

EFFECTS OF METHYL SUBSTITUTION
ON THE PHOTOPROCESSES
OF ALKYL PHENYL KETONES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
EUGENE GEORGE HARRIS
1973

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ABSTRACT

EFFECTS OF METHYL SUBSTITUTION ON THE PHOTOPROCESSES OF ALKYL PHENYL KETONES

By

Eugene George Harris

Photochemical studies were conducted to determine the effects of methyl substituents on the rates of hydrogen abstraction (k_r) and radiationless decay (k_d) from the triplet states of butyro and valerophenone. Methyl groups were added in the series: meta methyl, para methyl, 3,4-dimethyl, and 3,5-dimethyl. Values for k_r and k_d were calculated from solvent studies and Stern Volmer quenching plots.

The rates of radiationless decay were found to be larger for the meta substituted phenyl ketones. The 3,4-dimethyl ketones possessed k_d values which were determined to be about the same as those for the para substituted ketones. The 3,5-dimethyl ketones possessed k_d values that were lower than those of the meta methyl ketones.

The faster rates of hydrogen abstraction for the meta substituted ketones were proposed to be the result of the larger $(n, \pi^*) - (\pi, \pi^*)$ triplet separations in the para isomers.

An additivity relationship was noted for the relative rates of hydrogen abstraction among the various isomers of the methylated ketones. These rates showed a reasonable correlation to $(n,\pi^*)-(\pi,\pi^*)$ triplet separations which had been determined from earlier phosphorescent excitation studies.

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By

Eugene George Harris

A THESIS

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G 80378

To Paula
for her endurance and
understanding

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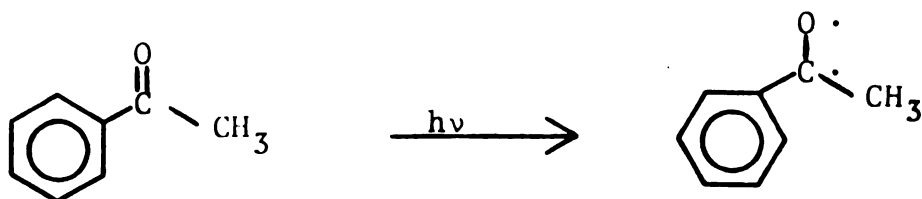
INTRODUCTION

The photochemistry of ketones has undergone extensive examination in recent years.¹⁻⁶ As a result the mechanisms for many photoprocesses are becoming fairly well understood. However, no general understanding of the steric and electronic effects of ring substituents on the photochemistry of phenyl ketones yet exists. The following study of the type II process of meta- and para-methylated phenyl ketones was initiated to clarify some of these electronic effects.

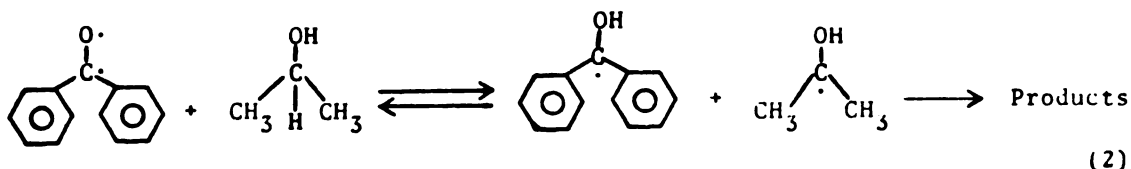
A. Substituent Effects on the Photoreduction of Ketones

1) Review of Photoreduction

The first experimental evidence of photoreduction came when Ciamician and Silber identified the pinacol and corresponding aldehyde or ketone from benzophenone irradiated in alcohols.⁷ Acetone and acetophenone were also found to photoreduce.^{7,8} Numerous hydrogen donor solvents have been employed in the photoreduction process.⁸ Hirshberg completed the first systematic studies in the late thirties. He proposed the first step of photoreduction to be a diradical formation, (Equation 1).



Hammond later found, as did Hirshberg, that optically active alcohols did not racemize and so concluded that disproportionation and reversal of the abstraction process did not take place (Equation 2).¹⁰ Quenching studies of



benzophenone with O_2 and olefins indicated that the reacting species was a triplet.¹¹

2) Substituent Effects - Meta and Para

The first substituent effects were noted by Bergman and Hirshberg in 1943.¹² They found that only a limited number of ketones were susceptible to photoreduction (Equation 3).



Acetyl naphthalenes, α naphthyl phenyl ketones, and di- α -naphthyl ketones did not undergo photoreduction. They found that meta-phenylbenzophenone forms a small amount of pinacol

whereas the para and ortho isomers do not. Methoxy-substituted acetophenones also do not react. The low reductivity for this group of ketones involves the nature of the lowest triplet state, with the $^3(n, \pi^*)$ state being generally reactive and the $^3(\pi, \pi^*)$ state nonreactive toward hydrogen abstraction.¹³ The $^3(n, \pi^*)$ state resembles an alkoxy radical in its reactivity and so possesses the greater electrophilicity (Figure 1).^{14,15}

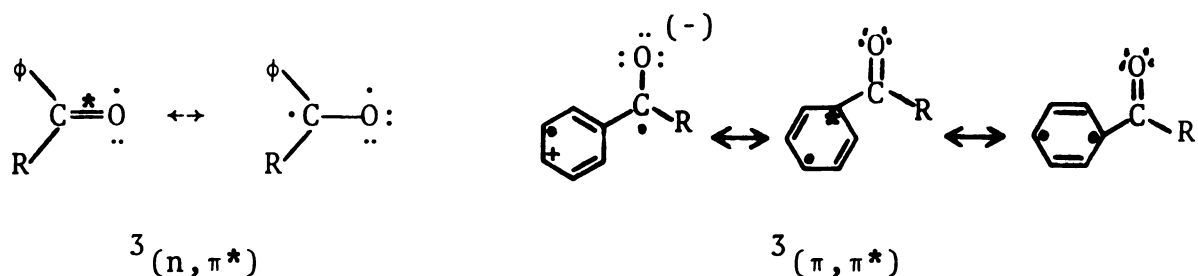
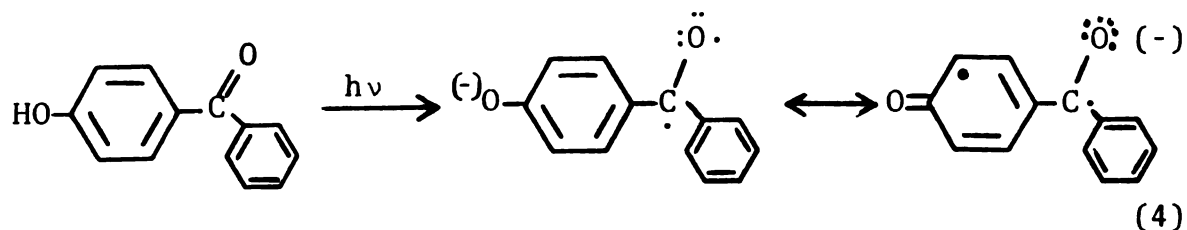


Figure 1. Electron density in $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ states.

Phosphorescence studies have shown that ketones such as para-phenyl and para-aminobenzophenone have low lying $^3(\pi, \pi^*)$ states.^{16,17} Pitts and workers photolyzed various p-aminobenzophenones and found little photoreduction by alcohols.¹⁸ Higher yields were noted, however, for para-methoxy and -phenyl substituents.¹⁹ Porter and Suppan studied, in some detail, the relationship between the spectroscopic and photochemical properties of substituted

benzophenones.²⁰ Amino, dimethylamino, or hydroxy groups substituted into the ring at the meta or para positions reduce the photoreduction quantum yield in alcohol to near zero. The pinacol yield increases in paraffins for the p-amino but not for meta-aminobenzophenone. This fact has been attributed to an inversion for the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states in the para isomer which can be deduced from spectroscopic data. Pinacol formation for the methoxy derivative was found to be 10 times that of the hydroxy, even though their spectra are nearly identical. A lowest charge transfer triplet, $^3CT^*$, was invoked to explain the large difference in reactivities, with deprotonation of the hydroxyl occurring in the excited state (Equation 4).

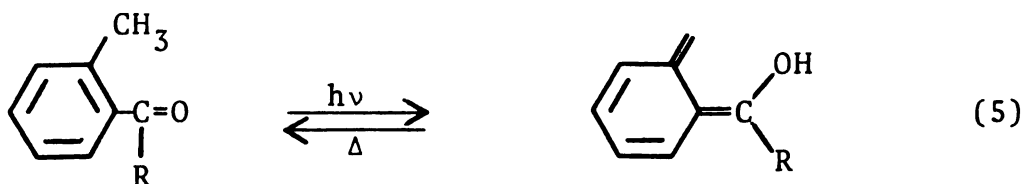


The intermediate reactivity of phenyl-substituted benzophenone was attributed to its lowest triplet being a $^3(\pi,\pi^*)$. Para and meta methyl substituents on benzophenone produce only a small reduction in quantum yield of pinacol formation while a para-trifluoromethyl group slightly increase the pinacol yield.²¹ Mixing of the lower $^3(n,\pi^*)$ state with the upper $^3(\pi,\pi^*)$ state was said to be the origin

of the former effect. The increase in pinacol formation in the latter case was rationalized as an inductive effect. Yang demonstrated, however, that methylation of acetophenone produces a lowest $^3(\pi, \pi^*)$ which still photoreduces with considerable quantum efficiency in 2-propanol.^{22,23} It was suggested that the reduction efficiency depends on the extent of vibronic coupling between the $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ states.²³ The methylated acetophenones have a considerably slower rate of non radiative decay than does acetophenone, which has a lowest $^3(n, \pi^*)$ state. Meta methyl and methoxy substituents lower pinacol quantum yields more than the para isomers do and also produce longer radiative lifetimes.

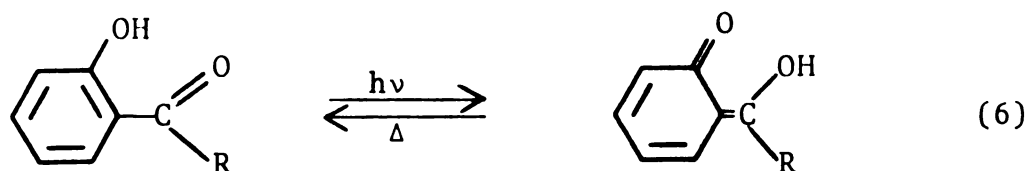
3) Ortho Substituent Effects

Yang, in 1961, provided evidence for the photoenolization (Equation 5) of o-methylbenzophenone, which had been proposed as the reason for the low photoreduction yields from ortho-alkyl phenyl ketones.²⁴ The following



year Yang demonstrated that the precursor of the photoenol was a triplet rather than a singlet.²⁵ The dependency of the rate of photoenolization on structure has been established.²⁶ Photoenolization has also been reported as

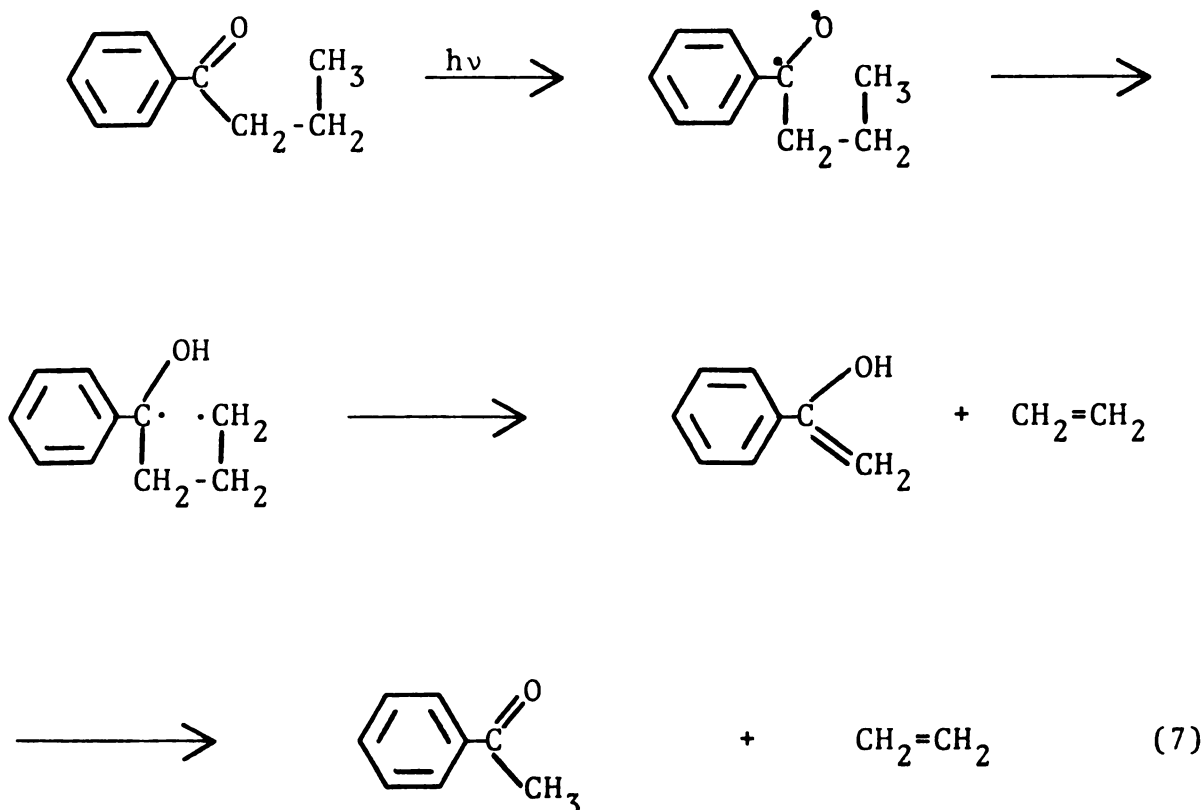
the pathway for the reduction of triplet activity for ortho-hydroxy phenyl ketones (Equation 6).^{18,19,20,27}



B. Substituent Effects on the Type II Reaction

1) Review of the Type II Reaction

Phenyl alkyl and dialkyl ketones containing gamma C-H bonds undergo, upon irradiation, 1,5 hydrogen shifts to yield cleavage and cyclization products (Equation 7).



