PHOTOENOLIZATION AND TYPE II PHOTOREACTION OF <u>ORTHO</u>-ALKYL PHENYL KETONES

A Dissertation
for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Andy Chi-Peng Chen
1977

This is to certify that the

thesis entitled

photoenolization and type II photoreaction of ortho-Alkyl phenyl ketones

presented by

Andy Chi-Peng Chen

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Chemistry

Peter Wagner
Major professor

Date July 14, 1977

O-7639

ABSTRACT

PHOTOENOLIZATION AND TYPE II PHOTOREACTION OF *ORTHO*-ALKYL PHENYL KETONES

By

Andy Chi-Peng Chen

Photochemical studies of a series of *ortho*-alkyl substituted phenyl ketones were conducted primarily to determine the mechanism and kinetics of photoenolization reaction, particularly conformational effects on photoreactivities. The other major objective was to determine the substituent effect of an *ortho*-methyl group on type II reactivity. The low type II quantum yields for *0*-methylbutyrophenone, *o*-methylvalerophenone, and *o*-methyl γ-methylvalerophenone results from a combination of low yield of long-lived triplet, low probability for product formation from the biradical intermediate, and competing enolization. An *ortho*-methyl substituent decreases the type II rate constant by a factor of 3.3, which is comparable to the decrease produced by a *meta*-methyl stustitution.

The ability of *ortho*-methyl phenyl ketones to photosensitize the *cis*-*trans* isomerization of 1,3-pentadiene indicates that such ketones form two triplets, one short-lived (∿0.3 nsec) and one long-lived (∿35 nsec). Quantitative studies of the type II photoelimination of *ortho*-alkyl ketones indicate that the reaction proceeds from the long-lived triplet. The competing reaction of this triplet is

presumed to be photoenolization, but its rate ($k_e = 3 \times 10^7$ sec^{-1}) is the same for _ortho_-CH_3, CD_3 and C_2H_5. Since k_e is independent of C-H bond strength, it must be concluded that the rate determining step for enolization of the long-lived triplet is not hydrogen abstraction. 8-Methyl-1-tetralone, a model for _syn_-_o_-methylacetophenone, also sensitizes the _cis_-_trans_ isormerization of 1,3-pentadiene, but displays a linear reciprocal quantum yield plot, and therefore has only one short-lived triplet.

It is concluded that the photoenolization of _ortho_-alkylphenyl ketones is dominated by conformational factors, in particular the ground state _syn_/_anti_ ratio and the rate for _anti_→_syn_ rotation in the excited state. The quantum yield for formation of long-lived triplet in fact measures the percentage of _anti_ ground states in what is presumably a rapid conformational equilibrium. The rate-determining step for enolization of the _anti_ triplet is rotation to a _syn_ conformation ($k_e = 3 \times 10^7$ sec^{-1}) in which enolization is very rapid ($k > 10^9$ s^{-1}).

Although the 2,6-disubstituted phenyl ketones probably have only one principal ground state conformation, two kinetically distinct triplets have been observed in sensitization studies. The long-lived triplet decays with a rate of 5×10^7 sec^{-1} but does not produce benzocyclobutenol; the short-lived one forms benzocyclobutenol with a rate of $\sim 10^9$ sec^{-1}.

PHOTOENOLIZATION AND TYPE II PHOTOREACTION OF *ORTHO*-ALKYL PHENYL KETONES

By

Andy Chi-Peng Chen

A DISSERTATION

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1977

To

My Wife

and

My Son

ACKNOWLEDGMENTS

First and formost, this author gratefully adknowledges Professor Peter J. Wagner for his guidance, support and encouragement throughout the course of this research.

The author thanks the Department of Chemistry for its excellent faculty and for the use of its fine research facilities.

Thanks is due my fellow graduate students, and especially those of the Wagner Group, for many enjoyable associations during my stay at Michigan State.

The author takes pleasure to thank Eastman Kodak Company, I.E. du Pont de Nemours & Co. Inc. and National Science foundation for a three-year Quill Fellowship administered by the Department of Chemistry at Michigan State University.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

DISCUSSION

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

INTRODUCTION

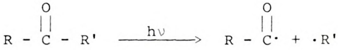
I. Photophysical processes

The creation of an electronically excited molecule results in the occurrence of photochemical as well as photophysical processes. An understanding of the photophysical processes is essential to fully appreciate the photochemical processes, and vice versa. A modified Jablonski diagram[1] is shown in Figure 1 to illustrate the photophysical processes for a typical organic molecule. Selection rules require that the spin angular momentum of the ground state be conserved in the light absorption process,[2] so that triplet states are generally populated by intersystem crossing from the directly excited singlet. Because of rapid vibrational relaxation in solution, only the lowest singlet and triplet excited states generally participate in chemical reactions.

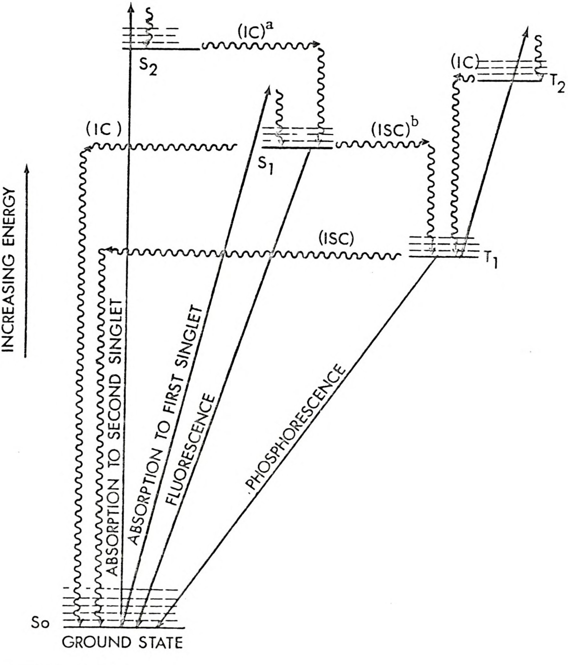
II. Photochemical Processes

1. The Norrish Type I Photoprocesses

The Norrish type I process of ketones involve the homolytic scission of the bond between the carbonly carbon and the α-carbon to give acyl and alkyl radicals[3] which go on to form various stable products.



$$R - \overset{\overset{\displaystyle O}{||}}{C} - R' \xrightarrow{h\nu} R - \overset{\overset{\displaystyle O}{||}}{C}\cdot + \cdot R'$$



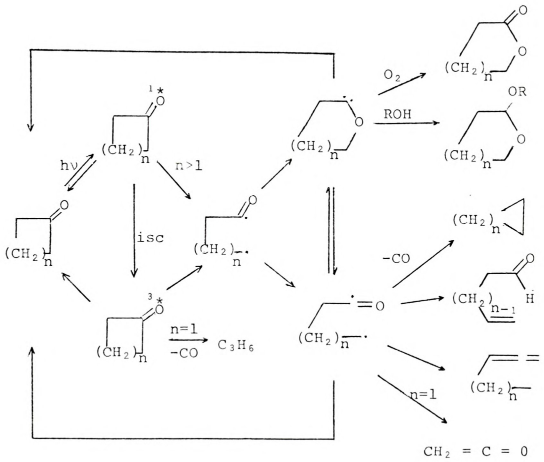
---

[a] Internal conversion.

[b] Intersystem crossing.

Figure 1. Photophysical transitions between electronic states in a typical organic molecule.

It is known that pivalophenone undergoes type I cleavage in solution through its triplet excited state.[4] Many investigations of type I reactions of cycloalkanones have been conducted.[5] The photochemical reaction pathways of cyclic ketones in solution are summarized in the following scheme.[6]

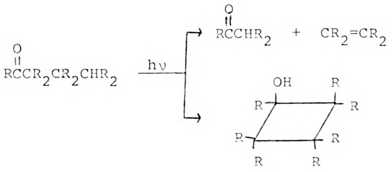


In the case of ketones with differing degrees of α-alkyl substitution, type I cleavage generally results in the formation of the more stable alkyl radical and the corresponding acyl radical.[5] The introduction of either α-methyl substituents,[7] or ring strain[8,9] in cyclic alkanones increases the rate constant for α-cleavage from the triplet state; it is likely that the rate constant for α-cleavage from the singlet excited state also increases.[10] Di-t-butyl ketone undergoes the type I process with a rate constant of 6 x 10^7 sec^{-1} from the singlet excited state and with a rate constant of 7 - 9 x 10^9 sec^{-1} from the triplet state.[11] An analogous difference of at least two orders of magnitude is also observed in the reactivities of the singlet and triplet excited states of cyclic alkanones toward α-cleavage.[10]

2. The Norrish Type II Photoprocesses

a. Definition

Carbonyl compounds containing γ C-H bonds undergo, upon electronic excitation, characteristic 1,5-hydrogen shifts to yield both cleavage and cyclization products. The cleavage reaction is commonly called Norrish type II photoelimination, after its discoverer.[12] Cyclobutanol formation, which generally accompanies cleavage, was first reported by Yang in 1958.[13] Together they are called the type II photoprocesses.[14] (Equation 1).



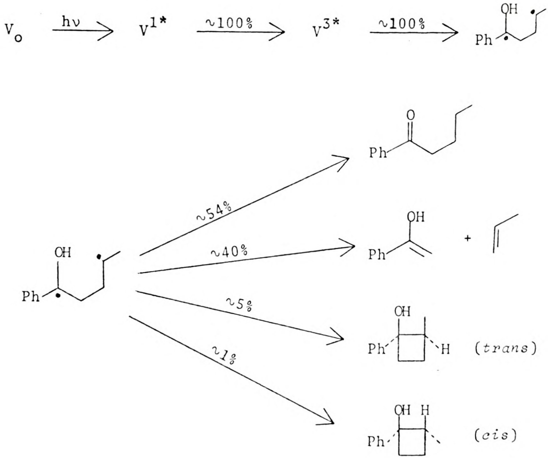
(1)

b. Multiplicity of Reactive Excited States

It is well established that aliphatic ketones undergo type II elimination from both singlet and triplet n,π^* states.[15-17] The evidence is that only part of the reaction can be quenched by conjugated dienes, which are very efficient triplet quenchers but inefficient singlet quenchers.[14] Cyclobutanol formation, however, occurs mostly from the triplet state.[15-17] This fact is evidenced by a significant decrease in the ratio of cyclization to elimination products with increasing concentrations of triplet quencher. The Type II cyclization and elimination reactions of aromatic ketones apparently occur only from triplet states since intersystem crossing quantum yields are generally unity.[18]

c. The 1,4-biradical Intermediates in Triplet-State Reactions

A 1,4-biradical intermediate has been demonstrated, with little doubt, to intervene in triplet state type II reactions.[19] The fact that this intermediate can undergo reversal of the hydrogen abstraction process, as well as product formation, was not taken into account by early studies which tried to compare quantum yields to triplet reactivity.[20-22] Wagner has shown that added Lewis bases maximize quantum yields by eliminating the reverse hydrogen transfer.[23] Furthermore, the biradical of γ-methoxy valerophenone was actually trapped using alkyl thiols as trapping agents. Using the photoprocesses of valerohenone, V, as an example, the following scheme reveals the mechanism of the type II process in phenyl alkyl ketones.[19]



The partitioning of the biradical between the various processes varies according to the structure of each specific ketone.

d. Effects of Ring Substituents in the Type II Photoreactions

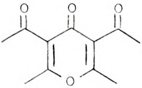
The effects of ring substituents on the type II reactions have been studied to ascertain structure-reactivity relationships. For meta and para substituents, there are two effects which determine quantum yields in type II reactions. The first is an inductive effect on the disproportionation of the biradical and the second is the lowering of the reactivity of the triplet through inversion of the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ triplets.[24] The increase in reactivity for the strongly electron withdrawing groups seems to be an inductive effect on the already electrophilic triplet.[25,26] It is now well established that ketones with π,π^* lowest triplet are appreciably less reactive than those with n,π^* triplets in type II reactions.[27,28] Since the $^3(\pi,\pi^*)$ lies only a few Kcal above the $^3(n,\pi^*)$ in phenyl alkyl ketones, electron donating substituents or a highly polar solvent can invert the ordering of the states.[29,31] It has been suggested that vibronic mixing [32,33] of the two triplets might induce n,π^*-like reactivity in the lowest triplet. Wagner has shown that when the two triplets are close enough in energy to equilibrate thermally before decaying, hydrogen abstraction can occur from low concentrations of n,π^* triplets even when the π,π^* triplets are lower.[28,34] The effects of ring methyl and polymethyl substitution on photoreactivity of butyrophenones and valerophenones has been determined by Wagner et al.[35] The effect of a _meta_ or _para_ methyl is to increase the energetic separation between the reactive n,π^* triplet and the lower π,π^* triplet. As the energy difference E_T between n,π^* and π,π^* triplets of the methylated ketones increased, the observed rate constants for the type II reaction decreases and is proportional to $(-\Delta E_T/RT)$. These results seem to indicate that reactivity arise from equilibrium levels of the upper n,π* states, rather than from vibronic mixing of the n,π* and π,π* states.

For *ortho* substituents, a steric effect will be operative along with the electronic effect. The substitution of an *o*-alkyl group also introduce a competing enolization reaction. This reaction has been known for a long time and has been subjected to flash spectroscopy studies but not to a combination of quenching and sensitization techniques. Further evidence concerning the mechanism and kinetics of the photoenolization reaction comprises a major part of the research presented herein. The photoenolization reaction will be reviewed and the kinetics involved will be derived in the next two sections.

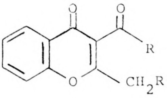
III. Photoenolization Reaction

1. Early Observations

In 1904 Collie[36] observed that crystals of pyrone **1**, upon exposure to sunlight, turned brilliant yellow and that the color faded upon melting the crystals or disolving them in a solvent. This early report of photochromism was followed by Ullman's observations on some chromone derivatives **2**.[37] Aryl ketones with *ortho* alkyl substituents are



1

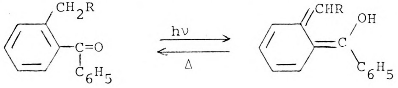


2a, $R=C_6H_5$

b, $R=CH_3$

noteworthy for their photochemical stability. For example, the photoreduction of benzophenone to benzopinacol is markedly suppressed when the ortho position is substituted by an alkyl group containing an α-hydrogen ($-CHR_2$). Thus, for o-methylbenzophenone, $\Phi_{reduction} = 0.055$ in 2-propanol.[38] In contrast, both 3-methylbenzophenone and 4-methylbenzophenone show high quantum yields, $\Phi_{reduction} =$ ca. 0.5.

In an important paper published in 1961,[39] Yang and Rivas showed that this effect was due neither to adverse electronic interactions nor to steric hindrance, but rather to an internal hydrogen abstraction which yields an enol isomer of the ketone (Equation 2). Photoenolization of this type has been demonstrated by the following observations. When a solution of 3a in Ch_3OD was irradiated, the recovered 3a was found to contain 1.04-1.09 atoms of deuterium per molecule. By nmr spectrometry all the deuterium atoms were found to be located at the benzylic position. Also, the photoenol 4b or o-methylbenzophenone reacts smoothly with dimethyl acetylenedicarboxylate, a dienophile, to give an adduct 5 in



(2)

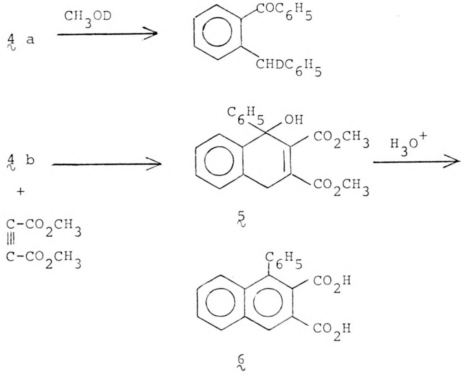
3a, $R=C_6H_5$

b, $R=H$

4a, $R=C_6H_5$

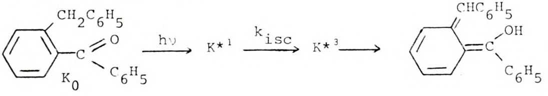
b, $R=H$

excellent yield. The structure of 5 was established by its conversion to 1-phenylnaphthalene-2,3-dicarboxylic acid 6, identical in all respects with an authentic sample.



2. The Mechanism

Most early studies of photoenolization were centered around 2-alkylbenzophenones. Detection of the triplet ketone species in a photoenolization reaction was first reported by Yang et al.[40] Thus, flash photolysis of 2-benzylbenzophenone produced two species of lifetimes ca. 10 S and 500 μs. The longer-lived species was assigned as a dienol and the shorter-lived species as the n,π* triplet (Equation 3).



(3)

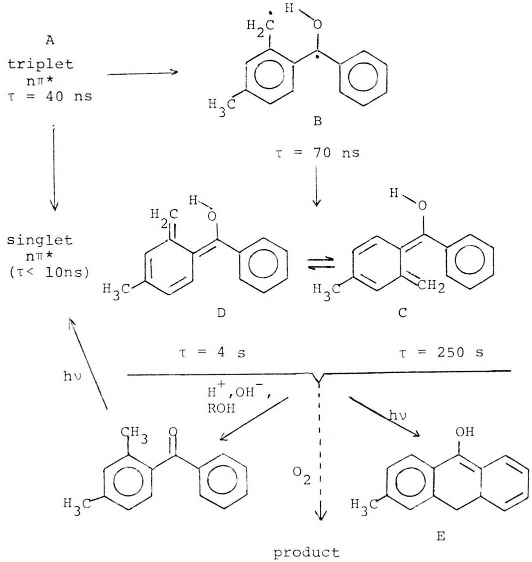
The latter assignment, however, was subsequently discounted by Porter and Tchir[41] on the basis of known lifetimes of triplet states for benzophenone in hydrogen donating solvents. In a more extensive investigation, Porter and Tchir[41,42] detected five transients in the conventional and laser flash photolysis of 2,4-dimethylbenzophenone. The transients observed and their lifetimes in ethanol and cyclohexane are listed in Table 1.

Table 1. Transients observed with 2,4-dimethylbenzophenone

		Lifetimes		
Transient	$\lambda_{max.}$/nm	Cyclohexane	Cyclohexane-O_2	EtOH
(A)	535	38 ns	38 ns	28 ns
(B)	420	67 ns	67 ns	1.7 μs
(C)	390	250 s	20 ms	1.9 s
(D)	430	3.9 s	9.5 ms	1.7 s
(E)	390	Hours		Hours

The reaction pathway and structural assignments of the transients is given in the following scheme. The initial n,π* singlet state is extremely short-lived (10 ps) and undergoes intersystem crossing with unit efficiency.

The corresponding triplet state has a lifetime of 40 ns (A) and further decays to a transient of lifetime 67 ns (B). The nature of this species will be discussed later. The transients C and D were assigned the two isomeric enol structures. The isomer C decays more slowly than D presumably because it cannot undergo internal tautomerization. The absorption



spectrum of transient E is the same as that reported by Ullman[43] for an intermediate to which he assigned a dihydroanthrone structure. The formation of transient E, by a "photo-Elbs" reaction, would be avoided when light of longer wavelength was filtered out.[42,44] A low yield of anthrone was isolated on addition of oxygen to this intermediate and further photooxidation would eventually give anthraquinone.

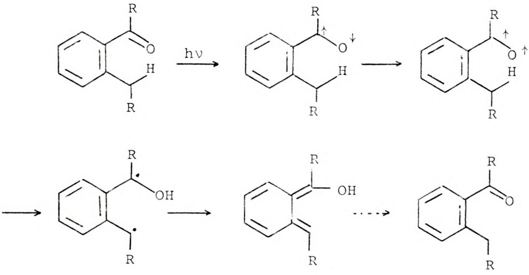
In a study of the photoenolization of some photochromic chromones, Ullman et al.[37] suggested that a triplet state of enol intervenes between the triplet state of the ketone and the ground state of the enol (step 3). This

$$\begin{array}{lll} K_o \longrightarrow {}^1K & & \\ {}^1K \longrightarrow {}^3K & & \text{(step 3)} \\ {}^3K \longrightarrow {}^3E & & \\ {}^3E \longrightarrow E_o & & \end{array}$$

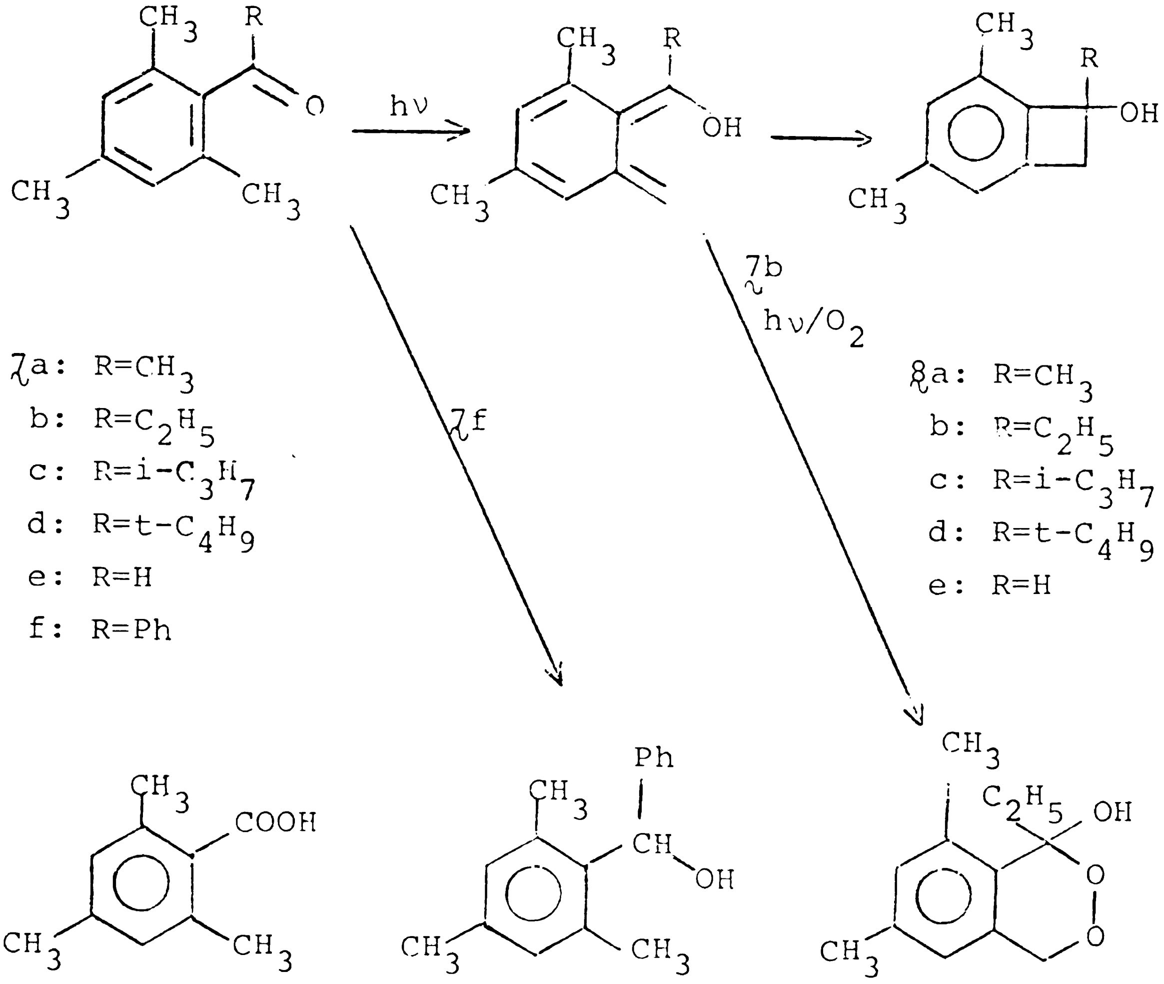
proposal was based on the fact that although the chromone 2a undergoes photoenolization, the corresponding 2-methyl analogue 2b does not. Ullman argured that since the chromophores of two compounds are virtually identical, their reactvities must be controlled by the nature of the products. However, the energies of the ground states of the two corresponding enols should be comparable since both have energy levels lying well below the level of their triplet state precursors. On the other hand if excited states of the enols were formed as intermediates, the more conjugated excited photoenol of the benzyl derivative 2a might be expected to be substantially less energetic than that of 2b.

Porter and Tchir suggested later[41] that this species, corresponding to transient B observed in flash photolysis, might be a "twisted" or "orthogonal" triplet state, a molecule which might be described as a 1,4-biradical. However, the destabilization of this species by a phenyl group and its insensitivity to oxygen would argue against this assignment. A further complication was that no single transient arising directly from the decay of this species was observed. Therefore, no definite assignment of this species was made.

The most commonly accepted mechanism for photoenolization is outlined in the following scheme.



The introduction of a second ortho-substituent into the ketones causes a drastic change in photobehaviour. For example, the transients observed in the flash photolysis of 2,6-dimethylbenzophenone[41] are not at all similar to those observed with ortho-substituted benzophenones and no assignments were suggested. In an extensive study of 2,4,6-trialkylphenylketones, Matsuura and Kitaura[45] noted that cyclobutenol formation was the preferred course of reaction. Even though no Diels-Alder adducts were observed, deuterium exchange was noted when the ketones were irradiated in CH_3OD fo long periods. They deduced that dienols were first formed and then underwent ring closure to give the cylobutenols. The following scheme describes some of the reactions of 2,4,6-trialkylphenylketones.

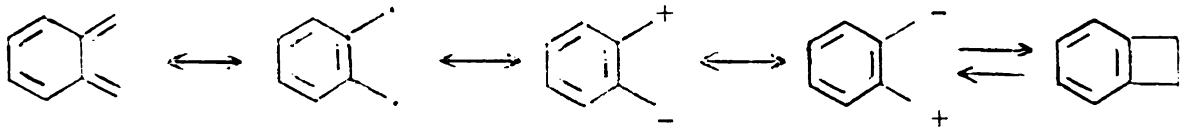


7a: R=CH_3
b: R=C_2H_5
c: R=i-C_3H_7
d: R=t-C_4H_9
e: R=H
f: R=Ph

8a: R=CH_3
b: R=C_2H_5
c: R=i-C_3H_7
d: R=t-C_4H_9
e: R=H

9 10 11

Since the photoinduced enols are hydroxy-o-quinodimethanes (o-xylylnes), it is worthwhile to examine the nature of the electronic structure of oxylylene. Commonly asked questions about its electronic structure involve the relative importance of structures such as 12a-12c in various electronic states; preferred geometry; and reaction modes of each state. Both theoretical arguments[46,47] and spectroscopic studies[48,49] suggest that o-xylylene has a ground state singlet. Its S_1



12 12a 12b 12c 13

state is planar (tight biradicaloid geometry, i.e., the two nonbonding orbitals in the same general region of space), while in T_1 loose geometries are preferred, i.e., one CH_2 group twisted out of the plane of the ring and the two orbitals in separate regions of space. Recent calculations based on Pariser-Parr-Pople (PPP) approximations suggest that the ground state of 12 deviates from the image of a "perfect" biradicaloid molecule.[48] The ionic configurations 12b and 12c make a noticeable contribution ($\sim$18%) to S_0. In standard symbolism, formula 12 then is a fair representation of the ground state S_0, although the contribution of structure 12a is higher than usual.

3. Singlet versus Triplet Reactivity

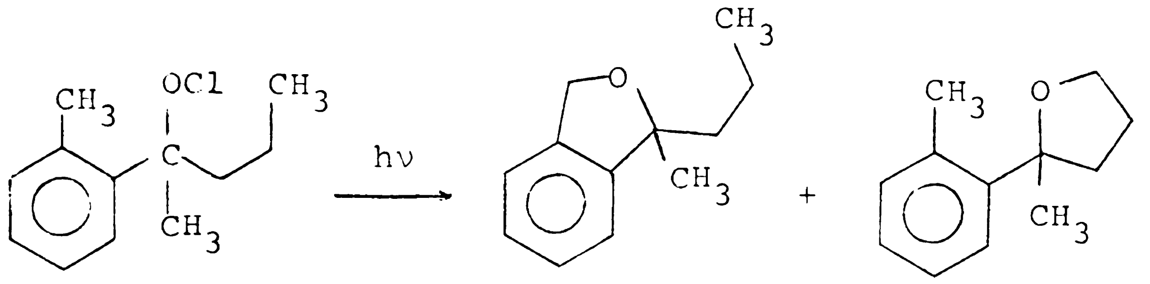
The photoenolization reaction of o-alkylbenzophenones and 3-benzoylchromones seems to proceed exclusively via the triplet state,[37,40] since addition of a triplet quencher can completely quench the reaction. The lack of signlet reaction probably results from the rapid rate of intersystem crossing in these ketones.

Exclusive triplet reaction is, however, not always true for alkyl phenyl ketones. In a study on the photoenolization for 2-methylacetophenone,[50] addition of 0.25 M cis-piperylene resulted in only a 20% depression of the enol formation observed by flash photolysis. Lindquist argued that since piperylene is a very efficient acceptor for the energy of ketone triplets, while it does not quench their singlet excited state,[50] it is apparent that the photoenolization of 2-methylacetophenone occurs to a large extent via the excited singlet state of the ketone. Since only a single concentration of piperylene was employed and also since the unquenchable species could either be a short-lived triplet or singlet, a conclusion[50] that 80% of the enolization occurs from the singlet state is not warranted.

Sammes[51] further substantiated the participation of the singlet state by the following argument. It is known that alkyl phenyl ketones containing -H atoms on the aliphatic chain undergo the type II process only from the triplet state,[19] and the efficiency of the type II reaction is much reduced for 2-methyl substituted phenyl alkyl ketones because of competing photoenolization. Because the observed triplet decay rate of 2-methylacetophenone is slower than those of analogous ketones bearing a γ-H atom it would be surprising if hydrogen abstraction from the *ortho*-methyl group in the triplet ketone could compete efficiently with that from a γ-C atom in the aliphatic chain. The singlet state pathway was then suggested as the alternative route.

However, Bergmark et al.[52] demonstrated a 30:1 preference for *o*-benzylic:γ-CH_2 in the corresponding alkoxy radical

(Equation 4_. If the alkoxyl radical could serve as a model



(4)

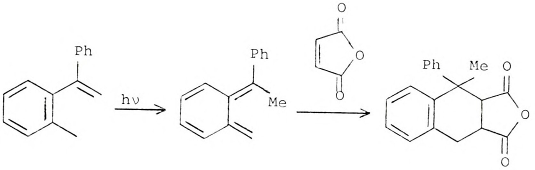
30 : 1

for the n,π* triplet state of the corresponding ketone, the rate of o-methyl hydrogen abstraction should be at least 10^9 sec^{-1} instead of the $\sim 10^7$ sec^{-1} found by flash photolysis. This result indicates that the unquenchable species observed by Lindqvist may well be a short-lived triplet rather than a singlet or a combination of the two. Further experiments are needed to ascertain the quantitative participation of the singlet state in photoenolization processes.

4. n,π* versus π,π* Reactivity

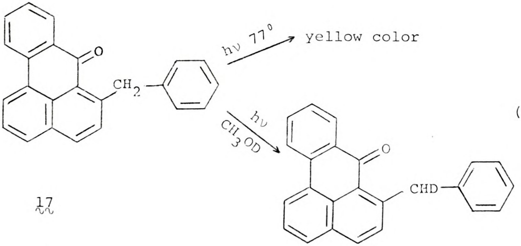
The relative reactivities of the n,π* and π,π* states in the Norrish type II reaction have been well studied.[27-34] Since the photoenzolization process strongly resembles the type II process in that γ-hydrogen migrates to the carbonyl oxyger, it is not suprising that the n,π*[38, 39, 41, 45] triplet was assumed to be the reactive species in the photoenolization reaction.

However, hydrogen abstractions are known for systems where a π,π* excited state must be reacting. For example the olefin 14 undergoes hydrogen scrambling[53] and chemical trapping[54] with maleic anhydride to give 16 (Equation 5). Similarly,



(5)

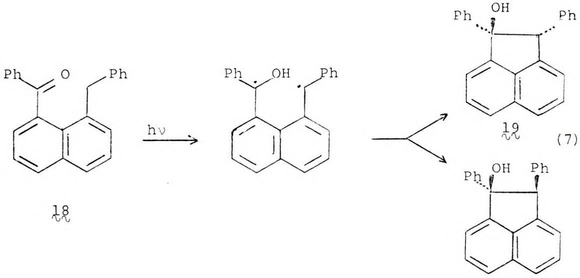
6-benzylbenzanthrone **17**, which would be expected to posses a low-lying π,π* triplet, does form a photoenol, as determined by formation of yellow coloration at low temperature and deuterium exchange at the benzylic position (Equation 6).



(6)

17

Similar π,π* state appears to be involved in the hydrogen abstraction reaction of the ketone **18**, which produces the alcohols **19** and **20** by a 7-membered transition state[55] (Equation 7). The π,π* character of the excited state was



18

19

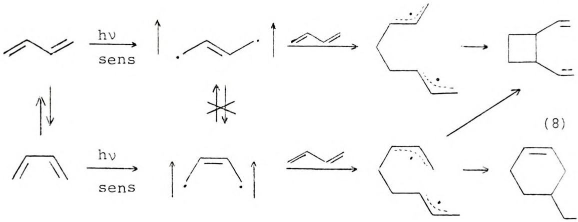
20

(7)

demonstrated by the small bathochromic shift for the 0-0 band in the phosphorescence spectrum of 18 when a non-polar solvent was replaced by a polar solvent.[56] There has been, however, little work done to determine quantitatively the relative reactivities of n,π* and π,π* states in the photoenolization process.

5. Conformational Effects

There is an increasing number of photochemical reactions for which the product composition apparently depends upon ground-state molecular conformation.[57] The first example where such a relationship was postulated is the sensitized dimerization of butadiene[57a] (Equation 8). Formation of vinylcyclohexene only upon excitation of the s-cis diene requires that the cis and trans triplets do not interconvert prior to addition. Conformational control of product in the photoisomerization of 1,3-cyclohexadienes to 1,3,5-hexatrienes has also

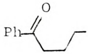
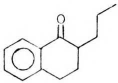
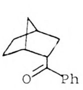


(8)

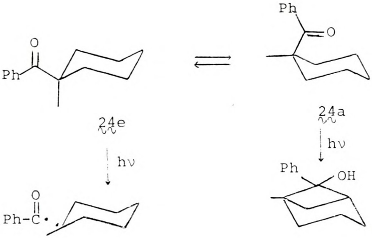
been investigated.[58]

Lewis has reported that γ-hydrogen abstraction in polycyclic ketones **22** and **23** is more rapid than in acyclic ketone **21**.[59] It was suggested that the rate increases are due to the increased number of "frozen" C-C bonds in the reactant based on the activation parameters (Table 2).

Table 2. Activation parameters of phenyl ketones

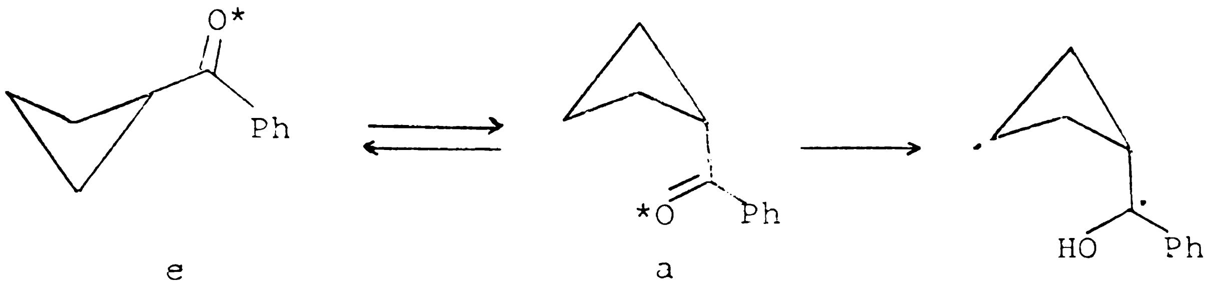
Ketone	$k_\gamma, 10^8 sec^{-1}$	E_a, Kcal	$\Delta S^\ddagger$, eu
21 	1.2	3.5	-12
22 	6.0	—	—
23 	70	3.7	-4

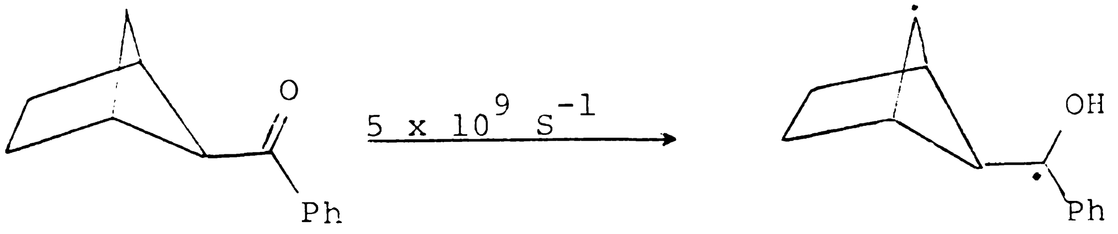
In an elegant study of the photochemistry of 1-benzoyl-1-methylcyclohexane **24**, Lewis *et al.*[60] have provided an example of a system in which excited state reactions are faster than conformational changes. Excitation of **24** yields two



discrete triplets: one with a lifetime of 10^{-7} sec which undergoes only α-cleavage to radicals, and one with a much shorter lifetime which undergoes only γ-hydrogen abstraction and cyclization. The rate of cyclohexane ring inversion ($\sim 10^5$ $\sec^{-1}$) is too slow to equilibrate excited conformers with the benzoyl group equatorial and axial. In this case, the excited state reactions are determined by ground state conformational preferences.

Cyclobutyl ketones provide another example of conformational effects on photochemistry. The quantum yield for the type II processes of benzoylcyclobutane is low[61] presumably because hydrogen abstraction can occur only when the benzoyl group is in a pseudoaxial conformation. The rapid γ-hydrogen abstraction of *exo*-5-benzoylbicyclo[2.1.1]hexane,[62]





a good model for a, certainly supports this interpretation.

However, little attention has been given to conformational effects on photoenolization processes.

