= 18.2 M^{-1}
$k_q\tau_2$= 16.2 M^{-1}

Quenching of the Products Formation in α-(Bromoethoxy)acetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 92:8
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 77. Quenching of the Products Formation in α-(Bromoethoxy)acetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$		Φ°/Φ	
	#1	#2	#1	#2
0.00	0.115	0.0025	1.00	1.00
0.0050	0.110	0.0024	1.05	1.05
0.010	0.104	0.0023	1.11	1.08
0.015	0.099	0.0022	1.16	1.15

[ketone]= 0.05 M, IS_{KET}= MB, $[IS_{KET}]$= 0.02 M, R_f (**55**)= 0.270, R_f (**58**)= 0.185; [Py]= 0.10 M. Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 3 hours. Irradiation wavelength= 313 nm.

#1 = acetophenone (**55**)
#2 = α-vinyloxyacetophenone (**58**)

$k_q\tau_1 = 10.8\ M^{-1}$
$k_q\tau_2 = 9.6\ M^{-1}$

Quenching of the Product Formation in α-(Iodoethoxy)acetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 92:8
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 78. Quenching of the Product Formation in α-(Iodoethoxy)acetophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.079	1.00
0.0050	0.077	1.04
0.010	0.074	1.07
0.020	0.069	1.15
0.030	0.065	1.22

[ketone]= 0.05 M, IS_{KET}= MB, $[IS_{KET}]$= 0.02 M, R_f (PP)= 0.185; [Py]= 0.10 M. Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 3 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 7.4\ M^{-1}$

Quenching of the Product Formation in β-(Chloroethoxy)propiophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 92:8
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 79. Quenching of the Product Formation in β-(Chloroethoxy)propiophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.271	1.00
0.0046	0.067	4.06
0.012	0.032	8.60
0.016	0.025	10.95
0.032	0.013	20.35

[ketone]= 0.05 M, IS_{KET}= MB, $[IS_{KET}]$= 0.02 M, R_f (PP)= 0.201; [Py]= 0.10 M. Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 24 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 604.8\ M^{-1}$

Quenching of the Product Formation in β-(Bromoethoxy)propiophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 92:8
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 80. Quenching of the Product Formation in β-(Bromoethoxy)propiophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.210	1.00
0.0051	0.063	3.33
0.010	0.038	5.56
0.015	0.027	7.85
0.020	0.021	10.0

[ketone]= 0.05 M, IS_{KET}= MB, [IS_{KET}]= 0.02 M, R_f (PP)= 0.201; [Py]= 0.10 M. Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 14 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 450.8\ M^{-1}$

Quenching of the Product Formation in β-(Iodoethoxy)propiophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

HPLC analysis: Rainin with Dynamax
Column: Dynamax normal phase
Solvent system: Hexanes: Ethyl Acetate
Solvent ratio: 92:8
Flow rate: 1.0 mL/min
Loop: 20 μL
Detection wave length: 270nm

Table 81. Quenching of the Product Formation in β-(Iodoethoxy)propiophenone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	0.054	1.00
0.0053	0.037	1.45
0.011	0.028	1.91
0.022	0.019	2.88

[ketone]= 0.05 M, IS_{KET}= MB, $[IS_{KET}]$= 0.02 M, R_f (PP)= 0.201; [Py]= 0.10 M. Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 10 hours. Irradiation wavelength= 313 nm.

$k_q\tau = 85.4\ M^{-1}$

Quenching of the Products Formation in β-Cyclopropylmethoxybutanone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

GC analysis: Varian 3400
Column: DB-210
Initial temperature: 70°C
Hold time: 3min.
Final temperature: 220°C
Rate: 7°C/min.
Injector temperature: 200°C
Detector temperature: 220°C

Table 82. Quenching of the Products Formation in β-Cyclopropylmethoxybutanone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(PP)}/A_{(IS)}$		$\Phi°/\Phi$	
	#1	#2	#1	#2
0.00	9.21	2.73	1.00	1.00
0.010	7.23	2.63	1.51	1.04
0.020	5.45	2.52	1.87	1.08
0.040	4.11	2.31	2.56	1.18
0.063	3.27	2.21	3.35	1.24
0.084	2.71	2.05	3.84	1.33
0.104	2.53	2.01	4.41	1.36
0.125	2.19	1.92	4.64	1.42
0.234	2.03	1.78	5.13	1.53
0.283	1.92	1.75	5.25	1.56

[ketone]= 0.2 M, IS_{KET}= C_{20}, [IS_{KET}]= 0.0033 M; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 402 hours. Irradiation wavelength= 313 nm.

#1 = cyclization products
#2 = rearrangement products

Quenching of Starting Material Disappearence in α-Cyclopropylmethoxyacetone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

^{1}HNMR analysis: Varian Unity+_500
Relaxation time (d1)= 10 sec

Table 83. Quenching of Starting Material Disappearence in α-Cyclopropylmethoxyacetone with 2,5-Dimethyl-2,4-hexadiene at 313 nm in Benzene

[Q]	$A_{(SM)}/A_{(IS)}$	$\Phi°/\Phi$
0.00	3.90	1.00
0.01309	4.29	1.10
0.03909	4.60	1.18
0.06218	4.72	1.21
0.08636	4.84	1.24
0.1374	4.95	1.27
0.2748	5.03	1.29
0.4122	5.06	1.30

[ketone]= 0.2 M, IS_{KET}= MB, $[IS_{KET}]$= 0.02 M; Q= 2,5-dimethyl-2,4-hexadiene. Irradiation time= 432 hours. Irradiation wavelength= 313 nm.

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