The cleavage reaction with ketones is commonly called Norrish type II photoelimination.²⁸ The cyclization reaction to form cyclobutanols was first discovered by Yang in 1958.²⁹ Both of these reactions involve the transfer of hydrogen from the γ carbon to the carbonyl oxygen. In the photoelimination reaction, ketone formation has been shown to proceed via the enol.^{30,31} Although dialkyl ketones react from both singlet and triplet, in the phenyl alkyl ketone system, where intersystem crossing from the singlet to triplet is extremely rapid, both elimination and cyclization occur only from the triplet.³²⁻³⁷ A 1,4-biradical intermediate has been demonstrated, with little doubt, to intervene in triplet state type II reactions.³⁸ 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 research groups who tried to compare quantum yields to triplet reactivity.^{13,39,40} Wagner has shown that added hydrogen bonding solvents maximize quantum yields by eliminating the reverse hydrogen transfer.⁴¹ Reactivities of the triplet may be obtained from Stern Volmer plots, of which more will be said later.

2) Effects of Ring Substituents on the Type II Photoreaction

The use of the Type II reaction to ascertain structure-reactivity relationships in ring substituted ketones was

thought to be preferable to analogous studies using intermolecular photoreduction, mainly because of the control of C-H bond strength during drastic solvent changes. Pitts, in 1966, found substituent effects on the quantum yield of butyrophenone reaction similar to those observed for benzophenones.¹³ The photoelimination quantum yield for *p*-hydroxy, *p*-amino, and *p*-phenyl were negligible and the phosphorescent lifetimes were long, ~ 0.08 sec. The lifetimes for *p*-methyl, *p*-fluoro, and *p*-acetoxybutyrophenones were shorter, ~ 0.004 sec, and displayed higher quantum yields. Pitts considered the latter ketones to possess $^3(n, \pi^*)$ lowest triplets. *p*-Methoxybutyrophenone had an intermediate lifetime and quantum yield. In a later communication Pitts found the meta substituted methoxy and acetoxy butyrophenones to have a quantum yield, in benzene, one tenth that of the ortho and para substituted ketones and a phosphorescent lifetime a factor of 10 longer.³⁹ The meta substituents were thought to lead to $^3(\pi, \pi^*)$ lowest triplets while the ortho and para substituted methoxy and acetoxy butyrophenones were not classified. The m,*p*-fluoro, methyl and chloro all behaved similarly and were held to have a $^3(n, \pi^*)$ lowest triplet. Pitts suggested that the energy separation of the $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ triplets might be rather small in certain solvents, as dual phosphorescent emission had been observed for similar ketones.^{40,42,43}

The most in depth work on the type II reaction has been completed by Kemppainen on the substituted valerophenone system.⁴³ Quenching studies in combination with spectroscopic data have somewhat clarified the effect of substituents on the photoelimination quantum yields and reactivities.^{44,1} 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.⁴⁵ The former effect is present with groups such as *p*-trifluoromethyl or a pyridyl ketone.^{1,46} Addition of alcohol promotes a ϕ_{II} of unity which indicates that these lowest $^3(n,\pi^*)$ triplet ketones have negligible direct decay from their triplets. The increase in reactivity for the strongly electron withdrawing groups seems to be an inductive effect on the already electrophilic triplet.^{21,47} 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.^{43,48,49} As well as having longer lifetimes, the type II quantum values for the chloro, methyl, and methoxy substituted alkyl phenyl ketones do not reach unity upon addition of increments of alcohol. Such behavior indicates some type of direct triplet decay competitive with γ -hydrogen abstraction.^{41,49} Quenching

studies also show that the ketones with lowest $^3(\pi, \pi^*)$ triplets show marked reduction in rates of hydrogen abstraction.⁵⁰ Yang and Dusenbergh, in their work with methylated acetophenones, also demonstrated reduced k_r values for these lowest $^3(\pi, \pi^*)$ triplets.²³ Wagner has shown that a reactive upper $^3(n, \pi^*)$ state in equilibrium with a lower unreactive $^3(\pi, \pi^*)$ state best explains the experimental data.⁵¹ Since spectroscopists have indicated that the triplets are vibronically mixed, some reactivity from the lowest $^3(\pi, \pi)^*$ state is not ruled out for ketones where the states are close (<2 kcal separation).^{40,43,47,48,52,53} Chloro and methyl substituted phenyl ketones would fall in this category.⁴⁴ It was also noted that meta-methyl and methoxy substitution produced shorter lifetimes and lower quantum yields. These observations point to a higher radiationless decay for these meta substituted ketones.

C. Objectives

The difference in the k_d values for the meta and para isomers poses an interesting question. Quenching by ground state ketone might possibly be an answer. This would be supported by an increase in type II yield with a concurrent decrease in ketone concentration. Perhaps the difference reflects vibronic effects leading to radiationless decay. The work described in this thesis was begun on the

proposition that varying the quantity and position of methyl groups in the phenyl ring of alkyl phenyl ketones might yield information on the excited triplet's electronic structure. As the number of methyl groups increase and their positions vary, one would expect a transition from the small effect of one methyl group to the large effect of one methoxy group.

D. Kinetics of Experimental Techniques

1) Representation of the Type II Process

Figure 2 is a modified Jablonski diagram which gives a pictorial view of the excitation to and possible modes of decay from the two lowest electronic states of valerophenone. A schematic of the photolysis of valerophenone is given in Figure 3.

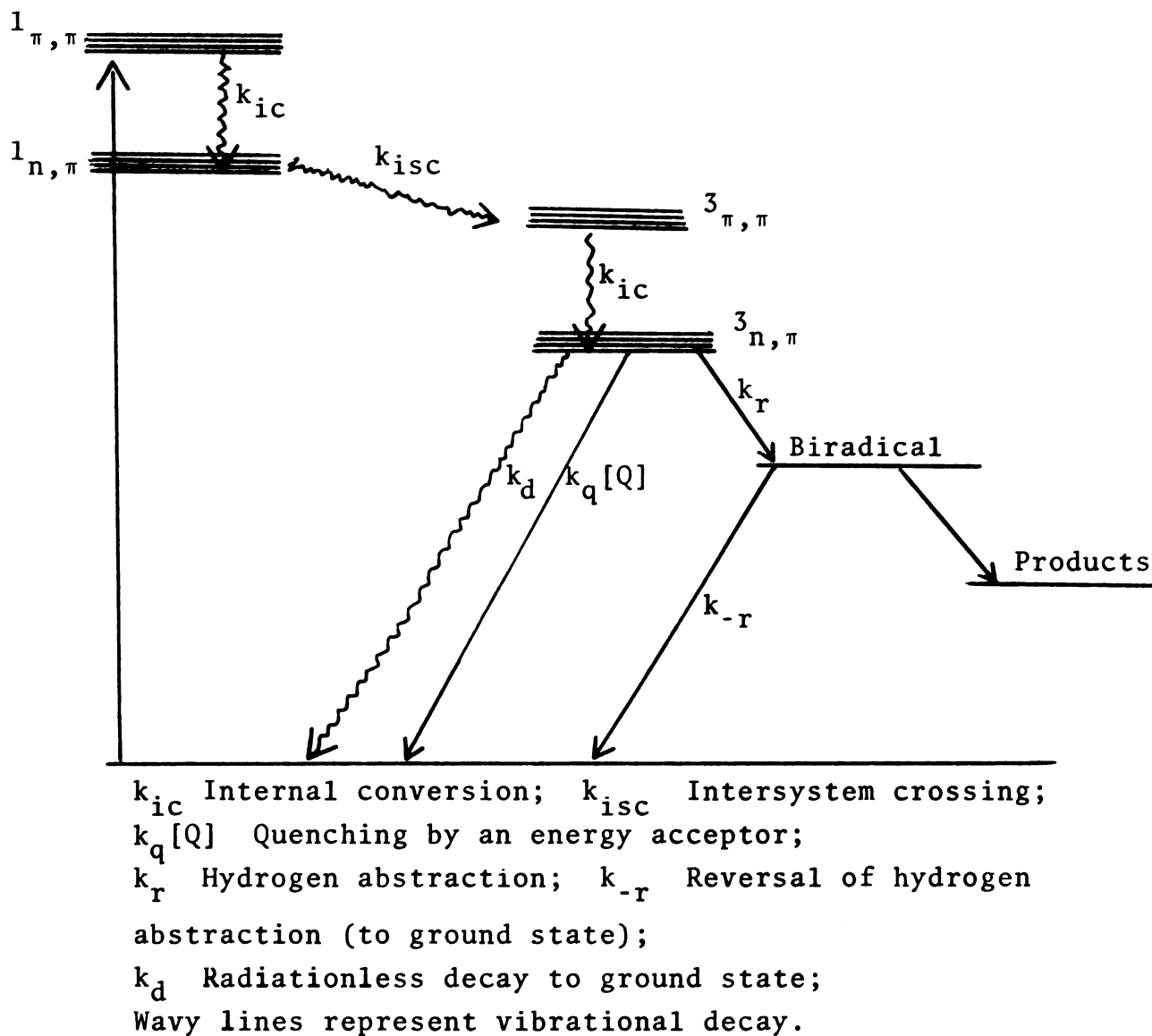


Figure 2. Jablonski diagram of the photolysis of valerophenone with a quencher present.

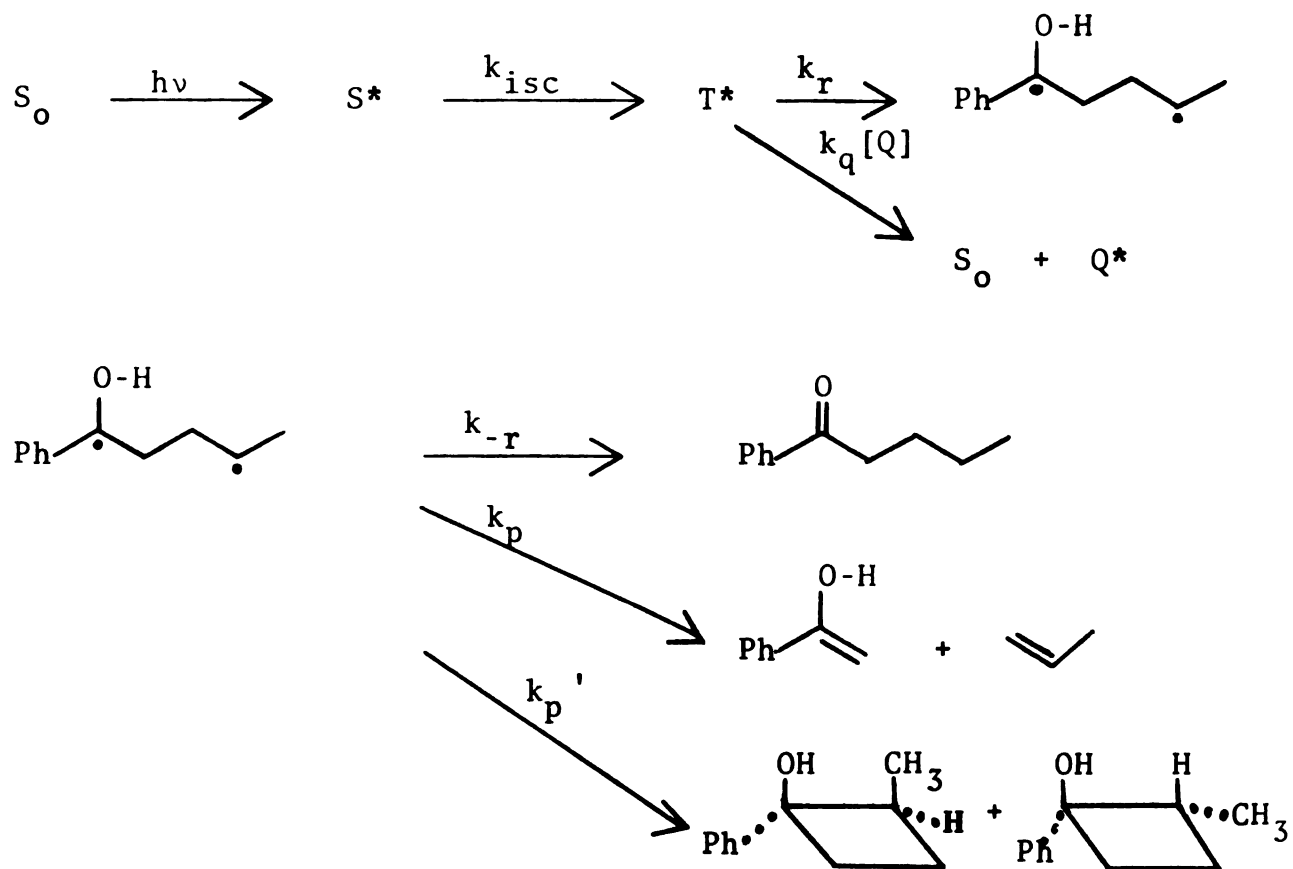


Figure 3. Photolysis of valerophenone.

2) Energy Transfer

The quenching portrayed in the Jablonski diagram, in fluid solutions, is a collisional interaction process and depends on the spatial overlap of the orbitals of the two molecules.^{54,55} It has often been assumed that triplet energy transfer was diffusion controlled and thus dependent only on the viscosity of the solvent.⁵⁶ Quenching rates were calculated using the modified Debye Equation 8:⁵⁷

$$k_q = k_{diff} = \frac{8RT}{2000 \eta} \quad 1/\text{mole} \cdot \text{sec} \quad (8)$$

In viscous solvents, the quenching rate has been determined to be inversely proportional to the viscosity.⁵⁴ In solvents of lower viscosity the rate still increases with decreasing viscosity but becomes lower than k_{diff} (Figure 4).