IV. Sensitization and Quenching Kinetics

The quantum yield is a measure of the efficiency of a photoreaction. It is also the only kinetic parameter which can be measured under steady state cinditions since photoreactions generally follow zero order kinetics. For a triplet reaction, the quantum yield may be defined as follow.

$$\Phi_{II} = \Phi_T \cdot \Phi_R \cdot P_p \qquad (9)$$

$$\Phi_{II} = k_{isc}\tau_s \cdot k_r\tau_T \cdot P_p \qquad (10)$$

$$1/\tau_T = \Sigma k_i \qquad (11)$$

i: all the chemical and physical pathways for T.

The intersystem crossing yield Φ_T is the probability of triplet formation from its singlet precursor. It is defined as $k_{isc}\ \tau_s$, where k_{isc} is the rate constant of intersystem crossing and τ_s is the lifetime of the singlet. Φ_R, the probability that the triplet will react, is defined as $k_r \tau_T$, where k_r is the rate constant for the reaction and τ_T is the lifetime of triplet. If an intermediate exists between the triplet and the final products, revertibility[63] should also be considered. Hence, the factor P_p is necessary to describe the probability that the intermediate will form product. If there are competing reactions from the triplet, the lifetime of the triplet will be determined by the rate of all reactions undergone by the triplet (Equation 11).

The lifetime of a particular excited state can be derived from quenching studies analyzed by the Stern-Volmer expression (Equation 12).

$$\Phi_o/\Phi = 1 + k_q[Q]\tau_o \qquad (12)$$

Φ_o is the quantum yield in the absence of quencher, Φ is the quantum yield in the presence of some quencher, and $[Q]$ is the concentration of the quencher. There is a linear relation between Φ_o/Φ and the quencher concentration, with slope $k_q\tau$, k_q being the bimolecular rate constant for quenching and τ_o being the lifetime of the particular excited state being quenched.

The general Stern-Volmer quenching equations for systems in which two different excited states both react and are quenched by a given quencher has been derived and analyzed by Wagner.[64] Similar kinetic analysis has been developed by Dalton and Synder[65] and by Shetlar.[66]

Intersystem crossing yields and lifetimes of triplets can be obtained by measuring the efficiency with which the ketones sensitize the *cis*-to-*trans* isomerization of various concentrations of 1,3-pentadiene. Equation 13 describes the

$$\Phi_{sens}^{-1} = \Phi_{isc}^{-1}\alpha^{-1}\left(1 + \frac{1}{k_q\tau_T[Q]}\right) \qquad (13)$$

reciprocal dependence of sensitized quantum yield on quencher concentration, where Φ_{isc} is the intersystem crossing quantum yield for the sensitizer, α is the probability that the quencher triplet will yield the observed product, τ_T is the sensitizer triplet lifetime, and [Q] is the diene concentration. With acetophenone as sensitizer, $\Phi_{c\rightarrow t}$ equals 0.56,[67] and this system can be used as an actinometer.

In systems where two conformers give rise to different photoproducts, the kinetics will be more complicated (Equation 14).

$$\begin{tikzcd}
A \arrow[r, "h\nu"] \arrow[d, shift left] & A^* \arrow[r, "k_x"] \arrow[d, shift right, "k'_a"'] & X \\
B \arrow[r, "h\nu"] \arrow[u, shift left] & B^* \arrow[r, "k_y"] \arrow[u, shift right, "k'_b"'] & Y
\end{tikzcd} \qquad (14)$$

There are three boundary conditions of interest: 1) excited state conformational changes are faster than triplet decay; 2) conformational changes are slower than triplet decay; 3) conformational changes are rate-determining.

In case one the activation energy for conformational isomerization is lower than those for formation of X or Y ($k'_a, k'_b >> k_x, k_y$). In this case the ratio of products will depend upon the difference in energy for the transition states leading to X and Y (Curtin-Hammett principle[68]). The observed rate is the rate for each conformation times the equilibrium percentage of molecules in that conformation.

$$k_x^{obs.} = X_A \cdot k_x$$

$$k_y^{obs.} = X_B \cdot k_y$$

There is only one lifetime, which is defined as follows:

$$1/\tau = X_A \tau_A^{-1} + X_B \tau_B^{-1}$$

In case two ($k'_a, k'_b \ll k_x, k_y$) the ratio of products depends upon the ground state populations of A and B and the efficiencies of product formation from their excited states. The lifetimes of A* and B* need not be the same. If the lifetimes of the two excited states differ greatly, the simple Stern-Volmer equation (Eq. 12) would be obtained for both excited states.

In the last case where conformational change is rate determining ($k'_b \ll k_x, k'_a \sim k_y$), the lifetime of A* would be different from that of B*, with $1/\tau_{A*} = k_x$, $1/\tau_{B*} = k_y + k'_a$. The boundary conditions and product ratios are summarized in the following scheme.

Conformational Equilibrium

$k'_a, k'_b \gg k_x, k_y$ $$\frac{X}{Y} = \frac{k'_a\, k_x}{k'_b\, k_y}$$

Ground State Control

$k'_a, k'_b \ll k_x, k_y$ $$\frac{X}{Y} = \frac{\varepsilon_A [A]\, k_x\, \tau_{A*}}{\varepsilon_B [B]\, k_y\, \tau_{B*}}$$

Rotational Control

$k'_b \ll k_x \quad k'_a \sim k_y$ $$\frac{X}{Y} = \frac{\tau_{A*} \{\varepsilon_A [A] + \varepsilon_B [B]\, k'_b \tau_{B*}\}\, k_x}{\varepsilon_B [B]\, k_y\, \tau_{B*}}$$

V. Research Objectives

The purpose of this research was to further investigate the photoenolization of o-substituted aryl ketones to provide more information about the relationship between molecular conformation and photochemical reactivity. The ring substituent effect of an o-methyl group on type II reactivity was also of interest.

The type II reaction was chosen as the monitoring system because certain problems inherent in other system can be avoided.[69] The C-H bond strength at the γ-carbon can be varied without significantly changing the environment of the excited state of the ketone. In addition, the type II reaction is well understood and the products of this reaction can, in most case, be easily analyzed by VPC.

The photochemistry of a series of o-methyl substituted butyrophenones, valerophenones, and γ-methylvalerophenones was studied. These compounds, upon irradiation, have two chemical options available: abstraction by oxygen of an *ortho* methyl hydrogen (photoenolization) or of a γ-hydrogen from the alkyl chain (type II reaction). The rate constant of enolization can be calculated if both the lifetime of the triplet and the rate constant of the type II reaction are known. In addition, o-ethylvalerophenone and deuterated 2,4-dimethylvalerophenone were studied to determine the effect of C-H bond strength on the photoenolization processes.

The lifetime and intersystem crossing yield of 8-methyltetralone, a good model for the *syn* conformer, was measured to compare with that o-methyl phenyl ketones, which have both the syn and anti conformers. Polymethylsubstituted 8-methyl tetralones were also studied in order to estimate the reactivity of compounds with a lowest π,π^* triplet state.

Since ^{13}C nmr spectra cold provide a generally applicable method to study the conformational preferences of these compounds,[70] the spectra of these ketones were taken to correlate the photoreactivity with ground state conformations.

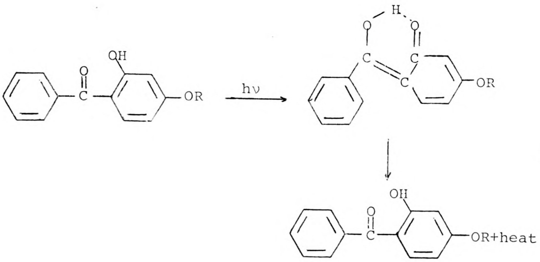
The effect of solvent polarity on the photoenolization reaction was also studied by triplet decay measurement in various organic solvents.

VI. Practical Application

The study of photoenolization will not only extend our knowledge about the nature of excited states of ketones but also has several practical applications:

1. Stabilization of Polymers

There are several ways in which a polymer can be protected from the action of ultraviolet light, apart from the obvious expedient of using an opaque screen or coating to prevent light from reaching the polymer. One way is to mix with the polymer a compound which will absorb most of the light and use up the energy in some way which does not harm the polymer. Compounds which have been found particularly effective with polyethylene, for example, are the substituted 2-hydroxybenzophenones. These compounds undergo a reversible photoenolization which gives a low energy path for the photochemical energy to be degraded to heat (Equation 15).



(15)

2. Photochromism

Photochromism is defined as a reversible change of a single chemical species between two states having distinguishably different absorption spectra. This definition can be represented by the following equation:

$$A\ (\lambda_1) \underset{}{\overset{h\nu}{\rightleftarrows}} B\ (\lambda_2) \qquad (16)$$

It is not surprising that a lot of photoenolizable ketones readily show photochromic characteristics. For example, 2-benzyl-3-benzoylchromones show photochromism even at room temperature. The lifetime of these colored enols can be

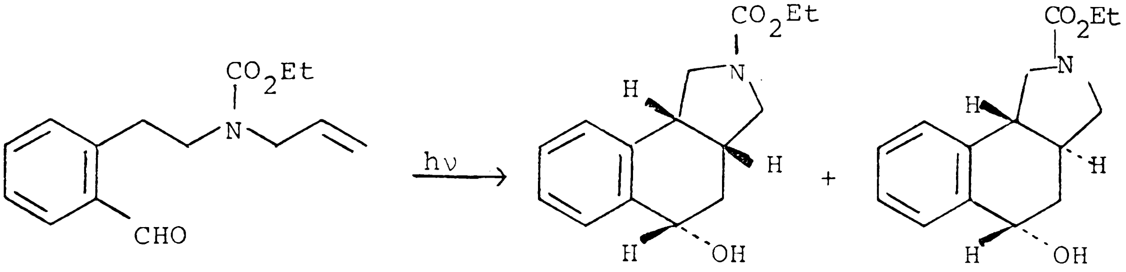
(17)

Colorless Orange

controlled over a wide range by the choice of solvents, by the use of an acid or base catalyst, and by the use of metal ions to form coordination complexes.

3. Synthetic Applications

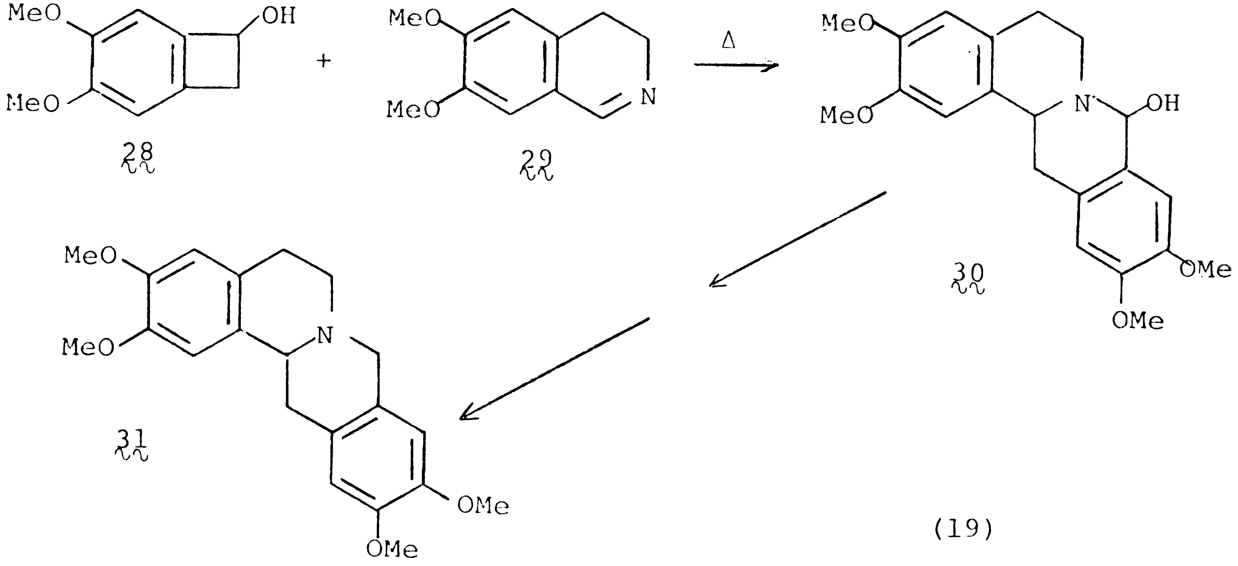
The photoinduced dienols are potentially useful for new synthetic methods of annelation. A variety of dienophiles will add to the photodienol from 2-methylbenzophenone. Some of the example are shown in Table 3.[71] An intramolecular addition between the photoenol and olefinic bond of **25** afford a major product **26** and a minor product **27**.[72]



(18)

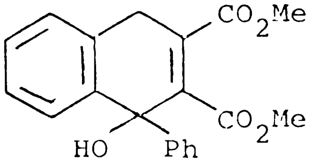
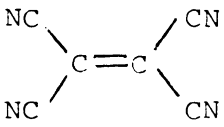
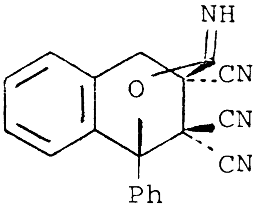
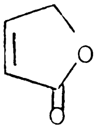
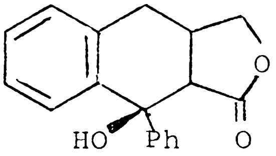
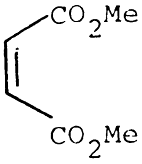
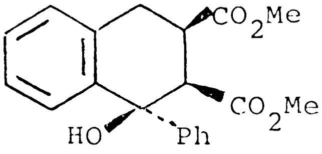
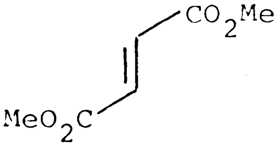
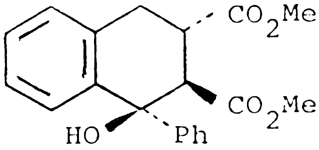
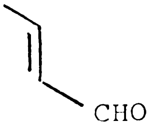
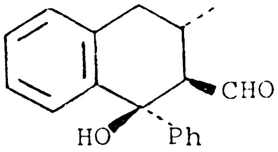
25 **26** **27**

Kametani has used the opening of benzocyclobutene derivatives as a source of the reactive o-quinonedimethides in some elegant alkaloid synthesis.[73] In particular the benzocyclobutenol **28** reacted with the imine **29** to give the adduct **30** which was then converted into the alkaloid xylopinine **31**.[74] The photochemical equivalent of this reaction has not so far been attemped.


MeO
MeO
OH
+
MeO
MeO
N
Δ
MeO
MeO
N
OH
OMe
OMe
MeO
MeO
N
OMe
OMe
28
29
30
31

(19)

Table 3. Cycloadducts from 2-Methylbenzophenone

Dienophile	Adduct	Yield(%)
$MeO_2C \cdot C{\equiv}C \cdot CO_2Me$		53
		22
		50
		35
		58
		27

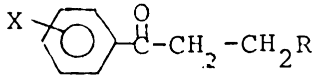
RESULTS

I. Ortho-Alkyl Phenyl Ketones

1. Quantum Yield of Photoproducts

Irradiation (313 nm) of degassed solutions of the ortho-alkyl phenyl ketones listed in Table 4 resulted in the production of the type II cleavage product, the substituted acetophenone. No other products were observed by VPC analysis in any of the solvents used. The disappearance quantum yield for o-methyl γ-methylvalerophenone in benzene is 0.036. This is somewhat larger than the 0.033 value of o-methylacetophenone formation, indicating that unidentified products may be formed, but is no more than 8% chemical yield. These unidentified products are most likely the type II cyclization products, 1-o-methylphenyl-2,2-dimethylcyclobutanols. Solvent effects on type II quantum yields were determined for all the ketones. This was usually done by measuring the type II quantum yield of the ketone at various concentrations of added t-butyl alcohol, pyridine, or 1,4-dioxane. Additions of large concentrations of tert-butyl alcohol caused type II yields to maximize, as previously noted.[14] Irradiation of ketone solutions containing pyridine produced a slight yellow color. No attempt was made to determine the origin of the color formation. A maximum quantum yield was usually obtained in 3.0 M 1,4-dioxane. Quantum yields of acetophenones in benzene and maximum quantum yields in 1,4-dioxane are listed in Table 4. Quantum yields in t-butyl alcohol are listed in Table 5.

Table 4. Photokinetics Parameters for *Ortho* Alkyl Ketones in Benzene[a]

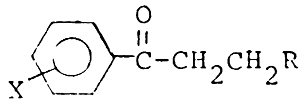


Ketone	X	R	Φ_{II}^{b}	Φ_{max}^{c}	Φ_{T}^{d}	$k_q\tau$, M^{-1}[e]
32	2-CH_3	CH_3	0.0014 ± 0.0001	0.0238 ± 0.0014	0.21 ± 0.01	150 ± 3
33	2-CH_3	CH_2CH_3	0.016 ± 0.0008	0.102 ± 0.004	0.21 ± 0.01	90 ± 2
34	2-CH_3	$CH(CH_3)_2$	0.033 ± 0.002	0.174 ± 0.008	0.21 ± 0.01	27 ± 1
35	2,3-$(CH_3)_2$	$CH(CH_3)_2$	0.026 ± 0.001	0.081 ± 0.003	0.16 ± 0.01	125 ± 3
36-h	2,4-$(CH_3)_2$	$CH(CH_3)_2$	0.024 ± 0.001	0.079 ± 0.004	0.23 ± 0.01	137 ± 2
36-d	2,4-$(CD_3)_2$	$CH(CH_3)_2$	0.039 ± 0.002	———	0.22 ± 0.01	102 ± 2
37	2,5-$(CH_3)_2$	$CH(CH_3)_2$	0.021 ± 0.001	0.071 ± 0.003	0.20 ± 0.01	117 ± 3
38	2,3,4,5-$(CH_3)_4$	$CH(CH_3)_2$	0.0134 ± 0.0008	0.040 ± 0.002	0.16 ± 0.01	481 ± 6
41	2-CH_2CH_3	CH_2CH_3	0.021 ± 0.002	0.069 ± 0.003	0.12 ± 0.01	94 ± 2

---

[a] 0.05 M ketone, 313-nm irradiation. [b] Acetophenone formation. [c] Acetophenone formation in 3.0 M dioxane. [d] Triplet yield determined by sensitizing isomerization of 0.2 M *cis*-1,3-pentadiene. [e] Slopes of linear Stern-Volmer plots with 2,5-dimethyl-2,4-hexadiene as quencher.

Table 5. Photokinetic Parameters for *Ortho* Alkyl Ketones in *t*-BuOH[a]



Ketone	X	R	Φ_{II}^{b}	Φ_T	$k_q\tau$, M^{-1}[d]
32	2-CH_3	CH_3	0.015 ± 0.001	0.112 ± 0.005	340 ± 6
33	2-CH_3	CH_2CH_3	0.060 ± 0.002	0.110 ± 0.005	156 ± 4
34	2-CH_3	$CH(CH_3)_2$	0.095 ± 0.004	0.110 ± 0.004	40 ± 3
35	2,3-$(CH_3)_2$	$CH(CH_3)_2$	0.052 ± 0.002	0.095 ± 0.003	253 ± 4
36-h	2,4-$(CH_3)_2$	$CH(CH_3)_2$	0.046 ± 0.001	0.140 ± 0.006	319 ± 5
36-d	2,4-$(CD_3)_2$	$CH(CH_3)_2$	0.078 ± 0.003	0.131 ± 0.006	——
37	2,5-$(CH_3)_2$	$CH(CH_3)_2$	0.045 ± 0.002	0.113 ± 0.004	261 ± 2
38	2,3,4,5-$(CH_3)_4$	$CH(CH_3)_2$	0.029 ± 0.001	0.091 ± 0.003	793 ± 10
41	2-CH_2CH_3	CH_2CH_3	0.048 ± 0.003	0.070 ± 0.003	120 ± 4

[a] 0.05 M ketone, 313-nm irradiation. [b] Acetophenone formation. [c] Triplet yield determined by sensitizing isomerization of 0.15 M *cis*-1,3-pentadiene. [d] Slopes of linear Stern-Volmer plots with 2,5-dimethyl-2,4-hexadiene as quencher.

2. Quenching of Photoproducts

Stern-Volmer quenching slopes for the ketones studied were obtained by irradiating them in solutions containing varying amounts of quencher and then plotting relative quantum yields according to Equation 12 in the Introduction. The intercept should be 1 and slope represents the value of $k_q\tau$. The quencher most commonly used in this study was 2,5-dimethyl-2,4-hexadiene. Figure 2 contains Stern-Volmer quenching plots for o-methylbutyrophenone, o-methylvalerophenone, and o-methyl γ-methylvalerophenone. Talbe 4 contains $k_q\tau$ values for the ortho-alkyl ketones in benzene; those in t-butyl alc hol are listed in Table 5.

It is of interest to compare $k_q\tau$ vales measured in similar solvents of differing viscosities since $k_q\tau$ would decrease with increasing solvent viscosity if energy transfer is "diffusion-controlled."[75] Table 6 compares $k_q\tau$ values obtained using, 2,5-dimethyl-2,4-hexadiene to quench excited o-methyl γ-methylvalerophenone 34 in primary alcohols. As solvent viscosity increases $k_q\tau$ value do in fact decrease, as shown in Figure 3. Figure 4 compares the $k_q\tau$ values obtained from quenching excited 34 against those obtained from quenching valerophenone, with each point corresponding to measurements in a particular solvent.

The irradiation of o-methyl-α-methoxyacetophenone 45 in degassed benzene solution results in the production of o-methylacetophenone and 1-(o-methylphenyl)-1-hydroxy-3-oxetane. The quantum yeild for the former product is 0.171 ± 0.009; that for oxetane formation is 0.029 ± 0.001. Values for α-methoxyacetophenone itself are 0.57 and 0.42.[72] The quenching of 45 by

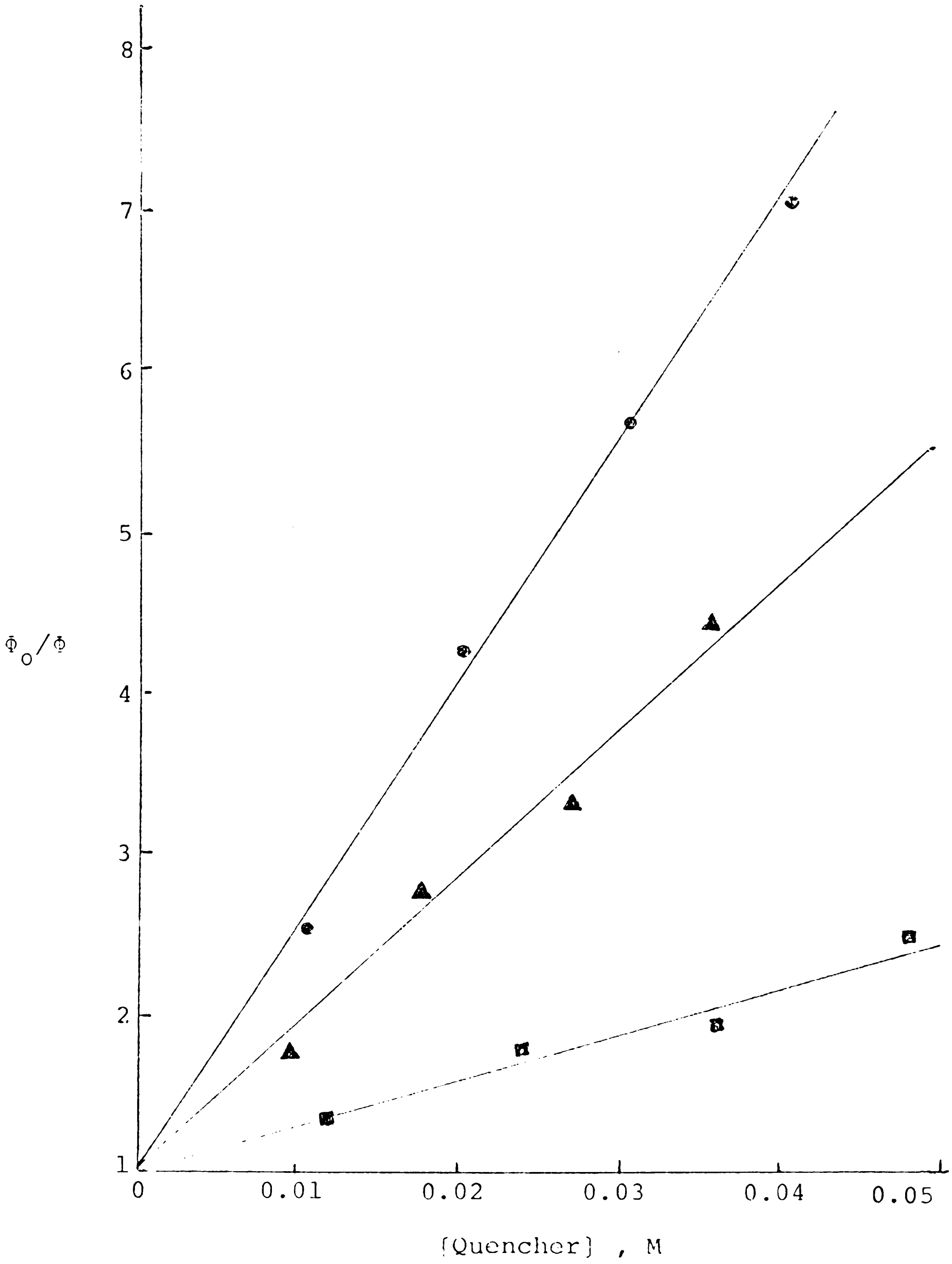


Figure 2. Stern-Volmer quenching plot for o-methylbutyrophenone (●), o-methylvalerophenone (▲), and o-methyl γ-methylvalerophenone (■).

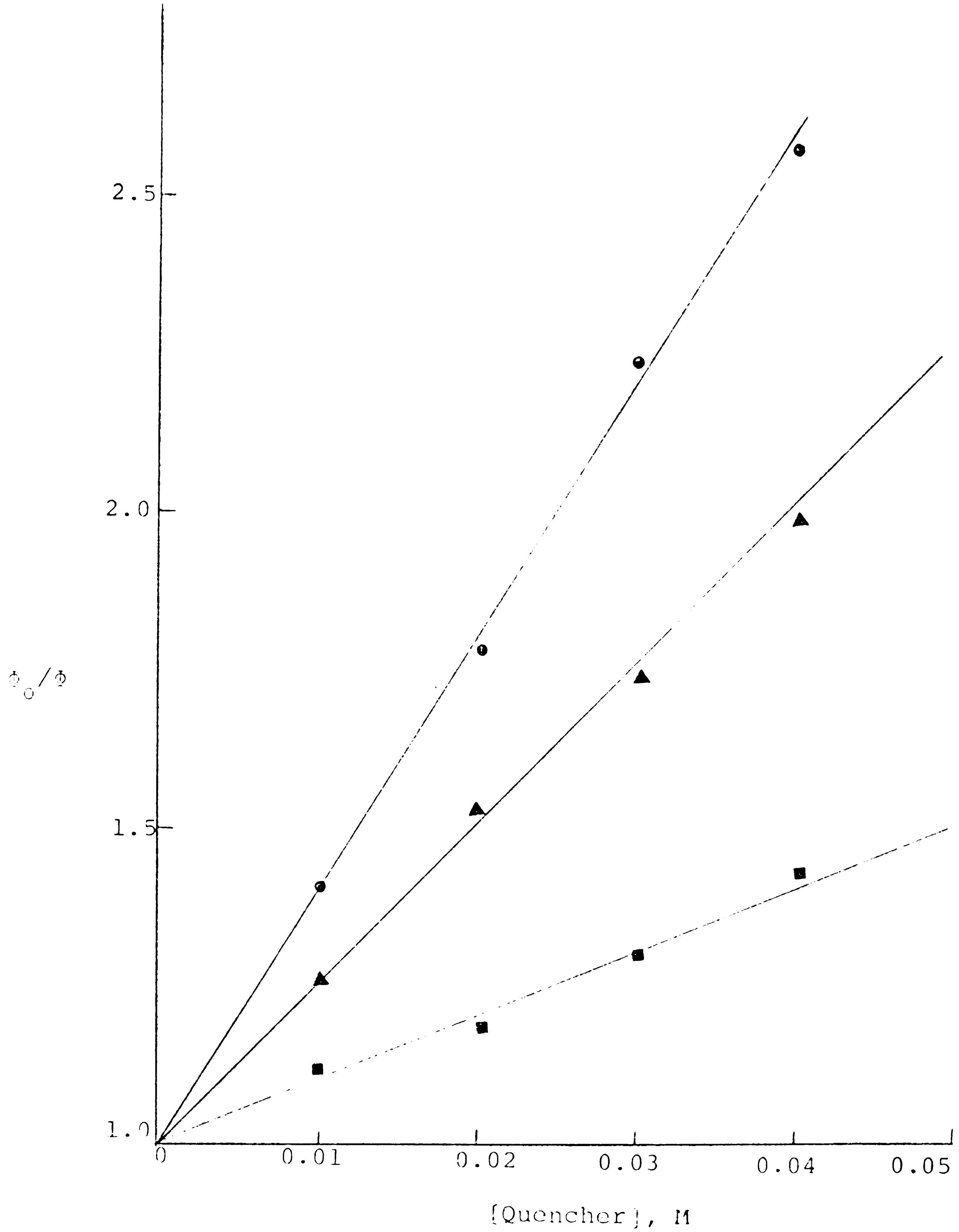


Figure 3. Stern-Volmer quenching plot for o-methyl γ-methylvalerophenone in 1-propanol (●), 1-pentanol (▲), and 1-heptanol (■).

Table 6. Quenching Constants for o-Methyl γ-methylvalerophenone in Primary Alcohol Solvents of Varying Viscosity

Solvent	Viscosity (η, cP)[a]	$k_q\tau$, M^{-1}	$k_q\tau$[b] (VP)
1-Propanol	1.9	37 ± 2	52
1-Pentanol	3.1	25 ± 1	36
1-Heptanol	5.5	14 ± 1	23
t-BuOH	3.9	40 ± 3	40

[a] Ref. 75. [b] From quenching excited valerophenone, ref. 75.

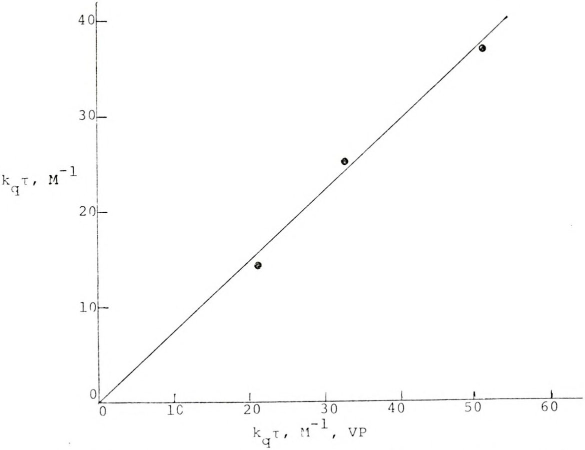


Figure 4. Quenching constant for ketone 34 versus quenching constant for valerophenone in same solvent.

1,3-pentadiene in benzene deserves some attention since it does not give a straight Stern-Volmer plot, as shown in Figure 5. Two $k_q\tau$ values of 4.9 M^{-1} and 1.4 M^{-1} are obtained based on equations 20 - 23[77] for cases in which two excited states react

$$\frac{\Phi_p^0}{\Phi_p} = \frac{(1+k_q\tau_1[Q])(1+k_q\tau_2[Q])}{1 + \dfrac{k_q[Q]\tau_2 + \Phi_2^0 k_q[Q]\tau_1/\Phi_1^0}{1+\Phi_2^0/\Phi_1^0}} \qquad (20)$$

$$\text{initial slope} = k_q\tau_1\left(\frac{\Phi_1^0}{\Phi_1^0+\Phi_2^0}\right) + k_q\tau_2\left(\frac{\Phi_2^0}{\Phi_1^0+\Phi_2^0}\right) \qquad (21)$$

$$\text{final slope} = \frac{k_q\tau_1 \cdot k_q\tau_2(1+\Phi_2^0/\Phi_1^0)}{k_q\tau_2 + \Phi_2^0 k_q\tau_1/\Phi_1^0} \qquad (22)$$

$$\begin{aligned}\text{final intercept } b_2 = {} & \frac{(1+\Phi_2^0/\Phi_1^0)(k_q\tau_1+k_q\tau_2)}{k_q\tau_2 + \Phi_2^0 k_q\tau_1/\Phi_1^0} \quad - \\ & \frac{(1+\Phi_2/\Phi_1)^2\, k_q\tau_1\, k_q\tau_2}{(k_q\tau_2 + \Phi_2^0 k_q\tau_1/\Phi_1^0)^2} \qquad (23)\end{aligned}$$

and are both quenched.

3. Sensitization Studies

The intersystem crossing quantum yields (Φ_T) of _ortho_-alkyl phenyl ketones were determined from the quantum efficiencies with which these ketones sensitize the _cis_-to-_trans_ isomerization ($\Phi_{c\rightarrow t}$) of various concentrations of _cis_-1,3-pentadiene in benzene. Normally, such plots are linear. As shown in Figure 6, the plot for _o_-methylacetophenone is not

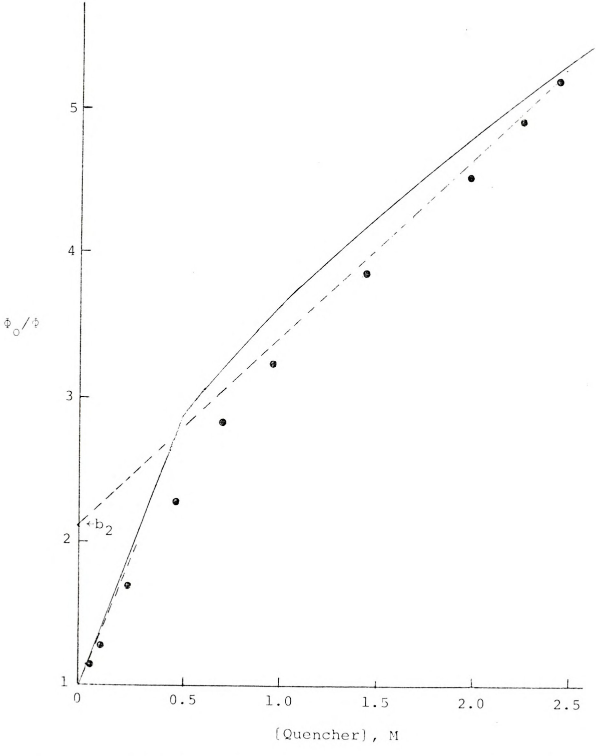


Figure 5. Quenching plot for o-methyl α-methoxyacetophenone in benzene with pentadiene as quencher. Solid curve is calculated from Equation 20.

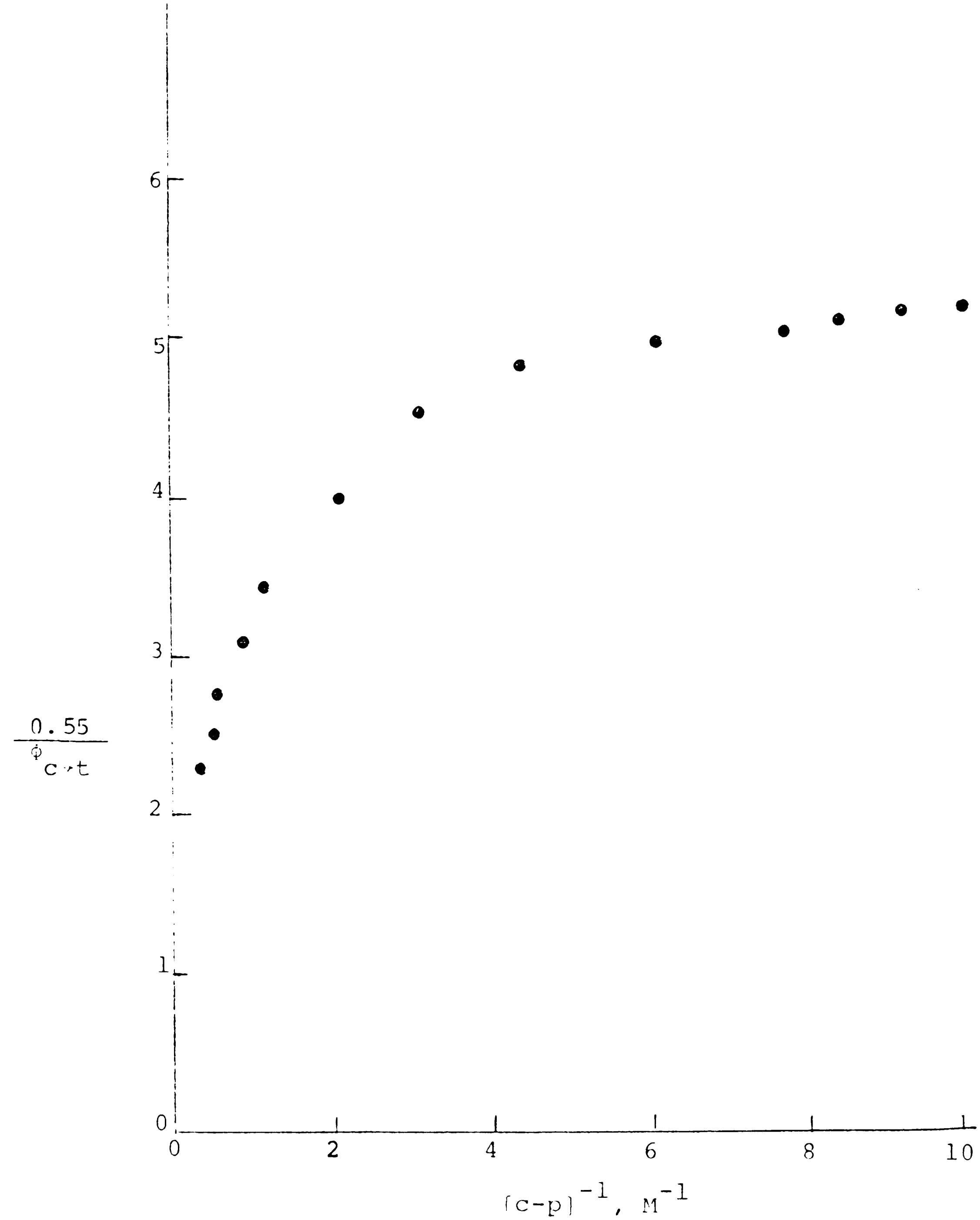


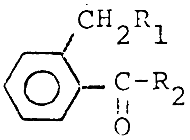
Figure 6. Concentration dependence of the cis-trans isomerization of cis-1,3-pentadiene (c-p) in benzene photosensitized by 0.05 M o-methylacetophenone.

linear but has a steep slope at high (>1 M) diene concentration[78] and a very low slope at low (<0.2 M) diene concentration. Kinetic analysis of this plot, which is derived in section VI, yileds $k_q\tau$ values of 150 M^{-1} for the triplet formed in 21% yield and 1.0 M^{-1} for a triplet formed in 31% yield. Such nonlinear plots signify two kinetically independent triplets. Similar sensitization plots for o-methylvalerophenone, o-ethylvalerophenone and o-methylbenzophenone in benzene and t-butyl alchol are shown in Figure 7, 8 and 9 respectively. The final slope and intercept of these sensitization plots are not considered reliable because the sensitized quantum yields are very close to each other at the lower concentrations of diene. As shown in Figure 10, a sensitization plot for o-methyl γ-methylvalerophenone at even lower concentration of diene (0.1 - 0.01 M) results in a straignt line with reasonably large variation in quantum yields. The $k_q\tau$ value thus obtained is 25 M^{-1}, in good agreement with the slope of the Stern-Volmer quenching plot for that ketone. It is assumed hereafter that the triplet lifetime of any ketone determined by sensitization studies at low concentrations of diene would be the same as that obtained from a Stern-Volmer quenching plot. Table 7 contains triplet yileds and lifetimes of both triplets for several ketones.

4. Deuterium Incorporation Experiments

Irradiation of o-methylacetophenone and o-methylbenzophenone in CH_3OD results in deuterium incorporation in the recovered starting ketone. The quantum yield of

Table 7. Triplet Formation and Decay Rate Constant for *Ortho* Alkyl Ketones in Benzene and *t*-BuOH



R_1	R_2	Long-lived		Short-lived		
		Φ_T^L	$1/\tau, 10^7 S^{-1}$	Φ_T^S	$1/\tau, 10^7 S^{-1}$	Φ_T^{total}
		Benzene				
H	CH_3	0.219	2.9	0.301	3.2	0.52
H	C_6H_5	0.376	13.8	0.624	5.8	1.0
CH_3	$(CH_2)_3CH_3$	0.120	5.1	0.20	6.9	0.32
H	$(CH_2)_3CH_3$	0.21	5.2	0.28	3.0	0.49
		t-BuOH				
H	CH_3	0.11	0.6	0.15	0.5	0.26
H	C_6H_5	0.35	6.4	0.65	1.4	1.0
CH_3	$(CH_2)_3CH_3$	0.07	1.5	0.15	0.8	0.22
H	$(CH_2)_3CH_3$	0.11	2.0	0.17	0.5	0.28

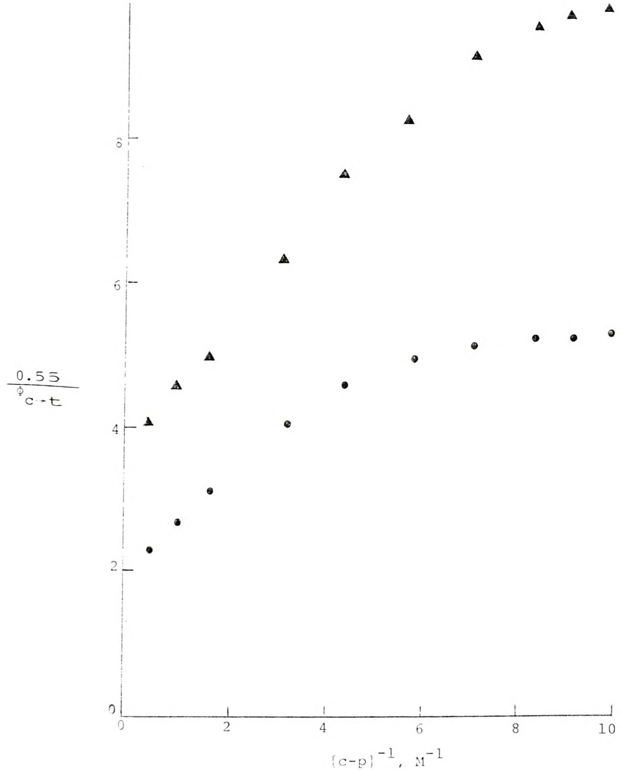


Figure 7. Sensitization studies for o-methylvalerophenone in benzene (●) and t-BuOH (▲).

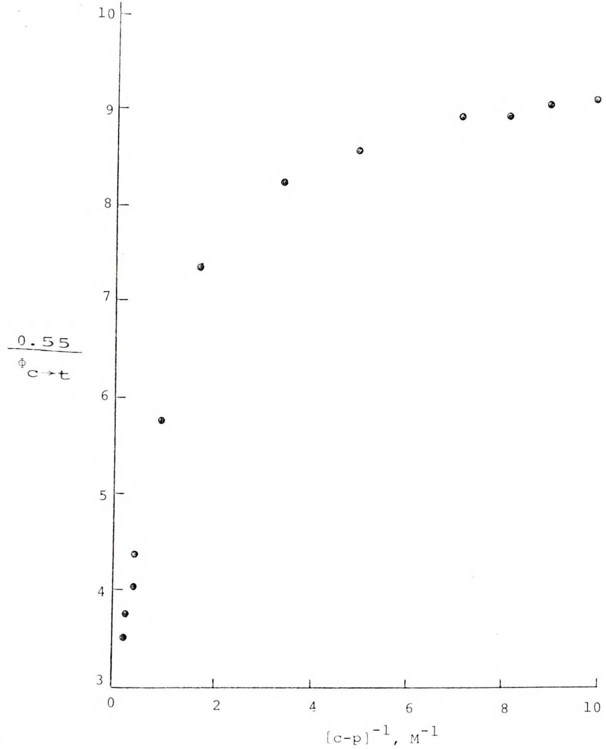


Figure 8. Sensitization studies for o-ethylvalerophenone in benzene.

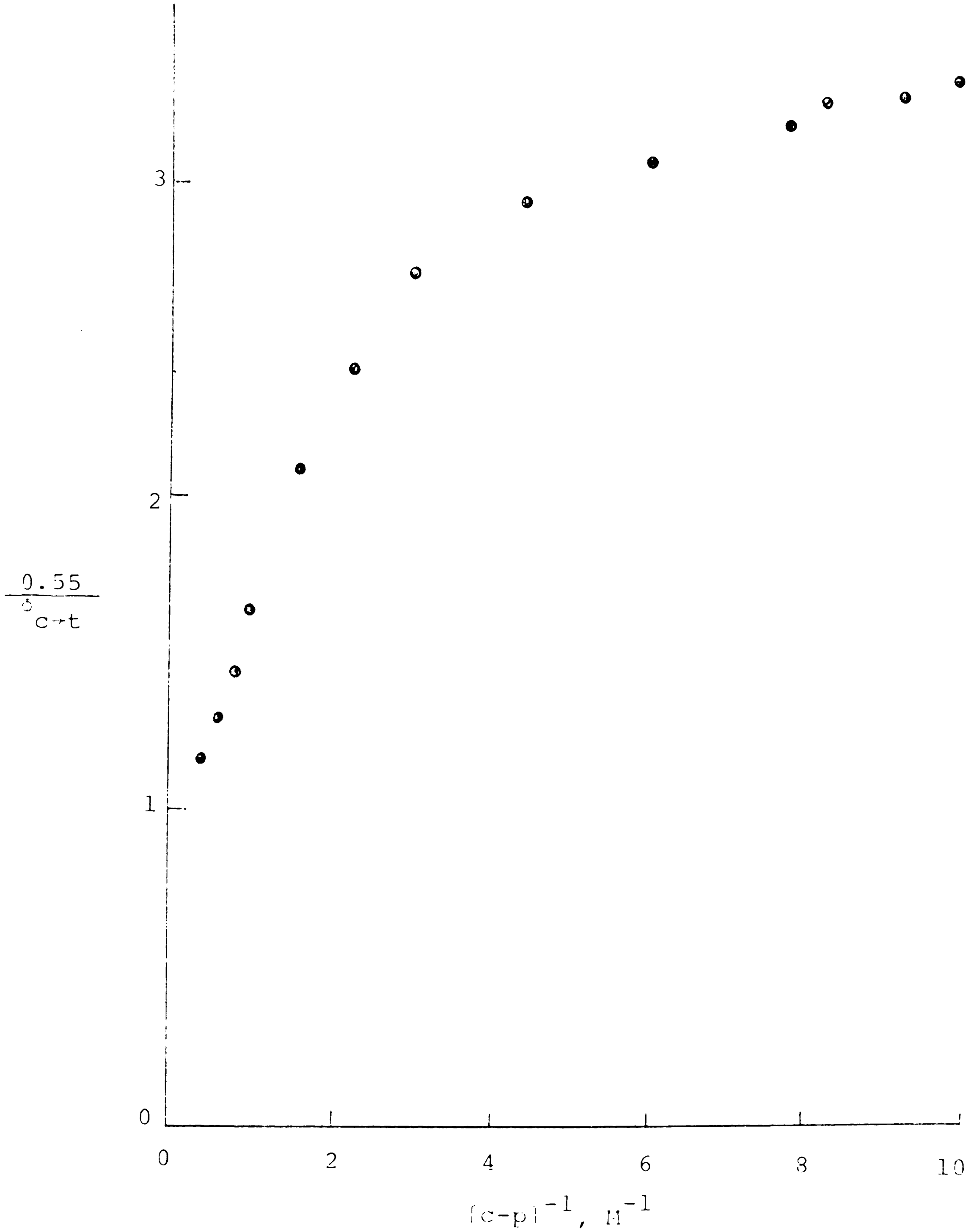


Figure 9. Sensitization studies for o-methylbenzophenone in benzene.

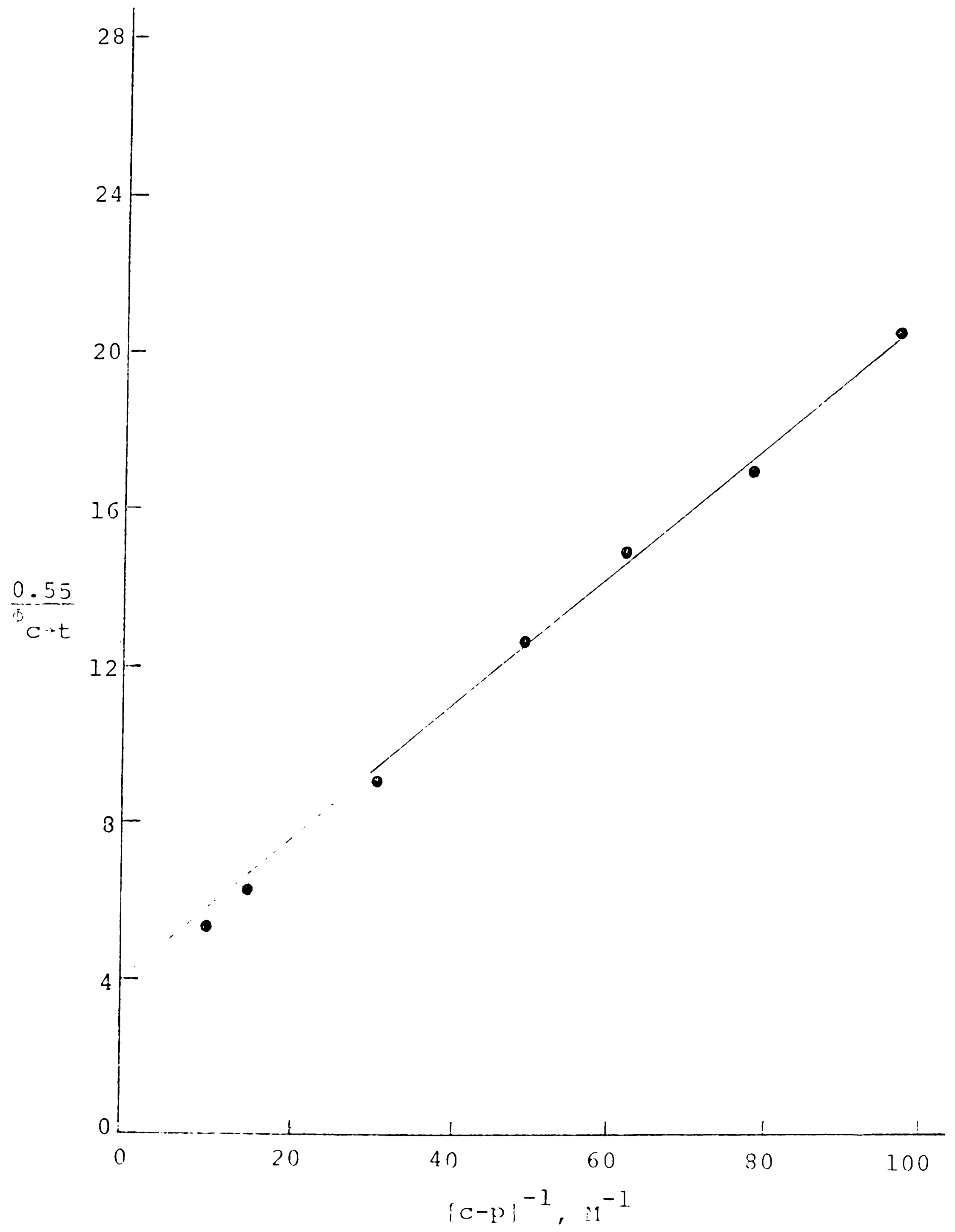


Figure 10. Sensitization studies for *o*-methyl ,-methylvalerophenone in Benzene.

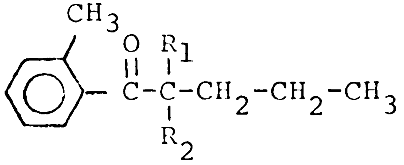
deuterium incorporation, determined by mass spectral analysis (m/e 91), is 0.21 ± 0.06 for o-methylacetophenone and 0.38 ± 0.06 for o-methylbenzophenone. Stern-Volmer quenching plots of this process for these ketones are shown in Figure 11. Small concentrations of pentadiene (<0.1 M) quench about two thirds the deuterium incorporation in o-methylacetophenone. Larger concentrations of pentadiene (>0.5 M) continue to quench the reaction, but with less efficiency. Application of eq. 20-23 suggests that this process arises from two triplets, one long-lived (11 ns) and one short-lived (0.2 ns). o-Methylbenzophenone also produces two triplets, but with a total Φ_T of unity. Moreover it undergoes photoinduced deuterium incorporation almost twice as efficiently as does o-methylacetophenone.

II. α-Methylated Ketones

1. Quantum Yields of Photoproducts

Irradiation (313) nm) of o-methyl α-methylvalerophenone 39 in benzene solution results in the type II cleavage product o-methylpropiophenone and the type II cyclization products, 1-o-methylphenyl-2,4-dimethylcyclobutanols. They are formed in comparable yields, just as reported for α-methylvalerophenone.[79] On the other hand, photolysis of o-methyl α,α-dimethylvalerophenone 40 gives the type I cleavage product o-methylbenzaldehyde in addition to the type II cleavage and cyclization products. The quantum yields of product formation for both ketones in benzene and in 4.0 M 1,4-diozane are listed in Table 8.

Table 8. Photokinetic Parameters for α-Methylated Valerophenones in Benzene[a]



Ke-tone	R_1	R_2	Φ_{AP}^{b}	Φ_{CY}^{c}	Φ_{I}^{d}	Φ_{T}^{long}	Φ_{T}^{short}	Φ_{T}^{total}	$k_q\tau^{long}$, M^{-1}	$k_q\tau^{s}$ M^{-1}
39	H	CH_3	0.005±0.0004	0.007±0.0005	—	0.112	0.241	0.353	123±3	1.67
			(0.031±0.002)	(0.033±0.002)					(119±2)[f]	
40	CH_3	CH_3	0.0024±0.0002	0.008±0.0006	0.0034±0.0002	0.071	0.219	0.290	167±3	1.10
			(0.014±0.0008)	(0.029±0.001)	(0.0065±0.003)[e]				(159±2)[f]	

---

[a] 0.05 M ketone. [b] Acetophenone formation; number in parenthesis is the maximum quantum yield obtained in ∿4 M dioxane. [c] Cyclobutanol formation; the maximum quantum yield is listed in parenthesis. [d] Type I product, o-methylbenzaldehyde. [e] In presence of 0.01-0.05 M RSH.

[f] From sensitization plots.

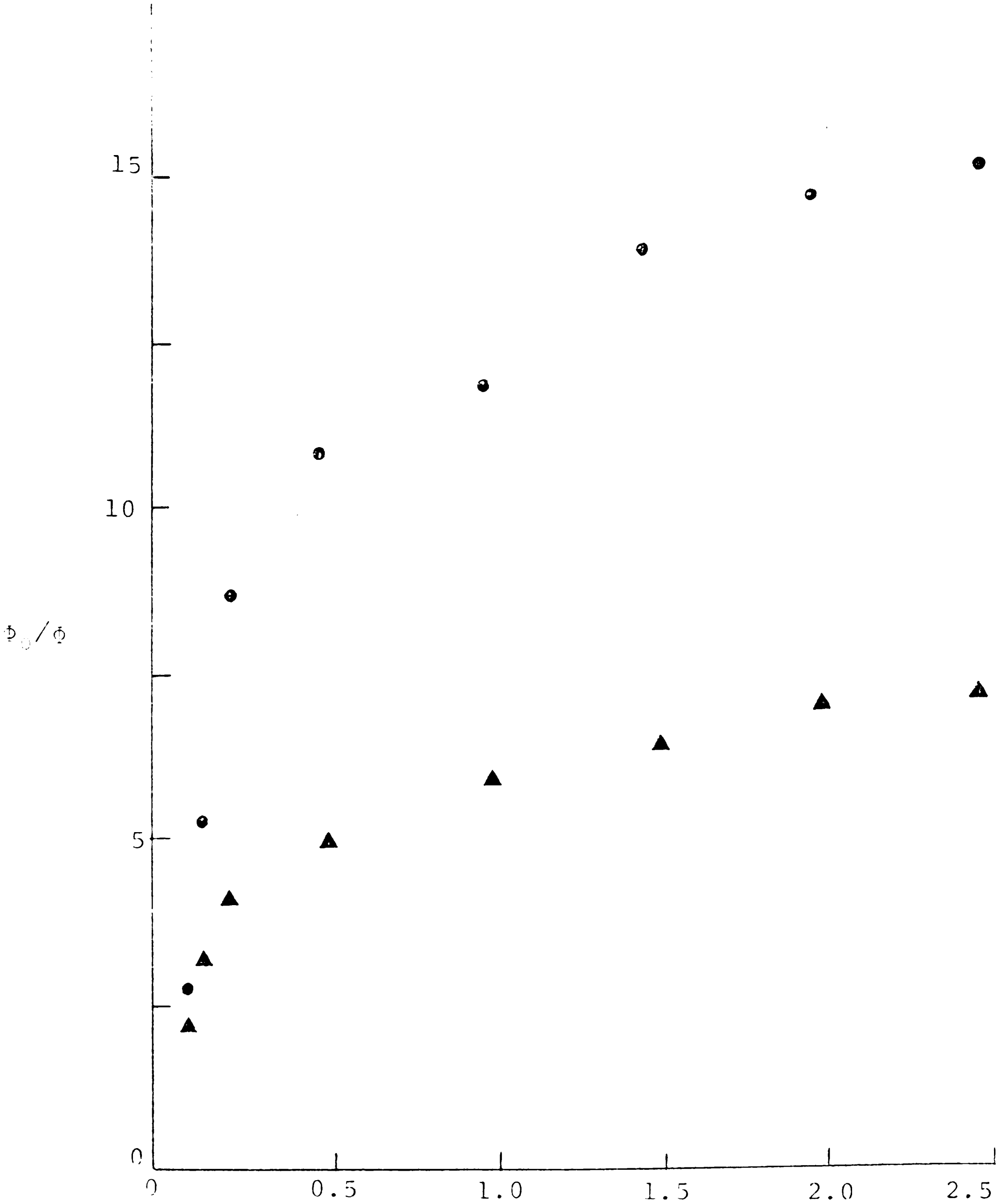


Figure 11. Quenching plot of deuterium incorporation for o-methylacetophenone (▲) and o-methylbenzophenone (●) in CH_3OD with pentadiene as quencher.

2. Radical Trapping Experiments

1-Dodecanethiol was employed at concentrations which would not directly quench the triplet[80] to trap the free radicals produced from type I cleavage of ketone **40**. The virtually identical quantum yields of o-methylbenzaldehyde with both 0.01 M and 0.05 M thiol indicates complete trapping of all noncage free radicals. Thus the quantum yield for α-cleavage product formation is approximately 0.0065. Allowing for ∿50% cage recombination of benzoyl and alkyl radicals[80] the quantum yields for α-cleavage can be estimated as 0.013.

3. Quenching of Photoproducts

All the photoproducts of **39** and **40** are quenchable by 2,5-dimethyl-2,4-hexadiene; Stern-Volmer plots were constructed using the data from the cyclobutanol products and are shown in Figure 12. Table 8 contains the values of $k_q\tau$ obtained from Figure 12.

4. Sensitization Studies

Sensitization of the cis-to-trans isomerization of cis-1,3-pentadiene by these two α-substituted ketones also indicates the existence of two triplets with discrete lifetime. The curved double reciprocal plots are shown in Figure 13. Application of equations in section 6 indicates the Φ_T and $k_q\tau$ values listed in Table 8.

III. 2,6-Dimethyl Ketones

Introduction of a second ortho-methyl substituent on the phenyl ring of the ketones causes dramatic changes in molecular conformations and photochemical behaviour. As indicated

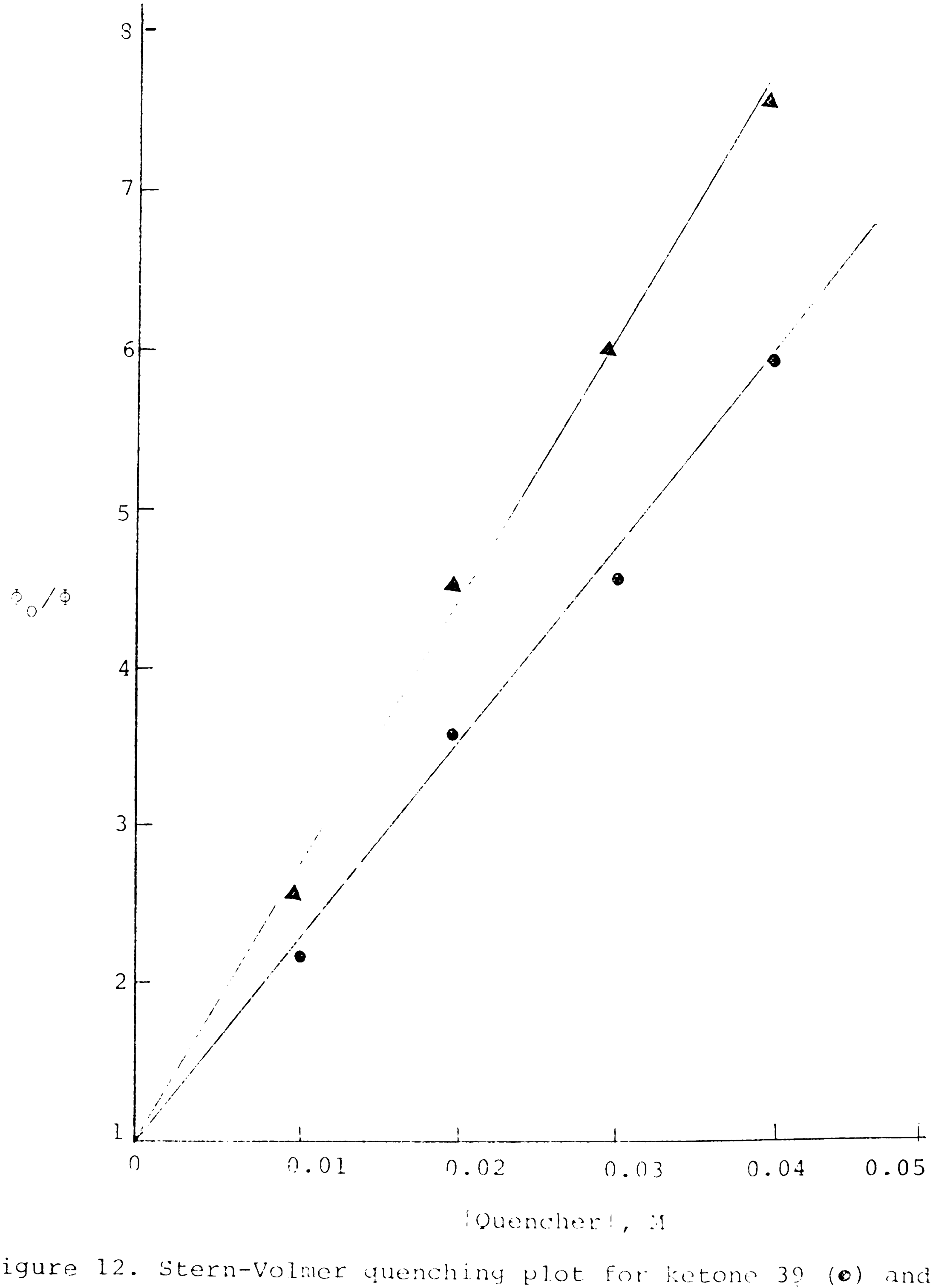


Figure 12. Stern-Volmer quenching plot for ketone 39 (●) and 40 (▲) in benzene.

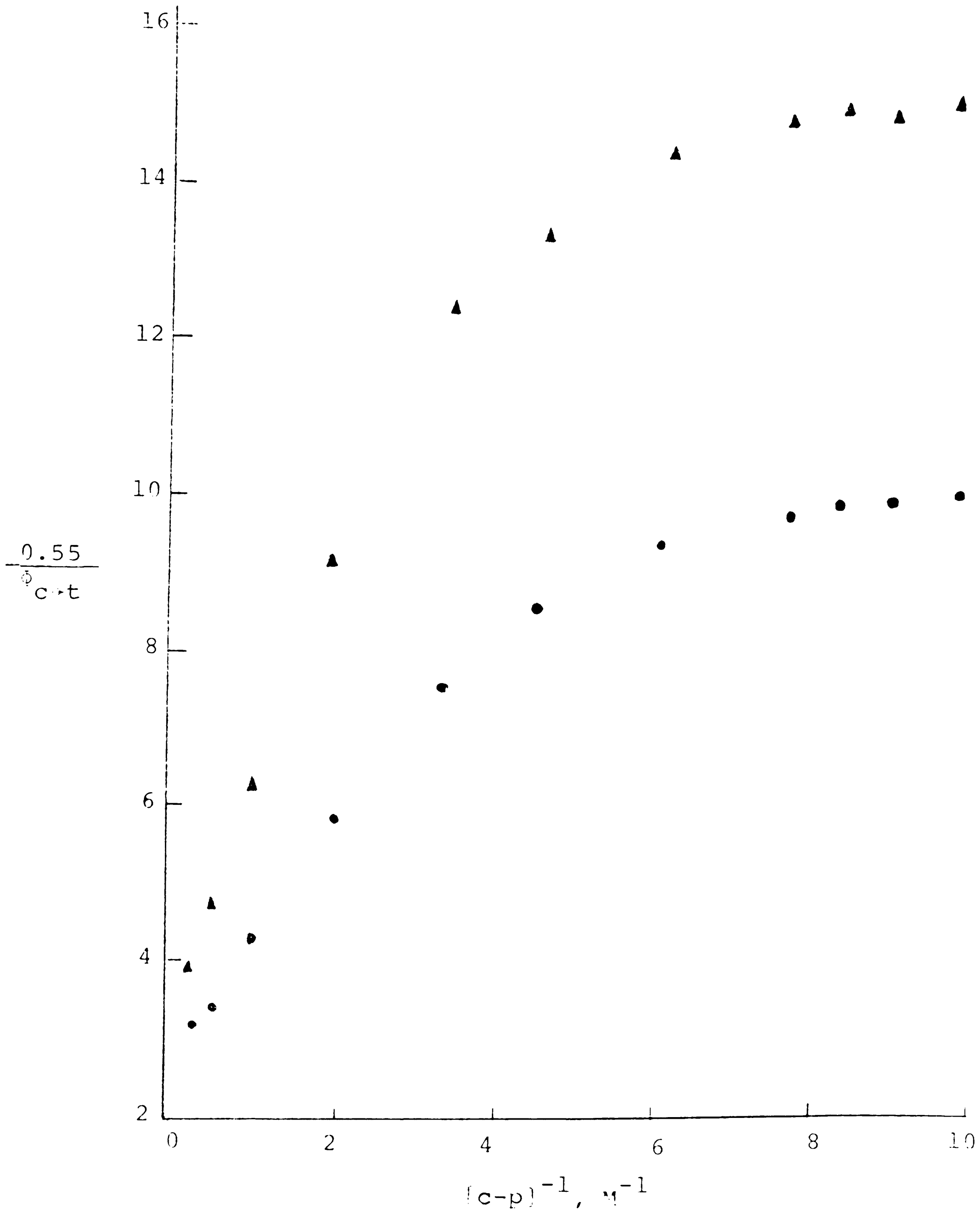
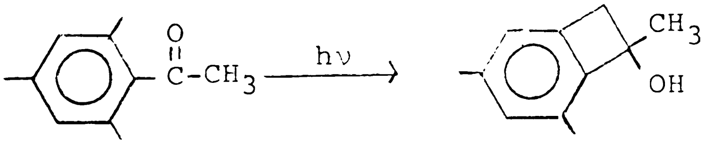


Figure 13. Sensitization studies for ketone 39 (●) and 40 (▲) in benzene.

from uv spectra and ^{13}C nmr signals, 2,6-disubstituted phenyl ketones are highly twisted in the ground state.[81]

Irradiation of 2,4,6-trimethylacetophenone in benzene solution results in the formation of benzocyclobutenol (eq. 24),



(24)

as has been reported before.[45] The quantum yield of this reaction is increased tenfold by 3.0 M 1,4-dioxane. Prolonged irradiation in the presence of concentrated 1,3-pentadiene results in some quenching of benzocyclobutenol formation and formation of a new product. The quantum yield of this unknown product increases with increasing 1,3-pentadiene concentration; the plot of reciprocal quantum yield versus reciprocal diene concentration gives a straight line (Figure 14), indicating that this product probably arises from a reaction between the excited state of ketone and 1,3-pentadiene. Oxetane formation from irradiation of ketones in the presence of dienes is well-known[82] and this type of cycloaddition reaction may well be responsible for the formation of the unknown product. No attempt was made to isolate and identify this unknown product. This complication could be avoided by using 1-methylnaphthalene as a quencher and irradiating at 366 nm. No product other than benzocyclobutenol was detected. The quenching plot thus obtained, as shown in Figure 15, give a straight line at high concentrations of quencher with a slope of 4.2 M^{-1}, which corresponds to a rate of triplet decay of 1.2 x 10^9 sec^{-1}.

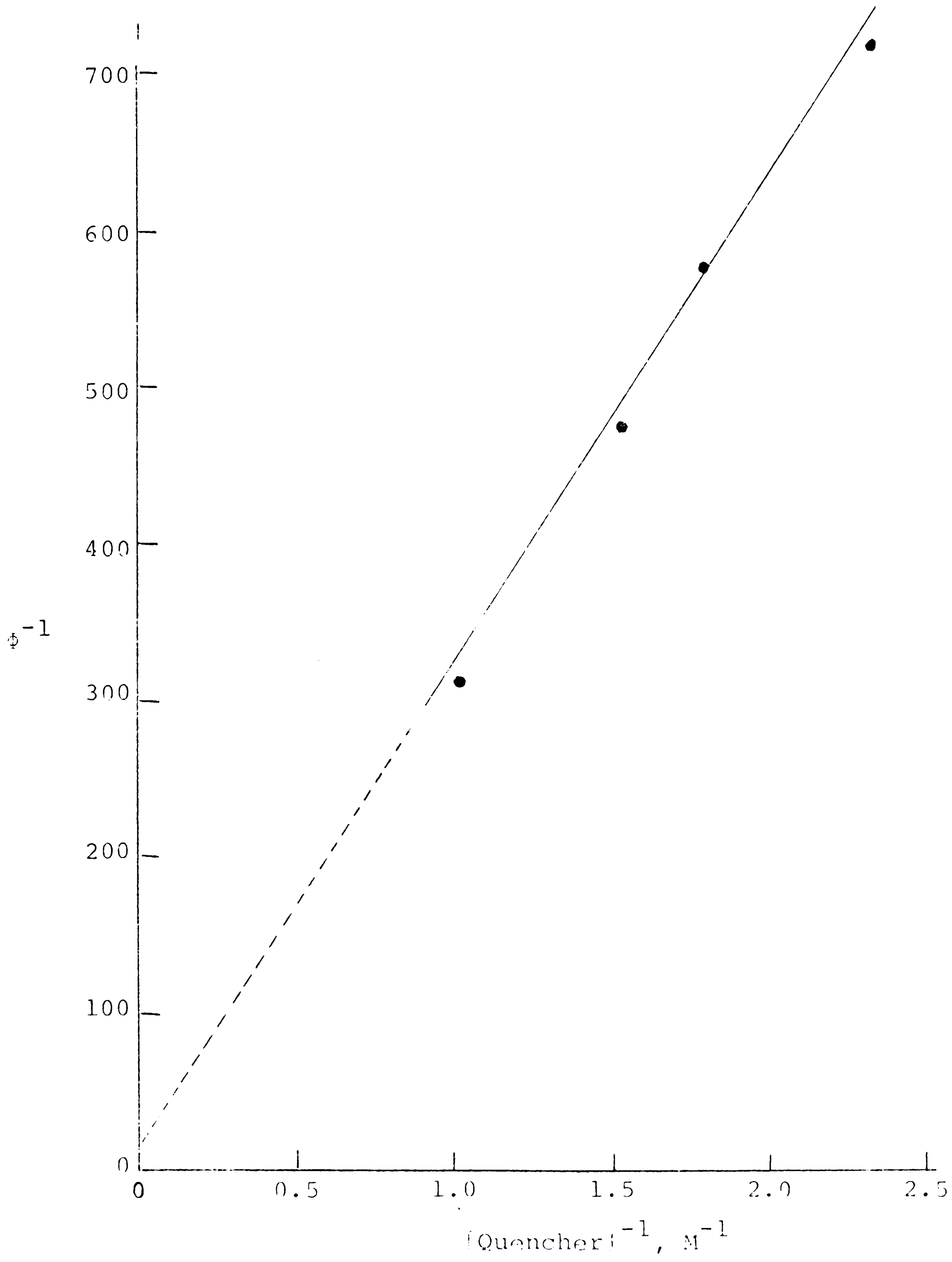


Figure 14. Reciprocal quenching plot for unknown product formation from 2,4,6-trimethylacetophenone.

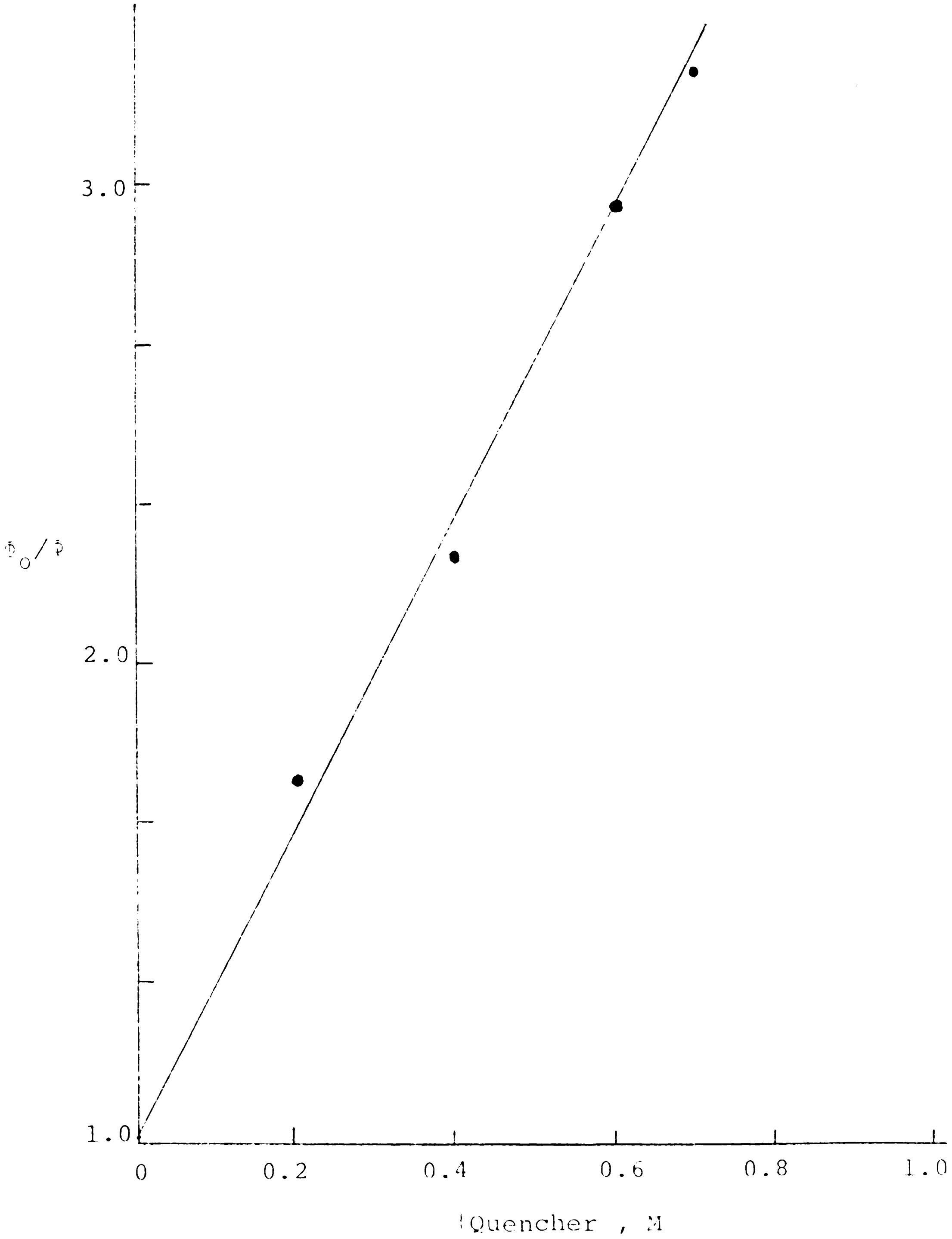


Figure 15. Stern-Volmer quenching of benzocyclobutenol formation from 2,4,6-trimethylacetophenone in benzene.