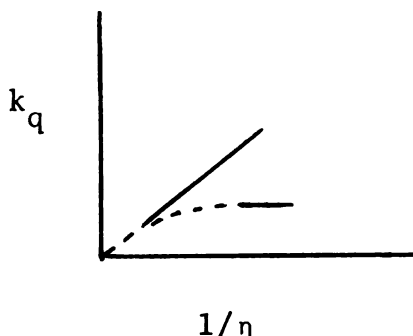
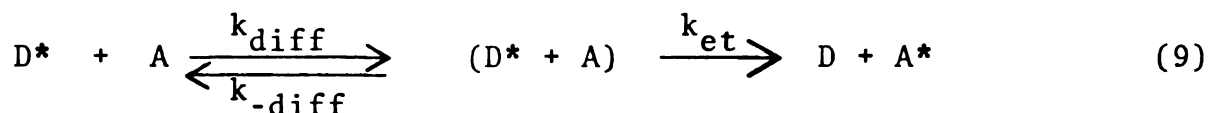


Figure 4. Dependence of k_q on low viscosity solvents.

Wagner proposed that in solvents of low viscosity diffusion apart competes with energy transfer (Equation 9).



Support for the idea that the energy transfer depends on a common process, i.e. the rate of diffusion together, comes from the observation that as long as the energy difference between a wide variety of donors and acceptors is 1 kcal exothermic, the rate for quenching in benzene is $5 \pm 1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.⁵⁴

3) Determination of Reactivity

Since photochemical studies are normally done under steady state conditions, the measureable quantities of a particular process are quantum yields for product formation or light emission. The quantum yields, with quencher present, for the type II process can be expressed as a series of probabilities (Equation 10).¹

$$\phi_{II} = \phi_{isc} \phi_{BR} \phi_p = \phi_{isc} [k_r / (k_r + k_d + k_q[Q])] [k_p / (k_p + k_{-r})] \quad (10)$$

ϕ_{isc} may be dropped from the expression since it is close to unity for alkyl phenyl ketones. The Stern Volmer expression (Equation 11) has been derived elsewhere.⁵⁷

ϕ_0 is the quantum yield for a process in the absence of

$$\phi_0/\phi = 1 + k_q\tau[Q] \quad (11)$$

quencher, ϕ is the quantum yield in the presence of quencher, $[Q]$ is the quencher concentration, and τ is the lifetime of the particular excited state being quenched. The Stern Volmer plot will be linear under various conditions.⁵⁸

4) Effect of Reversible Hydrogen Transfer

The expression $k_p/(k_{-r} + k_p)$ in Equation 10 is due to the probability of disproportionation of the biradical back to starting ketone. Wagner demonstrated that Lewis bases appreciably enhanced type II efficiency and attributed it to hydrogen bonding of the hydroxyl biradical intermediate. If it is found that the quantum yield becomes unity upon addition of increasing amounts of hydrogen bonding solvent, then it is possible to say that $k_r = 1/\tau_0$.

If however, the maximum quantum yield does not reach unity, or within experimental error, then $k_r \neq 1/\tau_0$. In this case, Equation 12 is appropriate.

$$\phi_{max} = k_r/(k_r + k_d) = k_r\tau \quad (12)$$

τ is obtained from a Stern Volmer plot and $\phi_{\max}$ is the maximum quantum yield in the hydrogen bonding solvent.

The value for radiationless decay, k_d , may then be computed from Equation 13.

$$k_d = 1/\tau - k_r \quad (13)$$

RESULTS

A. Absolute Type II Quantum Yields

Absolute quantum yields of substituted acetophenone formation were determined for 3130-Å irradiation of degassed solutions of the ketones listed in Table 1. The formation of substituted acetophenone relative to a known concentration of an internal standard was analyzed by vapor phase chromatography (VPC). Valerophenone actinometry was used with its type II quantum yield known to be .33 for a .1M solution in benzene.⁵⁹ The values for para- and meta-methyl valerophenone agree with results obtained earlier in this laboratory.⁴⁴ However, the values for meta and para-methylbutyrophenone are lower than those reported by Pitts.^{13,39} The values for 3,5- and 3,4-dimethyl substituted ketones have not been previously recorded.

B. Cyclobutanol Quantum Yields

The cyclobutanols that are referred to in this study were not isolated and directly identified. However, cyclobutanols are known to always accompany elimination.¹ The presumed cyclobutanols were formed in the expected

yields of 5 to 25%, and possessed appropriate VPC retention times.^{43,44} Two peaks attributable to the cis and trans isomers from the substituted valerophenones appeared on the VPC traces (Figure 14). Since the presumed cyclobutanols from the butyrophenones appeared under the tail of the parent ketones, the ketones had to be photolyzed to almost complete conversion to provide measureable ratios for quantum yield determinations. Data for cyclobutanol formation appears in Table 1.

C. Stern Volmer Quenching Slopes

The Stern Volmer quenching slopes were obtained by varying the amounts of quencher in succeeding solutions and plotting the ratio of quantum yield with no quencher over quantum yield with quencher against quencher concentrations. 2,5-Dimethyl-2,4-hexadiene was the quencher of choice for this study. Stern Volmer plots were linear for ϕ_0/ϕ values of 1 to 3, the region of study. Previous work has demonstrated the linearity of the plots for similar ketones out to large ϕ_0/ϕ values.⁴⁹ Experimental $k_q\tau$ values are found in Table 1 and the corresponding plots in Figures 6 through 10. The $k_q\tau$ value for para-methylvalerophenone was a repeat of earlier work and agrees with the previously determined value.⁵⁰ For a reason not discernable, the scattering of data points for the Stern Volmer plots of para-methylbutyrophenone was particularly large and therefore the plot in Figure 7

represents the average of three runs. The Stern Volmer plot for 3,4-dimethylbutyrophenone (Figure 6) contains the data points for two runs. The other $k_q\tau$ values were the result of one run plus a preliminary point used to estimate the desired concentration range. The $k_q\tau$'s represent the average of the individual points and the average deviation is given.

D. Solvent Studies

Maximum quantum yields were obtained for the ketones by gradually increasing the concentration of an added Lewis base in solutions of 0.1M ketone in benzene. With added t-butyl alcohol, the quantum yields for several ketones were found to decrease at higher concentrations, after having reached maximum values (Figures 11 and 12). Pyridine has then chosen for its increased basicity and lower polarity. However, in some cases the quantum yields also decreased at higher pyridine concentrations. This effect will be discussed later. The values given in Table II for $\phi_{\max}$ are the result of enough data points (either one or two runs) to yield a plot that either had a maximum or leveled off. The data are listed in Table II.

E. Dependence of Quantum Yields on Ketone Concentration

Figures 4 and 5 show the variation of type II quantum yields with changes in ketone concentration. Earlier work had shown that quantum yields normally rise with increasing

ketone concentration because of increasing solvent polarity.⁵⁰ A decrease could indicate either the presence of a quenching impurity in the ketone or quenching by ground state ketone.^{59,62} Aspects of this will be discussed later. The results are listed in the last section of the kinetic data.

F. Disappearance Quantum Yields

It was necessary to find out whether the ketone was decaying to some other product(s) and therefore lowering the $\phi_{\max}$ yield. This was accomplished by comparing the parent ketone to standard ratio before photolysis to the parent ketone plus the summation of type II and cyclobutanol formation after photolysis. The results are given in Table 1 as a percentage difference. It was assumed that olefin is formed in the same yield as acetophenone and that the VPC response of each cyclobutanol equalled that of its isomeric starting ketone.

G. UV Absorption of Methylated Butyrophenones

Table 3 lists the $\lambda_{\max}$ and corresponding molar extinction coefficients of the 1L_a band of methylated butyrophenones. The second column in Table 3 lists the difference, in kcal, of the $\lambda_{\max}$ relative to that of butyrophenone itself. The uv absorption curves are given in the last section.

Table 1. Photokinetic Parameters

Ketone	$k_q \tau \text{ M}^{-1} \text{ s}^a$	$1/\tau \times 10^7 \text{ s}^b$	$\phi_{II} \text{ }^c$	$\phi \text{ (cyc)}$	Excess Ketone ^{d,h} Disappearance
meta-methylbutyrophenone	1140 $\pm$ 100	4.4 $\pm$.4	.14 $\pm$.01 ^g	.012	0
meta-methylvalerophenone	128 $\pm$ 4 ^e	39.0 $\pm$ 1.0 ^e	.35 $\pm$.3	.049	7
para-methylbutyrophenone	3600 $\pm$ 400	1.4 $\pm$.1	.27 (.22) ^f	.019	0
para-methylvalerophenone	270 $\pm$ 6	18.5 $\pm$.3	.39 $\pm$.3	.075	0
3,5-dimethylbutyrophenone	3100 $\pm$ 260	1.6 $\pm$.1	.13 (.08) ^f	.008	13
3,5-dimethylvalerophenone	366 $\pm$ 10	13.8 $\pm$.4	.30 $\pm$.02	.038	0
3,4-dimethylbutyrophenone	6050 $\pm$ 300	.83 $\pm$.04	.13 $\pm$.01	.010	2
3,4-dimethylvalerophenone	1170 $\pm$ 50	4.3 $\pm$.20	.37 (.30) ^f	.050	0

^a $k_q \tau$ is the Stern-Volmer quenching slope;

^b $K_q = 5 \pm 1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$;

^c Values at .1 M ketone concentration;

^d Percent starting ketone not accounted for by type II and cyclobutanol formation in mass balance - before and after irradiation;

^e Taken from the Ph.D. Thesis of A. E. Kemppainen, Michigan State University;

^f Values not in parenthesis were extrapolated from Figures 4 and 5;

^g Error limits were taken as $\pm 8\%$;

^h Error limits were taken as ± 10 to 15% .

Table 2. Data for Solvent Studies^a

Ketone $\cdot 1M^a$	[ϕ_{II} in added t-Butyl Alcohol]									
	0	.05	1.0	1.5	2.0	2.5	3.0	4.0	5.0	
meta-methylvalerophenone	.35	.60	.62		.74		.735			.74
3,5-dimethylvalerophenone	.24	.40	.46		.55		.50			.41
3,4-dimethylvalerophenone	.30	.49	.59	.65	.65		.69			
3,4-dimethylbutyrophenone	.13	.33	.32	.40	.40	.39				
	[ϕ_{II} in added Pyridine]									
	0	.05	.1	.15	.20	.25	.30	.40	.45	.55
meta-methylbutyrophenone	.14	.32	.39	.41	.44	.46	.47	.55	.54	.54
para-methylbutyrophenone	.18	.32	.33	.43	.53	.51	.50	.49	.47	.43
3,5-dimethylbutyrophenone	.08			.28	.29	.29	.29	.28	.27	.26

^a in benzene.

Table 3. Substituent Effect on the $S_0 \rightarrow {}^1L_a$ Transitions of Acylbenzenes

Substituent	Butyrophenone ^a	
	λ_{max} , nm	$-\Delta v$, Kcal/mole
H	238 (14,000)	0
m-CH ₃	240 (11,000)	1.0
p-CH ₃	245 (18,000)	3.3
3,4-dimethyl	247 (15,000)	4.2
3,5-dimethyl	244 (11,400)	2.8

^ain heptane; molar extinction coefficients in parenthesis

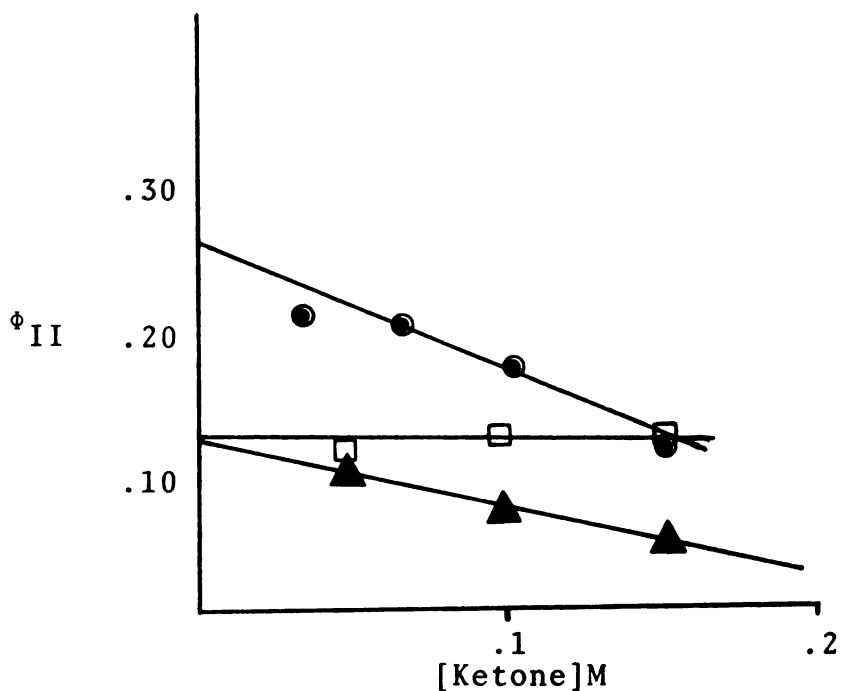


Figure 5. Relationship of type II quantum yield to ketone concentration ● p-methylbutyrophenone, □ 3,4-dimethylbutyrophenone, ▲ 3,5-dimethylbutyrophenone.