2,4,6-Trimethyl-γ-methylvalerophenone 46, 2,3,5,6-tetramethylvalerophenone 47, 2,3,4,5,6-pentamethylvalerophenone 48 and 2,4,6-trimethyl α-methylvalerophenone 49 undergo competitive type II elimination and benzocyclobutenol formation. Stern-Volmer quenching plots of type II elimination for ketones 46 - 49 are shown in Figure 16. The kinetic parameters for these ketones are listed in Table 9. Whereas elimination is readily quenchable with dienes, cyclization is quenched only at high diene concentrations. Use of any of these ketones to photosensitize 1,3-pentadiene isomerization reveals both a long-lived triplet and a short-lived triplet. The long-lived triplet is presumably the one responsible for type II reaction; the latter probably is the precursor of benzocyclobutenol. Figure 17 contains the sensitization plots for these 2,6-dimethyl substituted ketones. Triplet yields and lifetimes are listed in Table 10.

Irradiation of 2,4,6-triisopropyl γ-methylvalerophenone 50 resulted in the formation of the type II cleavage product (Φ = 0.0024) and of a benzocyclobutenol (Φ = 0.006). The Stern-Volmer quenching plot of type II product is linear with a slope of 115 M^{-1}. A sensitization plot, on the other hand, shows only a short-lived triplet, ($k_q\tau = 0.6\ M^{-1}$ $\Phi_T = 0.084$). The long-lived triplet could not be observed in the sensitization study down to 0.2 M of 1,3-pentadiene (Figure 18). Irradiation of 2,4,6-triisopropylacetophenone in benzene gives only the benzocyclobutenol in low quantum yield (Φ = 0.006). Formation of this benzocyclobutenol can be quenched by

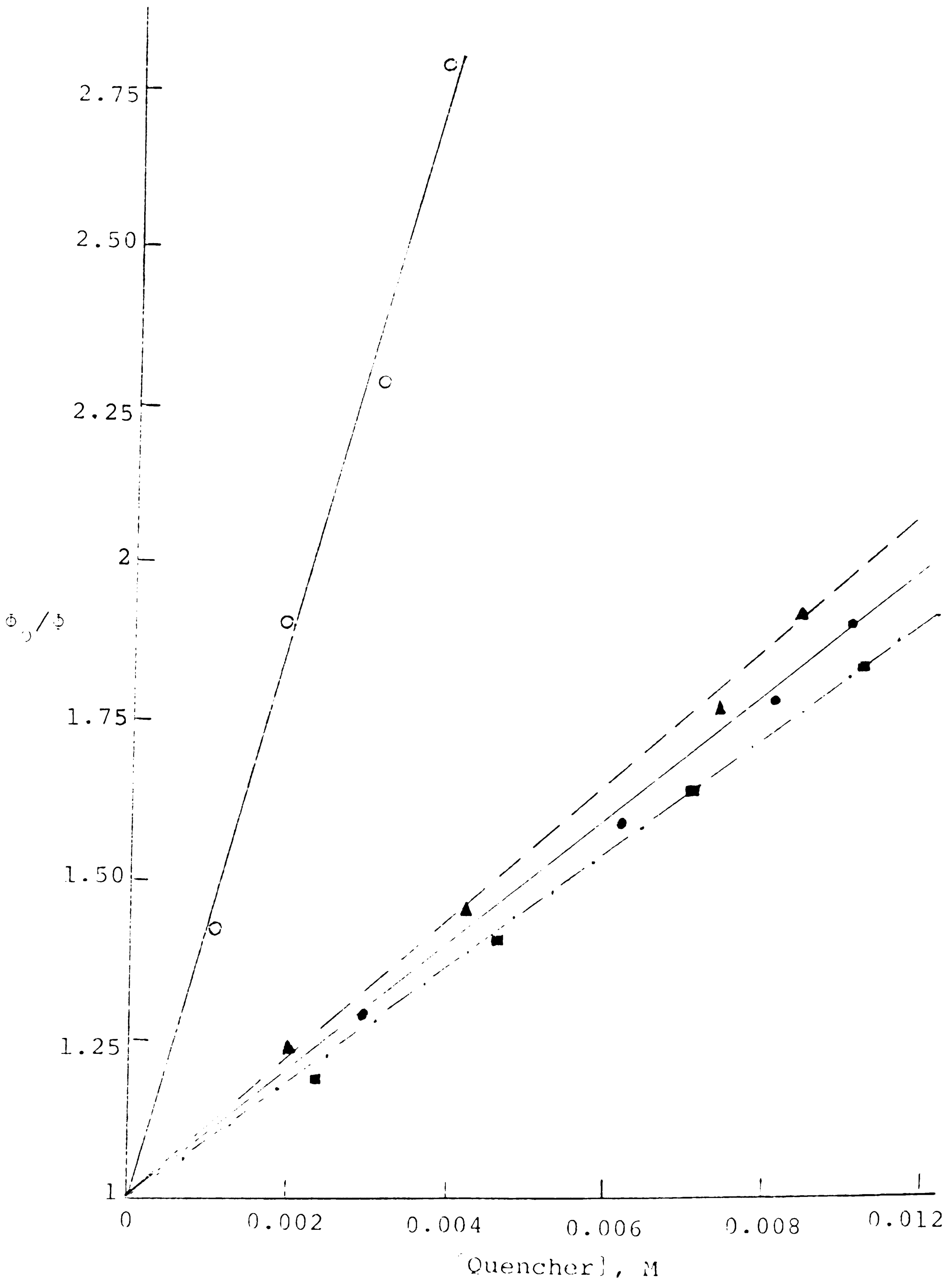


Figure 16. Stern-Volmer quenching plots for ketone 46 (■), 47 (●), 48 (▲) and 49 (o) in benzene.

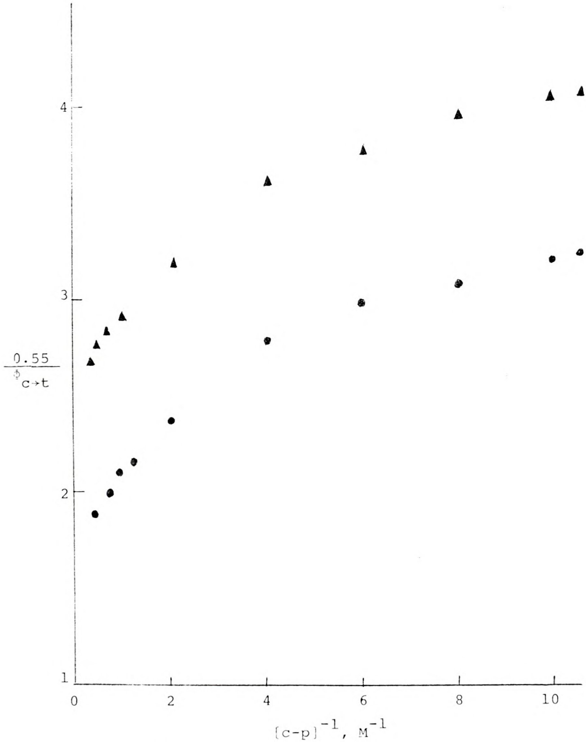


Figure 17. Sensitization studies of 2,4,6-trimethyl γ-methylvalerophenone (●) and 2,3,4,5,6-pentamethylvalerophenone (▲) in benzene.

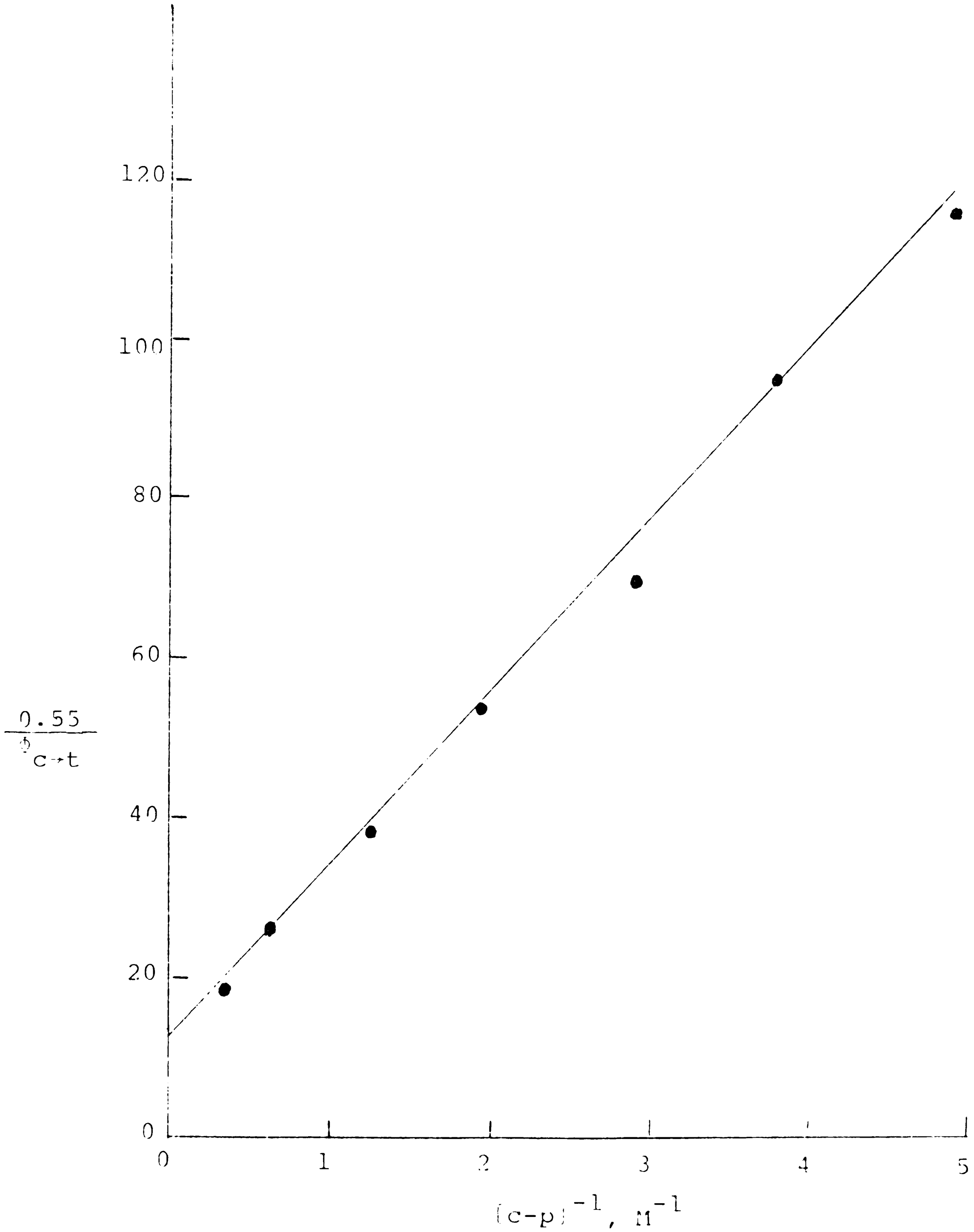
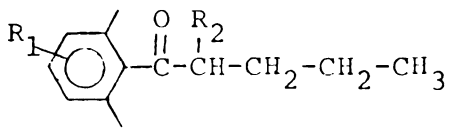


Figure 18. Sensitization plot for 2,4,6-triisopropyl γ-methylvalerophenone.

Table 9. Photokinetic Parameters for 2,6-Disubstituted Ketones



Ketones	R_1	R_2	Φ_{AP}[a]	Φ_{CB}[b]	Φ_T	$k_q\tau$, M^{-1}[c]
46	4-CH_3	H	0.0037±0.0002 (0.027±0.001)	0.022±0.001 (0.212±0.010)	0.345±0.006	91±5
47	3,5-$(CH_3)_2$	H	0.0004±0.0001 (0.003±0.0004)	0.020±0.001 (0.184±0.007)	0.251±0.004	101±8
48	3,4,5-$(CH_3)_3$	H	0.0002±0.00003 (0.0006±0.00005)	0.0012±0.0001 (0.013±0.001)	0.254±0.003	109±10
49	4-CH_3	CH_3	0.0018±0.0002 (0.011±0.001)	0.026±0.001 (0.271±0.014)	0.130±0.002	454±17

[a] Acetophenone formation; maximum quantum yield is obtained in 3.0 M dioxane and listed in parenthesis. [b] Cyclobutenol formation. [c] Based on acetophenone formation.

Table 10. Triplet Formation and Decay Rate Constant obtained from Sensitization Plots for 2,6-Disubstituted Ketones

Keytones	Long-lived triplet		Short-lived triplet		
	Φ_T^{Long}	$k_q\tau^{Long}$, M^{-1}	Φ_T^{Short}	$k_q\tau^{Short}$, M^{-1}	Φ_T^{total}
46	0.34	89	0.28	4.2	0.62
47	0.25	99	0.19	5.6	0.44
48	0.26	107	0.12	7.6	0.38
49	0.13	439	0.07	4.5	0.20

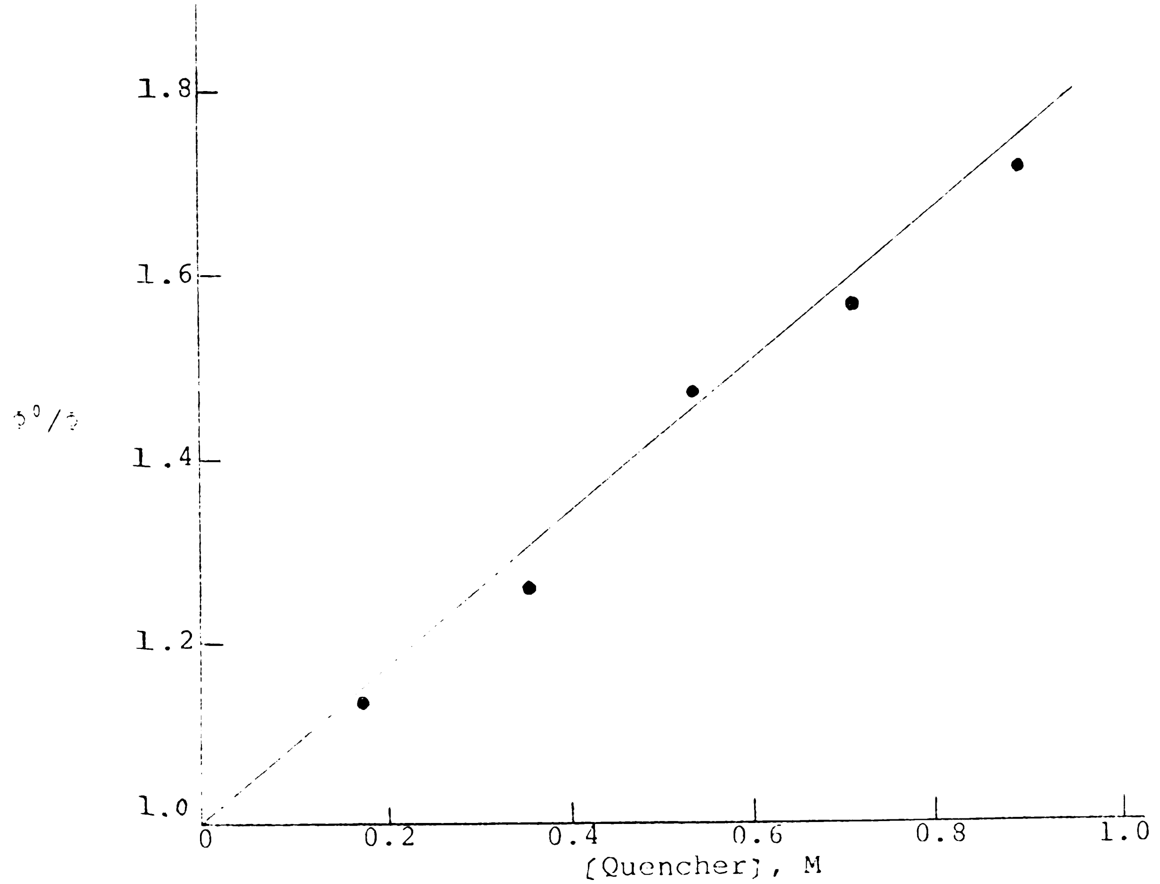


Figure 19. Quenching plot of benzocyclobutenol formation from 0.1 M 2,4,6-triisopropylacetophenone in benzene.

1-methylnaphthalene and a $k_q\tau$ of 0.8 M^{-1} is obtained from the quenching plot (Figure 19).

Irradiation of 2,4,6-trimethylpivalophenone **51** in benzene gives only the type I cleavage product, 2,4,6-trimethylbenzaldehyde. The quantum yield of product formation is 0.091 ± 0.004 and is maximized to 0.184 ± 0.005 in the presence of 0.01 M 1-dodecanethiol. Quenching of benzaldehyde formation from **51** with 1-methylnaphthalene as quencher using 366-nm irradiation led to a linear Stern-Volmer plot with slope of 680 M^{-1} (Figure 20).

IV. Methyl-Substituted 1-Tetralones

Sensitization studies with several methyl-substituted 1-tetralones, such as 8-methyl-1-tetralone **52**, 3,3,6,7-tetramethyl-1-tetralone **53**, and 5,6,7,8-tetramethyl-1-tetralone **54**, were carried out to determine the intersystem crossing yields and triplet lifetimes for comparison to those of the acyclic analogues such as *o*-methylvalerophenone, 2,4,6-trimethylvalerophenone, and 2,3,4,5,6-pentamethylvalerophenone. Figure 21 portrays the sensitization plots for these tetralones over the same concentration range employed in the study of the acyclic analogues. In contrast to *o*-methylacetophenone, 8-methyl-1-tetralone displays a linear sensitization plot: only one short-lived triplet is indicated. Table 11 contains the triplet yields and lifetimes of methyl-substituted 1-tetralones and of 4,7-dimethyl-1-indanone.

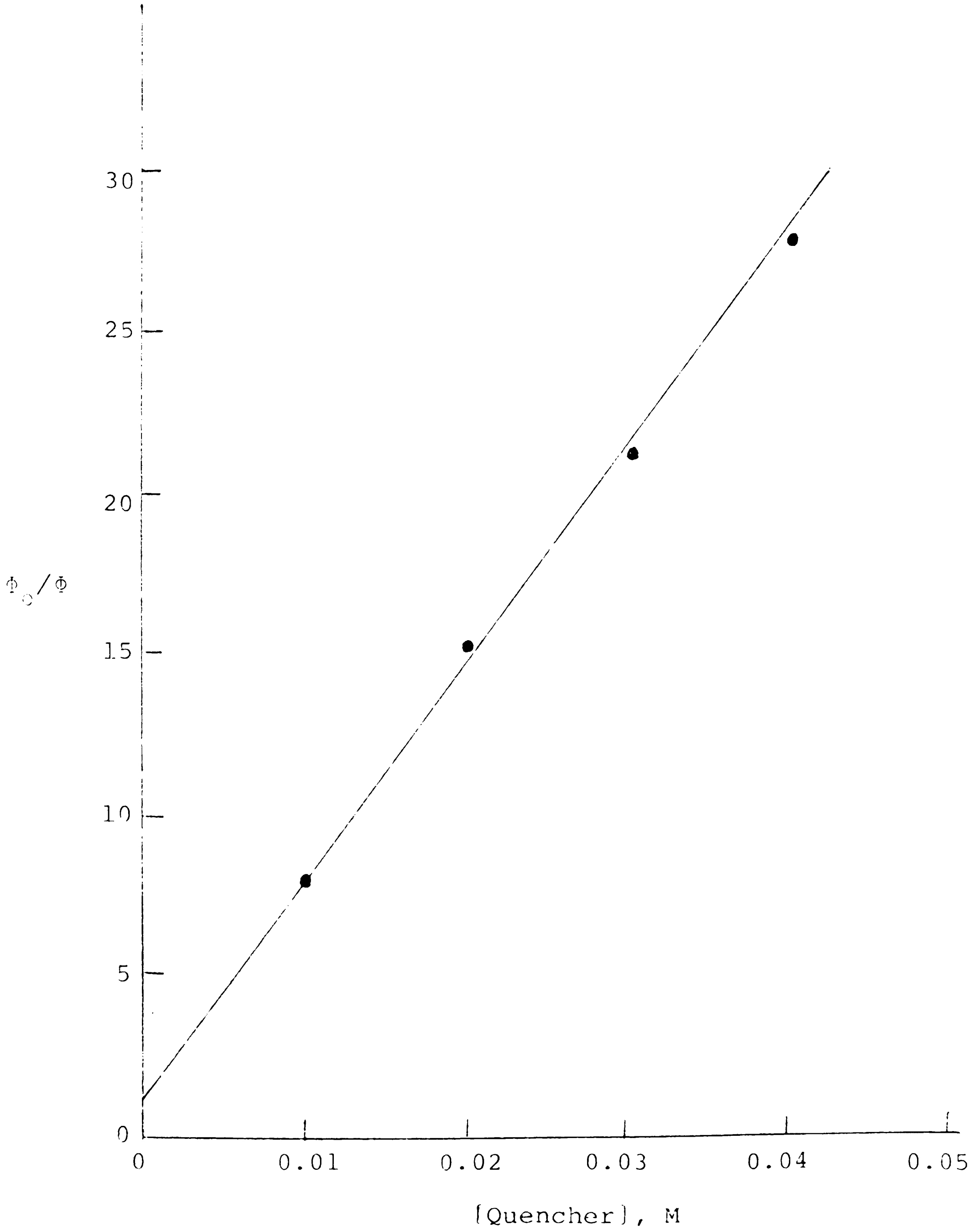


Figure 20. Quenching plot for 2,4,6-trimethylpivalophenone.

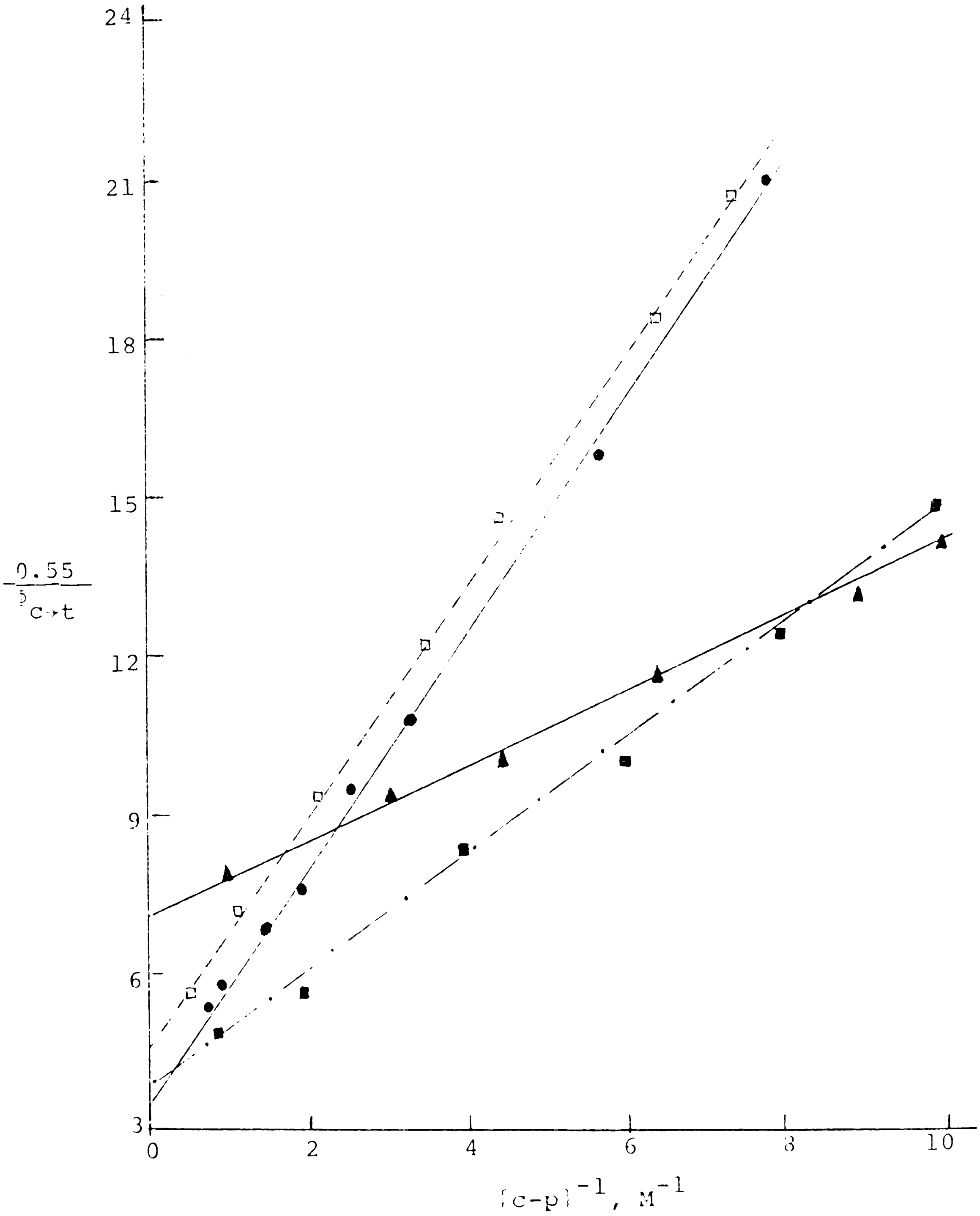


Figure 21. Sensitization studies of 8-methyl-1-tetralone (●), 5,6,7,8-tetramethyltetralone (▲), 3,3,6,8-tetramethyltetralone (■) and 4,7-dimethyl-α-indanone (□).

Table 11. Triplet Yield and Decay Rate Constant for Cyclic Ketones

Ketone[a]	Intercept[b]	Slope, M	$\Phi_T$total	$1/\tau$ 10^9 S^{-1}[c]
1-Tetralone				
8-methyl-	3.50	2.2	0.28	3.1
3,3,6,8-tetramethyl-	3.85	1.2	0.26	1.5
5,6,7,8-tetramethyl-	7.14	0.7	0.14	0.4
1-Indanone				
4,7-dimethyl-	4.76	2.1	0.21	2.2

[a] 0.05 M in benzene, 313-nm irradiation

[b] Extrapolate at infinite concentration of diene

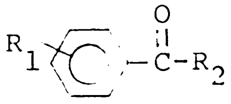
[c] $k_q = 5 \times 10^9 \ M^{-1} \ S^{-1}$

V. Spectroscopic Studies

Uv spectra of each ketone in n-heptane were measured; λ_{max} and extinction coefficients are listed in Table 12. Special attention is aimed at any correlation between L_a band intensities and molecular conformational preference and this aspect will be discussed later. All ortho-alkyl substituted ketones phosphoresce at 77°K, but they generally display structureless spectra with much weaker intensity relative to that of unsubstituted counterparts.

The phosphorescence spectra of o-methylacetophenone and 2,4,6-trimethylacetophenone in methycyclohexane glass at 77°K

Table 12. UV Spectra of o-Substituted Ketones in n-Heptane



ketone	Substituent on Ar	n,π* λ_{max}	n,π* ε_{max}	L_b λ_{max}	L_b ε_{max}	L_a λ_{max}	L_a ε_{max}
32	2-CH_3	309	72	283	1300	237	11550
33	2-CH_3	306	70	284	1350	238	11700
34	2-CH_3	307	68	283	1320	236	11450
35	2,3-$(CH_3)_2$	—	—	282	1010	241	8610
36	2,4-$(CH_3)_2$	304	89	283	1010	243	11170
37	2,5-$(CH_3)_2$	—	—	291	1430	241	9900
38	2,3,4,5-$(CH_3)_4$	—	—	290	1010	251	8600
39	2-CH_3, α-CH_3	—	—	281	1050	238	7500
40	2-CH_3, α,α-$(CH_3)_2$	—	—	276	870	236	3500
41	2-CH_2CH_3	—	—	280	1030	242	8570
45	2-CH_3, α-OCH_3	307	70	284	1340	238	11640
46	2,4,6-$(CH_3)_3$	308	110	273	386	240	2580
47	2,3,5,6-$(CH_3)_4$	306*	82	279	719	212	11500
48	2,3,4,5,6-$(CH_3)_5$	306*	80	278	746	214	12050
49	2,4,6-$(CH_3)_3$, α-CH_3	—	—	271	398	215	10860
50	2,4,6-$CH(CH_3)_{2\ 3}$	305*	99	267	410	208	12380
51	2,4,6-$(CH_3)_3$, α,α-$(CH_3)_2$	—	—	—	—	210	11480

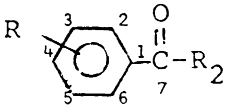
Table 12. Continued.

Ketone	R_1	n,π*		Lb		L_a	
		λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
1-Tetralones							
52	8-CH_3	301	2310	—	—	250 246	10100 10390
53	3,3,6,8-$(CH_3)_4$	300	3405	—	—	258 242	11450 10940
54	5,6,7,8-$(CH_3)_4$	304	1822	—	—	263 256	14900 15340

* Shoulder, not a maximum

\- No maximum

Table 13. ^{13}C NMR Chemical Shifts Values of o-Substituted Pheynl Ketones.



Key-tones	δ, ppm						
	1	2	3	4	5	6	7
34 2-CH_3	137.8	138.4	129.3	132.0	125.7	131.5	201.5
35 2,3-$(CH_3)_2$	137.9	140.6	134.6	131.9	125.2	124.9	205.9
36 2,4-$(CH_3)_2$	135.5	138.4	132.8	141.5	126.3	128.9	204.2
37 2,5-$(CH_3)_2$	138.5	134.6	128.9	131.8	135.0	131.6	204.0
38 2,3,4,5-$(CH_3)_4$	136.5	137.8	133.3	138.4	132.0	126.0	207.1
39 2-CH_3, α-CH_3	137.6	139.0	127.6	131.7	125.6	130.7	208.3
40 2-CH_3, α,α-$(CH_3)_2$	134.2	141.1	124.8	130.9	124.4	128.6	213.8
41 2-CH_2CH_3	138.8	143.7	130.2	130.8	125.6	128.0	205.1
46 2,4,6-$(CH_3)_3$	143.1	138.2	131.9	141.2	126.1	134.1	211.0
47 2,3,5,6-$(CH_3)_4$	143.3	134.3	127.6	131.5	127.6	134.3	209.2
48 2,3,4,5,6-$(CH_3)_5$	135.2	127.0	133.0	141.1	133.0	126.9	209.5
49 2,4,6-$(CH_3)_3$, α-CH_3	143.0	138.3	131.7	141.2	126.0	134.0	217.4
50 2,4,6-$CH(CH_3)_{2\ 3}$	144.2	138.5	127.1	141.9	126.5	135.2	211.9
51 2,4,6-$(CH_3)_3$, α,α-$(CH_3)_2$	143.1	138.2	131.8	141.1	126.2	134.3	218.9
1-Tetralones							
52 8-CH_3	131.2	142.4	127.9	132.4	126.8	140.6	199.2
53 3,3,6,8-$(CH_3)_4$	131.3	142.9	128.3	144.0	127.9	141.3	199.5
54 5,6,7,8-$(CH_3)_4$	139.4	142.8	141.0	141.3	138.6	143.0	199.7

Table 13. Continued.

Ketones	δ, ppm						
	1	2	3	4	5	6	7
Acetophenone	137.1	128.2	128.4	132.9	128.4	128.2	197.6
α-Tetralone	133.2	127.0	126.5	132.6	128.7	144.4	197.8
2,4,6-Tri-t-butylacetophenone[a]	137.1	144.9	122.8	149.4	122.8	144.9	212.9

[a] From reference 70.

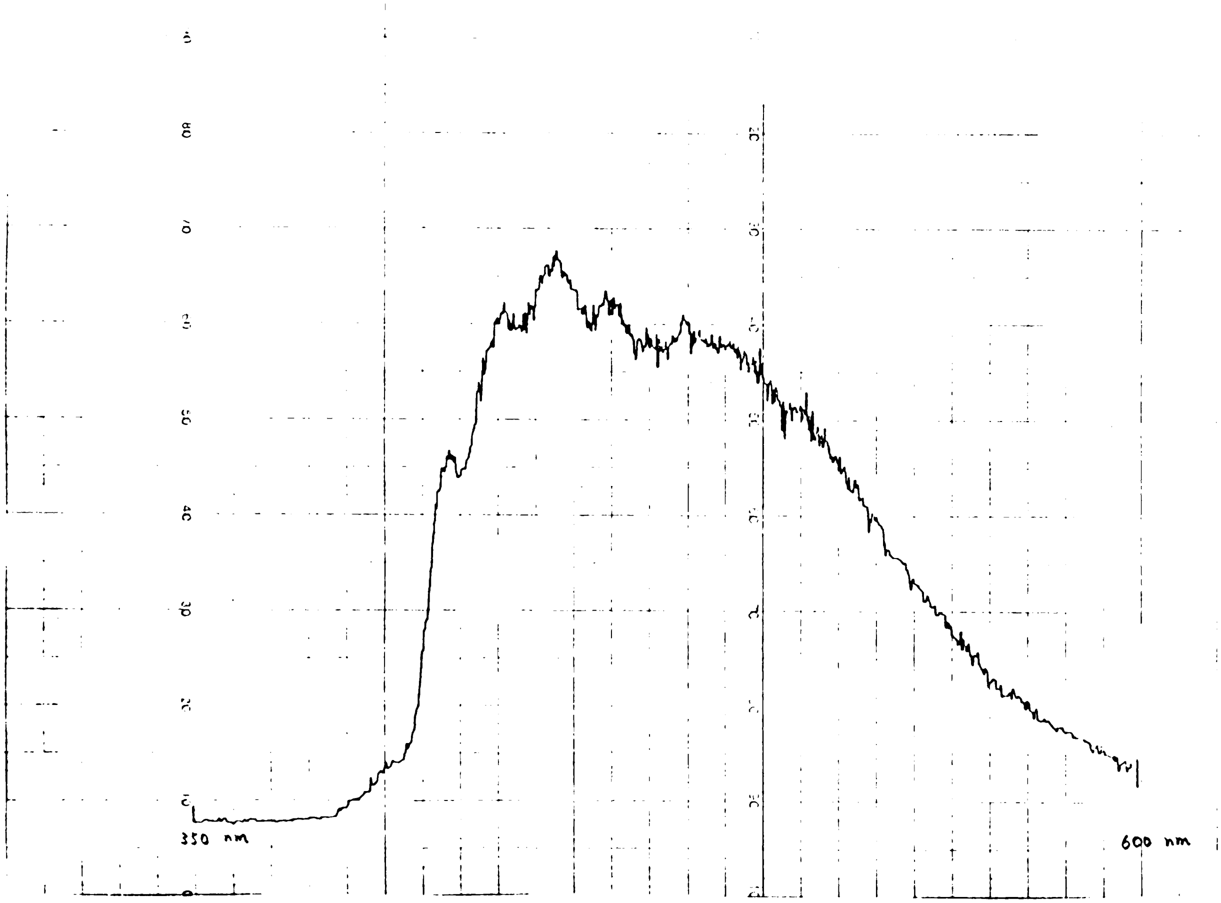


Figure 22. Phosphoresce spectra of *o*-methylacetophenene in methylcyclohexane.

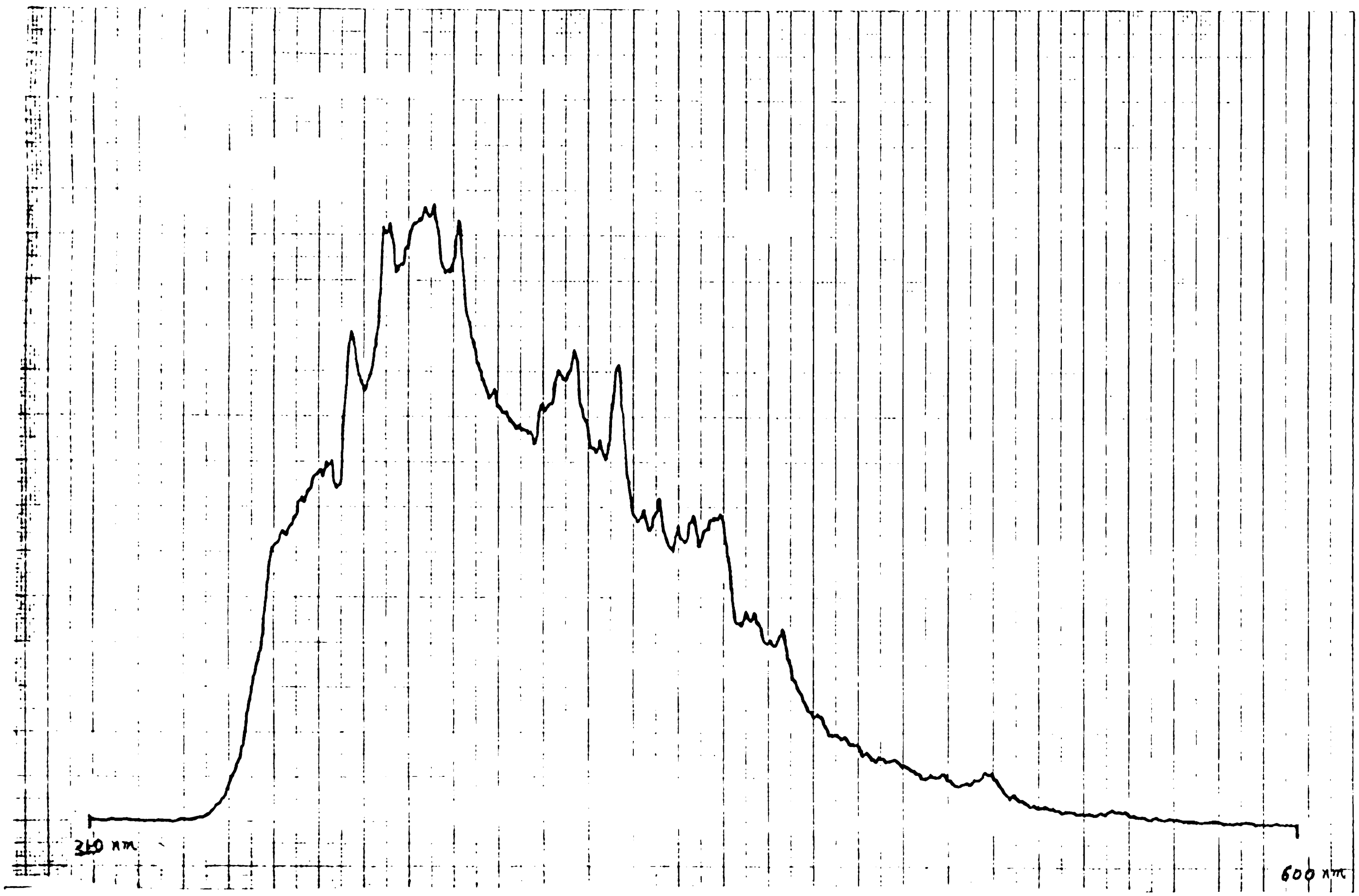


Figure 23. Phosphoresce spectra of 2,4,6-trimethylacetophenone in methylcyclohexane.

are shown in Figure 22 and 23 respectively.

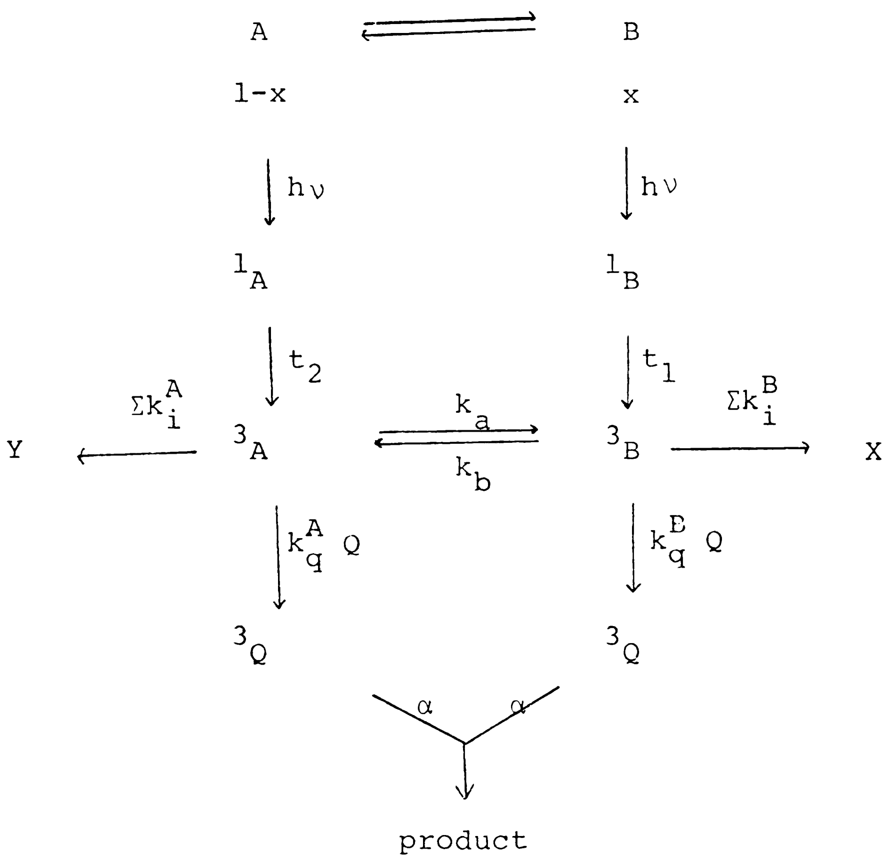
^{13}C nmr spectra of each ketone were measured in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard; the chemical shift values of aromatic and carbonyl carbons are listed in Table 13. It seems that the ^{13}C nmr signal of the carbonyl carbon atom moves to lower fields with increasing steric hindrance by ortho-substituent. Thus, the carbonyl carbon of acetophenone has a chemical shift of δ 199.9 ppm, while the ortho-substituted ketones o-methylvalerophenone, o-ethylvalerophenone, 2,3-dimethylvalerophenone 2,4,6-trimethylacetophenone and 2,4,6-triisopropylacetophenone show resonances at progressively lower fields: δ 201.54, 208.82, 205.98, 210.01, and 211.87, respectively.

VI. Sensitization Kinetic Analysis

In order to describe the behavior of sensitization plots where two triplet states can react with quencher Q, it is desired to derive a general expression relating the inverse of the total quantum yield for product formation, $1/\Phi_T$, and $1/[Q]$.

If species A and B are interconvertible both in the ground state and in the excited triplet state, product formation can occur from either species, say A, either directly or indirectly through interconversion from the other depending on the relative rate of interconversion and the rate of other processes available to these species.

The processes of interest are summarized in the following scheme and the parameters involved are defined below:



X : the fraction of species B in equilibrium

t_1 : the intersystem crossing quantum yield of B

t_2 : the intersystem crossing quantum yield of A

k_a : the rate of conversion from ^3A to ^3B

k_b : the rate of conversion from ^3B to ^3A

k_q^A : the bimolecular quenching constant of A

k_q^B : the bimolecular quenching constant of B

Σk_i^A : all the unimolecular reaction rates other than k_a

Σk_i^B : all the unimolecular reaction rates other than k_b

α : the probability of product formation from ^3Q

The total quantum yield for product formation, Φ_T, will equal the sum of the quantum yield for formation of T from

^3A and ^3B:

$$\Phi_T = \Phi_T^A + \Phi_T^B$$

Expressions for Φ_T^A and Φ_T, derived from

$$\Phi_T^A = (1 - x)t_2 \frac{k_q^A[Q]}{\frac{1}{\tau_A} + k_q^A[Q]} \alpha + x\, t_1 \frac{k_b}{\frac{1}{\tau_B} + k_q^B[Q]} \frac{k_q^A[Q]}{\frac{1}{\tau_A} + k_q^A[Q]} \alpha$$

(25)

$$\Phi_T^B = x\, t_1 \frac{k_q^B[Q]}{\frac{1}{\tau_B} + k_q^B[Q]} \alpha + (1-x)t_2 \frac{k_a}{\frac{1}{\tau_A} + k_q^A[Q]} \frac{k_q^B[Q]}{\frac{1}{\tau_B} + k_q^B[Q]} \alpha$$

(26)

where τ_A, τ_B are the triplet lifetimes of A and B and

$$\tau_A = \frac{1}{\sum_i k_i^A + k_a}$$

$$\tau_B = \frac{1}{\sum_i k_i^B + k_b}$$

combining eqs 25 and 26 would give Φ_T which can be rearranged to eq 27.

$$\Phi_T = \frac{1}{(k_q^B[Q] + \frac{1}{\tau_B})(k_q^A[Q] + \frac{1}{\tau_A})} \cdot \begin{Bmatrix} xt_1\ \alpha\ \{k_q^B[Q](k_q^A[Q] + \frac{1}{\tau_A}) + k_q^A[Q]K_b\} \\ +(1-x)t_2\ \alpha\{k_q^A[Q](k_q^B[Q] + \frac{1}{\tau_B}) + k_q^B[Q] \end{Bmatrix}$$

(27)

inversion of eq 27 and multipy α on both side would yield

$$\frac{\alpha}{\Phi_T} = (k_q^B[Q] + \frac{1}{\tau_B})(k_q^A[Q] + \frac{1}{\tau_A})/xt_1\{k_q^B[Q](k_q^A[Q]+\frac{1}{\tau_A}) + k_q^A[Q]k_b\} + (1-x)t_2\{k_q^A[Q](k_q^B[Q]+\frac{1}{\tau_B}) + k_q^B[Q]k_a\} \tag{28}$$

The right-handed side of eq. 28 is multiplied by $\tau_A\tau_B/\tau_A\tau_B$ to give

$$\frac{\alpha}{\Phi_T} = (k_q^B\tau_B[Q]+1)(k_q^A\tau_A[Q]+1)/xt_1\ k_q^B\tau_B[Q](k_q^A\tau_A[Q]+1) + k_q^A\tau_A\ k_b\tau_B[Q] + (1-x)t_2\{k_q^A\tau_A[Q](k_q^B\tau_B[Q]+1) + k_q^B\tau_B\ k_a\tau_A(Q)\} \tag{29}$$

Now dividing the numerator and denominator of the right-hand side of eq. 29 by $[Q]^2$, we obtain

$$\frac{\alpha}{\Phi_T} = (k_q^B\tau_B + \frac{1}{[Q]})(k_q^A\tau_A + \frac{1}{[Q]})/xt_1\{k_q^B\tau_B(k_q^A\tau_A + \frac{1}{[Q]}) + \frac{1}{[Q]}(k_q^A\tau_A\ k_b\tau_B)\} + (1-x)t_2\{k_q^A\tau_A(k_q^B\tau_B+\frac{1}{[Q]}) + \frac{1}{[Q]}k_q^B\tau_B k_a\tau_A \tag{30}$$

Eq. 30 gives the inverse of the total quantum yield for product formation as a function of $1/(Q)$. Since the numerator of eq. 30 is a polynomial linear in $1/[Q]$, the sensitization plot will approach a straight line, i.e., an oblique asymptote, when $1/[Q]\to\infty$ The equation for this oblique asymptote can be determined by mathematical procedures,[83] and is given by

$$\text{Obique asymptote} = \frac{1}{c}\ \frac{1}{[Q]} + \frac{1}{c^2}\{(k_q^A\tau_A+k_q^B\tau_B)C - k_q^A\tau_A k_q^B\tau_B\ \{xt_1 + (1-x)t_2\}$$

where $C = xt_1\{k_q^B\tau_B + k_q^A\tau_A k_b\tau_B\} + (1-x)t_2\{k_q^A\tau_A + k_q^B\tau_B k_a\tau_A\}$

Therefore,

$$\text{intercept} = \frac{1}{C^2}\{(k_q^A\tau_A + k_q^B\tau_B)C - k_q^A\tau_A k_q^B\tau_B\ xt_1 + (1-x)t_2\}$$

$$\text{slope} = \frac{1}{C}$$

$$\frac{\text{intercept}}{\text{slope}} = \frac{1}{C}\{(k_q^A\tau_A + k_q^B\tau_B)C - k_q^A\tau_A k_q^B\tau_B\{xt_1 + (1-x)t_2\}\}$$

Case I.

If $k_a \ll \sum_i k_i^A$ and $k_b \gg \sum_i k_i^B$, and also $k_q^A = k_q^B$

i.e. $k_a \ll \frac{1}{\tau_A}$ and $k_b = \frac{1}{\tau_B}$

then $C = xt_1\{k_q(\tau_B + \tau_A k_b\tau_B)\} + (1-x)t_2 \cdot k_q(\tau_A + \tau_B k_a\tau_A)$

$= k_q\ \{xt_1(\tau_A + \tau_B) + (1-x)t_2(\tau_A + \tau_B k_a\tau_A)\}$

$= k_q\tau_B\ \{xt_1(\tau_A/\tau_B + 1) + (1-x)t_2(\tau_A/\tau_B + k_a\tau_A)\}$

Furthermore, if $\tau_A \ll \tau_B$

then $C = k_q\tau_B\{xt_1\}$

Therefore,

$$\text{intercept} = \frac{k_q(\tau_A + \tau_B)}{k_q\tau_B\ x\ t_1} - \frac{k_q^2\tau_A\tau_B\ xt_1 + [(1-x)t_2]}{(k_q\tau_B xt_1)^2}$$

$$\simeq \frac{1}{xt_1}$$

∴ The 1/intercept is actually a measure of fraction x when $t_1 = 1$.

$$\frac{\text{intercept}}{\text{slope}} = k_q(\tau_A + \tau_B) - \frac{\tau_A k_q}{xt_1}[xt_1 + (1-x)t_2]$$

$$= k_q(\tau_A + \tau_B) - k_q\tau_A[1 + \frac{xt_1 + (1-x)t_2}{xt_1}]$$

$$= k_q[\tau_B - \tau_A \cdot \frac{xt_1 + (1-x)t_2}{xt_1}]$$

if $\tau_A << \tau_B$, then intercept/slope = $k_q\tau_B$

<u>Case II.</u>

If $k_a >> \Sigma k_i^A$ and $k_b >> \Sigma k_i^B$; $k_q^A = k_q^B$

i.e. $k_a = \frac{1}{\tau_A}$ and $k_b = \frac{1}{\tau_B}$

Then $C = xt_1 \cdot k_q(\tau_B + \tau_A) + (1-x)t_2 \cdot k_q(\tau_A + \tau_B)$

$$= k_q(\tau_A + \tau_B)[xt_1 + (1-x)t_2]$$

$$\frac{1}{\text{slope}} = k_q(\tau_A + \tau_B)[xt_1 + (1-x)t_2]$$

$$\text{intercept} = \frac{k_q(\tau_A+\tau_B)}{k_q(\tau_A+\tau_B)[xt_1+(1-x)t_2]} - \frac{k_q^2 \cdot \tau_A\tau_B[xt_1+(1-x)t_2]}{k_q^2(\tau_A+\tau_B)^2[xt_1+(1-x)t_2]^2}$$

$$= \frac{1}{xt_1 + (1-x)t_2}[1- \frac{\tau_A\tau_B}{(\tau_A+\tau_B)^2}]$$

$$\frac{\text{intercept}}{\text{slope}} = k_q(\tau_A + \tau_B)[1 - \frac{\tau_A\tau_B}{(\tau_A + \tau_B)^2}]$$

Case III.

If $k_a << \sum_i k_i^A$ and $k_b << \sum_i k_i^B$

i.e. $k_a << \frac{1}{\tau_A}$ and $k_b << \frac{1}{\tau_B}$

then $$C = k_q x t_1[\tau_B + \tau_A\, k_b\tau_B] + k_q(1-x)t_2[\tau_A + \tau_B k_a \tau_A]$$

$$= k_q\{\tau_A x t_1[\frac{\tau_B}{\tau_A} + k_b\tau_B] + \tau_B(1-x)t_2[\frac{\tau_A}{\tau_B} + k_a\tau_A]\}$$

$$= k_q\{x t_1\tau_B + (1-x)t_2\tau_A\}$$

$$\text{intercept} = \frac{\tau_A + \tau_B}{x t_1\tau_B + (1-x)t_2\tau_A} - \frac{\tau_A\tau_B[x t_1 + (1-x)t_2]}{[x t_1\tau_B + (1-x)t_2\tau_A]^2}$$

$$\frac{\text{intercept}}{\text{slope}} = k_q(\tau_A + \tau_B) - \frac{k_q\tau_A\tau_B[x t_1 + (1-x)t_2]}{x t_1\tau_B + (1-x)t_2\tau_A}$$

Furthermore, if $\tau_A >> \tau_B$ then

$$\text{intercept} = \frac{1 + \tau_B/\tau_A}{x t_1\tau_B/\tau_A + (1-x)t_2} - \frac{\tau_B/\tau_A[x t_1 + (1-x)t_2]}{[x t_1\tau_B/\tau_A + (1-x)t_2]^2}$$

$$\simeq \frac{1}{(1-x)t_2}$$

$$\frac{\text{intercept}}{\text{slope}} = k_q(\tau_A + \tau_B) - \frac{k_q\tau_A\tau_B[x t_1 + (1-x)t_2]}{(1-x)t_2\tau_A}$$

$$\simeq k_q\tau_A$$

Now turns to the sensitization plot as $1/[Q]\to 0$

The initial slope of this plot can be determined by evaluating the derivative of eq. 30 with respect to $1/[Q]$ at $1/[Q] = 0$, and is given by

$$\text{initial slope} = \frac{k_q^2\tau_A\tau_B[xt_1+(1-x)t_2]\cdot k_q(\tau_A+\tau_B) - k_q^2\tau_A\tau_B\cdot C}{(k_q^2\tau_A\tau_B[xt_1+(1-x)t_2])^2}$$

$$= \frac{(\tau_A + \tau_B)}{k_q\tau_A\tau_B[xt_1+(1-x)t_2]} - \frac{\{xt_1(\tau_B+\tau_A\tau_B k_b)+(1-x)t_2(\tau_A+\tau_B\tau_A k_a)\}}{k_q[xt_1+(1-x)t_2]^2\cdot\tau_A\tau_B}$$

$$\frac{1}{\text{intercept}} = xt_1 + (1-x)t_2$$

Case I. If $k_a << \Sigma k_i^a$ and $k_b >> \Sigma k_i^B$

i.e. $k_a << \frac{1}{\tau_A}$ and $k_b = \frac{1}{\tau_B}$, then

$$\text{initial slope} = \frac{\tau_A + \tau_B}{k_q\tau_A\tau_B[xt_1+(1-x)t_2]} - \frac{\tau_B\{xt_1(\frac{\tau_A}{\tau_B}+1)+(1-x)t_2(\frac{\tau_A}{\tau_B})\}}{k_q[xt_1+(1-x)t_2]^2\tau_A\cdot\tau_B}$$

$$= \frac{1}{k_q\tau_A}\{\frac{(\tau_A+\tau_B)}{\tau_B[xt_1+(1-x)t_2]} - \frac{xt_1(\tau_A/\tau_B)+(1-x)t_2\tau_A/\tau_B}{[xt_1+(1-x)t_2]^2}$$

$$\therefore \frac{\text{intercept}}{\text{slope}} = k_q\tau_A\frac{xt_1 + (1-x)t_2}{(1+\frac{\tau_A}{\tau_B})[xt_1+(1-x)t_2] - xt_1(\frac{\tau_A}{\tau_B}+1)+(1-x)t_2(\frac{\tau_A}{\tau_B})}$$

Furthermore, if $\tau_A << \tau_B$, then

$$\frac{\text{intercept}}{\text{slope}} = k_q\tau_A\{\frac{xt_1 + (1-x)t_2}{xt_1 + (1-x)t_2}\}$$

$$= k_q\tau_A$$

Case II. If $k_a >> \Sigma k_i^A$ and $k_b >> \Sigma k_i^B$

then $C = k_q(\tau_A + \tau_B)[xt_1 + (1-x)t_2]$

$$\text{initial slope} = \frac{\tau_A + \tau_B}{k_q\tau_A\tau_B[xt_1+(1-x)t_2]} - \frac{\tau_A + \tau_B}{k_q\tau_A\tau_B[xt_1(1-x)t_2]}$$

$$= 0$$

This means that there is only one triplet lifetime in this case i.e. $^3A \rightleftarrows {}^3B$ reaches equilibrium before they are quenched.

Case III. If $k_a << \Sigma k_i^A$ and $k_b << \Sigma k_i^B$

i.e. $k_a << \frac{1}{\tau_A}$ and $k_b << \frac{1}{\tau_B}$

then $C = k_q\{xt_1\tau_B + (1-x)t_2\tau_A\}$

$$\text{initial slope} = \frac{\tau_A + \tau_B}{k_q\tau_A\tau_B[xt_1+(1-x)t_2]} - \frac{xt_1\tau_B + (1-x)t_2\tau_A}{k_q[xt_1+(1-x)t_2]^2 \cdot \tau_A\tau_B}$$

$$\therefore \frac{\text{intercept}}{\text{slope}} = \frac{k_q\tau_A\tau_B[xt_1 + (1-x)t_2]}{(\tau_A + \tau_B)[xt_1+(1-x)t_2] - xt_1\tau_B+(1-x)t_2\tau_A}$$

DISCUSSION

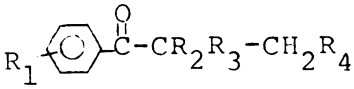
I. Effects of o-Methyl Substitution on Type II Photoreactivity

Type II quantum yields for o-methylbutyrophenone, o-methylvalerophenone, and o-methyl γ-methylvalerophenone are low and depend on γ-hydrogen lability, as expected if another triplet-state reaction such as enolization (rate = k_e) is competitive with γ-hydrogen abstration (rate = k_r). The rate constants of type II reaction in benzene and t-BuOH can be calculated based on equation 31.

$$\begin{aligned}\Phi_{II}^{max} &= \Phi_T^{long}\, k_r\, \tau_T \\ &= \Phi_T^{long}\, k_r\, (k_r + k_e)^{-1}\end{aligned} \qquad (31)$$

Since type II reaction comes only from the long-lived triplet, Φ_T^{long} is the yield of long-lived triplet measured by extrapolation of low concentration pentadiene data in a sensitization plot to $[\text{pentadiene}]^{-1} = o$. Table 14 contains the triplet lifetime data and rate constants for the o-alkyl phenyl ketones. Compared to the k_r values of the unsubstituted ketones,[14] the rate decrease produced by the ortho-methyl group is found to be a factor of 3.3. As indicated in Table 12 and 14, the solvent effect of t-butyl alcohol represents not only P_p maximizing, but also Φ_T, k_r and k_e decreasing. Generally, k_e in t-butyl alcohol is only 1/5 that in benzene. Similar

Table 14. Triplet Lifetime and Rate Constants for *o*-Alkyl Phenyl Ketones



Ketones	R_1	R_2	R_3	R_4	$1/\tau^a$, 10^7 s^{-1}	k_r 10^7 s^{-1}	k_e 10^7 s^{-1}
			In Benzene				
32	2-CH_3	H	H	CH_3	3.4	0.4	3.0
33	2-CH_3	H	H	CH_2CH_3	5.6	2.7	2.9
34	2-CH_3	H	H	$CH(CH_3)_2$	18.0	15.0	3.0
35	2,3-$(CH_3)_2$	H	H	$CH(CH_3)_2$	4.0	2.0	2.0
36-h	2,4-$(CH_3)_2$	H	H	$CH(CH_3)_2$	3.6	1.2	2.4
36-d	2,4-$(CD_3)_2$	H	H	$CH(CH_3)_2$	4.9	2.6	2.3
37	2,5-$(CH_3)_2$	H	H	$CH(CH_3)_2$	4.3	1.6	2.7
38	2,3,4,5-$(CH_3)_4$	H	H	$CH(CH_3)_2$	1.0	0.3	0.7
39	2-CH_3	CH_3	H	CH_2CH_3	4.0	2.4	1.6
40[b]	2-CH_3	CH_3	CH_3	CH_2CH_3	3.0	1.9	0.4
41	2-CH_2CH_3	H	H	CH_2CH_3	5.3	3.0	2.3
			In *t*-BuOH				
32	2-CH_3	H	H	CH_3	0.7	0.1	0.6
33	2-CH_3	H	H	CH_2CH_3	1.5	0.8	0.7
34	2-CH_3	H	H	$CH(CH_3)_2$	5.7	4.9	0.8
35	2,3-$(CH_3)_2$	H	H	$CH(CH_3)_2$	0.9	0.5	0.4
36-h	2,4-$(CH_3)_2$	H	H	$CH(CH_3)_2$	0.7	0.2	0.5
37	2,5-$(CH_3)_2$	H	H	$CH(CH_3)_2$	0.9	0.4	0.5
38	2,3,4,5-$(CH_3)_4$	H	H	$CH(CH_3)_2$	0.3	0.1	0.2
41	2-CH_2CH_3	H	H	CH_2CH_3	2.0	1.3	0.7

Table 14. continued

ketone	R_1	R_2	R_3	R_4	$1/\tau$ $10^7\ s^{-1\,a}$	k_r $10^7\ s^{-1}$	k_e $10^7\ s^{-1}$
				In 3.0 M 1,4-Dioxane			
33	2-CH_3	H	H	CH_2CH_3	5.8	2.6	3.2
34	2-CH_3	H	H	$CH(CH_3)_2$	18.6	14.6	4.0

[a] $k_q = 5.0 \times 10^9\ M^{-1}\ s^{-1}$ in benzene, $2.3 \times 10^9\ M^{-1}\ s^{-1}$ in t-BuOH (C. Steel and L. Giering, unpablished work).

[b] Also undergoes type I cleavage reaction, $k_I = 0.6 \times 10^7\ s^{-1}$.

decreases in triplet decay rates of o-methylacetophenone in polar solvents were reported by Lindqvist.[50] On the other hand, 3.0 M 1,4-dioxane maximizes P_p without significantly changing Φ_T and triplet lifetime values.

The effects of meta-and para-methyl substitution on the photoreactivity of phenyl ketones have been thoroughly studied by Wagner, Thomas and Harris.[35] It has been shown that a meta-methyl decreases k_r by a factor of 3, which is comparable to the reduction produced by an ortho-methyl. On the other hand, a factor of 8 rate decrease is observed for para-methyl. The fact that ortho-methyl has a rate decrease comparable to that of meta-methyl rather than para-methyl is not without precedent.[84,85] Simple MO calculations[85] of excited state electron distribution in substituted benzenes indicate selective electron transmission from the o- and m-positions by electron-donating groups. This ortho-meta transmission in the lowest excited singlet of substituted benzene is obviously in

contrast to the ortho-para transmission in the ground state.

The comparable rate constant for ortho-methyl and meta-methyl phenyl ketones also indicates that the assumed diffusion-controlled values of k_q is reasonable. This assumption is further verified by the quenching study of o-methyl γ-methylvalerophenone **34** in primary alcohols with various viscosities. It has been shown that in moderately viscous alcohols the diffusion-controlled rate of quenching, k_{dif}, is inversely proportional to viscosity η, according to equation 32, a slightly modified Debye equation.[80,86] As described

$$k_q = k_{dif} = 8RT/2000\ \eta \qquad (32)$$

in Table 6 and Figure 4, exothermic energy transfer from triplet **34** is just as "diffusion-controlled" as for the unhidered valerophenone. This kind of sterically indifferent triplet energy transfer was observed before with α,α-dimethylvalerophenone.[79]

Type II quantum yields and k_r values demonstrate a progressive decrease as more methyl groups are placed onto the ring, presumably because the energy difference ΔE_T between n,π* and π,π* triplet increases with additional methyl groups.

It is interesting that no cyclobutanol products were detected for ketones **32** - **34**, although cyclobutanols averge 18% of the total products from various unsubstituted phenyl ketones. This decreased tendency for cyclization versus elimination may be due to the steric interaction between the o-methyl group and 1,4-biradical intermediates. On the other hand, cyclobutanols are formed during the irradiation of ketones 39 and 40. The increase in the cyclization:elimination ratio (ketone 33 : 39 : 40 = 0 : 1.4 : 3.3) by α-methyl substituents indicates a change in the behavior of the 1,4-biradicals. The Lewis[87] and Wagner[79] groups have independently observed this α-methyl effect on cyclization: elimination ratios. It seems that α-methyl substitution destabilizes the conformation of the biradical which leads to cleavage relative to the conformation which leads to cyclization.[79,87]

The values of k_r, 2.4×10^7 sec^{-1} for *o*-methyl α-methylvalerophenone 39 and 1.9×10^7 sec^{-1} for *o*-methyl α,α-dimethylvalerophenone 40, together with *o*-methylvalerophenone's $k_r = 2.7 \times 10^7$ sec^{-1}, indicate that α-methyl substitution produces a small decrease in rates of γ-hydrogen abstraction. Similarly, a slight decrease in type II reactivity was also observed in the case of α,α-dimethylvalerophenone.[76] These decreases are likely due to a weak inductive effect on the n,π* triplet rather than to a steric effect. It is known that strong electron-withdrawing groups on the α-carbon greatly enhance the reactivity of phenyl ketone triplets.[88,89] Therefore, methyl substitution should produce a week inductive effect in the opposite direction.

The estimated quantum yield for type I cleavage of 40, together with Φ_T and $k_q\tau$ values, indicates a rate constant

$$\Phi_{BA} = 0.5 \cdot \Phi_T \cdot \tau \cdot k_I$$

of type I cleavage at 0.58×10^7 sec^{-1}. In this case, the formation of a stable tertiary alkyl radical make the α-cleavage process thermodynamically favorable and enables it

to compete with the type II process. The value of k_I is somewhat lower than that of α,α-dimethylvalerophenone ($k_I = 1.4 \times 10^7$).[79] The reduced reactivity of **40** probably is due to the increased π,π* character in the lowest triplet state caused by o-methyl substitution, which is the same reason for lower reactivity in type II processes for these o-methyl substituted phenyl ketones.

II. Comparisons between Type II Reaction and Photoenolization Reaction

At first glance the photoenolization process strongly resembles the type II process in that a γ-hydrogen migrates to the carbonyl oxygen in the excited state of phenyl ketones. Compounds similar to o-methylvalerophenone **33** upon irradiation can potentially undergo both enolization and type II reaction. Bergmark[52] showed that **33** does undergo type II photoelimination in low yield ($\Phi_{max} = 0.04$). Assuming no significant radiationless decay for **33**, Bergmark suggested a selectivity factor of 26 : 1 for abstraction of o-methyl versus α-methylene hydrogens. Furthermore, Bergmark demonstrated a 30 : 1 preference for o-methyl : γ-CH_3 in the corresponding alkoxyl radical. The closeness of these ratios Bergmark argued, affirms the usefulness of the alkoxy radical model in aryl ketone photochemistry and also demonstrates that no kinetic difference can be detected between photoenolization and the photoelimination reaction.

Analysis of the kinetic data for **33** reveals two facts: (1) The low type II quantum yield actually results from a combination of low yield of triplet ($\Phi_T = 0.21$), low

probability for product formation from the diradical intermediate (P_p = 0.16), and competing enolization, not just from the latter as previously assumed.[52]

(2) The value of k_e(2.9×10^7 sec^{-1}) is comparable to that of k_r(2.7×10^7 sec^{-1}), which is quite different from the 30 : 1 preference ratio observed in the alkoxy radical system.

Additional methyl substitution on the phenyl ring may have effects on both k_r and k_e. A comparison of k_r and k_e should provide more information about the mechanism of photoenolization since the mechanism and kinetics of the type II reaction are well understood.[14] For 2,3-dimethyl-, 2,4-dimethyl-, 2,3-dimethyl-, and 2,3,4,5-tetramethyl γ-methylvalerophenone the additional methyl groups lower k_r progressively as shown in Table 14 and discussed in Section I, while k_e remains unchanged (2-3 x 10^7 sec^{-1}). The differences in k_r and k_e indicate that different mechanisms might be involved in the photoenolization and type II reactions.

This hypothesis is further supported by the following experimental data. First, *o*-ethylvalerophenone **41** has the same triplet lifetime as *o*-methylvalerophenone **33** and there is no increase in k_e from **33** to **41** even though the C-H bond strength decreases from **33** (primary C-H) to **41** (secondary C-H). On the other hand, the k_r values increases by a factor of 16 when γ C-H bond changes from primary to secondary.[14] Equally interesting is the behavior of 2,4-dimethylvalerophenone **36h** and 2,4-dimethyl-d_6-valerophenone **36d**, which also display comparable k_e values. Therefore, there is no significant isotope effect on enolization, while a k_H/k_D value of 4.8

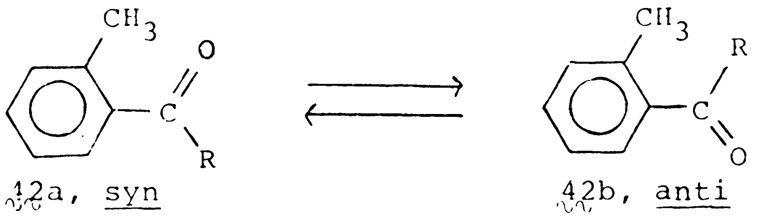
obtains in type II γ-hydrogen abstraction.[90]

The fact that k_e is independent of C-H bond strength, the lack of a kinetic isotope effect and the insensitivity of k_e to additional methyl groups on the ring together indicate that the rate determining step for enolization is not hydrogen abstraction.

This conclusion suggests that conformational factors may play an important role in the rate determing step for enolization reactions. Before a detailed correlation is made, it is appropriate first to examine the conformational analysis of these o-substituted phenyl ketones.

III. Conformational Considerations

Ortho-substituted phenyl ketones can exist both in syn **42a** and anti conformations **42b**. Montaudo and co-workers[91] have studied the conformational preferences of ortho-substituted acetophenones and benzophenones by proton nmr data and dipole moment measurements. The nearly identical chemical shift and dipole moment values of o-substituted ketones and the corresponding unsubstituted ketones suggested that these molecules exist preferentially in the conformation **42a** rather than **42b**. Conformations such as **42b** are disfavored in these compounds presumably because the steric interaction between the ortho-methyl and the R group would force the molecules



42a, syn   **42b**, anti

out of planarity.

The use of electronic absorption spectra to interpret molecular geometries has been well recognized.[92] Specifically, it has been shown that introduction of a methyl substituent at the ortho position of acetophenone decreases the intensity of the π,π^* charge-transfer (L_a) band.[93] The hypsochromic effect of the ortho substituent is explained as steric inhibition of resonance.[93] Analysis of the uv spectra of the o-substituted ketones employed in this study (Table 9) reveals the following: (1) the L_a band intensities are essentially the same for o-methylbutyrophenone, o-methylvalerophenone, and o-methyl γ-methylvalerophenone. This indicates that γ-substituents do not increase the steric hindrance between the o-methyl and the side chain of the benzene ring. (2) An additional methyl group at the 3-position, such as in 2,3-dimethyl-, 2,3,4,5-tetramethyl-, and 2,3,5,6-tetramethylvalerophenone, further depresses the L_a band intensity. The marked enhancement of the steric interference by meta-substitution can be attributed to the so-called buttressing effect.[94] (3) Substitution of methyl at the α position, such as in o-methyl α-methylvalerophenone and o-methyl α,α-dimethylvalerophenone, also remarkably depresses the L_a band intensity, presumably because of the bulkier size of the side chain.

The disadvantage of using uv spectra to determine ground state conformations are twofold. First, it is difficult to obtain accurate band intensity measurements. Second, one is employing an energy difference between an electronically excited state and ground state to evaluate a property of the

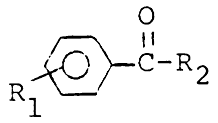
ground state. ^{13}C nmr spectra measurements could avoid these drawbacks since ^{13}C chemical shifts arise from the electronic ground state only and the possibility of overlapping bands is remote due to the characteristic low field resonance of the carbonyl carbon atom. It has been suggested[70] that the angle of twist between the C=O group and the benzene ring (θ) of a substituted ketone can be calculated using equation 33, where

$$\cos^2\theta = \left| \frac{\delta_x - \delta_{90^o}}{\delta_{0^o} - \delta_{90^o}} \right|_{*C=O} \qquad (33)$$

δ_x is the carbonyl chemical shift of the ketone in question and δ_{0^o} and δ_{90^o} are chemical shift values (carbonyl carbon) of model molecules which exist in planar ($\theta = 0^o$) and orthogonal ($\theta = 90^o$) conformations, respectively.

In this study 1-tetralone ($\theta = 0^o$) and 2,4,6-tri-tert-butylacetophenone ($\theta = 90^o$) are chosen as the reference molecules. Since acetophenone has previously been used as the model compound for $\theta = 0$ in a similar study,[70] it is interesting to compare the θ values based on the two different models. Table 15 contains the carbonyl carbon chemical shifts (downfield from internal TMS) and the angle of twist θ for the ketones. There seems to be a good correlation between the angle of twist and steric hindrance to planarity in these ketones. Thus, the angle of twist increases from 0^o to 25.4^o and 45.9^o in proceeding from 1-tetralone to 2-methyl- and 2,3-dimethyl γ-methylvalerophenone. Additional

Table 15. ^{13}C nmr Chemical Shifts and Angle of Twist



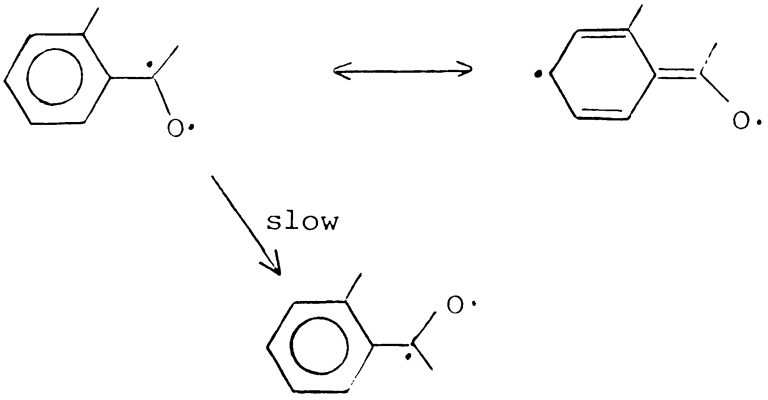
Ketone	Substituent on Ar	$\delta_{C=O}$* ppm	angle of twist θ	
			acetophenone	1-tetralone
34	2-CH_3	201.5	20.8	25.4
35	2,3-$(CH_3)_2$	205.9	43.1	45.9
36	2,4-$(CH_3)_2$	204.2	35.4	38.8
37	2,5-$(CH_3)_2$	204.0	34.8	38.2
38	2,3,4,5-$(CH_3)_4$	207.1	48.2	50.5
39	2-CH_3, α-CH_3	208.3	49.2	51.4
40	2-CH_3, α,α-$(CH_3)_2$	213.8	61.8	63.5
41	2-CH_2CH_3	205.1	39.2	42.4
46	2,4,6-$(CH_3)_3$	211.0	68.0	69.4
47	2,3,5,6-$(CH_3)_4$	209.2	65.3	66.5
48	2,3,4,5,6-$(CH_3)_5$	209.5	66.2	67.6
49	2,4,6-$(CH_3)_3$, α-CH_3	217.4	70.4	71.6
50	2,4,6-$[CH(CH_3)_2]_3$	211.9	73.1	74.3
51	2,4,6-$(CH_3)_3$, α,α-$(CH_3)_2$	218.9	87.3	87.8
Acetophenone		197.6	0	0[b]
α-tetralone		197.8	0[b]	0
2,4,6-tri-t-butylacetophenone		212.9[a]	90[b]	90[b]

[a] from reference 70.