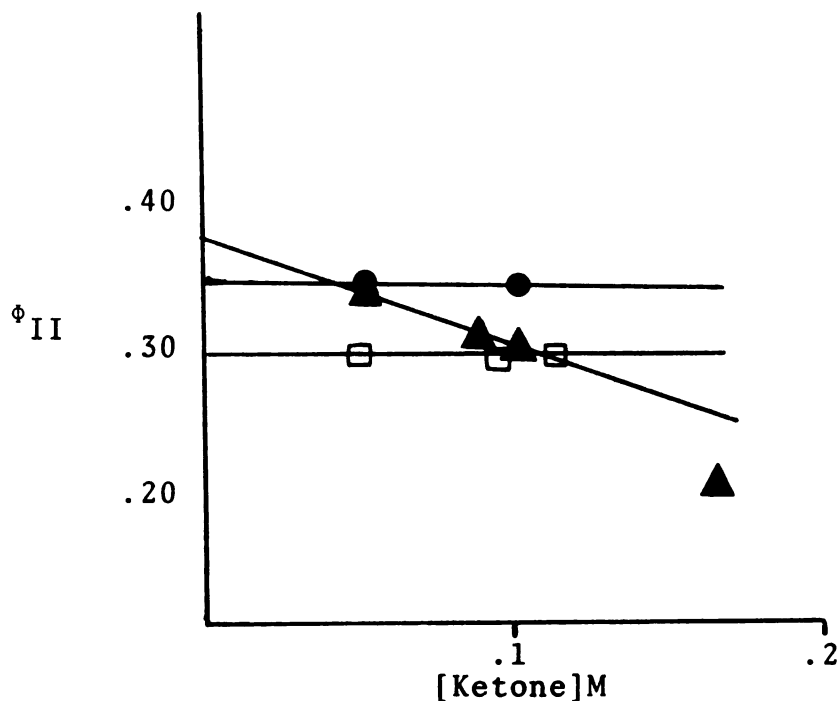


Figure 6. Relationship of type II quantum yield to ketone concentration; ● m-methylvalerophenone, □ 3,5-dimethylvalerophenone, ▲ 3,4-dimethylvalerophenone.

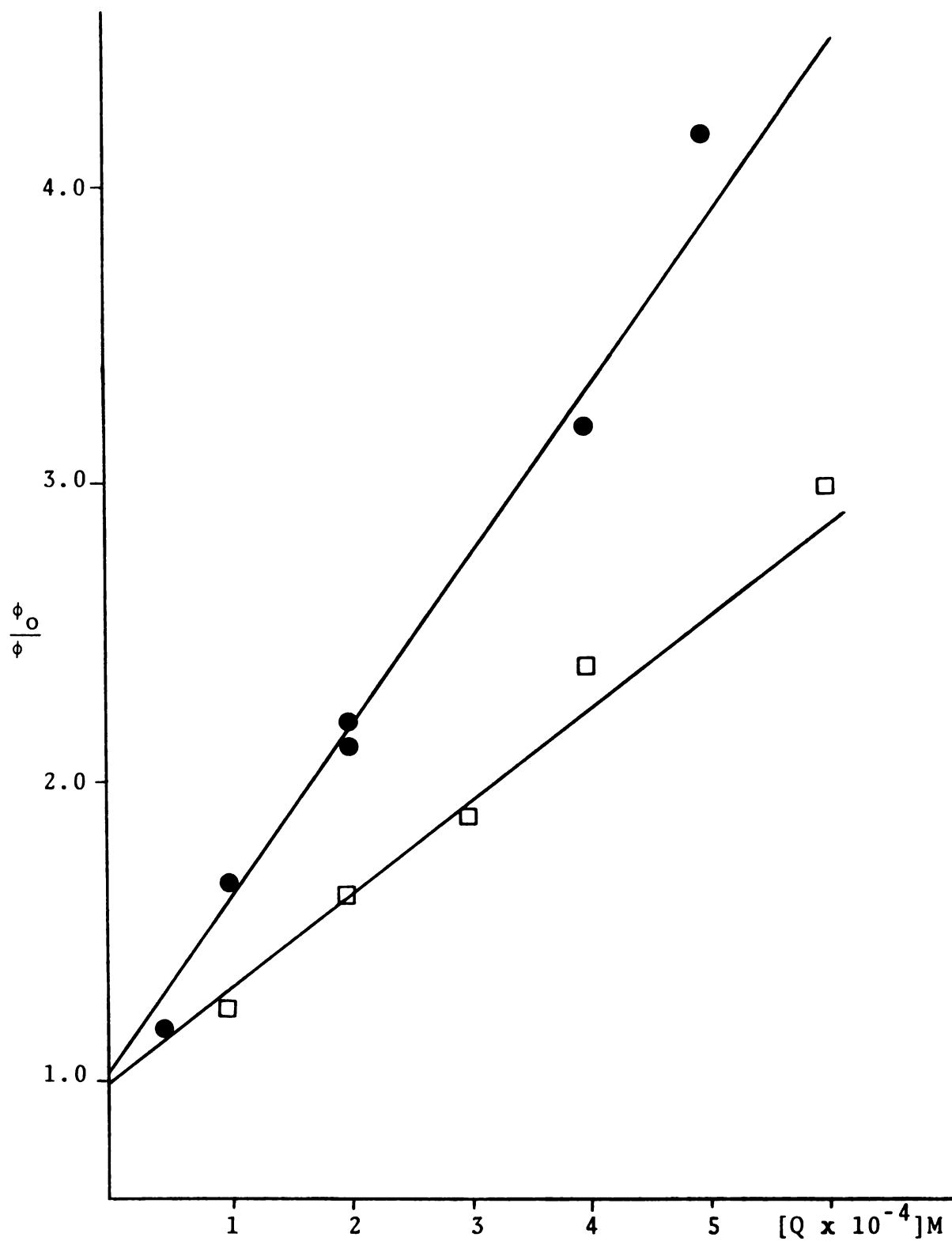


Figure 7. Stern Volmer quenching plots for ● 3,4-dimethylbutyrophenone, □ 3,5-dimethylbutyrophenone.

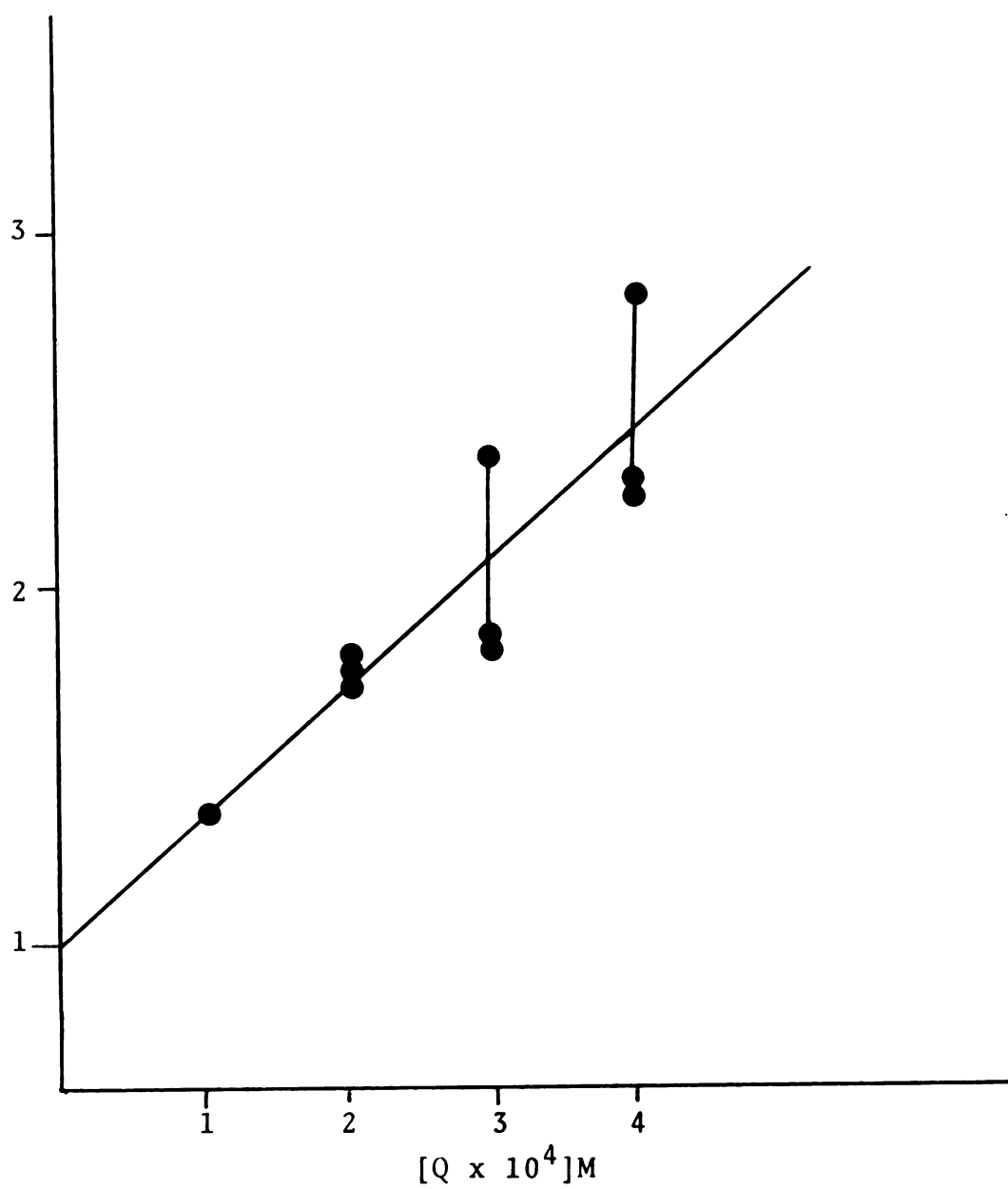


Figure 8. Stern Volmer quenching plot for p-methylbutyrophenone.

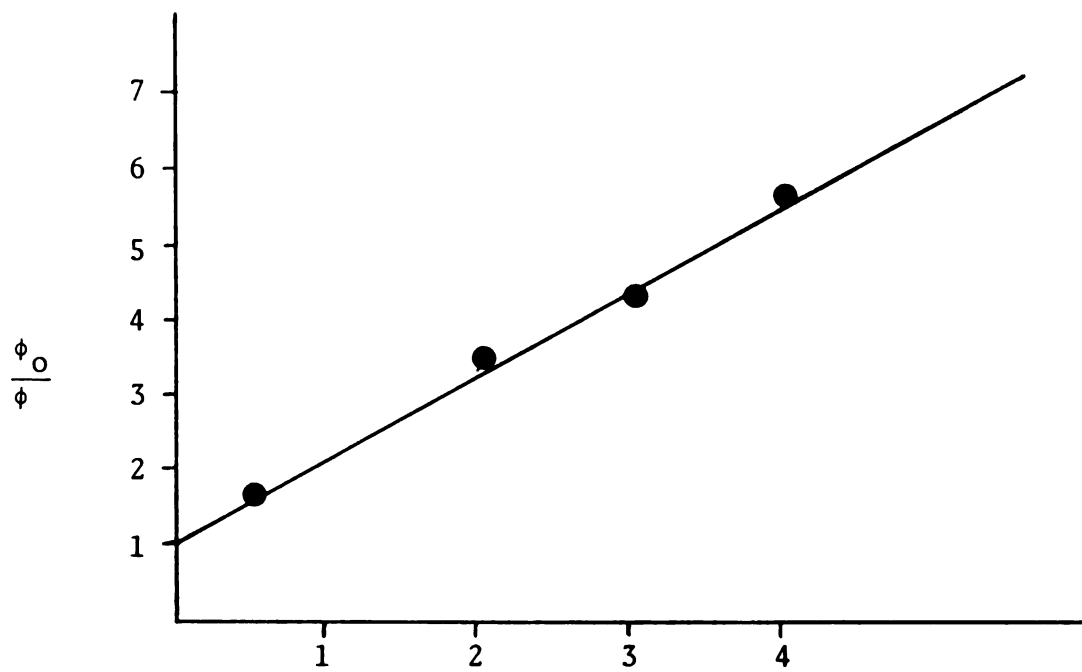


Figure 9. Stern Volmer quenching plot for 3,4-dimethylvalerophenone.

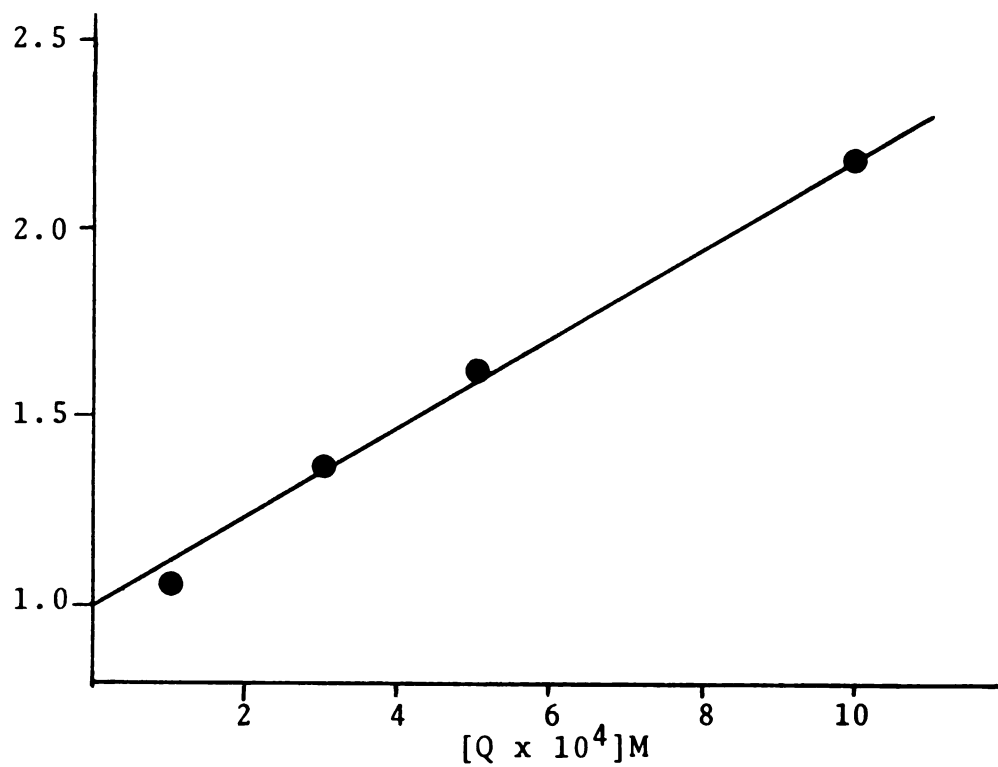


Figure 10. Stern Volmer quenching plot for meta-methylbutyrophenone.