[b] assumed value.

α-methyl substitution, such as in *o*-methyl α-methylvalerophenone and *o*-methyl α,α-dimethylvalerophenone also makes the ketones out of plane more, presumably due to the severe steric interference between the *o*-methyl group and the bulky α-methyl substituted side chain. All of the 2,6-disubstituted ketones are highly twisted with 2,4,6,α,α-pentamethyl substitution resulting in the greatest out of plane twist.

It should be noted that the conformational distribution and behavior in the excited state may not be the same as in the ground state and that the alkoxy radical obtained from the corresponding hypochlorite[52] actually is not a perfect model for the excited ketone. The alkoxy radical has a freely rotating acyl group whereas the excited ketones do not, presumably because population of the $\pi^*\pi$ orbital enhances the bond order between the benzene ring and the carbonyl carbon increases the barrier to rotation,[95] and makes the excited state more planar than the ground state. Therefore, the rate of rotation from *anti* to *syn* (and *vice versa*) in the excited



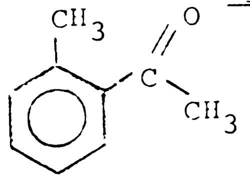
state would be expected to be slower than that in the ground

state. In other words, the rapid equilibrium existing between these conformers in the ground state may not be established in the excited state if some rapid reactions other than rotation are available for one or both of the excited conformers.

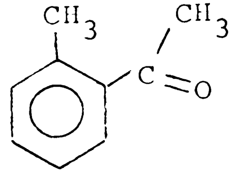
IV. Conformational Effect on Photoenolization

This investigation of *o*-alkyl substituted ketones was undertaken primarily to determine how conformational factors effect the photoenolization reaction and to provide more information about the mechanism and kinetics of this reaction. Previous discussion indicates that hydrogen abstraction is not rate-determining in photoenolization and some other process must be involved in the rate-determining step.

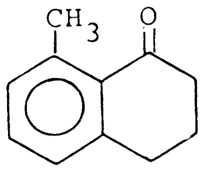
In order to substantiate the involvement of conformational factors in the rate determining step, the sensitization efficiencies of *o*-methylacetophenone **43** and 8-methyl-1-tetralone **44** were measured. The difference between **43** and **44** is that **43** can exist both in *syn* and *anti* conformations whereas **44** is fixed in the *syn* conformation and can therefore serve as a model for *syn*-**43**. It should be pointed out, however, that this nomenclature does not imply two planar conformers but rather two rotational minima in which the *ortho* methyl and the carbonyl oxygen are either on the same side or on opposite sides of the plane perpendicular to the benzene ring and bisecting the *para*-carbon and the carbonyl carbon.



43-*syn*



43-*anti*

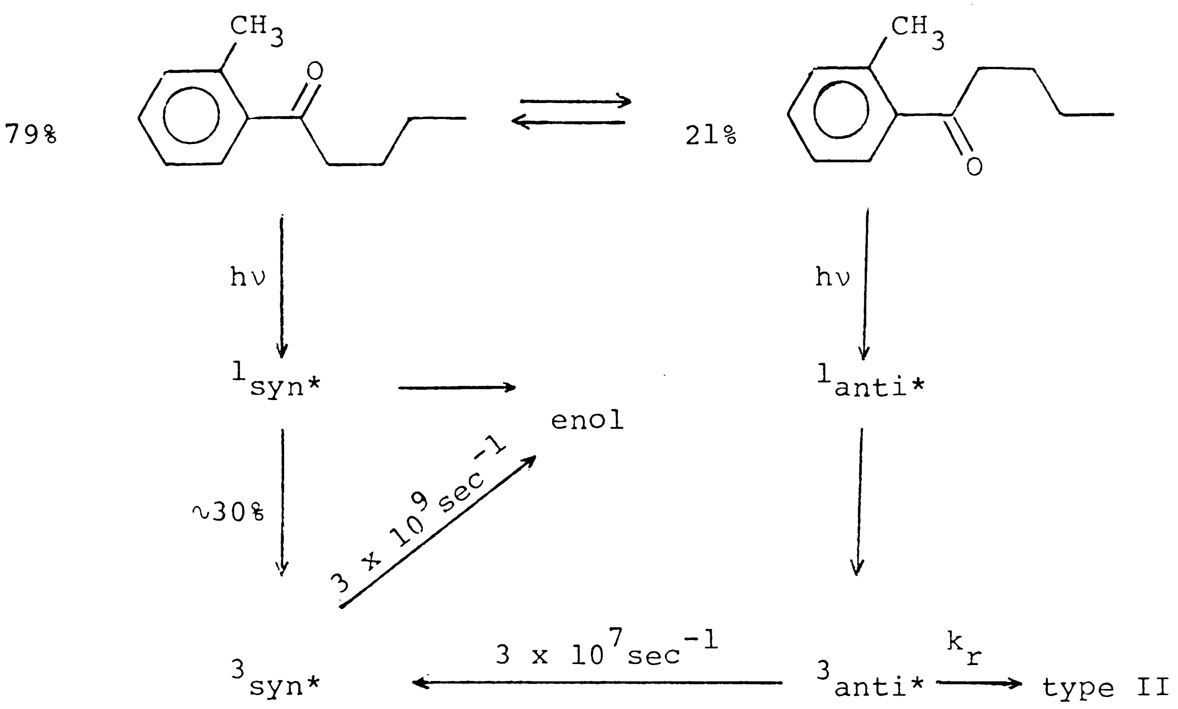


44

As shown in Figure 16, the sensitization plot for **43** indicates the presence of two distinct triplets. Kinetic analysis of this plot, which is similar to that derived by Dalton and Synder,[96] yields $k_q\tau$ values of 158 M^{-1} for the triplet formed in 21% yield and 1.0 M^{-1} for a triplet formed in 31% yield. Since the quenching rate is diffusion controlled, as indicated for *o*-methyl γ-methylvalerophenone, $K_q = 5 \times 10^9\ M^{-1}\ S^{-1}$ in benzene.[97] The two triplets are then calculated to have decay rate of 3×10^7 and $5 \times 10^9\ S^{-1}$, respectively. The former apparently is the one observed by Lindqvist[50] while no subnanosecond triplet has been detected before. On the other hand, 8-methyl-1-tetralone **44**, displays a linear sensitization plot which indicates a triplet yield of 0.28 and a triplet decay rate of $3 \times 10^9\ S^{-1}$.

If we make the reasonable assumption that only rapid enolization can be responsible for the unusually rapid triplet decay of both **43** and **44**, we conclude that the very short-lived triplet of 43 is the *syn* conformer while the long-lived triplet is the *anti* conformer. The comparable triplet decay rates for **44** and the short-lived triplet of **43** are certainly consistent with this conclusion.

Therefore, study of the type II photoelimination of various *ortho* alkyl ketones (**32** - **41**), together with the sensitization studies of **43** and **44**, shows that the triplet state *anti*→*syn* rotation is most likely the rate-determining step in photoenolization. The following scheme summarizes what we believe to be the mechanism for photoenolization of *o*-tolyl alkyl



ketones. The process competing with normal triplet reactions of the anti triplet is irreversible rotation into a syn conformation which enolizes so rapidly that other reactions with rate constants ∿10^7 S^{-1} cannot compete. The 100-fold greater reactivity of the o-methyl relative to the γ-methylene is actually expected on the basis of their intrinsic labilities[98] and the two frozen rotations in the former, and is close to what Bergmark observe for the o-methyl alkoxy radical.[52] Previoualy, Lewis, Johnson and Ruden[99] have shown that endo-2-benzoylnorbornane has two frozen rotations and has a rate constant of γ-hydrogen abstraction (7 x 10^9 sec^{-1}) similar to that for syn-**43**.

The Φ_T^{long} values determined from the sensitization study in fact measure the percentage of anti ground states in what is presumably a rapid conformational equilibrium. If this argument holds true, then the more sterically hindered the ketone is, the lower the percentage of <u>anti</u> conformers would be and consquently the lower Φ_T^{long} should be. The relatively low Φ_T^{long} values of <u>o</u>-ethylvalerophenone, <u>o</u>-methyl α-methylvalerophenone, and <u>o</u>-methyl α,α-dimethylvalerophenone and their relatively large ground state angles of twist, as indicated by their ^{13}C nmr and uv spectra, are consistent with this line of reasoning.

The $\sim 10^7$ s^{-1} rate of rotation in the triplet would indicate a barrier of some 8 Kcal, if a normal preexponential factor of 10^{12-13} is assumed. Because of severe nonbonded interactions in the totally planar forms, this barrier would certainly be expected to be smaller than that in the excited benzaldehyde, for which a value of some 20 Kcal has been calculated.[100] The decrease in k_e caused by α-methyl substitution may indicate that the rotation process is slowed down somewhat by interference between the <u>o</u>-methyl and the bulky α-methyl substituted side chain.

It should be noted that the triplet enole has been suggested by Ullman[37,43] to intervene between the triplet of ketone and the ground state of the enol in the photoenolization of chromone systems. The results in this study establish that the long-lived triplet detected by sensitization experiments is a ketone triplet and not, say, a triplet enol, which would not be expected to undergo type II elimination.

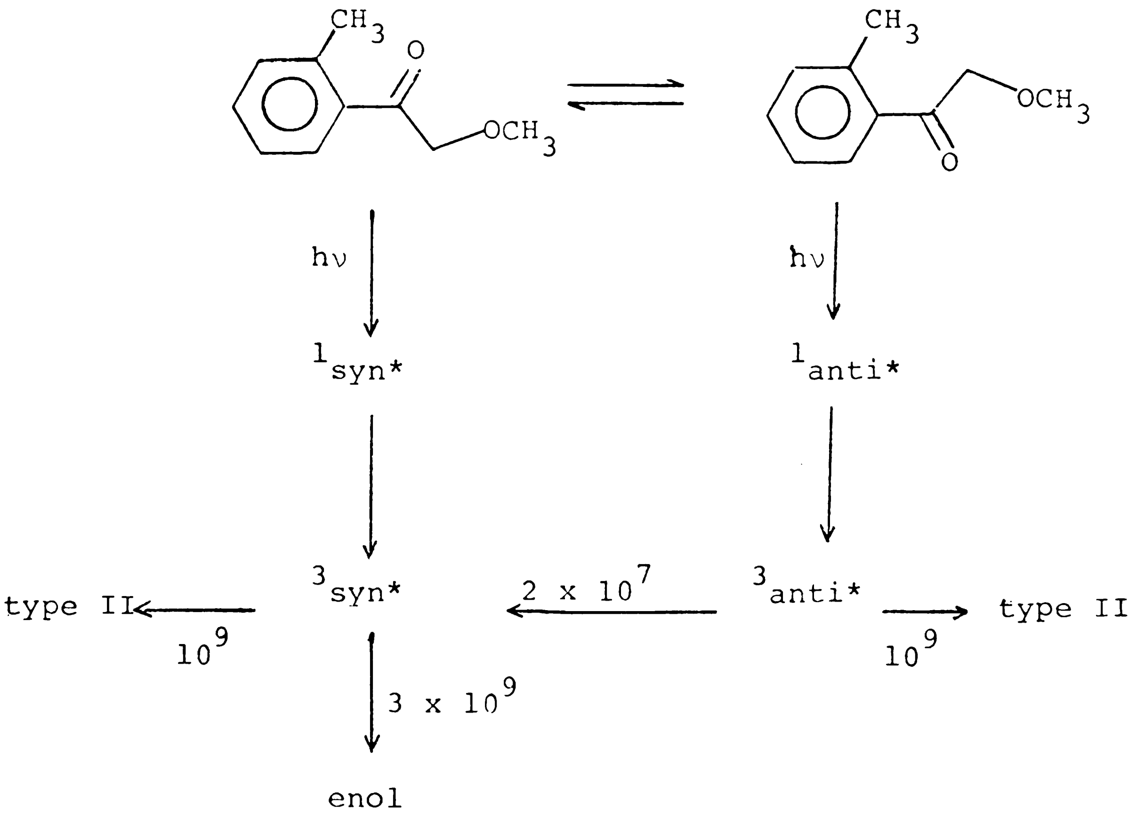
It could also be argued that the two triplets observed in sensitization studies are kinetically distinct n,π* and π,π* triplets rather than the syn and anti triplets of the ketone. Ortho-methylbenzophenone sensitizes the cis-trans isomerization of 1,3-pentadiene and two kinetically independent triplets similar to that of o-methylacetophenone are also detected in the reciprocal quantum yield plot. The two triplets observed for o-methylbenzophenone remove the possibility that kinetically distinct n,π^* and π,π^* triplets are involed since it is well known that there is a large energy separation between n,π^* and π,π^* triplets in benzophenone.[101]

Since only 26 - 39% of the syn singlets intersystem cross, it is interesting to know what the other singlets do. The first guess would be that they undergo singlet-state enolization. It is known that n,π^* singlets react some 5 - 10 times faster than n,π^* triplets in type II γ-hydrogen abstraction.[14,102] A similar relative rate of singlet enolization could make it compete well with the rapid intersystem crossing of phenyl ketones.[103] However, the following results do not agree with that argument. Small concentrations of pentadiene (<0.1 M) quenched two-thirds of the deuterium incorporation when o-methylacetophenone was irradiated in methanol O-d. Large concentrations continue to quench the process, but with less efficiency. It appears that over 85% of the deuterium incorporation (Φ_D = 0.2) arises from two triplets, one long lived (>11 nsec) and one short-lived (∿0.2) nsec). o-Methylbenzophenone undergoes photoinduced deuterium incorporation more efficiently than o-methylacetophenone (Φ_D = 0.38), again from two triplets with a total Φ_T of unity. If deuterium incorporation can serve as a quantitative measure of enol formation, the low quantum yields of both triplet formation and deuterium incorporation in *o*-methylacetophenone indicate that the majority of singlet reaction is strictly quenching rather than enolization. It is quite possible that radiationless decay occurs via partial hydrogen abstraction for the singlet excited state of *o*-methylphenyl ketones,as is now established for singlet state γ-hydrogen abstraction.[104,105]

As pointed out earlier, k_e in *tert*-butyl alcohol is only 1/5 that in benzene. This decrease in triplet decay rate was interpreted[50] as being due to solvent-induced shifts in the relative energy levels of the closely spaced n,π^* and π,π^* configurations. This possibility is very real for the rate decreases in k_r,[106] but is unlikely for the long-lived *anti* triplet since the rate is the measure of *anti*→*syn* rotation rather than of hydrogen abstraction and does not change with ring substitution. It is possible that the decrease in k_e in *tert*-butyl alcohol is due to the higher viscosity and/or to the bulkier size of the *anti* triplet resulting from hydrogen bonding between the *tert*-butyl alcohol and the triplet of ketone. Sensitization studies revealed an approximate five-fold rate decrease for enolization by the *syn* triplet when the solvent is changed from benzene to *tert*-butyl alcohol. This change presumably occurs because the population of the n,π^* triplet state is lowered by a polar solvent.

Irradiation of *o*-methyl α-methyloxyacetophenone **45** gives both the type II cleavage product and oxetanols. The percentage yield of cyclobutanol is 15%, which is lower that the 43%

reported for α-methoxyacetophenone.[76] The Stern-Volmer quenching plot of **45** is nonlinear and two $k_q\tau$ values of 4.9 M^{-1} and 1.4 M^{-1} are obtained based on eq. 20 - 23. Notice that both triplets are extremely short-lived ($\tau_1 = 1$ ns; $\tau_2 = 0.3$ ns) and no long-lived triplet is observed. The very rapid γ-hydrogen abstraction for both *syn*-**45** and *anti*-**45** triplets would result in measurable reaction from both conformers. A rate constant of 3.2×10^9 sec^{-1} for γ-methoxyacetophenone has previously been reported by Lewis and Turro.[76] As shown in the following scheme, *anti*-**45** triplet undergoes only type II reaction while



syn-**45** triplet can undergo both type II reaction and enolization competitively. Therefore, the longer-lived triplet would correspond to *anti*-**45** which gives $k_r = 1.0 \times 10^9$ sec^{-1}. The same 3-fold decrease in k_r is observed upon *o*-methyl substitution. The shorter-lived triplet would correspond to *syn*-**45** and a k_e of 2.6×10^9 sec^{-1} is calculated based on equation 34. This value compares favorably with that measured for the 8-methyltetralones.

$$1/\tau_2 = k_r + k_e = 1.0 \times 10^9 \ \mathrm{S}^{-1} + k_e = 3.6 \times 10^9 \ \mathrm{S}^{-1} \quad (34)$$

Thus, the reactions of *o*-substituted phenyl ketones are totally controlled by ground state conformations for ketones which undergo type II reaction extremely fast (e.g. **45**) whereas rotationally-controlled excited-state reactions take over for ketones which undergo type II reaction with a rate comparable to the rate of rotation(e.g. *o*-methylvalerophenone).

V. 2,6-Disubstituted Ketones

In an extensive study of 2,4,6-trialkylphenyl ketones, Kitaura and Matsuura[45] noted that cyclobutenol formation was often the preferred course of reaction. In no case could ground state dienols be trapped by dienophiles, but deuterium exchange processes do occur. "Anomalous" photochemical behavior has also been noted for 2,6-disubstituted benzophenones.[107,108] No detailed kinetics for the photoenolization of these 2,6-disubstituted ketones have been reported.

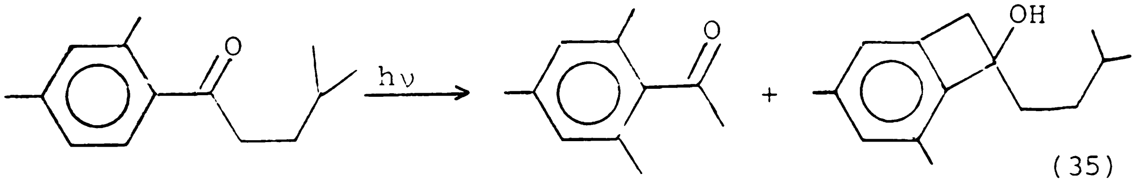
As far as ground state conformation is concerned, 2,6-disubstituted phenyl ketones are highly twisted, as indicated earlier by ^{13}C nmr and uv spectra. They cannot have *syn* and *anti* conformers because of symmetry. Nonetheless, two kinetically distinct triplets were observed in the sensitization studies. Triplet yields and decay rates for some

2,6-disubstituted acetophenones and 8-methyltetralones are listed in Table 16. The long-lived triplets have a decay rate of 5 x 10^7 $\sec^{-1}$ which is almost double that of monosubstituted acetophenones. The short-lived triplets have a decay rate similar to their tetralone analogs which produce only one short-lived triplet.

Table 16. Triplet Yield and Lifetimes for 2,6-Disubstituted Acetophenones and Tetralones.

Ketone	long-lived		short-lived	
	Φ_T^{long}	$1/\tau, 10^7 S^{-1}$	Φ_T^{short}	$1/\tau, 10^7 S^{-1}$
	Acetophenone			
2,4,6-trimethyl-	0.34	5.2	0.28	125
2,3,5,6-tetramethyl-	0.24	5.0	0.20	100
2,3,4,5,6-pentamethyl-	0.26	4.5	0.12	66
	1-Tetralone			
8-methyl	-	-	0.28	300
3,3,6,8-tetramethyl-	-	-	0.26	150
5,6,7,8-tetramethyl-	-	-	0.14	48
	1-Indanone			
4,7-dimethyl-	-	-	0.21	220

For 2,4,6-trimethyl γ-methylvalerophenone, 2,3,5,6-tetramethyl- and 2,3,4,5,6-pentamethylvalerophenone, both acetophenone and benzocyclobutenol products are formed (equation 35). The type II product is readily quenched with diene whereas

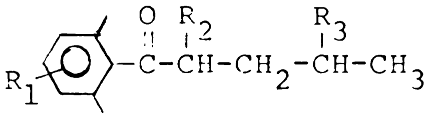


(35)

benzocyclobutenol is not. Use of the ketones to photosensitize the isomerization of 1,3-pentadiene also indicates two triplets with lifetimes similar to those of the 2,6-disubstituted acetophenones. The short-lived triplet with a lifetime of 0.8 ns is probably the precursor of benzocyclobutenol.

The rate constant of type II reaction can be calculated based on equation 31. Table 17 contains the long-lived triplet lifetime data and rate constants for these 2,6-disubstituted ketones.

Table 17. Long-lived Triplet Lifetime and Rate Constants for 2,6-Disubstituted Ketones in Benzene.



Ketone	R_1	R_2	R_3	$1/\tau^{long}$, $10^7 s^{-1}$	k_r $10^7 s^{-1}$	k_e $10^7 s^{-1}$
46	4-CH_3	H	CH_3	5.5	0.43	5.1
47	3,5-$(CH_3)_2$	H	H	5.0	0.06	4.9
48	3,4,5-$(CH_3)_3$	H	H	4.6	0.01	4.6
49	4-CH_3	CH_3	H	1.1	0.09	1.0

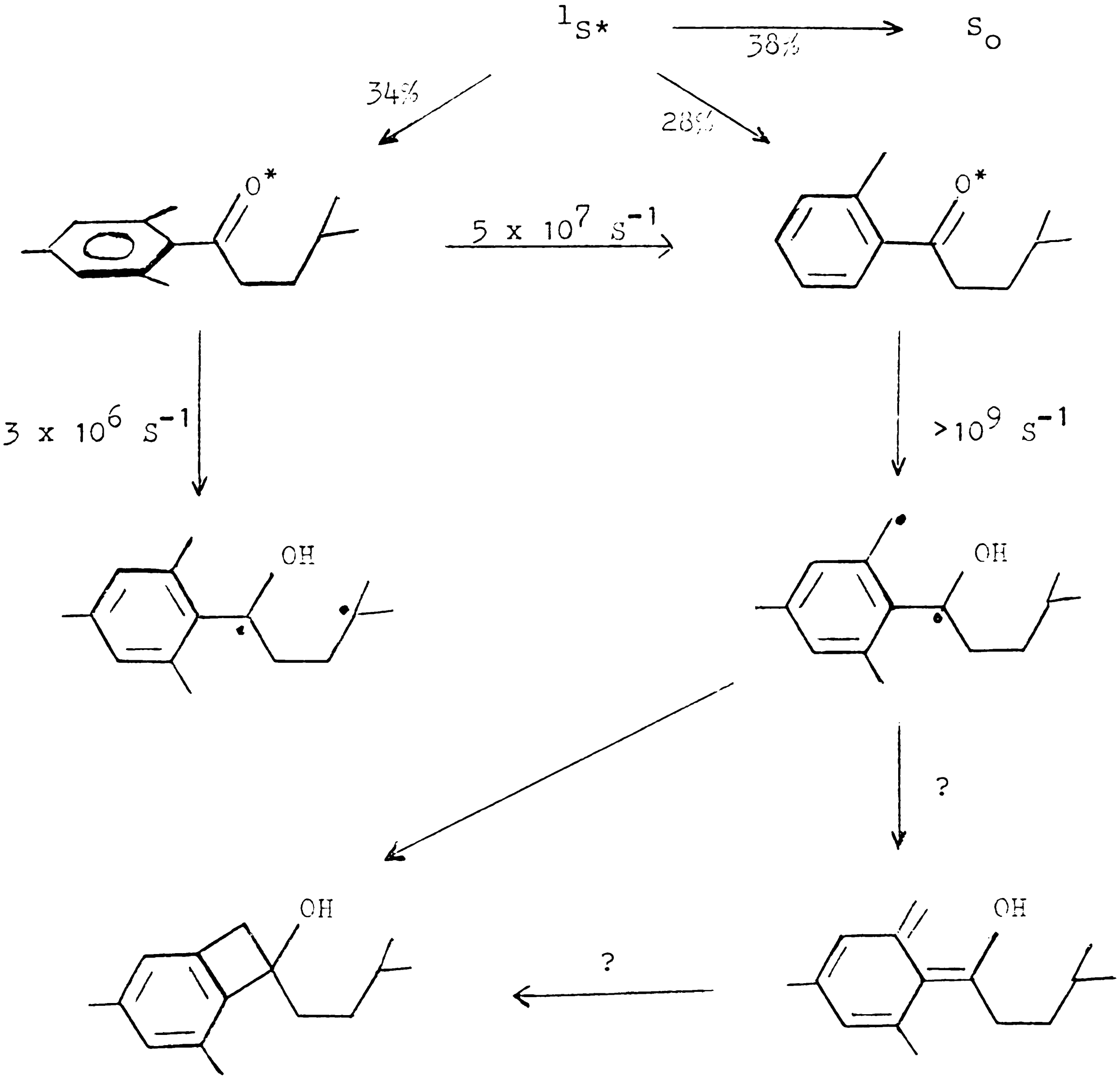
Therefore, the type II reaction rates constant for ketone

46, **47**, **48**, and **49** is only 1/104, 1/135, 1/800 and 1/90 of the corresponding unsubstituted phenyl ketones. These ratio are actually expected considering the methyl ring substitution effect, i.e. 1/8 for each *para* methyl and 1/3 for each *ortho* and *meta* methyl group. The k_e values for ketone **46**, **47** and **48** are close to the long-lived triplet decay rate for the corresponding acetophenone obtained from sensitization studies.

Although the acyclic ketones have only one triplet ground-state conformer, they may well form two triplets with different twist angles and different lifetimes. The more twised one can undergo type II hydrogen abstraction or rotate with a rate constant 5 x 10^7 sec^{-1} to the more planar form, which can readily abstract an *ortho* benzylic hydrogen. The proposed mechanism for 2,6-disubstituted ketones is summarized in the following scheme.

As shown in Table 16, the short-lived triplet decay rate decreases as more methyl groups are added to the phenyl ring. The triplet decay rate for 2,3,4,5,6-pentamethylacetophenone is only 1/8 that for 2-methylacetophenone, wheareas a 100-fold decrease is realized in the type II reaction. The rate decreases presumably are due to less population of the reactive n,π^* triplet state caused by electron-donating methyl group.

There seems to be no difference in short-lived decay rate between methyl-substituted 1-tetralone and corresponding indanone indicating the carbonyl group in both ketones has roughly the same proximity to the benzylic hydrogen, i.e. both carbonyl groups are fixed in the *syn* conformation to the enolizable


$^1S*$
38%
S_o
34%
28%
O^*
$5 \times 10^7\ s^{-1}$
O^*
$3 \times 10^6\ s^{-1}$
$>10^9\ s^{-1}$
OH
OH
?
OH
?
OH

methyl group. This conclusion is supported by the uv spectra, in that both ketones show normal L_a band intensities. When the ring size become larger than eight the carbonyl group might start to twist out of plane[109] and conformational factors may well be important again.

Finally, it is noticable that a ten-fold increase of quantum yield for benzocyclobutenol formation is obtained upon addition of 3 M dioxane. This very large solvent effect can be explained as stabilization by a Lewis base of an intermediate which leads to cyclobutenol product. This intermediate could either be a hydroxy diradical similar to that involved in type II reaction[14] or a dienol species.

VI. Summary

The studies conducted with the _o_-alkyl phenyl ketones have significant implications for both photoenolization reactions and type II reactions. The effect of _o_-methyl substituents on the type II reaction has been shown to be comparable to that of _m_-methyl, in that both lower reactivity by a factor of 3. The steric effect of an _o_-methyl group on exothermic energy transfer is small as indicated by quenching of _o_-methyl γ-methylvalerophenone being "diffusion-controlled." _Ortho_-methyl substitution does not seem to lower rates of type I α-cleavage beyond the factor of three caused by inversion of triplet states.

The low type II quantum yields for _o_-methyl substituted phenyl ketones bearing a γ hydrogen result from a combination of low yield of triplet ($\Phi_T = 0.21$), low probability for product formation from the diradial intermediate ($P = 0.08 - 0.18$),

and competing photoenolization reaction.

Analysis of type II quantum yields and triplet lifetimes of ortho-tolyl alkyl ketones indicates a rate for triplet state enolization of 3 x 10^7 sec^{-1}, similar to rates which have been measured by flash spectroscopic kinetics. Although the rate of γ-hydrogen abstraction decreases as additional methyl group are substituted onto the benzene ring, the rate of triplet state enolization remains unchanged. The rate is also the same for ortho-ethyl, CH_3, and CD_3. Sensitization studies reveal that ortho-methylphenyl alkyl ketones yield two triplets with distinctly different lifetimes, while their cyclic analogs, namely 8-methyl substituted 1-tetralones yield only one short-lived triplet. Therefore, this work suggests that syn triplets enolize rapidly ($k = 4 \times 10^9$ sec^{-1}) such that formation of this conformer is rate-determining in enolization of anti triplets.

Although the 2,6-disubstituted phenyl ketones probably have only one principal ground state conformation, two kinetically distinct triplets have been observed in sensitization studies. The long-lived triplet decays with a rate of 5 x 10^7 sec^{-1} but does not produce benzocyclobutenol; the short-lived one forms benzocyclobutenol with a rate of $\sim 10^9$ sec^{-1} for 2,4,6-trimethyl-, 2,3,5,6-tetramethyl-, and 2,3,4,5,6-pentamethylvalerophenone.

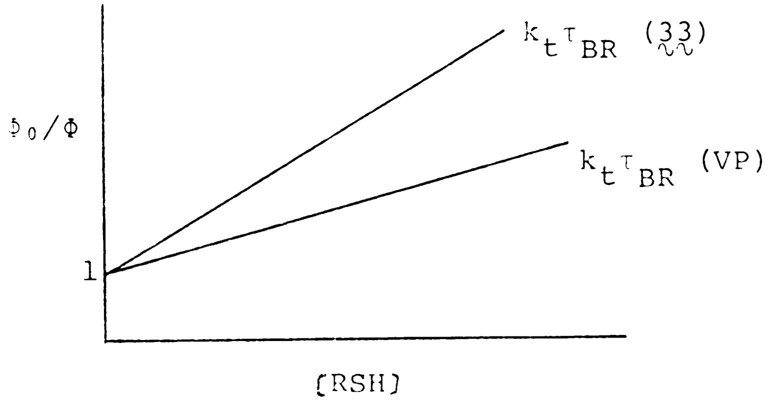
In conclusion, the photochemistry of ortho-alkylphenyl ketones is dominated by conformational factors, in particular the ground state syn/anti ratio and the rate for anti→syn rotation in the excited state. Although the importance of

ground-state conformations in photochemical processes is now well documented,[110] photoenolization is a rare case[111] where an excited-state conformational change appears to be rate limiting.

VII. Suggestions for Further Research

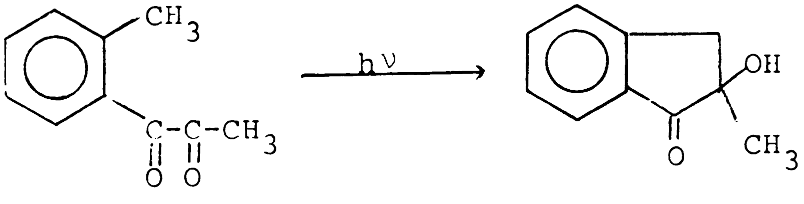
1. Effects of o-Alkyl Substituents on the Lifetime of 1,4-Biradical Intermediates.

o-Alkyl substituents effect the 1,4-biradicals since o-methyl phenyl ketones have relatively low probability of product formation. Determination of the biradical lifetimes should provide valuable information about the origin of such changes. This can be done by comparing the quenching efficiencies with which a given thiol quenches type II elimination from valerophenone (VP) and o-methylvalerophenone **33**. The relative biradical lifetimes can be calculated from the ratio of the quenching slopes.



2. o-Methylphenyl α-Diketones

Photocyclization of 1-(o-tolyl)-1,2-propanedione **46** to 2-hydroxy-2-methylindanone **47** has been reported.[112-114] Product **47** can either be formed directly by a 1,6-hydrogen migration from the ortho methyl to the excited acetyl carbonyl

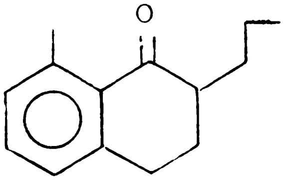


46 47

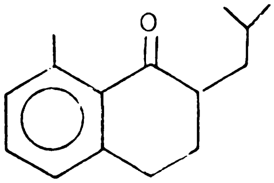
oxygen or by a 1,5-hydrogen shift (to give an enol) followed an aldol cyclization. Ogata and Takagi[115] provided some evidence of the intermediacy of the enol by trapping it with dimethyl acetylenedicarboxylate. However, no detailed kinetic data on this reaction have been reported. It would be interesting to study this raction by a combination of quenching and sensitization studies similar to that conducted in the monoketone system and to explore the possibility of conformational involvements in these o-methylphenyl α-diketone molecules.

3. Competition between Photoenolization and Type II Reaction in 2-Alkyl-8-methyl-1-tetralone

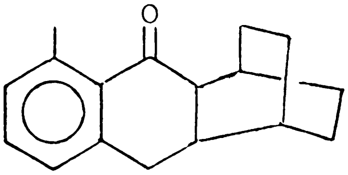
Investigation of the photochemistry of ketones such as 48-50 would provide information about the competition between



48



49



50

Photoenolization and type II reaction. Lewis and co-workers[116] have studied the photochemistry of 2-propyl-1-tetralone and measured a rate constant of 5.9×10^8 sec^{-1} for type II hydrogen

abstraction. Therefore, it is expected that the type II reaction will be able to compete with enolization reaction (3×10^9 sec^{-1}) more efficiently in **48** than in syn-o-methylvalerophenone and even more so in compound **49**. In this fashion we can monitor the photoenolization reaction of syn triplet by type II product formation, which is directly measurable.

Photochemical study of compound **50** would prove even more beneficial. In this molecule both the benzylic hydrogen and the side chain γ-hydrogen are fixed in the same proximity to the carbonyl oxygen. The rate of type II reaction should be very rapid and the rate difference, if any, between type II reaction and enolization would reflect the intrinsic lability[98] of the benzilic hydrogen.

It is also of interest to investigate the phoeokinetics of 2,4,6-trimethyl α,α-dimethylvalerophenone which would be extremely hindered such that a planar triplet may not be formed at all.

4. Temperature-dependent Studies

It has been shown in this study that anti→syn triplet rotation seems to be rate-limiting in photenolization for acyclic o-methyl-substituted ketones. A temperature-dependent study on k_e would give us a more accurate determination of the barrier to rotation in the excited state. The conformational equilibrium between syn and anti conformers is faster in the ground state than in the excited state. Although both uv and ^{13}C nmr spectra indicate predominately

syn conformations, conformer distribution in the ground state have not been determined quantitatively. Use of dynamic nmr techniques, either through ^{1}H or ^{13}C nmr spectroscopy, may resolve this problem and display the distinct existence of these two isomers at very low temperature. The ratio and the rate of interconversion of these two isomers at various temperatures can also be derived from such a study.

EXPERIMENTAL

I. Chemicals

1. Solvents

a. Benzene

Analytical reagent grade benzene supplied by Mallinckrodt Chemical Works was purified by stirring gallon quantities with 300-ml portions of concentrated sulfuric acid several times. The sulfuric acid was discarded and a new portion added until the acid layer remained colorless. The benzene was then stirred over 10% aqueous sodium hydroxide for 24 hours, washed with saturated aqueous sodium chloride, and dried over anhydrous magnesium sulfate. The benzene was distilled from 100 g of phosphorous pentoxide through a 95 cm column packed with glass helices. A high reflux ratio was maintained, and the central cut (∿80%) was collected for use. The boiling point was 79.8 ± 0.2 C, uncorrected.

b. t-Butyl Alcohol

The *t*-butyl alcohol (J. T. Baker Co.) was distilled from freshly cut sodium at atmospheric pressure (bp 82.0 ± 0.2 C, uncor.)

c. Pyridine

"Certified A.C. S. grade" pyridine from Fisher Scientific Co. was distilled from barium oxide and the middle fraction retained. The boiling point was 115.6 ± 0.2 C, uncor.

d. 1-Propanol

Fisher Scientific Co. 1-propanol was distilled from calcium hydride at atmospheric pressure (bp 97.8 ± 0.2 C, uncor).

e. 1-Pentanol

1-Pentanol (Fisher Scientific Co.) was purified in the same manner as 1-propanol. The boiling point was 138.1 ± 0.2 C, uncor.

f. 1-Heptanol

Matheson Coleman Bell 1-heptanol was purified in the same manner as 1-propanol. The boilling point was 176.5 ± 0.3 C, uncor.

g. 1,4-Dioxane

"Scintanalyzed" 1,4-dioxane (Fisher Scientific Co.) was allowed to stand over ferrous sulfate for two days, then mixed with concentrated hydrochloric acid (5 : 2 ether : acid), and then refluxed at 120 - 130 °C for 10 h under nitrogen.[117] A resinous material was separated from the cooled liquid by filtration and the filtrate was neutralized with sodium carbonate. The 1,4-dioxane was distilled twice from sodium hydroxide and once from sodium under nitrogen. The boiling point was 101.4 ± 0.2 C, uncor.

h. Methyl Alcohol-d

Methyl alcohol-d, 99% pure, supplied by Aldrich Co. was used as received.

i. n-Heptane

n-Heptane (J. T. Baker Co.) was purified in the same manner as benzene, except on a smaller acale. The boiling point was 98.4 ± 0.3 C, uncor.

2. Ketones

Several methods of preparation were used depending on the availability of the starting materials and the characteristics of the reaction. The general methods employed are listed below with the ketones prepared by that method. The structure of each ketone was verified by its spectroscopic properties. Mass, ^{1}H nmr, ^{13}C nmr, ir and uv spectra were obtained on a Hitachi Perkin-Elmer RMU-6 mass spectrometer operated by Mrs. Lorraine A. Guile, a Varian T-60 nmr spectrometer; a Varian CFT-20 nmr spectrometer; a Perkin-Elmer model 237-B infrared spectrometer; and a Cary 17 spectrometer, respectively. The purity of each ketone was carefully checked by VPC analysis. Unless otherwise indicated, all the ketones used were obtained with >99% purity.

Method A

The ketone was prepared by dropwise addition of 0.12 mole of the Grignard of an o-alkylbromobenzene to 0.1 mole of the appropriate aliphatic nitrile in 200 ml of ether.[118] The resulting solution of imine salt was carefully stirred into 300 g of ice containing 30 ml of concentrated HCl (4.8 mole). The aqueous layer was extracted with ether to remove any soulble impurities, such as the starting nitrile and biphenyls. The imine hydrochloride was then hydrolyzed to the desired ketone by heating the solution on a steam bath for one hour. The ketone was then extracted into ether and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed and the ketone was purified by vacuum distillation. For further purification, the ketone was run through a short column of alumina and then vacuum distilled. The following ketones were prepared by this method:

a. o-Methylbutyrophenone

Made form o-bromotoluene (Eastman) and butyronitrile (Aldrich): bp 93°C (3 Torr); MS (70 eV) m/e 162, 134, 119, 91; ^{1}H nmr ($CDCl_3$) δ 0.99 (t, 3 H), 1.74 (m, 2 H), 2.40 (s, 3 H), 2.84 (t, 2 H), 7.38, 7.75 (4 H, aromatic H); ir (neat) 1685 cm^{-1}, 1602 cm^{-1}, 1450 cm^{-1}.

b. o-Methylvalerophenone

Made from o-bromotoluene and valeronitrile (Eastman): bp 84°C (3 Torr); MS (70 eV) m/e 176, 148, 134, 119, 91; nmr ($CDCl_3$) δ 0.99 (t, 3 H), 1.57 (m, 4 H), 2.38 (s, 3 H), 2.58 (t, 2 H), 7.38, 7.75 (4 H, aromatic H); ir (CCl_4) 1683 cm^{-1}, 1600 cm^{-1}, 1452 cm^{-1}.

c. o-Ethylvalerophenone

Made from o-ethylbromobenzene (Aldrich) and valeronitrile: bp 134°C (7 Torr); MS (70 eV) m/e 190, 162, 105, 91; nmr ($CDCl_3$) δ 1.05 (t, 3 H), 1.30 (t, 3 H), 1.58 (m, 4 H), 2.84 (m, 4 H), 7.34, 7.65 (4 H, aromatic H); ir (CCl_4) 1680 cm^{-1}, 1602 cm^{-1}, 1450 cm^{-1}.

d. 8-Methyl-1-tetralone

o-Methyl-γ-chlorobutyrophenone was prepared from o-bromotaluene and 4-chlorobutyronitrile (Aldrich) as described in Method A. bp 126-129°C (5 Torr); nmr δ 2.11 (m, 2 H), 2.37 (s, 3 H), 2.91 (t, 3 H), 3.48 (t, 3 H), 7.12 and 7.44 (4 H, aromatic H). Aluminum chloride (0.05 mole) in CS_2 (50 ml) was added slowly to a cooled solution of the chloroketone (0.1 mole) in CS_2 (80 ml). When the addition was complete the mixture was stirred at room temperature for one hour and then poured into a solution of dilute HCl. The mixture was extracted with 125 ml ether. The extract was washed first with 20 ml dilute aqueous sodium hydroxide and then with water (20 ml) and dried over sodium sulfate. The ether was removed, and 8-methyl-1-tetralone was obtained by vacuum distillation: bp 121°C (3 Torr); MS (70 eV) m/e 160, 145, 132, 119, 91; nmr ($CDCl_3$) δ 2.04 (t, 2 H), 2.39 (s, 3 H), 2.92 (m, 2 H), 3.50 (t, 2 H), 7.04, 7.16, 7.44 (3 H, aromatic H); ir (CCl_4) 1689 cm^{-1}, 1606 cm^{-1}, 1446 cm^{-1}.

e. 4,7-Dimethyl-1-indanone

Made from 2,4-dimethyl 3-chlorobutyrophenone which was prepared from p-xylene and 3-chloropropionitrile (Aldrich): mp 46°C; MS (70 eV) m/e 160, 145, 132, 105; nmr ($CDCl_3$) δ 2.05 (s, 3 H), 2.34 (s, 3 H), 2.69 (t, 2 H), 3.05 (t, 2 H), 7.10, 7.25 (2 H, aromatic H); ir (CCl_4) 1690 cm^{-1}, 1604 cm^{-1}, 1435 cm^{-1}.

Method B

The ketone was prepared by dropwise addition of 0.12 mole of the Gridnard of 3-methylbutylchloride to 0.1 mole of the appropriate benzonitrile in 200 ml of ether. The work-up procedure is the same as described in Method A. The following ketones were prepared by this method.

f. o-Methyl γ-methylvalerophenone

Made from o-tolunitrile and 3-methylbutylchloride (Aldrich): bp 98°C (4 Torr); MS (70 eV) m/e 190, 162, 134, 119, 91; nmr ($CDCl_3$) δ 0.90 (d, 6 H), 1.59 (m, 3 H), 2.40 (s, 3 H), 2.85 (t, 2 H), 7.31 and 7.85 (4 H, aromatic H); ir (CCl_4) 1683 cm^{-1}, 1600 cm^{-1}, 1452 cm^{-1}.

g. 2,3-Dimethyl γ-methylvalerophenone

Made from 2,3-dimethylbenzonitrile and 3-methylbutyl-chloride. bp 146°C (6 Torr); MS (70 eV) m/e 204, 176, 161, 105; nmr ($CDCl_3$) δ 1.05 (d, 6 H), 1.62 (m, 3 H), 2.40 (s, 3 H), 2.48 (s, 3 H), 2.83 (t, 2 H), 7.18 and 7.41 (3 H, aromatic H); ir (CCl_4) 1681 cm^{-1}, 1604 cm^{-1}, 1452 cm^{-1}.

Method C

The ketone was prepared by Fridel-Crafts acylation of appropriate substituted benzenes. In a typical preparation 0.2 mole of 4-methylvaleryl chloride was slowly added to a cooled solution of meta-xytene (0.2 mole) in 1,2-dichloroethane in the presence of aluminum chloride (0.21 mole). When the addition was complete the mixture was stirred at room temperature for an hour and then poured into a stirred solution of ice water and hydrochloric acid. The mixture was extracted with ether. The combined extracts were washed with dilute aqueous sodium hydroxide and then with water and dried. The ether was removed, and the residue was vacuum distilled. The purification method was the same as in method A. The following ketones were prepared by this method:

h. 2,4-Dimethyl-γ-methylvalerophenone

Made from m-xylene (Matheson Coleman & Bell) and 4-methylvaleryl chloride. The latter was prepared from 4-methylvaleric acid (Eastman) and thionyl chloride (Fisher Scientific Co.): bp 122°C (3 Torr); MS (70 eV) m/e 204, 176, 161, 133, 105; nmr ($CDCl_3$) δ 0.91 (d, 6 H), 1.59 (m, 3 H), 2.31 (s, 3 H), 2.48 (s, 3 H), 2.77 (t, 2 H), 7.01, 7.32 (3 H, aromatic H); ir

(CCl_4) 1685 cm^{-1}, 1600 cm^{-1}, 1450 cm^{-1}.

i. 2,4-Dimethyl-d_6-γ-methylvalerophenone

Made from *m*xylene-d_6 (Mercks) and 4-methylvaleryl chloride: bp 145°C (6 Torr); MS (70 eV) m/e 210, 182, 164, 139, 111; nmr ($CDCl_3$) δ 0.93 (d, 6 H), 1.58 (m, 3 H), 2.75 (t, 2 H), 7.01, 7.32 (3 H, aromatic H); ir (CCl_4) 1685 cm^{-1}, 1600 cm^{-1}, 1450 cm^{-1}.

j. 2,5-Dimethyl-γ-methylvalerophenone

Made from *p*-xylene (Mallincrodt) and 4-methylvaleryl chloride: bp 146°C (5.5 Torr); MS (70 eV) m/e 204, 176, 161, 133, 105; nmr ($CDCl_3$) δ 0.90 (d, 6 H), 1.57 (m, 3 H), 2.28 (s, 3 H), 2,38 (s, 3 H), 2.73 (t, 2 H), 7.11, 7.28 (3 H, aromatic H); ir (CCl_4) 1685 cm^{-1}, 1601 cm^{-1}, 1448 cm^{-1}.

k. 2,3,4,5-Tetramethyl γ-methylvalerophenone

Made from 1,2,3,4-tetramethylbenzene (Aldrich) and 4-methylvaleryl chloride: bp 139°C (1 Torr); MS(70 eV) m/e 232, 204, 289, 262, 246, 233; nmr ($CDCl_3$) δ 0.94 (d, 6 H), 1.58 (m, 3 H), 2.18 (s, 6 H), 2.26 (s, 6 H), 2.71 (t, 2 H), 7.01 (s, 1 H); ir (CCl_4) 1678 cm^{-1}, 1602 cm^{-1}, 1441 cm^{-1}.

l. 2,4,6-Trimethyl γ-methylvalerophenone

Made from mesitylene (Matheson Coleman & Bell) and 4-methylvaleryl chloride: bp 114°C (1 Torr); MS (70 eV) m/e 218, 190, 175, 147, 132, 119; nmr ($CDCl_3$) δ 0.90 (d, 6 H), 1.55 (m, 3 H), 2.13 (s, 6 H0, 2.21 (s, 3 H), 2.68 (t, 2 H), 6.90 (s, 2 H); ir (CCl_4) 1695 cm^{-1}, 1598 cm^{-1}, 1450 cm^{-1}.

m. 2,3,5,6-Tetramethylvalerophenone

Made from 1,2,4,5-tetramethylbenzene (Aldrich) and valeryl chloride (Eastman): bp 130°C (3 Torr); MS (70 eV) m/e 218, 190, 175, 147, 133, 118; nmr ($CDCl_3$) δ 0.97 (d, 3H), 1.55 (m, 4 H), 2.12 (s, 6 H), 2.20 (s, 3 H), 2.81 (t, 2 H), 7.23 (s, 1 H); ir (CCl_4) 1687 cm^{-1}, 1598 cm^{-1}, 1450 cm^{-1}.

n. 2,3,4,5,6-Pentamethylvalerophenone

Made from pentamethylbenzene (Eastman) and valeryl chloride: bp 128°C (2 Torr); MS (70 eV) m/e 232, 204, 189, 161, 147; nmr ($CDCl_3$) δ 0.99 (d, 3 H), 1.57 (m, 4 H), 2.14 (s, 6 H), 2.21 (s, 9 H), 2.84 (t, 2 H); ir (CCl_4) 1685 cm^{-1}, 1600 cm^{-1}, 1450 cm^{-1}.

o. 5,6,7,8-Tetramethyl-1-tetralone

Made from 1,2,3,4-tetramethylbenzene and 4-chlorobutyryl chloride: bp 154°C (2 Torr); MS (70 eV) m/e 202, 174, 162, 147, 131, 115; nmr ($CDCl_3$) δ 2.22 (m, 13 H), 2.38 (s, 3 H), 3.12 (t, 2 H); ir (CCl_4) 1689 cm^{-1}, 1604 cm^{-1}, 1442 cm^{-1}.

p. 2,4,6-Triisopropylacetophenone

Made from 2,4,6-triisopropylbenzene (Aldrich) and acetyl chloride (Mallincrodt): mp 58°C; MS (70 eV) m/e 246, 218, 203, 160; nmr ($CDCl_3$) δ 1.31 (d, 18 H), 2.05 (s, 3 H), 2.76 (m, 3 H), 7.01 (s, 2 H); ir (CCl_4) 1680 cm^{-1}, 1588 cm^{-1}, 1450 cm^{-1}.

q. 2,4,6-Triisopropyl γ-methylvalerophenone

Made from 2,4,6-triisopropylbenzene and 4-methylvaleryl chloride: bp 134°C (1 Torr); MS (70 eV) m/e 302, 274, 231, 203; nmr ($CDCl_3$) δ 0.99 (d, 6 H), 1.30 (d, 18 H), 1.60 (m, 3 H), 2.83 (t, 5 H), 7.02 (s, 2 H); ir (CCl_4) 1680 cm^{-1}, 1586 cm^{-1}, 1452 cm^{-1}.

Method D

The ketone was prepared by the coupling reaction between a phenyl magnesium bromide and aliphatic acid chloride. The work-up procedure is the same as that used in method B. The following ketones were prepared by this method.

r. o-Methyl α-methylvalerophenone

Made from o-bromotoluene and α-methylvaleryl chloride. The latter was prepared by Dr. J. McGrath and was distilled before use: bp 72°C (0.3 Torr); MS (70 eV) m/e 190, 162, 147, 119, 91; nmr ($CDCl_3$) δ 0.6-1.6 (m, 10 H), 2.38 (s, 3 H), 3.32 (m, 1 H), 7.02, 7.28 (4 H, aromatic H), the 10 proton multiplet includes δ 1.05 (d, 3 H, $-CH_3$), 0.91 (t, 3 H, $-CH_3$) and 4 methylene protons; ir (CCl_4) 1675 cm^{-1}, 1602 cm^{-1}, 1443 cm^{-1}.

s. o-Methyl α,α-dimethylvalerophenone

Made from o-bromotoluene and α,α-dimethylvaleryl chloride. The latter was prepared by Dr. J. McGrath and was distilled before use: bp 74°C (0.3 Torr); MS (70 eV) m/e 204, 176, 161, 119, 91; nmr ($CDCl_3$) δ 0.82 (m, 5 H), 1.21 (s, 6 H), 1.51 (m, 2 H), 2.20 (s, 3 H), 7.06 (4 H, aromatic H); ir (CCl_4) 1670 cm^{-1}, 1598 cm^{-1}, 1450 cm^{-1}. This compound was purified via its oxime, which was prepared by refluxing 0.1 mol of the ketone and 0.75 mol of hydroxylamine hydrochloride in 200 ml of 10% aqueous sodium hydroxide solution for 2 days. Upon cooling the oxime was obtained as a white solid. The oxime was then purified by recrystallization from ethanol, mp 135-6°C (uncor.). Hydrolysis of 10 g of the oxime by refluxing with 120 ml of 10 % aqueous hydrochloric acid for 4 hr was followed by steam distillation. The distillate was extracted with 200 ml ether. The combined extracts were washed with 20 ml water and dried over 10 g sodium sulfate. The o-methyl α,α-dimethylvalerophenone was then vacuum distilled. bp 74°C (0.3 Torr); MS (70 eV) m/e 204, 176, 161, 119, 91; nmr ($CDCl_3$)

δ 0.82 (m, 5 H), 1.21 (s, 6 H), 1.51 (m, 2 H), 2.20 (s, 3 H), 7.06 (4 H, aromatic H); ir (CCl_4) 1670 cm^{-1}, 1598 cm^{-1}, 1450 cm^{-1}.

The following ketones were purchased and were purified before use:

t. o-Methylacetophenone (Aldrich). This ketone was purified by passing through a short column of alumina and then distilled.

u. o-Methylbenzophenone (Aldrich). Purification method is the same as that of o-methylacetophenone.

v. 2,4,6-Trimethylacetophenone (Aldrich). Purified as above two ketones.

w. 3,3,6,8-Tetramethyl-1-tetralone (Aldrich). This ketone was purified by recrystalizing it from methanol twice, mp 58.5-59°C (uncor.).

3. Quenchers

a. 1,3-Pentadiene

When 1,3-pentadiene was used in obtaining Stern-Volmer plots, a mixture of the cis and trans isomers was used. Before use, the 1,3-pentadiene (Aldrich Chemical Co) was run through a 50 cm column of neutral alumina and then distilled. When the isomerization of 1,3-pentadiene was studied, cis-1,3-pentadiene (Chemical Samples Co.) was used as received. VPC analysis indicated that this cis-1,3-pentadiene was > 99.7% pure.

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

2,5-Dimethyl-2,4-hexadiene (Chemical Samples Co.) sublimed in the bottle at refrigerator temperature (∿0°C) and atmospheric pressure. The sublimed compound was used.

c. 1-Methylnaphthalene

1-Methylnaphthalene (Aldrich Chemical Co.) was distilled twice prior to use. The boiling point was 107.3 ± 0.5 C (10 Torr).

4. Internal Standards

The internal standards used were all high molecular weight alkanes which were previously purified.[119]

Standard	Supplier	bp or mp
Tetradecane (C_{14})	Columbia Organic Chem.	119-120°C at 10mm Hg
Pentadecane (C_{15})	Columbia Organic Chem.	132°C at 10mm Hg
Hexadecane (C_{16})	Aldrich Chemical Co.	146°C at 10mm Hg
Heptadecane (C_{17})	Aldrich Chemical Co.	158°C at 8mm Hg
Octadecane (C_{18})	Aldrich Chemical Co.	mp = 29-30°C
Eicosane (C_{20})	Matheson Coleman & Bell	mp = 35-33.5°C

II. Methods

1. Preparation of Samples for Photolysis

Using class A volumetric glassware and an analytical balance sensitive to tenths of milligrams, solutions containing the requisite amounts of ketone, internal standard, quencher, and other additives were prepared at room temperature (about 25°). Generally, duplicate 2.8 ml samples of each solution were syringed into Pyrex photolysis tubes. These photolysis tubes were prepared from carefully sorted and cleaned 100 x 13mm Pyres culture tubes by heating them 3 cm from the neck and drawing out the softened tubes to a length of approximately 18 cm. The samples were attached to the stopcocks of a vacuum line using 1 hole rubber stoppers and degassed by freezing them in liquid nitrogen followed by evacuating them to 1×10^{-3} torr for 30 min; the samples were then isolated from the vacuum pump by closing the stopcocks and allowed to thaw. This freeze-pump-thaw sequence was carried out two more times, the tubes being sealed with a torch before the final thawing. Each tube was inverted several times after being sealed to ensure adequate mixing.

2. Photolysis

The sample tubes were irradiated in parrallel using a water bath immersed merry-go-round apparatus[120] to insure that all the samples received the same amount of incident light and that the temperature remained constant (22-24°C). A 450 watt Hanovia medium pressure mercury lamp was used as light source, and the 3130 Å region was isolated by a 1 cm path of a 0.002 M potassium chromate - 1% potassium carbonate aqueous filter solution. The 3660 Å line, used in quenching studies with 1-methylnaphthalene, was isolated by a set of Corning No. 7083 filters. The samples were generally irradiated until ∿5% of the starting ketone was converted to products.

3. Photolysate Analysis

a. <u>Gas Chromatography</u>

The analysis of products or of the disappearance of reactants in photolyzed solutions was carried out in all cases by gas-liquid partition chromatography. Two Varian Aerograph gas chromatograph models with flame ionization detecters were used: Hy-Fi III Series 1200; and Hy-Fi Model 600 C. An Infortronics Model CRS-208 Automatic Digital Integrator was used to integrate peaks.

Nitrogen (about 25 ml/min) was used as the carrier gas, and hydrogen (about 25 ml/min) and air (about 250 ml/min) were used for the flame. Ten foot x 1/8" aluminum columns packed with a mixture of 4% QF-1 and 1% carbowax 20 M on chromosorb G usually separate the photolysate mixture effectively. A 20' x 1/8" aluminum column packed with 25% 1,2,3-tris(2-cyanoethoxy)propane on 60/80 chromosorb P in an Aerograph Hy-Fi Model 600 D was used to analyze *cis-trans* isomerization of 1,3-pentadiene.

Further information regarding the VPC conditions employed to analyze a particular run may be found in the tables of photokinetic data.

b. Identification of Photoproducts

The photoproducts, *o*-methyl-, *o*-ethyl-, 2,3,-dimethyl-, 2,4-dimethyl-, 2,5-dimethyl-, and 2,3,4,5-tetramethylacetophenone were identified by comparing their retention time with authentic compounds on analytical VPC columns. Two photoproducts were formed from irradiation of *o*-methyl α-methylvalerophenone: (1) *o*-methylpropiophenone was identified by comparing retention time on analytical VPC columns with authentic sample. (2) Cyclization product, the cyclobutanol, was identified as 1-(*o*-methylphenyl)-2,4-dimethylcyclobutanol which had the following spectral data: δ 2.28 (s, 6 H), 1.04 (d, 6 H), 1.64 (d, 2 H), 2.87 (m, 2 H), 3.20 (s, 1 H), 7.25 (m, 4 H); ir (CCl_4) 3485 cm^{-1}. Peaks in the VPC traces of the photolysates of *o*-methyl α,α-dimethylvalerophenone not assigned to the parent ketone or to *o*-methylphenyl *t*-butyl ketones were assumed to be the cyclobutanols on the basis of their expected and observed proximity to the parent ketone peak.

The photoproduct of 2,4,6-trimethylacetophenone was isolated and identified as 2,4-dimethylbenzocyclobutenol based on the following spectral data: IR (Nujol) 3250 cm^{-1}(OH); nmr ($CDCl_3$) δ 6.68 (s, 2, aromatic protons), 3.15 (g, 2, $-CH_2$), 2.27 (s, 3, benzylic $-CH_3$), 2.22 (s, 3, aromatic CH_3) and 1.64 (s, 3, aliphatic CH_3). Mass spectrum (70 eV): m/e 162 (parent peak). Two products were formed during the photolysis of 2,4,6-trimethyl-, 2,3,5,6-tetramethyl-, 2,3,4,5,6-pentamethylvalerophenone: (1) Type II photoproducts, 2,4,5-trimethyl-, 2,3,5,6-tetramethyl-, 2,3,4,5,6-pentamethylacetophenone, were identified by comparing retention times on analytical VPC columns with authentic compounds which were independently synthesized. (2) Cyclization products, the benzocyclobutenols, were identified by their IR spectra (3250 cm^{-1}, -OH) and by their VPC retention times relative to the parent ketone peak.

Two products were formed during the irradiation of o-methyl αmethoxyacetophenone **45**. A benzeze solution containing 0.5 g **45** was irradiated for 2 days with a 450-W Hanovia medium-pressure mercury vapor lamp through Pyrex. The products were separated and collected by preparative VPC on a 5' x 3/8" column packed with 20% SE 30 on Chromosorb W at 165°. The first product was identified as o-methylacetophenone which had an nmr spectrum identical with that of a commercial sample. The second product was identified as 1-(o-methylphenyl)-1-hydroxy-3-oxetane from the following spectral data: nmr ($CDCl_3$) δ 2.42

(s, 3 H), 3.72 (s, 1 H), 5.21 (s, 4 H) and 7.24 (m, 4 H); MS (70 eV) m/e 146, 91; ir (CCl_4) 3480 cm^{-1}.

c. Standardization Factors for Internal Standards

In order to obtain the concentrations of the various photoproducts by VPC, known concentrations of internal standards were used in the photolysis solutions. To determine the concentration of a photoproduct P, the response of the VPC detector to a given measured concentration of P was compared to the response to a similar concentration of internal standard, S. Thus, a standardization factor, SF was calculated according to equation 25.

$$SF = \frac{[P]}{[S]} \times \frac{\text{area S peak}}{\text{area P peak}} \qquad (25)$$

In the deuterium incorporation experiments 0.1 M degassed solutions of o-methylacetophenone in CH_3OD with various concentrations of 1,3-pentadiene were irradiated at 313 nm for 2 hr. After the irradiation was complete the tubes containing the photolysate were broken at the top and CH_3OD was let evaporate in the hood. The mass spectral was then taken for each tube sample. The toluene ion peak (m/e = 91) was used as reference peak for the determination of deuterium incorporation based on the following equation

$$\%\ D = \left(\frac{m+1}{m}\right) - \left(\frac{m+1}{m}\right)_o + 2\left\{\left(\frac{m+2}{m}\right) - \left(\frac{m+2}{m}\right)_o\right\}$$
$$m = 91$$

where (m + 1/m) and (m + 2/m) are the peak ratio of the photolysate and $(m + 1/m)_o$ and $(m + 2/m)_o$ are the peak ratio before irradiation. The irradiation and anslysis for o-methylbenzophenone was the same as o-methylacetophenone.

When analysis of P and S in a photolyzed sample was carried out under the same conditions that the SF was determined, the concentration of P could be calculated as follow:

$$[P] = SF \times [S] \times \frac{\text{area P peak}}{\text{area S peak}} \qquad (26)$$

Table 18 contains the SF's which were determined for this stidy.

Table 18. Standardization Factors

Internal Standard	SF	Product
Tetradecane (C_{14})	2.00	Acetophenone
Pentadecane (C_{15})	1.97	2-Methylacetophenone
Hexadecane (C_{16})	1.75	2-Ethylacetophenone
Pentadecane (C_{15})	1.70	2,3-Dimethylacetophenone
Hexadecane (C_{16})	1.73	2,4-Dimethylacetophenone
Hexadecane (C_{16})	1.75	2,5-Dimethylacetophenone
Octadecane (C_{18})	1.65	2,3,4,5-Tetramethylacetophenone
Octadecane (C_{18})	1.80	2,4,6-Trimethylacetophenone
Hexadecane (C_{16})	1.77	2-Methylpropiophenone
Octadecane (C_{18})	1.82	2-Methylisobutyprophenone
Eicosane (C_{20})	1.25	2,4,6-Triisopropylacetophenone
Octadecane (C_{18})	1.64	2,3,5,6-Tetramethylacetophenone
Eicosane (C_{20})	1.70	2,3,4,5,6-Pentamethylacetophenone
Pentadecane (C_{15})	2.15	2-Methylbenzaldehyde

4. Actinometry and Quantum Yields

The quantum yield of formation of a given product is calculated by dividing the number of photoproduct molecules produced by the number of photons absorbed by the molecules. The actinometer provides the number of photons when it is irradiated in parallel with samples for which quantum yields are desired.

Two chemical system were used for actinometers in this work. One system contained approximately 0.1 M valerophenone with a known concentration (usually in the range of 0.004 M) of tetradecane as the internal standard. The quantum yield for acetophenone formation in this system in benzene is known to be 0.33.[121] Thus, the photon count in einsteins l^{-1} is as follows:

$$\text{number of photons} = \frac{[\text{acetophenone}]}{0.33}$$

o-Methyl γ-methylvalerophenone, $\Phi_{II} = 0.033$ based on valerophenone, was used as a actinometer in case where the quantum yields are too low to be determined accurately by valerophenone.

The other system used consisted of some known concentration of cis-1,3-pentadiene and an amount of sensitizer such that the same amount of light was absorbed by the actinometer and by the samples for which quantum yields were desired. The photon count in einsteins l^{-1} is as follows:[118]

$$\text{number of photons} = [\text{cis-p}]_{\text{initial}} \ln \frac{0.555}{0.555 - \%\ \text{trans-p}}$$

The % *trans*-1,3-pentadiene (% *trans*-p) was measured on a 25' x 1/8' aluminum column cotaining 25% 1,2,3,-tris(2-cyanoethoxy) propane on 60/80 chromosorb P held at 50-55°C.

III. Photokinetic Data

There follow tabulations of data obtained from experiments involving quantum yield determinations, quenching of photoproducts, and sensitization of *cis*-to-*trans* isomerization of *cis*-1,3-pentadiene. Table include the VPC peak areas of the photoproduct of a given kinetic run relative to the peak area of an internal standard. Quenching data include relative quantum yields (Φ), which are obtained by dividing the peak area ratio found in the absence of quencher by that found in the presence of quencher. In tables of sensitization experiments, *trans*-1,3-pentadiene peak areas are tabulated as the percent of the sum of the *cis*- and *trans*-1,3-pentadiene peak areas.

The reproducibility of the relative VPC peak areas and consequently of the concentrations of the major photoproducts is on the order of $\sim$5%. The quantum yields incorporate an additional ±3% uncertainty in reproducibility because of the precision of the actinometry. Errors in actinometry, either in the precision or the accuracy, do not affect $k_q\tau$ since they cancel out in the ratio Φ^0/Φ. The $k_q\tau$ values obtained were generally reproducible to within ±5%. All $k_q\tau$ values are reported with their average deviations.

I. Stern-Volmer Quenching Studies.

Table 19. o-Methylbutyrophenone in Benzene at 313 nm

Additive concentration	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	0.982	0.00212	0.0014	1
[Quencher[b]], M				
0.0101	0.393	0.00084	0.00056	2.51
0.0202	0.234	0.00051	0.00034	4.20
0.0303	0.175	0.00038	0.00025	5.61
0.0404	0.140	0.00030	0.00020	7.02
[t-BuOH], M				
1.0	6.451	0.0139	0.0092	
2.0	9.702	0.0209	0.0138	
4.0	10.520	0.0227	0.0149	
[1,4-Dioxane], M				
1.0	11.082	0.0227	0.0158	
2.0	14.701	0.0317	0.0209	
3.0	16.694	0.0360	0.0238	

Photon count: 1.520 E l^{-1}

Internal standard: 0.0011 M C_{15}; SF = 1.97

Analytical conditions: 4% QF-1, 1% carbowax (column A) at 130°C.

---

[a] Type II elimination product, o-methylacetophenone.

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

Table 20. o-Methylvalerophenone in Benzene at 313 nm

Additive concentration	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	1.246	0.00344	0.016	1
[Quencher[a]], M				
0.0901	0.729	0.00201	0.0094	1.710
0.0182	0.463	0.00128	0.0059	2.694
0.0273	0.369	0.0010	0.0047	3.381
0.0364	0.284	0.0008	0.0036	4.387
[t-BuOH], M				
2.0	3.942	0.0109	0.051	
4.0	4.673	0.0129	0.060	
[1,4-Dioxane], M				
2.0	6.872	0.0190	0.088	
3.0	7.943	0.0273	0.102	

Photon count: 0.215 ξ l^{-1}

Internal standard: 0.0014 M C_{15}; SF = 1.97

Analytical conditions: Column A at 135°C

---

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

Table 21. o-Methyl γ-methylvalerophenone in Benzene

Additive concentration	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	0.812	0.00208	0.0330	1
[Quencher[a]], M				
0.0122	o.624	0.00160	0.0254	1.301
0.0244	0.474	0.00121	0.0193	1.712
0.0366	0.428	0.00109	0.0174	1.897
0.0488	0.338	0.00087	0.0138	2.399
[t-BuOH], M				
2.0	1.976	0.0050	0.0803	
4.0	2.338	0.0059	0.0950	
[1,4-Dioxane], M				
2.0	3.475	0.0089	0.1412	
3.0	4.281	0.0109	0.1740	

Photon count: 0.063 E l^{-1}

Internal standard: 0.0013 M C_{15}; SF = 1.97

Analytical conditions: Column A at 140°C

---

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

Table 22. 2,3-Dimethyl γ-methylvalerophenone in Benzene

Additive concentration	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	0.974	0.00162	0.0260	1
[Quencher[a]], M				
0.0103	0.429	0.00071	0.0115	2.267
0.0206	0.269	0.00045	0.0072	3.616
0.0309	0.199	0.00033	0.0053	4.893
0.0412	0.159	0.00026	0.0043	6.109
[t-BuOH], M				
2.0	1.472	0.00245	0.0393	
4.0	1.948	0.00324	0.052	
[1,4-Dioxane], M				
2.0	2.678	0.00445	0.0715	
3.0	3.034	0.00505	0.0809	

Photon count: 0.0624 ξ 1^{-1}

Internal standard: 0.00098 M C_{15}; SF = 1.70

Analytical conditions: 5% QF-1, 1% carbowax (column B) at 145°C.

---

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

Table 23. 2,4-Dimethyl γ-methylvalerophenone in Benzene

Additive concentration	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	0.876	0.00158	0.0242	1
[Quencher[a]], M				
0.0094	0.386	0.00069	0.0107	2.269
0.0188	0.245	0.00044	0.00678	3.576
0.0282	0.207	0.00033	0.00501	4.835
0.0376	0.141	0.00025	0.00389	6.226
[t-BuOH], M				
2.0	1.265	0.00228	0.0349	
4.0	1.679	0.00303	0.0464	
[1,4-Dioxane], M				
1.5	2.045	0.00369	0.0565	
3.5	2.883	0.00520	0.0796	

Photon count: 0.0657 ξ l^{-1}

Internal standard: 0.00104 M C_{16}; SF = 1.73

Analytical conditions: Column A at 140°C

---

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

Table 24. 2,5-Dimethyl γ-methylvalerophenone in Benzene

Additive concentration	$\frac{\text{AP peak area}}{C_{16}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	0.944	0.00185	0.02099	1
[Quencher[a]], M				
0.0121	0.385	0.00075	0.0086	2.452
0.0242	0.246	0.00048	0.0055	3.831
0.0363	0.177	0.00035	0.0039	5.320
0.0484	0.144	0.00028	0.0032	6.566
[t-BuOH], M				
2.5	1.786	0.00350	0.0397	
4.0	2.023	0.00396	0.0450	
[1,4-Dioxane], M				
2.0	2.782	0.00545	0.0619	
3.0	3.192	0.00626	0.0710	

Photon count: 0.0881 $\xi\ 1^{-1}$

Internal standard: 0.00112 M C_{16}; SF = 1.75

Analytical conditions: Column B at 155°C

---

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

Table 25. 2,3,4,5-Tetramethyl γ-methylvalerophenone in Benzene and t-BuOH

[Quencher[a]], M	$\frac{\text{AP peak area}}{C_{18}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
	Benzene solution			
0	1.478	0.00234	0.01339	1
0.00095	1.017	0.00161	0.00921	1.454
0.00180	0.792	0.00125	0.00718	1.866
0.00285	0.622	0.00098	0.00563	2.377
0.00380	0.525	0.00083	0.00476	2.813
	t-BuOH solution			
0	3.199	0.00506	0.0289	1
0.00095	1.820	0.0029	0.0165	1.758
0.00180	1.321	0.0021	0.0119	2.422
0.00285	0.986	0.0016	0.0089	3.243
0.00380	0.797	0.0013	0.0072	4.013
	1,4-Dioxane in Benzene			
1.0	3.276	0.00519	0.0297	
2.0	3.841	0.00608	0.0348	
3.0	4.412	0.00698	0.0399	

Photon count: 0.1747 E l^{-1}

Internal standard: 0.00096 M C_{18}; SF = 1.65

Analytical conditions: Colimn A at 167°C

---

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

Table 26. o-Ethylvalerophenone in Benzene and t-BuOH

[Quencher[a]], M	$\frac{\text{AP peak area}}{C_{16}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
	Benzene solution			
0	0.841	0.001648	0.02099	1
0.0103	0.432	0.000846	0.0108	1.948
0.0206	0.284	0.000557	0.0071	2.957
0.0309	0.215	0.000422	0.0054	3.905
0.0412	0.177	0.000347	0.0044	4.749
	t-BuOH solution			
0	1.922	0.003767	0.0479	1
0.0103	0.863	0.001692	0.0216	2.226
0.0206	0.544	0.001066	0.0136	3.534
0.0309	0.403	0.000789	0.0100	4.770
0.0412	0.328	0.000643	0.0082	5.862
	1,4-Dioxane in Benzene			
2.0	2.014	0.003947	0.0503	
3.0	2.763	0.005414	0.0689	

Photon count: 0.07849 ξ l^{-1}

Internal standard: 0.00112 M C_{16}; SF = 1.75

Analytical conditions: Column B at 145°C

---

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

Table 27. Stern-Volmer Quenching of o-Methylbutyrophenone in t-BuOH[a]

[Quencher[b]], M	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	1.462	1
0.0051	0.533	2.744
0.0102	0.284	5.156
0.0153	0.235	6.232
0.0204	0.182	8.018

Table 28. Stern-Volmer Quenching of o-Methylvalerophenone in t-BuOH[a]

[Quencher[b]], M	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	1.294	1
0.0102	0.495	2.631
0.0204	0.316	4.091
0.0306	0.223	5.793
0.0408	0.178	7.280

[a] Analytical conditions are the same as that in Table 19.

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

Table 29. o-Methyl γ-Methylvalerophenone in t-BuOH[a]

[Quencher[b]], M	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	1.073	1
0.0201	0.608	1.764
0.0402	0.399	2.688
0.0603	0.314	3.412
0.0804	0.270	3.975

Table 30. o-Methyl γ-Methylvalerophenone in 3.0 M Dioxane[a]

[Quencher[b]], M	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	1.470	1
0.0104	1.111	1.323
0.0208	0.917	1.603
0.0312	0.724	2.029
0.0416	0.679	2.165

[a] Analytical conditions are the same as that in Table 21.

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

Table 31. *o*-Methyl γ-Methylvalerophenone in Primary Alcohols[a]

[Quencher[b]], M	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
	1-Propanol	
0	1.274	1
0.0101	0.934	1.364
0.0202	0.721	1.768
0.0303	0.618	2.061
0.0404	0.495	2.575
	1-Pentanol	
0	1.087	1
0.0101	0.870	1.249
0.0202	0.713	1.525
0.0303	0.630	1.724
0.0404	0.551	1.973
	1-Heptanol	
0	1.240	1
0.0101	1.096	1.131
0.0202	0.952	1.303
0.0303	0.871	1.424
0.0404	0.772	1.600

[a] Analytical conditions and quencher used are the same as that in Table 21.

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

Table 32. 2,3-Dimethyl γ-methylvalerophenone in t-BuOH[a]

[Quencher[b]], M	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	0.745	1
0.00081	0.617	1.207
0.00162	0.529	1.408
0.00243	0.458	1.625
0.00324	0.409	1.819

[a] Analytical conditions are the same as that in Table 22.

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

Table 33. 2,4-Dimethyl- and 2,5-dimethyl γ-methylvalerophenone in t-BuOH[a]

[Quencher], M	$\frac{\text{AP peak area}}{C_{16}\text{ peak area}}$[b]	$(\frac{\Phi^0}{\Phi})^b$	$\frac{\text{AP peak area}}{C_{16}\text{ peak area}}$[c]	$(\frac{\Phi^0}{\Phi})^c$
0	0.842	1	0.876	1
0.00092	0.650	1.295	0.708	1.238
0.00184	0.532	1.581	0.590	1.484
0.00276	0.445	1.891	0.509	1.718
0.00368	0.387	2.178	0.449	1.949

[a] Analytical conditions are the same in Table 23 for 2,4-dimethylacetophenone and in Table 24 for 2,5-dimethylacetophenone.