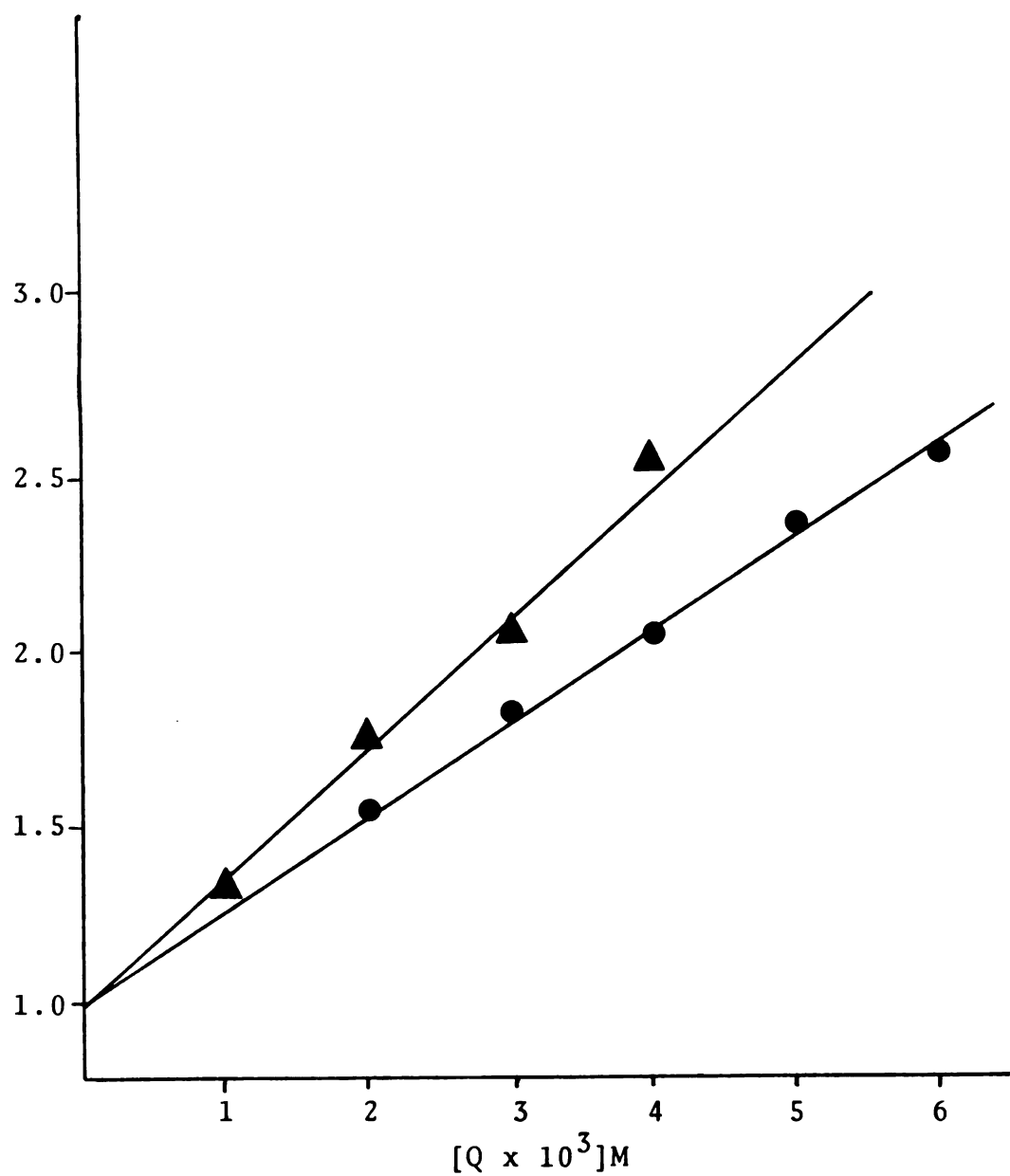


Figure 11. Stern Volmer quenching plots for
● para-methylvalerophenone,
▲ 3,5-dimethylvalerophenone.

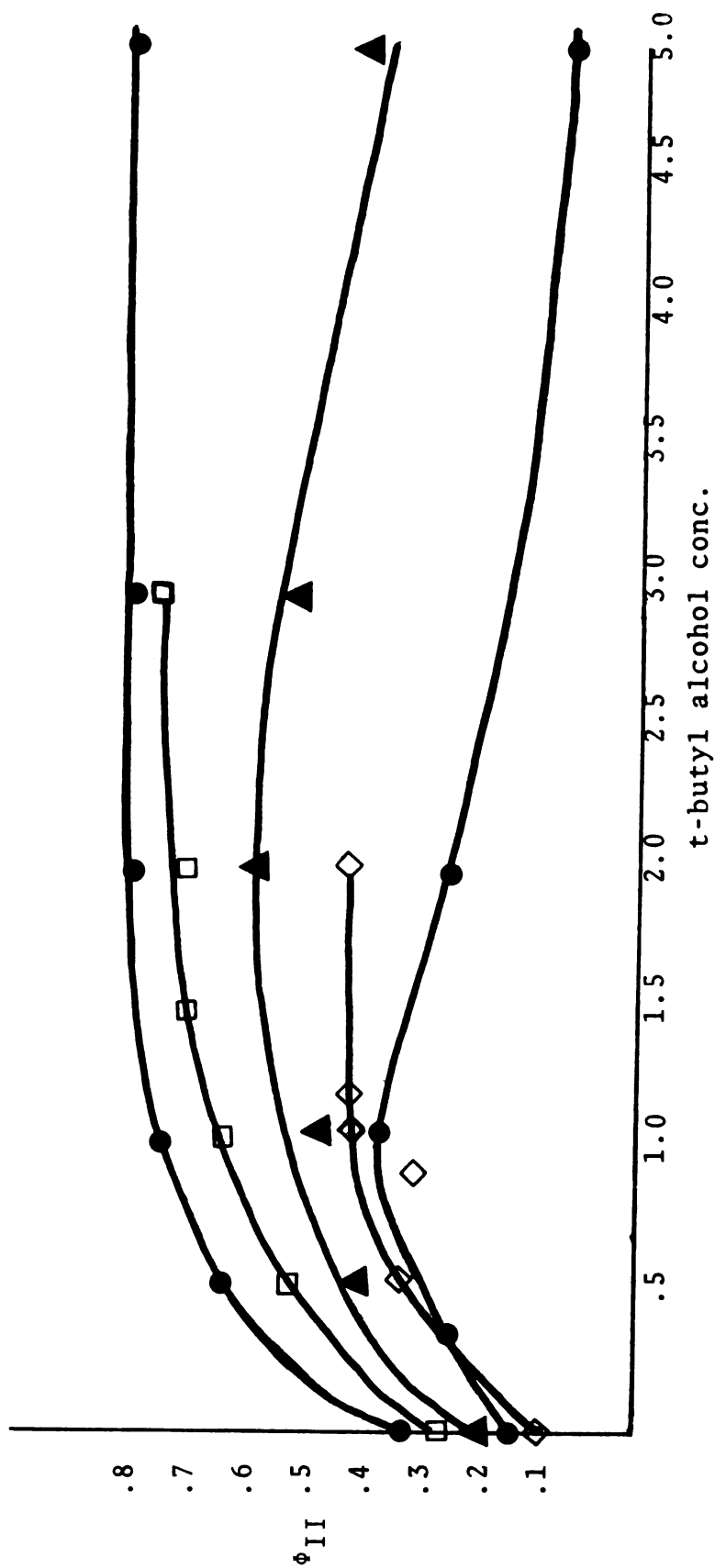


Figure 12. Relationship of type II quantum yield to added amounts of t-butyl alcohol in benzene. ● meta-methylvalerophenone, ▲ 3,5-dimethylvalerophenone, □ 3,4-dimethylvalerophenone, ◇ 3,4-dimethylbutyrophenone, Meta-methylbutyrophenone.

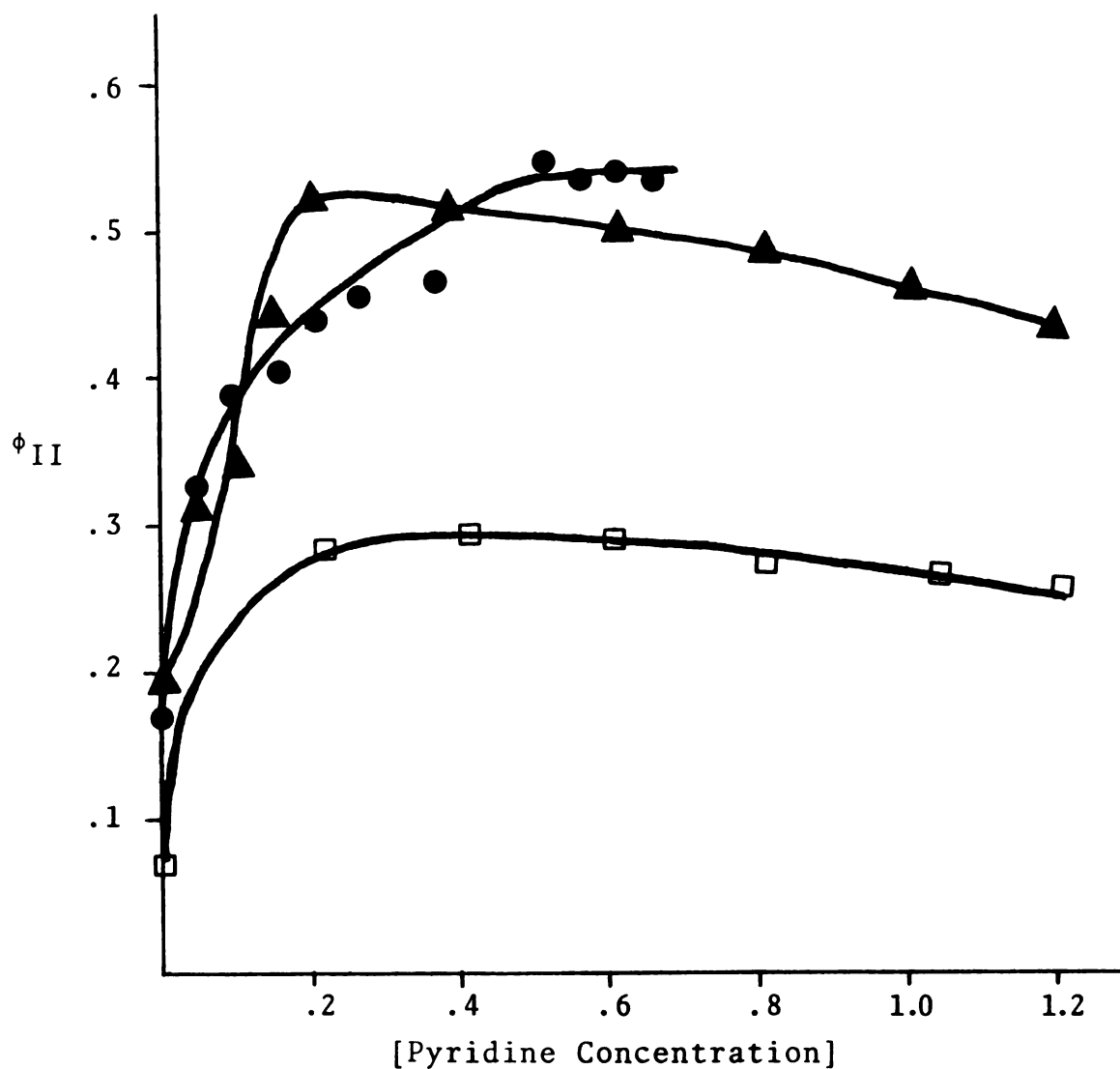


Figure 13. Effect of pyridine on type II reaction in benzene. ● meta-methylbutyrophenone, ▲ para-methylbutyrophenone, □ 3,5-dimethylbutyrophenone.

DISCUSSION

A. Effects of Methyl Substitution on Reactivities and Radiationless Decay of Triplet State

As previously discussed, the reactive state of the alkyl phenyl ketones is usually the triplet, due to the high efficiency of isc from the lowest $^1(n, \pi^*)$ state of the excited singlet to the nearby $^3(\pi, \pi^*)$ state of the triplet. In solution, the only competing modes of decay from the triplet will be hydrogen abstraction and radiationless decay. Wagner and Schott have shown that the hydrogen abstraction most likely originates from the upper $^3(n, \pi^*)$ state of ketones which possess lowest $^3(\pi, \pi^*)$ triplet states.⁵¹ The type II system was chosen for study because the effects of the substituents on the excited states may be readily measured through the change in the reactivity of the triplet towards hydrogen abstraction. If the reactivity is coming from an upper n, π triplet in equilibrium with a lower π, π triplet, a parallel effect should be observed between the reduction in reactivity and the increase in the separation of the excited triplet states. Since the rate of hydrogen abstraction is

independent of k_d , and if one can assume an insignificant change in k_q with substitution, then experimental k_r values will represent the change in reactivity of the triplets. The $1/\tau$ values from the Stern Volmer plots will give the sum of the rates of decay from the triplets. Equation 12 indicates that if we know the maximum total quantum yield for product formation then k_r and k_d values may be determined. To eliminate any inefficiency in product formation due to the reversal of the hydrogen abstraction process, a hydrogen bonding solvent was added. Figures 11 and 12 demonstrate that a maximum is reached in the ϕ_{II} value in the addition of the Lewis bases, t-butyl alcohol and pyridine. At this point, the value for the probability of the biradical going to product is presumably unity, and $\phi_{\max} = k_r \tau$. Ketones such as valerophenone and butyrophenone which have a $\phi_{\max}$ of unity must possess radiationless decay rates which cannot compete with the rate for hydrogen abstraction. Therefore the $1/\tau$ obtained from the Stern Volmer slope will equal k_r . The $\phi_{\max}$ values from Tables 4 and 5, and Figures 11 and 12, indicate that all of the ketones in this study possess k_d rates which do indeed compete with hydrogen abstraction and the extent of this competition varies. The decrease in $\phi_{II\max}$ at high alcohol concentration is probably due to the increasing competitiveness of the radiationless decay via an increase in the separation of the triplet states with the increasing polarity of the solvent.⁶³ The decrease when pyridine was

Table 4. Substituent Effects on Triplet State Reactivities of Butyrophenone

Ketone	$\phi_{\max}^a$	$k_r \times 10^6^b$	$k_d \times 10^6^c$	relative k_r
butyrophenone	1.0 ^d	7.6 ^d	-	1.0
<u>meta</u> -methyl	.60 $\pm$.085	2.7 $\pm$.4	1.3	.35 $\pm$.03
<u>para</u> -methyl	.69 ^e	.97 $\pm$.15	.45	.14 $\pm$.02
3,5-dimethyl	.32 $\pm$.02	.51 $\pm$.05	1.1	.067 $\pm$.009
3,4-dimethyl	.43 $\pm$.030	.35 $\pm$.003	.48	.045 $\pm$.005
p-methoxy	.04 ^f	.06	1.5	.008

^aIncludes $\phi_{II_{\max}}$ plus $\phi(\text{cyc})_{\max}$, all at .1M ketone;

^bobtained from equation 12;

^cobtained from equation 13;

^dvalue taken from A. E. Kemppainen's Ph.D. Thesis, Michigan State University;

^eThis value is an 18% increase from experiment value due to increase in ϕ_{II} in later runs after purification;

^fObtained from Ph.D. Thesis of H. N. Schott, Michigan State University.

Table 5. Substituent Effects on Triplet State Reactivities of Valerophenone

Ketone	$\phi_{\max}^a$	$k_r \times 10^6^b$	$k_d \times 10^6^c$	relative k_r
valerophenone	1.0 ^d	122 ^d	-	1.0
<u>meta</u> -methyl	.84 ± .07	32 ± .5	7	.25
<u>para</u> -methyl	1.0 ^d	18.5 ± 1.4	~ .45	.15 ± .01
3,5-dimethyl	.65 ± .05	9.0 ± .9	4.7	.074 ± .007
3,4-dimethyl	.80 ± .06	3.4 ± .4	0.9	.028 ± .003
p-methoxy	.26 ^e	.56	1.6	.005

^aIncludes $II_{\max}$ plus $(cyc)_{\max}$, all at .1M ketone;

^bobtained from equation 12;

^cobtained from equation 13;

^dvalue taken from A. E. Kemppainen's Ph.D. Thesis, Michigan State University;

^eObtained from Ph.D. Thesis of H. N. Schott, Michigan State University.

used might be attributed to charge transfer quenching, if the ionization potential of pyridine is low enough.⁶⁴

Any discussion of the effect of substituents on reactivity would not be complete without the presentation of spectral data, i.e., how the substituents affect the relative energies of the triplet states. The data from Table 3 indicate that the 1L_a state is stabilized to a greater extent by a methyl group in the para position. Progressive methylation also lowers the $^3(\pi, \pi^*)$ energy, as demonstrated by Yang's phosphorescent studies.²² His work points to a destabilizing effect on both the $^1(n, \pi^*)$ and $^3(n, \pi)$ from methylation in the para position, whereas the meta-methyls show little effect on the (n, π^*) states. The result of this is a larger $(n, \pi^*) - (\pi, \pi^*)$ triplet separation for the 3,4-dimethyl ketone relative to the same separation in the para and 3,5-dimethyl isomers (Table 6). By analogy, the meta-methyl ketone should have a smaller triplet separation than the para. Although the spectroscopically

Table 6. Phosphorescent Excitation 0-0 Bands of Several Methylated Acetophenones^a

Ketone	$\pi - \pi^*$ -nm-	n, π^*	$^3(n, \pi^*) - ^3(\pi, \pi^*)$ kcal
p-Methylacetophenone	386	368	3.7
m-Methylacetophenone	$\sim 384^b$	$\sim 372^b$	2.4^b
3,4-Dimethylacetophenone	392	367	5.0
3,5-Dimethylacetophenone	390	371	3.7

^aReference 22

^bextrapolated values

determined triplet energies are higher in a polar glass than in solution, the relative energies should be very nearly the same. In a non polar solution, the energies of the meta- and para-methyl (n, π^*) and (π, π^*) triplets must be very close and the nature of the lowest triplet is not agreed upon.^{47,53,65}

Data for methoxy and methyl ketones has shown that the meta isomer has a shorter lifetime and smaller quantum yield than the para isomer.⁵⁰ The ϕ_{II} and $1/\tau$ values in Table 1 agree with these results. k_d values for the 3,5-dimethylketones are observed to be slightly lower than those for the meta-methyl ketones. The origin of this effect is not clear. The radiationless decay rates of the para-methyl ketones and 3,4-dimethyl ketones lie within experimental error of coinciding. There is a large drop in the k_d rate upon the placement of a para group on the meta-methyl ketone. It follows that the placement of a methyl group at the para position has the predominate effect on k_d . Yang found that methylated acetophenones are less reactive than acetophenone, which has a lowest (n, π^*) triplet, and also exhibit slower nonradiationless decay processes.²² Here again the para and 3,4-dimethylketones had similar k_d rates, with the rate of the 3,5-dimethylketone being slightly faster. Any conclusive statement about the rates of radiationless decay in the present study is prevented by the scatter of the rates of decay data. The general conclusion is that the meta isomers have the

higher k_d values. The data seem to indicate that the k_d value is larger when the lowest state is more (n, π^*) like. However, the larger k_d value may also be the consequence of quenching by the ground state ketone. Such quenching has been demonstrated with meta- and para-methoxy acetophenones.⁵⁹ This data must be cautiously viewed since the three ketones had similar triplet energies. This type of decay has also been demonstrated for Michler's ketone and Michler's thione.^{60,61} The concentration studies in Figures 4 and 5 indicate no general self quenching effect in either series of ketones and therefore the slopes most likely represent the presence of a quenching impurity, which is also the probable origin of the scatter in the k_d data. Since meta-methoxyvalerophenone displayed such a large value for radiationless decay, any self quenching mechanism would also have to show up in a concentration study. However, a slight increase in ϕ_{II} with increasing ketone concentration actually occurs, making the self quenching proposal less likely. The rate of self quenching that was proposed for the methoxyketones ($8 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$) would surely be competitive here.⁵⁹

The values of the k_r from Tables 4 and 5 indicate that the meta isomer is more reactive in hydrogen abstractions than the para. This is reasonable considering the earlier statement that the meta and para-methyl both slightly stabilize the (π, π^*) levels, the para more than the

meta, whereas the meta methyl has a small effect on the (n, π^*) and the para significantly destabilizes it. This also is true in the case of the 3,4 and 3,5-dimethylketones. The meta substitution might also be less effective in decreasing the electrophilicity of the reactive triplet.

The relative k_r values demonstrate a progressive decrease in reactivity for the series of methylated butyro- and valerophenones. The last entry in Tables 4 and 5 show that the effect of a single p-methoxy group is much larger than that of dimethyl substitution.

B. Additivity of Substituents Effects

A systematic investigation of the additivity of substituents on excited state reactivity has not, to the author's knowledge, yet been reported. If the average of the relative reactivities for both series of ketones is compiled (Table 7) the results qualitatively indicate the

Table 7. Additivity of Substituent Effects on Reactivities

<u>Substituent</u>	<u>Average Relative k_r</u>	<u>Predicted Additivity</u>
H	1	-
<u>m</u> -Methyl	.30 $\pm$.03	-
<u>p</u> -Methyl	.14 $\pm$.02	-
3,5-dimethyl	.070 $\pm$.009	.090 ^a
3,4-dimethyl	.037 $\pm$.005	.042 ^b

^a 0.3 x 0.3; ^b 0.3 x 0.14

occurrence of such an additivity pattern in this system. The correlation is admittedly rough, but this is very probably the result of accumulative experimental error. A reasonable correlation is observed in Yang's data (Table 6) on the effects of methylation upon the phosphorescence emission from acetophenones.²² The last column in the Table 6 lists the splitting in the triplet's energies, which is at least proportional to what it should be in solution. It would be informative to also have the experimental values for the meta isomer. The values for the 3,4 and 3,5-dimethyl ketones are what would be expected if they were to be correlated to the reactivities. This is also what would be expected if the reaction was originating from a thermally equilibrated upper (n, π^*) triplet. It would be helpful to be able to get phosphorescent data in a non polar glass. Although the values listed in Table 8 cannot be compared to the reactivities, they do indicate that the effects on the lowest $^3(\pi, \pi^*)$ state seem to be additive. It would now be interesting to see if the 3,4,5-trimethylketone and also different groups would display parallel additive behavior.

Table 8. Additivity of Substituent Effects in Spectroscopic Data.^a

<u>Substituent</u>	<u>Phosphorescence Emission</u>	<u>$\Delta\nu$ in kcal</u>	<u>Expected Correlation</u>
H	386	0	
P	392	1.0	
M	394	1.4	
3,4-	400	2.4	2.4 ^b
3,5- ^e	402	2.9	2.8 ^c
3,4,5-	406	3.6	3.8 ^d

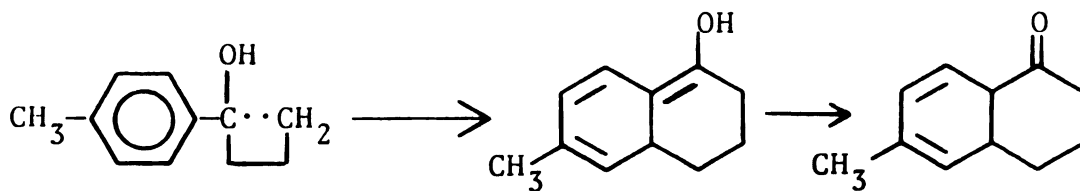
^aFrom reference 23; ^b1.0 + 1.4; ^c1.4 + 1.4; ^d1.0 + 1.4 + 1.4.

^eFrom reference 22.

C. The High Rate of Radiationless Decay of Valerophenones

Examination of the k_d values indicate an exceptionally high k_d value for both meta-methyl and 3,5-dimethyl-valerophenones. Reasonable answers to the high rate would be an undetected or reversibly-formed product, or more likely, a quenching impurity. The term reversible is used because of the absence of any extraneous VPC product peaks for these compounds.

Peaks of unknown origin in a one or two percent yield were evident in the VPC traces in the photolysis of the butyrophenones. Similar products were found by Pitts in his work with butyrophenones and were attributed to ring addition by the biradical (Equation 14).¹³



(14)

D. Summation

1) The reactivity of triplet phenyl ketones is reduced to a greater extent by a methyl group in the para position than by a meta-methyl. This effect is what would be expected from the differences in the triplet splitting.

2) The rate of radiationless decay was found to be larger for the ketones with a single meta methyl group. The reason for the increase is still not clear.

3) Of the greatest significance, a qualitative additivity correlation was noted for the effect of methylation on the reactivities of the triplet. A parallel was noted with the effects of methylation on the $n, \pi^* - \pi, \pi^*$ triplet splitting determined by phosphorescent excitation methods.

E. Further Studies

1) Further work is needed to discover the reason for the high k_d values in the valerophenones.

2) The 3,4,5-trimethyl ketones need to be studied to determine if the observed additivity is maintained by the third group.

3) Studies on varying the types of substituents need to be completed to determine if the additivity correlation in the excited state may be extended.

EXPERIMENTAL

A. Chemical

1) Dependence on Purity

For a ketone such as 3,4-dimethylbutyrophenone, which has a solution lifetime of 1.2×10^{-6} sec, a ketone impurity of .01% could result in a significant amount of triplet quenching. This would have led to erroneous results for lifetimes and k_T values. It was thus imperative to make certain that the ketones used were checked (by VPC) very carefully before using. In all cases, the ketones used were run through a short alumina column and recrystallized several times from heptane, pentane, and mixtures of ethanal and heptane. They were then distilled as carefully as possible on a Nester Faust model NFT 61 Spinning Band Distillation unit with a maximum theoretical plate limit of 250. The purification cycle was repeated until the ketones were considered suitably pure by VPC analysis. The qualification for purity was no observable impurity greater than .005%.

2) Preparation of Ketones

a) Method I - The ketone was prepared by using a dropwise addition of a relative mole ratio of .12 moles

of the Grignard of a n-bromo alkane to .1 mole of the respective methylated benzonitrile in 200 ml of ether. The resulting imine salt was carefully stirred into 300 gm of ice containing 30 ml of concentrated HCl. The aqueous layer was extracted with ether or benzene to take out any soluble impurities, such as the starting nitrile. The organic salt was then hydrolyzed to the desired ketone through a heating period of one half to one hour. The ketone was then extracted and the organic layer dried over anhydrous magnesium sulfate. The solvent was removed and the ketone purified by the given procedure.

b) Method II

The ketone was prepared from the addition of the correct alkyl lithium compound to the lithium salt of the methylated benzoic acid on a .1M scale. The lithium acid salt was prepared from the reaction of the methylated benzoic acid and lithium hydride in dry T.H.F. The white salt was formed after a few hours of reflux. The alkyl-lithium reagent was prepared from the corresponding alkyl bromide and lithium suspension with the reaction temperature kept below -20°C . The alkyl lithium reagent was then added slowly to the acid salt and refluxed to complete the reaction and to break up any excess lithium reagent. The entire procedure up to this point was completed under an atmosphere of inert gas. The dilithium salt was then hydrolyzed to the ketone in a well stirred and cooled

aqueous acid solution. The solution must be well stirred to insure the fast hydrolysis of any remaining lithium reagent. The aqueous layer was then extracted and the organic layer dried. After evaporation of the solvent, the resulting ketone was purified.

c) Method II-a

The same procedure was followed as in Method II except that the alkyl lithium reagent was added to the methylated benzoic acid. This procedure resulted in a large amount of alcohol by-product and therefore was used only once.