[b] 2,4-Dimethylacetophenone.

[c] 2,5-Dimethylacetophenone.

Table 34A. Deuterium Incorporation in 0.05 M o-Methylacetophenone and o-Methylbenzophenone

	o-Methylacetophenone (M=119)					o-Methylbenzophenone (M=119)				
$[Q]^a$	$\frac{M+1}{M}$	$\frac{M+2}{M}$	$[D]^b$	Φ_D	$\frac{\Phi^0_D}{\Phi_D}$	$\frac{M+1}{M}$	$\frac{M+2}{M}$	$[D]^b$	Φ_D	$\frac{\Phi^0_D}{\Phi_D}$
				Before irradiation						
0	8.80	0.54	0	0		8.80	0.54	0	0	
				After irradiation for 15 hrs.						
0.000	9.36	0.643	0.0384	0.223	1	9.94	0.64	0.0672	0.391	1
0.051	9.01	0.590	0.0155	0.090	2.48	9.17	0.60	0.0243	0.141	2.7
0.102	8.93	0.590	0.0116	0.067	3.32	8.96	0.59	0.0126	0.073	5.3
0.204	8.87	0.581	0.0085	0.050	4.50	8.90	0.56	0.0069	0.045	8.8
0.500	8.85	0.580	0.0076	0.044	5.06	8.90	0.55	0.0063	0.036	10.8
1.000	8.86	0.572	0.0064	0.037	6.04	8.91	0.54	0.0054	0.032	12.4
1.500	8.86	0.571	0.0062	0.036	6.22	8.94	0.54	0.0048	0.028	14.3
2.000	8.85	0.562	0.0054	0.031	7.11	8.89	0.54	0.0043	0.025	15.6

Actinometry: 0.1 M valerophenone + 0.021 M $C_{14}H_{30}$

Acetophenone/C_{14} = 1.318 S.F. = 2.05, $\Phi_{II} = 0.33$

Photon count: 0.172 $\varepsilon\ l^{-1}$

---

[a] 1,3-Pentadiene

[b] Deuterated ketone formed during irradiation in CH_3OD

$$\% D = \{(M + 1/M) - (M + 1/M)_o\} + \{(M + 2/M) - (M + 2/M)_o\} \times 2$$

Table 34B. Deuterium Incorporation in 0.05 M o-Methylacetophenone and o-Methylbenzophenone

$[Q]^a$	o-Methylacetophenone (M=91)					o-Methylbenzophenone (M=91)				
	$\frac{M+1}{M}$	$\frac{M+2}{M}$	$[D]^b$	Φ_D	$\frac{\Phi_D^0}{\Phi_D}$	$\frac{M+1}{M}$	$\frac{M+2}{M}$	$[D]^b$	D	$\frac{\Phi_D^0}{\Phi_D}$
				Before irradiation						
0	7.68	0.25	0	0		7.68	0.25	0	0	
				After irradiation for 15 hrs.						
0	7.98	0.46	0.0362	0.210	1	8.28	0.607	0.0657	0.382	1
0.051	7.86	0.32	0.0161	0.091	2.32	7.94	0.37	0.0246	0.143	2.75
0.102	7.81	0.31	0.0123	0.067	3.13	7.83	0.30	0.0126	0.0736	5.26
0.204	7.78	0.29	0.0088	0.051	4.14	7.80	0.27	0.0076	0.044	8.71
0.500	7.76	0.28	0.0072	0.042	4.98	7.76	0.27	0.0062	0.036	10.7
1.000	7.75	0.28	0.0062	0.036	5.87	7.73	0.28	0.0057	0.033	11.7
1.500	7.73	0.28	0.0057	0.033	6.30	7.70	0.29	0.0048	0.028	13.8
2.000	7.76	0.26	0.0050	0.029	7.08	7.70	0.29	0.0045	0.026	14.5

Actinometry: 0.1 M valerophenone + 0.0210 M $C_{14}H_{30}$

Acetophenone/C_{14} = 1.318 S.F. = 2.05, Φ_{II} = 0.33

Photon count: 0.172 ξ 1^{-1}

---

[a] 1,3-Pentadiene

[b] Deuterated ketone formed during irradiation in CH_3OD

$\% D = \{(M + 1/M - (M + 1/M)_o\} + \{(M + 2/M) - (M + 2/M)_o\} \times 2$

Table 35. o-Methyl α-methoxyacetophenone in Benzene with 1,3-pentadiene as Quencher

[Quencher], M	$\frac{\text{AP peak area}}{C_{15}\text{ peak area}}$	[AP]	Φ	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0.104	1.284	0.0306	0.170	1
0.251	0.769	0.0183	0.102	1.67
0.502	0.568	0.0135	0.075	2.26
0.753	0.447	0.0107	0.059	2.87
1.004	0.395	0.0094	0.052	3.25
1.506	0.333	0.0079	0.044	3.86
2.008	0.283	0.0068	0.038	4.53
2.510	0.247	0.0059	0.033	5.20

Photon count: 0.180 ξ l^{-1}

Internal standard: 0.0121 M C_{15}; SF = 1.97

Analytical conditions: Column A at 135°C

Table 36. *o*-Methyl α-methylvalerophenone in Benzene

Additive Concentration	$\frac{\text{AP peak area}}{C_{16}\text{ peak area}}$	$\frac{\text{CB peak area}^{a}}{C_{20}\text{ peak area}}$	$\frac{\Phi^0_{CB}}{\Phi_{CB}}$	[CB]	[AP]
0	0.456	0.723	1	0.0014	0.001
[Quencher[b]], M					
0.010	—	0.332	2.18	0.0006	—
0.020	—	0.204	3.54	0.0004	—
0.030	—	0.160	4.52	0.0003	—
0.040	—	0.123	5.90	0.0002	—
[1,4-Dioxane], M					
1.0	2.055	2.745	—	0.0053	0.005
2.0	2.574	3.112	—	0.0060	0.006
3.0	2.827	3.408	—	0.0066	0.006

Photon count: $0.201\ \xi\ l^{-1}$

Internal standard: 0.00124 M C_{16}; SF = 1.77

0.00118 M C_{20}; SF = 1.65

Analytical conditions: 10% QF-1, 1% carbowax (column D) at 155°C

---

[a] Type II cyclization product, cyclobutanoles.

[b] 1,3-Pentadiene.

Table 37. Photolysis of Ketone 40 in Benzene

Additive concentration	$\frac{\text{AP peak area}}{C_{18}\text{ peak area}}$	$\frac{\text{CB peak area}}{C_{20}\text{ peak area}}$	$\frac{\text{BA}^{a}\text{ peak area}}{C_{15}\text{ peak area}}$	$\frac{\Phi^0_{CB}}{\Phi_{CB}}$	[CB] x 10^3	[BA] x 10^3	[AP] x 10^3
0	0.312	1.258	0.335	1	2.12	0.90	0.64
[Quencher], M							
0.001	0.120	0.493	0.130	2.55	0.83	0.35	0.25
0.002	0.068	0.279	0.072	4.51	0.47	0.19	0.14
0.003	0.052	0.210	0.056	5.98	0.35	0.15	0.11
0.004	0.042	0.166	0.045	7.58	0.28	0.12	0.09
[Dioxane], M							
2.0	1.625	4.142	0.342		6.98	0.92	3.33
3.0	1.820	4.560	0.351		7.68	0.94	3.73
[Thio^{b}], M							
0.01			0.640			1.72	
0.03			0.641			1.72	
0.05			0.641			1.72	

Photon count: 0.265 ξ 1^{-1}

Analytical conditions: Column D at 158°C

Internal standards: 0.00125 M C_{15}; SF = 2.15 (for BA)

0.00112 M C_{18}; SF = 1.82 (for AP)

0.00108 M C_{20}; SF = 1.56 (for CB)

---

[a] Type I product, 2-methylbenzaldehyde (BA).

[b] 1-Drodecanethiol.

Table 38. 2,4,6-Trimethyl γ-methylvalerophenone in Benzene

Additive concentration	$\frac{\text{AP peak area}}{C_{18}\text{ peak area}}$	$\frac{\text{BCB}^{a}\text{ peak area}}{C_{20}\text{ peak area}}$	$\frac{\Phi^{0}_{AP}}{\Phi_{AP}}$	[AP]x 10^3	[BCB]x 10^3
0	0.218	1.251	1	0.41	2.29
[Quencher[b]], M					
0.0023	0.181	1.260	1.205	0.34	2.30
0.0046	0.152	1.248	1.432	0.29	2.28
0.0069	0.134	1.253	1.628	0.25	2.29
0.0092	0.119	1.241	1.828	0.22	2.27
0.0115	0.108	1.240	2.012	0.20	2.27
[Dioxane], M					
2.0	1.357	9.47		2.55	17.33
3.0	1.591	10.18		2.99	18.63

Photon count: 0.1116 ξ l^{-1}

Internal standard: 0.00105 M C_{18}; SF = 1.80 for AP

0.00125 M C_{20}; SF = 1.47 for BCB

Analytical conditions: Column A at 145°C

---

[a] Cyclization product, benzocyclobutenol.

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

Table 39. 2,3,5,6-Tetramethylvalerophenone in Benzene

Additive Concentration	$\frac{\text{AP peak area}}{\text{C}_{18}\text{ peak area}}$	$\frac{\text{BCB}^{a}\text{ peak area}}{\text{C}_{18}\text{ peak area}}$	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$	[AP]x 10^3	[BCB]x 10^3
0	0.0952	5.825	1	0.168	8.43
[Quencher[b]], M					
0.0031	0.0728	5.816	1.307	0.128	8.42
0.0062	0.0577	5.827	1.651	0.102	8.43
0.0093	0.0471	5.814	2.023	0.083	8.41
0.0124	0.0432	5.808	2.203	0.076	8.40
[1,4-Dioxane], M					
2.0	0.594	51.8		1.05	74.9
3.0	0.714	53.6		1.26	77.5

Photon count: 0.4215 E l^{-1}

Internal standard: 0.00108 M C_{18}; SF = 1.64 for AP

SF = 1.34 for CB

Analytical conditions: Column A at 153°C

---

[a] Cyclization product, benzocyclobutenol.

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

Talbe 40. 2,3,4,5,6-Pentamethylvalerophenone in Benzene

Additive Concentration	$\frac{\text{AP peak area}}{C_{20}\text{ peak area}}$	$\frac{\text{BCB}^{a}\text{ peak area}}{C_{20}\text{ peak area}}$	$\frac{\Phi^{0}_{AP}}{\Phi_{AP}}$	$[AP] \times 10^{3}$	$[BCB] \times 10^{3}$
0	0.0374	0.293	1	0.075	0.449
[Quencher[b]], M					
0.0042	0.0258	0.291	1.449	0.052	0.441
0.0084	0.0193	0.290	1.941	0.039	0.440
0.0126	0.0162	0.293	2.310	0.032	0.449
0.0168	0.0129	0.287	2.898	0.026	0.439
[1,4-Dioxane], M					
2.0	0.0949	2.984		0.190	4.57
3.0	0.1122	3.174		0.225	4.86

Photon count: 0.3750 $\xi\ 1^{-1}$

Internal standard: 0.00118 M C_{20}, SF = 1.70 for AP

SF = 1.30 for CB

Analytical conditions: Column B at 158°C

---

[a] Cyclization product, benzocyclobutenol.

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

Table 41. Stern-Volmer quenching of Benzocyclobutenol Formation from 2,4,6-trimethylacetophenone in Benzene Irradiated at 366 nm

[Quencher[a]], M	$\frac{\text{BCB peak area}^{b}}{C_{18}\text{ peak area}}$	$\frac{\Phi^0_{BCB}}{\Phi_{BCB}}$
0	0.945	1
0.204	0.532	1.775
0.408	0.425	2.224
0.612	0.319	2.958
0.716	0.292	3.233

[a] 1-Methylnaphthalene.

[b] Benzocyclobutenol formation.

Table 42. Stern-Volmer Quenching of Benzocyclobutenol Formation from 2,4,6-triisopropylacetophenone in Benzene Irradiated at 366 nm

[Quencher[a]], M	$\frac{\text{BCB peak area}^{b}}{C_{20}\text{ peak area}}$	$\frac{\Phi^0_{BCB}}{\Phi_{BCB}}$
0	1.475	1
0.174	1.283	1.150
0.348	1.169	1.261
0.522	1.001	1.475
0.696	0.941	1.568
0.879	0.857	1.721

[a] 1-Methylnaphthalene. [b] Benzocyclobutenol formation.

Table 43. 2,4,6-Trimethylpivalophenone in Benzene

Additive concentration	$\frac{BA^a}{C_{18}}$	[EA] x 10^3	Φ	$\frac{\Phi^0}{\Phi}$
0	0.874	6.81	0.0909	1
[Quencher[b]], M				
0.010	0.109	0.86	0.0114	7.96
0.020	0.056	0.44	0.0059	15.48
0.030	0.041	0.32	0.0042	21.47
0.040	0.031	0.24	0.0032	27.94
[RSH[c]], M				
0.01	1.767	13.77	0.1838	
0.02	1.768	13.78	0.1839	

Photon count: 0.0749 ξ l^{-1}

Internal standard: 0.00402 M C_{18}; SF = 1.94

Analyatical conditions: 4% QF-1. 1% carbowax at 145°C

---

[a] Type I product, 2,4,6-trimethylbenzaldehyde.

[b] 1,3-Pentadiene.

[c] 1-Dodecanethiol.

Table 44. 2,4,6-Trimethyl α-methylvalerophenone

Additive concentration	$\frac{\text{AP peak area}}{C_{18}\text{ peak area}}$	$\frac{\text{BCB peak area}}{C_{20}\text{ peak area}}$	[AP] x 10^3	[BCB] x 10^3	$\frac{\Phi^0_{AP}}{\Phi_{AP}}$
0	0.197	3.427	0.35	5.0	1
[Quencher[a]], M					
0.0011	0.138	3.490	0.25	5.0	1.424
0.0022	0.103	3.421	0.18	5.0	1.903
0.0033	0.086	3.409	0.15	5.0	2.276
0.0044	0.071	3.394	0.13	4.9	2.778
[1,4-Dioxane], M					
2.0	1.098	32.96	1.95	48.1	
3.0	1.204	35.72	2.14	52.1	
4.0	1.206	35.71	2.14	52.0	

Photon count: 0.1936 ξ l^{-1}

Internal standard: 0.00112 M C_{18}; SF = 1.58 for AP

0.00108 M C_{20}; SF = 1.36 for BCB

Analytical condition: Column A at 155°C

---

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

II. Sensitization Studies

Table 45. Various Ketones with 0.2 M cis-1,3-pentadiene in Benzene

Ketone	$[c\text{-}P]_0$	% t-P	$[t\text{-}P]^{a}_{corr.}$, M	Φ_T
32	0.202	2.28	0.00472	0.208
33	0.198	2.39	0.00477	0.210
34	0.201	2.38	0.00479	0.211
35	0.198	1.86	0.00370	0.163
36-h	0.203	2.57	0.00522	0.230
36-d	0.202	2.54	0.00515	0.227
37	0.210	2.11	0.00445	0.196
38	0.208	1.73	0.00361	0.159
41	0.214	1.29	0.00277	0.122
Acetophenone	0.207	9.45	0.0227	1.00

Analytical conditions: 25' x 1/8" aluminum column packed with 25% 1,2,3-tri(2-cyanoethoxy)propane on 60/80 chromosorb P at 58°C (column C)

---

[a] Corrected for back reaction according to:

$$\%\ t\text{-}P_{corr.} = 0.55 \ln \frac{0.55}{0.55 - \%\ t\text{-}P_{uncorr.}}$$

Table 46. Various Ketones with 0.15 M *cis*-1,3-pentadiene in *t*-BuOH

Ketone	$[c\text{-}P]_o$	% t-P	$[t\text{-}P]^a_{corr.}$, M	Φ_T
32	0.198	2.81	0.00558	0.110
33	0.204	2.71	0.00553	0.109
34	0.206	2.65	0.00547	0.108
35	0.194	2.48	0.00482	0.095
36-h	0.189	3.79	0.00725	0.143
36-d	0.196	3.28	0.00654	0.129
37	0.203	2.79	0.00568	0.112
38	0.206	2.26	0.00466	0.092
41	0.211	1.70	0.00359	0.071
Acetophenone[b]	0.198	20.50	0.0507	1.00

Analytical conditions: Column C at 58°C

---

[a] Corrected for back reaction.

[b] 0.1 M in benzene.

Table 47. 0.05 M o-Methylacetophenone in Benzene

$\{c\text{-}P\}^{-1}$, M^{-1}	% $t\text{-}P_{corr.}$[a]	$\{t\text{-}P\}$, M	$\frac{0.555}{\Phi_{c\to t}}$
0.202	0.60	0.0297	2.21
0.410	1.10	0.0269	2.44
0.503	1.22	0.02433	2.70
0.801	1.74	0.02176	3.02
0.998	1.93	0.01938	3.39
1.981	3.33	0.01685	3.90
2.994	4.45	0.01487	4.42
4.371	6.08	0.01392	4.72
6.012	8.08	0.01344	4.89
7.658	10.18	0.01330	4.94
8.383	10.99	0.01311	5.01
9.182	11.88	0.01293	5.08
10.012	12.90	0.01288	5.10

Photon count: 0.1184 $\xi\ l^{-1}$

Analytical concitions: As in Table 45

---

[a] Corrected for back reaction and also for the increases in isomerization quantum yield above 1 M diene.[78]

Table 48. 0.05 M o-Methylbenzophenone in Benzene

[c-P]$^{-1}$, M^{-1}	% t-P$_{corr.}$	[t-P], M	$\frac{0.555}{\Phi_{c\to t}}$
0.387	1.88	0.0486	1.165
0.597	2.59	0.0435	1.302
0.789	3.06	0.0388	1.458
0.992	3.39	0.0342	1.653
1.984	5.33	0.0269	2.102
2.330	5.41	0.0232	2.436
2.586	5.34	0.0206	2.744
4.285	8.22	0.0192	2.950
6.092	11.21	0.0184	3.074
7.986	14.27	0.0179	3.168
8.404	14.65	0.0174	3.248
8.694	15.08	0.0173	3.263
10.042	15.66	0.0156	3.631

Photon count: 0.1020 ξ l^{-1}

Analytical conditions: As in Table 45

Table 49. 0.05 M o-Methylvalerophenone in Benzene and t-BuOH

$[c\text{-}P]^{-1}$, M^{-1}	Benzene			t-BuOH		
	% t-P	[t-P], M	$\frac{0.555}{\Phi_{c\to t}}$	% t-P	[t-P], M	$\frac{0.555}{\Phi_{c\to t}}$
0.404	0.76	0.0190	2.266	0.24	0.0058	4.120
1.006	0.90	0.0091	2.667	0.52	0.0052	4.601
1.598	1.22	0.0076	3.133	0.78	0.0048	4.932
3.196	1.88	0.0059	4.064	1.21	0.0038	6.293
4.461	2.30	0.0052	4.639	1.42	0.0032	7.533
5.840	2.83	0.0048	4.933	1.70	0.0029	8.227
7.203	3.38	0.0047	5.094	1.89	0.0026	9.119
8.406	3.87	0.0046	5.201	2.11	0.0025	9.533
9.912	4.22	0.0046	5.213	2.26	0.0025	9.706
10.02	4.54	0.0045	5.279	2.45	0.0024	9.799

Photon count: 0.0431 ξ l^{-1}

Analytical conditions: As in Table 45

Table 50. 0.05 M o-Methyl γ-methylvalerophenone in Benzene

$[c\text{-}P]^{-1}$, M^{-1}	% $t\text{-}P_{corr.}$[a]	$[t\text{-}P]$, M	$\frac{0.555}{\Phi_{c \to t}}$
10.02	5.29	0.00528	5.28
15.91	7.07	0.00444	6.27
31.92	9.87	0.00309	9.01
49.02	10.91	0.00223	12.52
63.73	11.99	0.00188	14.81
79.81	13.24	0.00166	16.79
98.04	13.38	0.00136	20.41

Photon count: 0.0502 ξ l^{-1}

Analytical conditions: As in Table 45

---

[a] Corrected for back reaction.

Table 51. o-Ethylvalerophenone in Benzene

[c-P], M^{-1}	% $t\text{-}P_{corr}$	[t-P], M	$\frac{0.555}{\Phi_{c \to t}}$
0.201	1.31	0.0653	3.782
0.394	2.37	0.0602	4.102
0.411	2.31	0.0561	4.401
0.975	4.16	0.0427	5.788
1.725	5.78	0.0335	7.374
3.402	10.20	0.0299	8.236
5.001	14.44	0.0289	8.550
7.182	19.94	0.0278	8.894
8.179	22.39	0.0273	9.021
9.004	23.97	0.0266	9.274
9.946	26.99	0.0271	9.102

Photon count: 0.445 ξ l^{-1}

Analytical conditions: As in Table 45

Table 52. o-Methyl α-methylvalerophenone (39) and o-Methyl α,α-dimethylvalerophenone (40) in Benzene

$[c\text{-}P]^{-1}, M^{-1}$	Ketone 39			Ketone 40		
	% t-P	[t-P],M	$\frac{0.555}{\Phi_{c\to t}}$	% t-P	[t-P],M	$\frac{0.555}{\Phi_{c\to t}}$
0.202	0.86	0.0426	3.204	0.69	0.0391	4.002
0.501	2.01	0.0401	3.402	1.42	0.0284	4.803
1.004	3.10	0.0310	4.398	2.18	0.0217	6.301
2.002	4.71	0.0235	5.802	2.97	0.0149	9.189
2.704	4.80	0.0177	7.694	2.98	0.0110	12.392
4.598	7.38	0.0161	8.502	4.72	0.0103	13.301
6.104	8.85	0.0145	9.411	5.79	0.0095	14.402
7.805	10.87	0.0139	9.796	7.24	0.0093	14.702
8.405	11.47	0.0136	10.001	7.64	0.0091	14.996
9.152	12.36	0.0135	10.110	8.33	0.0091	15.001
10.004	13.38	0.0134	10.205	8.98	0.0089	15.204

Photon count: 0.246 $E\ l^{-1}$

Analytical conditions: As in Table 45

Table 53. 2,4,6-Trimethyl γ-methylvalerophenone (46) and 2,3,4,5,6-Pentamethylphenone (48) in Benzene

$[c\text{-}P]^{-1}, M^{-1}$	Ketone 46			Ketone 48		
	% $t\text{-}P_{corr.}$	[t-P],M	$\frac{0.555}{\Phi_{c\rightarrow t}}$	% t-P	[t-P],M	$\frac{0.555}{\Phi_{c\rightarrow t}}$
0.402	1.16	0.0289	1.884	0.81	0.0203	2.684
0.581	1.58	0.0272	1.998	1.13	0.0194	2.802
0.989	2.56	0.0259	2.101	1.85	0.0188	2.901
1.201	3.03	0.0253	2.153	2.19	0.0183	2.976
2.002	4.59	0.0229	2.372	3.41	0.0170	3.189
4.004	4.81	0.0195	2.786	6.05	0.0151	3.602
6.006	10.94	0.0182	2.984	8.71	0.0145	3.752
8.003	14.09	0.0176	3.089	11.02	0.0138	3.950
9.989	16.96	0.0169	3.204	13.51	0.0135	4.022
10.568	17.70	0.0167	3.248	14.20	0.0134	4.047
11.201	18.74	0.0167	3.251	15.01	0.0134	4.058

Photon count: 0.098 ξ l^{-1}

Analytical conditions: As in Table 45

Table 54. 8-Methyl-1-tetralone (51) and 5,6,7,8-Tetramethyl-1-tetralone (52) in Benzene

$[c\text{-}P]^{-1}, M^{-1}$	Ketone 51			Keotne 52		
	% t-$P_{Corr.}$	[t-P], M	$\frac{0.555}{\Phi_{c\rightarrow t}}$	% t-P	[t-P], M	$\frac{0.555}{\Phi_{c\rightarrow t}}$
0.801	1.75	0.0218	5.667	1.28	0.0159	7.766
0.987	2.04	0.0206	5.999	1.52	0.0154	8.033
1.582	2.79	0.0177	7.001	2.34	0.0148	8.349
1.994	3.22	0.0161	7.667	2.84	0.0142	8.694
2.601	3.39	0.0130	9.490	3.59	0.0138	8.945
3.372	3.79	0.0113	10.998	4.39	0.0130	9.499
5.752	4.24	0.0074	16.799	6.33	0.0110	11.233
7.801	4.66	0.0060	20.702	7.63	0.0098	12.658

Photon count: 0.223 E l^{-1}

Analytical conditions: As in Table 45

Table 55. 2.4.6-Triisopropyl γ-methylvalerophenone in Benzene

$[c\text{-}P]^{-1}$, M^{-1}	% $t\text{-}P_{corr.}$	$[t\text{-}P]$, M	$\frac{0.555}{\Phi_{c\to t}}$
0.315	0.55	0.0175	18.62
0.682	0.88	0.0129	25.27
1.269	1.09	0.0036	37.79
1.921	1.16	0.0060	53.92
2.802	1.27	0.0045	71.85
3.784	1.30	0.0034	94.98
4.903	1.33	0.0028	116.01

Photon tount: o.587 E l^{-1}

Analytical conditions: As in Table 45

Table 56. Reciprocal Quenching Study for the Unknown Product Formation from 2,4,6-Trimethylacetophenone in Benzene[a]

[Quencher[b]], M	[Quencher]$^{-1}$, M^{-1}	$\frac{\text{Product peak area}}{C_{18}\text{ peak area}}$	Φ_{product}	Φ^{-1}
0	∞	0	0	∞
0.4265	2.344	0.00816	0.00139	716
0.5541	1.805	0.01031	0.00175	518
0.6559	1.525	0.01244	0.00213	471
0.9467	1.056	0.01899	0.00324	308

[a] 0.05 M ketone, 313 nm irradiation.

[b] 1,3-Pentadiene as quencher.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. A. Jablonski, *Z. Physik*, **94**, 38(1935).
2. E. F. Ullman, *Accts. Chem. Res.*, **1**, 353(1968).
3. C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1531(1938).
4. H. -G. Heine, *Justus Liebigs Ann. Chem.*, **732**, 165(1970).
5. P. Yates, *Pure Appl. Chem.*, **16**, 93(1968).
6. P. Yates and R. Loutfy, *Accts. Chem. Res.*, **8**, 209(1975).
7. P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437(1969).
8. P. Dunion and C. N. Trumbone, *ibid.*, **87**, 4211(1965).
9. R. Simonaitis, G. W. Cowell and J. N. Pitts, Jr., *Tetrahedorn Lett.*, 3735(1967).
10. J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2564(1970).
11. N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro and J. C. Dalton, *ibid.*, **92**, 6974(1970).
12. R. G. W. Norrish, *Trans. Faraday Soc.*, **33**, 1512(1937).
13. N. C. Yang and D. H. Yang, *J. Amer. Chem. Soc.*, **80**, 2913 (1958).
14. P. J. Wagner, *Accts. Chem. Res.*, **4**, 169(1971).
15. D. R. Coulson and N. C. Yang. *J. Amer. Soc.*, **88**, 4511(1966).
16. P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009(1965).
17. N. C. Yang, S. P. Elliot, and B. Kim, *ibid.*, **91**, 7551(1969).
18. P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245(1966).

19. P. J. Wagner, P. A. Kelso and R. G. Zepp, *ibid.*, **94**, 7408 (1972).

20. E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., *ibid.*, **88**, 2652(1966).

21. J. N. Pitts, Jr., D. R. Burley, J. C. Mani and A. D. Broadbent, *ibid.*, **90**, 5902(1968).

22. D. R. Kearns and W. A. Case, *ibid.*, **88**, 5087(1966).

23. P. J. Wagner, *ibid.*, **89**, 5898(1967).

24. P. J. Wagner and H. N. Schott, *ibid.*,**91**, 5383(1969).

25. N. C. Yang and R. C. Dusenbery, *Mol. Photochem.*, **2**, 159(1969).

26. Y. H. Li and E. C. Lim, *Chem. Phy. Lett.*, **7**, 15(1970).

27. E. J. Baum, J. K. S. Wan and J. N. Pitts, *J. Amer. Chem. Soc.*, **88** , 2652(1966).

28. P. J. Wagner, A. E. Kemppainen and H. N. Shott, *ibid.*, **95**, 5604(1973).

29. A. A. Lamola, *J. Chem. Phys.*, **47**, 4810(1967).

30. J. B. Gallivan and J. S. Brinen, *Chem. Phys, Lett.*, **10**, 455(1971).

31. P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5806(1968).

32. (a) N. C. Yang, D. S. McClure and R. Dusenbery, *ibid.*, **89**, 5466(1967).

    (b) N. C. Yang and R. Dusenbery, *ibid.*, **90**, 5899(1968).

33. (a) T. H. Liu and E. C. Lim, *Chem. Phys. Lett.*, **7**, 159(1970).

    (b) L. Goodman and M. Koyanagi, *Mol. Photochem*, **4**, 369(1972).

34. P. J. Wagner and T. Nakahira, *J. Amer. Chem. Soc.*, **95**, 8474(1973).

35. P. J. Wagner, M. T. Thomas and E. Harris, *ibid*, **98**, 7675(1976).

36. J. N. Collie, *J. Chem. Soc.*, **85**, 971(1904).

37. K. R. Huffman, M. Loy and E. F. Ullman, *J. Amer. Chem. Soc.*, **87**, 5417(1965).

38. A. Backett and G. Porter, *Trans Faraday Soc.*, **58**, 2038(1963).

39. N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, **83**, 2217(1961).

40. E. F. Zwicker, L. I. Grossweiner and N. C. Yang, *ibid.*, **85**, 2671(1963).

41. G. Porter and M. F. Tchir, *J. Chem. Soc.*, *A*, 3772(1971).

42. G. Porter and M. F. Tchir, *Chem. Comm.* 1372(1970).

43. E. F. Ullman and K. R. Huffman, *Tetrahedron Lett.*, 1863 (1965).

44. N. D. Heindel, J. Molnar and M. Pfau, *Chem. Comm.*, 1373 (1970).

45. T. Matsuura and Y. Kitaura, *Tetrahedron*, **25**, 4487(1969).

46. J. Michl, *Mol. Photochem.*, **4**, 257(1972).

47. J. Michl, *Top. Current Chem.*, **46**, 1(1974).

48. J. Michl and C. R. Flynn, *J. Amer. Chem. Soc.*, **96**, 3280 (1974).

49. E. Migirdicyan and J. Baudet, *ibid.*, **97**, 7400(1975).

50. H. Lutz, E. Breheret and Lindqvist, *J. Chem. Soc.*, *Faraday Trans.*, *I*, 2096(1973).

51. P. G. Sammers, *Tetrahedron*, **32**, 405(1976).

52. W. R. Bergmak, B. Beckman and W. Lindenberger, *Tetrahedron Lett.*, 2259(1971).

53. F. Sclly and H. Morrison, *J. Chem. Soc.*, *Chem. Comm.*, 529(1973).

54. A. C. Pratt, *ibid.*, *Chem. Comm.*, 183(1974).

55. A. G. Schultz, C. D. Deboer, W. G. Herkstroeter and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **92**, 6086(1970).

56. G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664(1965).

57. (a) R. S. H. Liu, N. J. Turro and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406(1965).
    (b) W. G. Dauben, R. G. Williams and R. C. McKelvery, *ibid.*, **95**, 3932(1973).
    (c) E, L. Eliel, "*Stereochemistry of Carbon Compounds*" McGraw Hill, New York, N. Y. 1962, pp. 151, 237.

58. J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, **91**, 8144(1969).

59. F. D. Lewis, R. W. Johnson and D. R. Kory, *ibid.*, **96**, 6100(1974).

60. F. D. Lewis, R. W. Johnson and D. E. Johnson, *ibid.*, **96**, 6990(1974).

61. E. C. Alexander and J. A. Uliana, *ibid.*, **96**, 5644(1974).

62. A. Padwa, W. Eiscngern, *ibid.*, **94**, 5859(1972).

63. P. J. Wagner, "*Creation and Detection of the Excited* State", Vol. 1A, p.173, New York, Marcel Dekker 1971.

64. P. J. Wagner, *Mol. Photochemistry*, **30**, 23(1971).

65. J. C. Dalton, J. J. Synder, *ibid.*, **6**, 291(1974).

66. M. D. Shetler, *ibid.*, **6**, 191(1974).

67. A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129(1965).

68. E. L. Eliel, "*Sterochemistry of Carbon Compounds*",McGraw Hill, New York, N. Y., 1962, pp. 151, 237.

69. E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **88**, 2652(1966).

70. D. Leibfritz, *Chem. Ber.*, **108**, 3014(1975).

71. E. Blok and R. Stevenson, *J. Chem. Soc. Perkin I*, 308 (1973).

72. W. Oppolzer and K. Keller, *Angew. Chem. Internat. Edn.*, **11**, 728(1972).

73. T. Kametani and K. Fukumoto, *Heterocycles*, **3**, 29(1975).

74. T. Kametani and K. Fukumoto, *Heterocycles*, **3**, 29(1975).

75. P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232(1968).

76. F. D. Lewis and N. J. Turro, *ibid*, **92**, 311(1970).

77. P. J. Wagner, in "*Creation and Detection of the Excited State*", Vol I, Part A (A. A. Lamola, ed.), Dekker, New York, 1971, p. 173.

78. R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 211(1970).

79. P. J. Wagner and J. H. McGrath, *ibid.*, **94**, 3849(1972).

80. P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232(1968).

81. (a) H. Suzuki, "*Electronic Absorption Spectra and Geometry of Organic Molecules*" Academic Press, New York, N. Y. 1946, p. 4334.
    (b) Leibfritz, *Chem. Ber.*, **108**, 3014(1975).

82. (a) J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, **93**, 4794(1971).
    (b) J. A. Barltrop and H. A. J. Carless, *ibid.*, **94**, 8761 (1972).

83. F. Ayres, Jr., "*Theory and Problems of Differential and Integral Calculus*", Schaum, New York, 1950, p. 70.

84. R. Grinter and E. Heilbronner, *Helv. Chim Acta*., **45**, 2496(1962).

85. H. Z. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc*., **85**, 922(1963).

86. A. D. Osborne and G. Porter, *Proc. Roy. Soc. (London)*, A, **284**, 9(1965).

87. F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852(1972).

88. F. D. Lewis and N. J. Turro, *ibid*., **92**, 311(1970).

89. P. J. Wagner and R. A. Leavitt, *ibid*., **92**, 5806(1970).

90. P. J. Wagner, P. A. Kelso and R. G. Zepp, *ibid*., **94**, 7480(1972).

91. G. Montaudo, P. Finocchiara and P. Maravigna, *ibid*., **93**, 4214(1971).

92. E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3755(1955).

93. G. D. Hedden and W. C. Brown, *J. Amer. Chem. Soc*., **75**, 3744(1953).

94. W. F. Forbes and W. A. Muller, *ibid*., **79**, 6495(1957).

95. R Hoffmann and J. R. Swenson, *J. Phy. Chem.*, **64**, 415(1970).

96. J. C. Dalton, and J. J. Synnder, *Mol. Photochem*., **6**, 291(1974).

97. C. Steel and L. Giering, unpublished work.

98. C. Walling and M. J. Gibiam, *J. Amer. Chem*. Soc., **87**, 3361(1965).

99. F. D. Lewis, R. W. Johnson and R. A. Ruden, *ibid*., **94**, 4292(1972).

100. R. Hoffmann and J. R. Swenson, *J. Phys. Chem.*, **64**, 415 (1970).

101. D. R. Kearns and W. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

102. J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499(1970).

103. R. M. Hochstrasser, H. Lutz and G. W. Scott, *Chem. Phys. Lett.*, **24**, 162(1974).

104. L. Salem, *J. Amer. Chem. Soc.*, **96**, 3486(1974).

105. L. Salem, C. Leforestier, G. Segal and R. Wetmore, *ibid.*, **97**, 479(1975).

106. P. J. Wagner, A. E. Kemppainer and H. N. Schott, *ibid.*, **95**, 5604(1973).

107. W. G. Herkstroeter, L. B. Jones and G. S. Hammond, *ibid.*, **88**, 4777(1966).

108. M. A. Pfau, N. D. Heidel and T. F. Lemke, *Acad. Sci., Paris*, **261**, 1017(1965).

109. W. C. Brown, *J. Amer. Chem. Soc.*, **75**, 3744(1953).

110. (a) J. E. Baldwin and S. M. Krueger, *ibid.*, **91**, 6144(1969).
    (b) W. G. Dauben, R. G. Williams and R. O. McKelvey, *ibid.*, **95**, 3932(1973).
    (c) F. D. Lewis and R. W. Johnson, *ibid.*, **94**, 8914(1972).

111. (a) R. Rosenfield, M. Ottolenghi and A. Y. Meyer, *Mol. Photochem.*, **5**, 39(1973).
    (b) E. Migirdicyan, A. Despres, V. Leieune and S. Leach, *J. Photochem.*, **3**, 383(1974).

112. R. Bishop and N. K. Hamer, *Chem. Comm.*, 804(1969).

113. R. Bishop and N. K. Hamer, *J. Chem. Soc.*, C, 1193(1970).

114. N. K. Hamer and C. J. Samuel, *J. Chem. Soc.*, *Perkin Trans.*, **2**, 1316(1973).

115. Y. Ogata and K. Takage, *J. Org. Chem.*, **39**, 1385(1974).

116. F. D. Lewis, R. W. Johnson and D. R. Kory, *J. Amer. Chem. Soc.*, **96**, 6100(1974).

117. A. I. Vogel, "*Practical Organic Chemistry*", 3rd ed., 1955, p. 177.

118. W. D. Totherow and G. J. Gleidier, *J. Amer. Chem. Soc.*, **91**, 7150(1969).

119. P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5898(1968).

120. F. G. Moses, R. S. H. Liu and B. H. Monroe, *Mol. Photochem.*, **1**, 245(1969).

121. P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5898(1968).

122. A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129(1965).