3) Photolysis Products

a) Acetophenone - (M.C.B.) distilled at 55° @ 3MM.

b) Meta-Methylacetophenone - (Aldrich) used without distilling.

c) Paramethylacetophenone - prepared by Method I from acetyl bromide (Aldrich) and para-cyanotoluene (Eastman Organic) b.p. 47° @ 1.5MM.

d) 3,4-Dimethylacetophenone (Eastman Organic) b.p. 78° @ 1.5MM.

4) Solvents

a) Benzene - Both Fisher Scientific Co. 99 mole % thiophene free benzene and Mallinckrodt Nanograde benzene were purified by stirring with concentrated sulfuric acid. This was usually performed in gallon quantities. The acid was changed every day until it remained colorless. The

Table 9. Physical Data for Synthesized Ketones

Formula and Molecular Weight	Physical Properties and Spectral Data	Method of Preparation and Supplier
<u>Para-methylbutyrophenone</u> 162.22 $C_{11}H_{14}O$	b.p. 72°C @ 1.0 MM; Mass spec peaks of m/e at 162, 91, 119; Nmr chemical shifts are: triplet (1.0 σ), sextet (1.75 σ), singlet (2.40 σ), triplet (1.83 σ), aromatic (7.15, 7.3, 6.8, 7.92 σ); $\lambda_{max_{245}}$ ($\epsilon=18,000$), $\epsilon_{310}=55$	Method I n-propylbromide - Aldrich para-methylbenzonitrile - Eastman Organic
<u>Meta-methylbutyrophenone</u> 162.22 $C_{11}H_{14}O$	b.p. 92°C @ 2.9 MM; Mass spec peaks of m/e 162, 91, 119; Nmr chemical shifts are: triplet (.98 σ), sextet (1.73 σ), singlet (2.40 σ), triplet (2.82 σ), aromatic (7.25, 7.35, 7.75 σ); $\lambda_{max_{240}}$ ($\epsilon=10,900$), $\epsilon_{313}=48$	Method I n-propylbromide - Aldrich Meta-methylbenzonitrile - Eastman Organic
<u>3,4-dimethylbutyrophenone</u> 176.26 $C_{12}H_{16}O$	b.p. 105°C @ 2.3 MM; Mass spec peaks of m/e 176, 105, 133; Nmr chemical shifts are: triplet (1.02 σ), sextet 1.85 σ), singlet (2.35 σ), triplet (2.85 σ), aromatic (7.1, 7.25, 7.6, 7.73 σ); $\lambda_{max_{247}}$ ($\epsilon=15,000$), $\epsilon_{313}=56$	Method I n-propylbromide - Aldrich 3,4-dimethylbenzonitrile - Aldrich Method II 3,4-dimethylbenzoic acid - Aldrich
<u>3,5-dimethylbutyrophenone</u> 176.26 $C_{12}H_{16}O$	b.p. 98°C @ 2.4 MM; Mass spec peaks at m/e 176, 105, 133; Nmr chemical shifts are triplet (.98 σ), sextet (1.70 σ), singlet (2.35 σ), triplet (2.85 σ), aromatic (7.15, 7.55 σ); $\lambda_{max_{244}}$ ($\epsilon=11,400$), $\lambda_{313}=62$	Method II n-propylbromide - Aldrich 3,4-dimethylbenzoic acid - Aldrich

Table 9. (Continued)

Formula and Molecular Weight	Physical Properties and Spectral Data	Method of Preparation and Supplier
<u>Para-methylvalerophenone</u> 176.22 $C_{12}H_{16}O$	Nmr chemical shifts are: triplet (.90 σ), multiplet (1.52 σ), singlet (2.35 σ), triplet (2.8 σ), aromatic (7.1, 7.25, 7.75, 7.9 σ); $\lambda_{max}^{245} (\epsilon=15,300)$, ϵ_{313}^{56}	Method I n-butylbromide - Matheson Coleman and Bell <u>para</u> -cyanotoluene - Aldrich
<u>Meta-methylvalerophenone</u> 176.22 $C_{12}H_{16}O$	b.p. 81° @ 2 MM; Nmr chemical shifts are: triplet (.98 σ), multiplet (1.55 σ), singlet (2.4 σ), triplet (2.87 σ), aromatic (2.70, 7.37, 7.75 σ); $\lambda_{max}^{240} (\epsilon=11,600)$, ϵ_{313}^{46}	Method I n-butyl bromide - Matheson Coleman and Bell <u>Meta</u> -benzonitrile - Aldrich
<u>3,4-Dimethylvalerophenone</u> 190.24 $C_{13}H_{18}O$	b.p. 110°C @ 1.0 MM; Mass spec peaks at m/e 190, 133, 105; Nmr chemical shifts are: triplet (.98 σ), multiplet (1.65 σ), singlet (2.35 σ), triplet (2.95 σ), aromatic (7.2, 7.34, 7.73, 7.85 σ); $\lambda_{max}^{247} (\epsilon=14,200)$, ϵ_{313}^{59}	Method II and I n-butylbromide - Matheson Coleman and Bell 3,4-dimethylbenzoic acid - Aldrich
<u>3,5-Dimethylvalerophenone</u> 190.24 $C_{13}H_{18}O$	b.p. 106°C @ 1.2 MM; Mass spec peaks at m/e 190, 133, 105; Nmr chemical shifts are triplet (.94 σ), multiplet (1.6 σ), singlet (2.45 σ), triplet (2.93 σ), aromatic (7.2, 7.65 σ)	Method II n-butyl
<u>Valerophenone</u> 162.22 $C_{11}H_{14}O$	b.p. 97°C @ 2.0 MM	Prepared by R. Zepp - Method I

benzene was then washed with a NaHCO_3 solution followed by a saturated NaCl solution. After being dried with anhydrous magnesium sulfate, the benzene was distilled at atmospheric pressure from 100 to 200 grams of phosphorous pentoxide through a 49 cm. glass helix packed column. A high reflux ratio to head takeoff was maintained. A forecut and endcut of 10 to 15% was not used.

b) t-Butyl alcohol - The t-butyl alcohol (Fisher Scientific Company) was refluxed and distilled from freshly cut sodium after one recrystallization from itself. It was pure enough to crystallize at room temperature.

c) Heptane - The heptane (Matheson Coleman and Bell) used was purified in a manner analogous to benzene.

d) Pentane - The pentane (Matheson Coleman and Bell and J. T. Baker) was purified in a manner analogous to benzene.

e) Pyridine - The pyridine (Mallinckrodt Chemical and Fischer Scientific Company) was distilled from barium oxide at atmospheric pressure.

f) Ethanol - 95% Ethanol (Supplier unknown) was refluxed and distilled from magnesium at atmospheric pressure.

5) Internal Standards

a) Tetradecane - Tetradecane (Columbia Organic Chemicals) was purified in a manner analogous to benzene and was distilled at reduced pressure. It was purified by Professor P. J. Wagner.

b) Pentadecane - Pentadecane (Columbia Organic Chemicals) was purified in a mannor analogous to benzene b.p. 92°C @ 1MM.

c) Hexadecane - Hexadecane (Aldrich Chemicals) was purified in a mannor analogous to benzene. b.p. 108°C @ 1.1MM.

6) Quenchers

a) cis-1,3-Pentadiene (piperylene) - Piperylene (Chemical Samples Company) was used as received. Analysis (V.P.C.) showed it to contain only 0.4% of the trans isomer.

b) 2,5-Dimethyl-2,4-hexadiene - 2,5-Dimethyl-2,4-hexadiene (Chemical Samples Company) was purified by sublimation at atmospheric pressure at -10°C.

B. Methods of Analysis

1) Preparing Ketones for Photolysis

a) Making Solutions - All solutions were made up using Class A volumetric glassware and an analytical balance sensitive to .0001 gm, at room temperature. A stock solution of ketone and standard was made and the required amount pipetted into individual flasks. For a quenching run, a stock quencher solution was prepared and the required amount then pipetted into the same flasks. For a solvent study, the required amount of Lewis base was weighed, in the case of pyridine, or pipetted from a

stock solution, in the case of t-butyl alcohol, into the individual flasks. The flasks were then filled to the mark with benzene and mixed well. Two 2.8 ml samples were then injected into pyrex photolysis tubes with a 5 ml hypodermic syringe. The tubes had been previously prepared by selecting cleaned pyrex 100 x 13 MM culture tubes, which met a set standard of width and lip deformation, and drawing out the heated tubes to give them a cappillary neck about 2 cm from the open end of the tube.

b) Degassing - The tubes were then attached to a vacuum line using no. 0,0 one hole rubber stoppers on individual stopcocks. The tubes were slowly frozen, emmersed into liquid nitrogen, and pumped to a vacuum of 10^{-3} to 10^{-4} MM. The stopcocks were then closed and the tubes allowed to thaw. The process was repeated five times and on the last cycle the tube was sealed off at the cappillary.

2) Photolysis

The tubes were then placed in a "merry-go-round" apparatus which was designed to ensure that each tube received an equivalent amount of light and was kept at the same temperature.⁶⁶ A 450 watt medium pressure mercury lamp was inserted into a water cooled quartz jacketed immersion well. The well was placed into a cyclindrical vycor jar allowing a 1 cm path through a .002 M potassium chromate 1% potassium carbonate filter

solution which isolated 3130 Å radiation.⁶⁶ The samples were photolyzed till a 4 to 10% conversion to product occurred. All quenching runs and solvent studies contained .1M ketone. Valerophenone actinometer tubes were sometimes irradiated to 10% conversion. Earlier work showed that the quantum yield was not affected.⁴⁴

3) Analysis of Photolyzed Solutions

The analysis for product formation were all completed through the use of vapor phase chromatography (VPC). The work was generally completed on two similar Varian 1200 VPC's equipped with flame ionization detectors and a Leeds and Northrup Speedomax W recorder. Approximately one quarter of the work was analyzed using a model 224 disc integrator, and the rest by an Infotronics Model CRS-208 Automatic Digital Integrator. An Aerograph HyFi Model 600D VPC fitted with a 25' x 1/8" aluminum column containing 25% 1,2,3-tris(2-cyanoethoxy)propane (β,β,β) on 60/80 mesh Chromosorb P was used in the analysis of a few piperylene actinometers. All the gas chromatographs had on column injection and used nitrogen as a carrier gas. The gas flows for compressed air and hydrogen were set to maximize the sensitivity of the detector. The nitrogen flow rate was kept between 15 and 20 ml/minute. The following columns were used in the analyses.

COLUMN 1 9' x 1/8" aluminum filled with 5% QF-1,
1.2% Carbowax 20M on DMCS treated
60/80 mesh A. W. chromosorb G.

COLUMN 2 6' x 1/8" aluminum filled with 4% QF-1
1.2% Carbowax 20M on 60/80 chromosorb G.

COLUMN 3 11' x 1/8" aluminum filled with 4% QF-1
1% Carbowax 20M on 80/100 DMCS
A. W. chromosorb G.

COLUMN 4 8 2/3' x 1/8" aluminum filled with 4% QF-1,
1% Carbowax 20M on 60/80 chromosorb G.

4) Product Identification

The methylated acetophenone products of the photolyses were identified by the retention time of the known compound. The peaks which appeared in the VPC trace after photolysis near the parent ketone was presumed to be the cyclobutanol. Separation and identification of cyclobutanol products has been shown, therefore it was felt that further identification was not necessary.^{67,68} Small peaks which appeared near the acetophenone with three of the ketones were not identified. Figure 14 is a typical VPC trace.

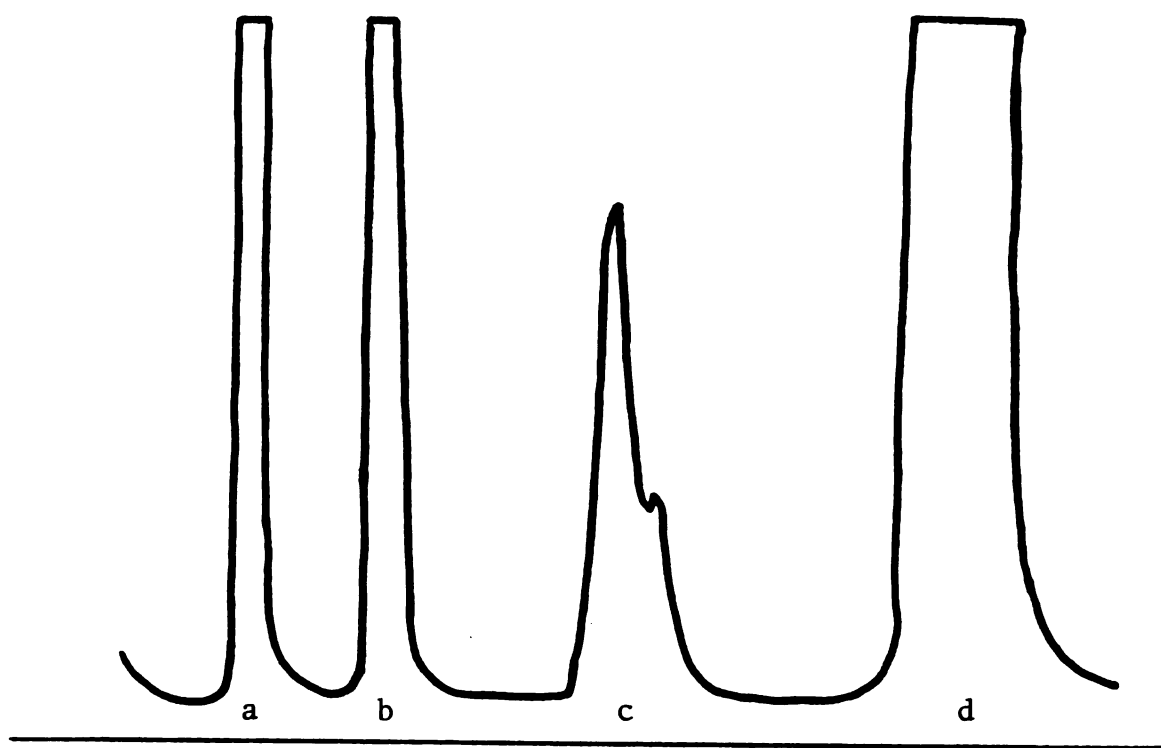


Figure 14. VPC trace of 3,4-dimethylvalerophenone
a) C_{16} b) 3,4-dimethylacetophenone
c) trans and cis cyclobutanols
d) parent ketone; integration was
accomplished using the automatic
integrator

5) Standardization Factors

To eliminate the error introduced by VPC injection technique, an internal standard was placed into the solution to be photolyzed. The VPC area for the photoproduct (PP) may then be compared to the area of the internal standard (IS). However, a standardizing factor (SF) needed to be introduced to account for the differences in molar response ratios, which Equation 15 depicts.

$$[PP] = SF[IS](PP)/(IS) \quad (15)$$

In this expression, brackets indicate concentration and parenthesis indicate VPC areas. The S.F value was determined by weighing out exact amounts of standard and photoproduct and determining the VPC response ratio (Equation 16).

$$SF = [PP]/[IS] \times (IS)/(PP) \quad (16)$$

The value of (IS)/(PP) was the average of six VPC injections.

6) Actinometry

The amount of light impinging upon the solutions during photolysis was usually determined by valerophenone actinometry. Actinometer tubes contained .1M valerophenone and ~.003 M tetradecane in benzene. The concentration of ketone used in all photolyses was large enough to absorb >99.9% of the incident light. For several runs, a .1M

solution of acetophenone and a varying concentration of piperylene in benzene was used as the actinometer. The kinetics of the expression used are reported elsewhere Equation 17.⁶⁹

$$[\text{pip}^A]^3 = [\text{cis-pip}]_0 \ln[(.555)/(.555 - \% \text{trans})] \quad (17)$$

The analyses were performed on the Aerograph HyFi Model 600 g.c. containing the β, β, β column. For an unidentified reason the light output was found to be higher using the piperylene actinometry. For the sake of consistency, all values are reported relative to those of valerophenone.

7) Ketone Disappearance and Cyclobutanol Yields.

The total quantum yield is determined by the sum of the acetophenone product and cyclobutanol formation, therefore the cyclobutanol VPC area must be standardized. The procedure to procure the SF factor for the cyclobutanols entailed the preparation of a solution of carefully weighed samples of the acetophenone and parent ketone and obtaining the VPC area response factor. The same procedure was used in obtaining the said SF value as for the similar value in the internal standard/acetophenone response. The values for the various ketones are recorded in Table 31. It was also necessary to insure that the photoproducts mentioned were the only resulting products of the photolysis. The procedure for determining this was reported in the results section. The results are reported in Table 32.

8) Reliability of Data

The reproducibility of the relative VPC peak areas is on the order of $\pm 5\%$ using the model 224 integrator and within $\pm 1\%$ for the digital integrator. The uncertainty for making the solutions and filling the tubes was on the order of 1 to 2%. Altogether, the uncertainty is within ± 5 to 8% including the uncertainty in the actinometer. The uncertainty in the $k_q\tau$ values should be less due to the lack of actinometer error. The variation in results due to O_2 quenching cannot be estimated, though inspection of the deviation for the higher $k_q\tau$ values suggests this occurrence. Unreliability due to quenching impurities in the glassware was reduced as much as possible by soaking in a commercial cleaner, rinsing 10 times with hot water, and rinsing 10 to 15 times in distilled water.

KINETIC DATA

A. Quenching Studies.

The following tables contain quencher concentrations, relative vpc areas of acetophenone type product relative to standard, the standard used, and its concentration. A reference to the column used and temperature of the column will be given.

Table 10. Stern-Volmer Quenching of .1 M para-Methyl-butyrophenone by 2,5-Dimethyl-2,4-hexadiene.

Run #1

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	.634	.00639	1.0
.0002	.372	.00375	1.70
.0003	.267	.00269	2.37
.0004	.224	.00225	2.83

^a0.00517 M C₁₅ internal standard. Column 4 - 132°C.
Incident Radiation .0296 Einstein/ℓ.

Run #2

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	.556	.00559	1.0
.0002	.320	.00322	1.74
.0003	.300	.00302	1.85
.0004	.240	.00241	2.31

^a.00516 M C₁₅ internal standard. Column 4 - 132°C.
Incident Radiation .0252 Einstein/ℓ.

Run #3

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	.594	.00600	1.0
.0001	.440	.00444	1.35
.0002	.332	.00335	1.78
.0003	.319	.00322	1.86
.0004	.262	.00265	2.27

^a.00520 M C₁₅ Internal Standard. Column 4 - 133°C.
Incident Radiation .0237 Einstein/ℓ.

Table 11. Photolysis of meta-Methylbutyrophenone.

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	1.04	.00705	1.0
.0001	.986	.00669	1.09
.0003	.764	.00518	1.35
.0005	.645	.00437	1.65
.0010	.475	.00322	2.12

^a.00348 C₁₅ internal standard. Column 3 - 135°C.
Incident Radiation .046 Einstein/l.

Table 12. Photolysis of 3,4-Dimethylbutyrophenone.

Run #1

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	.258	.00136	1.0
.00005	.217	.00114	1.19
.0001	.153	.00080	1.67
.0002	.121	.00060	2.13

^a.00301 M C₁₆ internal standard. Column 1 - 129°C.
Incident Radiation .0216 Einstein/l.

Run #2

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	.338	.00308	1.0
.0002	.153	.00140	2.21
.0004	.106	.0097	3.19
.0005	.081	.00074	4.17

^a.00522 M C₁₆ Internal Standard. Column 4 - 148°C.

Table 13. Photolysis of 3,5-Dimethylbutyrophenone.

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.000	.902	.00776	1.0
.0001	.344	.00296	1.26
.0002	.266	.00229	1.63
.0003	.230	.00198	1.88
.0004	.182	.00157	2.38
.0005	.200	.00172	2.17
.0006	.165	.00142	2.98

^a.00506 M C₁₅ internal standard. Column 4 - 133°C.
Incident Radiation .0308 Einstein/l.

Table 14. Photolysis of .1 M Para-methylvalerophenone.

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	0.353	.00348	1.0
.002	0.226	.00223	1.56
.003	0.194	.00192	1.82
.004	0.174	.00172	2.03
.005	0.150	.00148	2.35
.006	0.138	.00136	2.56

^a.00506 C₁₅ internal standard. Column 4 - 133°C.
Incident Radiation .0111 Einstein/l.

Table 15. Photolysis of .1 M 3,5-Dimethylvalerophenone.

Run #1

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	1.15	.00676	1.0
.001	.850	.00500	1.35

^a.00336 M C₁₆ internal standard. Column 1 - 125°C.
Incident Radiation .0228 Einstein/l.

Run #2

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	.770	.00402	1.0
.002	.441	.00230	1.75
.003	.372	.00194	2.07
.004	.304	.00159	2.53

^a.00298 M C₁₆ internal standard. Column 1 - 125°C.
Incident Radiation .0132 Einstein/l.

Table 16. Photolysis of .1 M 3,4-Dimethylvalerophenone.

Run #1

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	.42	.00247	1.0
.0005	.26	.00153	1.6

^a.00336 M C₁₆ internal standard. Column 1 - 129°C.
Incident Radiation .0147 Einstein/l.

Run #2

Quencher Concentration	Product/Standard Ratio ^a	[AP]	ϕ_o/ϕ
0.0	0.920	.00510	1.0
.002	0.265	.00147	3.45
.003	0.212	.00118	4.35
.004	0.166	.00092	5.55

^a.00317 M C₁₆ internal standard. Column 1 - 129°C.
Incident Radiation .0172 Einstein/l.

B. Solvent Studies

Included in the following tables are data for the formation of type II product versus added alcohol or pyridine to a solution of the ketone and standard.

Table 17. Solvent Study of a Para-methylbutyrophenone.

Run #1

Pyridine Concentration (M)	Product/Standard Ratio ^a	[AP]	ϕ_{II}
0.0	.228	.00249	.188
.40	.628	.00685	.514
.60	.615	.00670	.506
.80	.603	.00657	.490
1.00	.567	.00618	.467
1.20	.527	.00574	.434

^a.00557 M C₁₅ internal standard. Column 3 - 133°C.
Incident Radiation .0143 Einstein/l.

Run #2

Pyridine Concentration (M)	Product/Standard Ratio ^a	[AP]	ϕ_{II}
.05	.646	.00504	.317
.10	.682	.00532	.335
.15	.883	.00689	.434
.20	1.07	.00835	.525

^a.00400 M C₁₅ internal standard. Column 3 - 133°C.
Incident Radiation .0150 Einstein/l.

Table 18. Photolysis of meta-Methylbutyrophenone.

Run #1

Pyridine Concentration	Product/Standard Ratio ^a	[AP]	ϕ_{II}
.00	.39	.00397	.170
.05	.73	.00737	.32
.10	.88	.00889	.39
.15	.92	.00929	.41
.20	.99	.00999	.44
.25	1.03	.01040	.46
.30	1.05	.01060	.47

^a.00518 M C₁₅ internal standard. Column 4 - 133°C.
Incident Radiation .0207 Einstein/l.

Run #2

Pyridine Concentration	Product/Standard Ratio ^a	[AP]	ϕ_{II}
.40	1.28	.0118	.55
.45	1.27	.0121	.54
.50	1.28	.0118	.55
.55	1.26	.0116	.54

^a.00475 C₁₅ internal standard. Column 4 - 133°C.
Incident Radiation .0216 Einstein/l.

Table 19. Photolysis of .1 M 3,4-Dimethylbutyrophenone.

t-Butyl Alcohol	Product/Standard Ratio ^a	[AP]	ϕ_{II}
0.0	.543	.00334	.127
0.5	1.40	.00862	.327
0.8	1.38	.00850	.322
1.0	1.73	.0107	.402
1.2	1.72	.0106	.401
2.0	1.66	.0102	.387

^a.00352 M C₁₆ internal standard. Column 4 - 133°C.
Incident Radiation .0264 Einstein/l.

Table 20. Photolysis of 3,5-Dimethylbutyrophenone

Pyridine Concentration	Product/Standard Ratio ^a	[AP]	ϕ_{II}
0.0 ^b	.433 ^b	.00372 ^b	.08 ^b
0.2	.916	.00796	.277
0.4	.965	.00838	.291
0.6	.951	.00825	.287
0.8	.943	.00819	.285
1.0	.902	.00783	.272
1.2	.852	.00739	.257

^a.00511 M C₁₅ Internal Standard COLUMN 4 - 133°C;
Incident Radiation .0308 Einstein/ℓ;

^b.00506 M C₁₅ and .0536 Einstein/ℓ.

Table 21. Photolysis of meta Methylvalerophenone

t-butyl alcohol	Product/Standard Ratio ^a	[AP]	ϕ_{II}
0.0	.813	.00548	.349
0.5	1.40	.00944	.602
1.0	1.67	.01126	.692
2.0	1.72	.01159	.740
3.0	1.71	.01153	.735
5.0	1.72	.01159	.740

^a.00346 M C₁₅ Internal Standard COLUMN 4 - 135°C
Incident Radiation .0157 Einstein/ℓ.

Table 22. Photolysis of 3,4-DMVP

t-butyl alcohol	Product/Standard Ratio ^a	[AP]	ϕ_{II}
0.0	.920	.00510	.277
.5	1.64	.00909	.49
1.0	1.96	.00109	.59
1.5	2.15	.00119	.65
2.0	2.15	.00119	.65
3.0	2.30	.00127	.69

^a.00317 M C₁₆ Internal Standard COLUMN 1 - 129°C
Incident Radiation .0176 Einstein/l.

Table 23. Photolysis of 3,5-DMVP

t-butyl alcohol	Product/Standard Ratio ^a	[AP]	ϕ_{II}
0.0	.770	.00402	.304
0.5	1.02	.00532	.403
1.0	1.17	.00611	.462
2.0	1.40	.00731	.553
3.0	1.26	.00658	.498
5.0	1.04	.00543	.411

^a.00298 C₁₆ Internal Standard COLUMN 1 - 129°C
Incident Radiation .0132 Einstein/l.

C. Variance of Type II Yields with Charges in Ketone
Concentration

Table 24. Photolysis of p-Methylbutyrophenone

Ketone Concentration	Product/Standard Ratio ^a	Acetophenone Concentration	ϕ_{II}
.03	.830	.00557	.227
.06	.781	.00524	.215
.1	.613	.00411	.167
.15	.420	.00282	.115

^a.00344 C₁₅ Internal Standard
Incident Radiation .0157 Einstein/l.

COLUMN 4 - 133°C

Table 25. Photolysis of 3,4-Dimethylbutyrophenone

Ketone Concentration	Product/Standard Ratio ^a	Acetophenone Concentration	ϕ_{II}
.05	.502	.00309	.117
.10	.543	.00334	.127
.15	.511	.00315	.119

^a.00352 M C₁₆ Internal Standard
Incident Radiation .0264 Einstein/l.

COLUMN 1 - 129°C

Table 26. Photolysis of 3,5-Dimethylbutyrophenone

Ketone Concentration	Product/Standard Ratio ^a	Acetophenone Concentration	ϕ_{II}
.05	.674	.00101	.113
.10	.433 ^b	.00383	.072
.15	.302	.00270	.050

^a.00511 M C₁₆; ^b.00506 M C₁₆ Internal Standard
COLUMN 4 - 133°C; Incident Radiation .0157 Einstein/ℓ.

Table 27. Photolysis of m-Methylvalerophenone

Ketone Concentration	Product/Standard Ratio ^a	Acetophenone Concentration	ϕ_{II}
.05	.808	.00545	.347
.10	.813	.00548	.349

^a.00346 M C₁₅ Internal Standard COLUMN 4 - 135°C
Incident Radiation .0157 Einstein/ℓ.

Table 28. Photolysis of 3,5-Dimethylvalerophenone

Ketone Concentration	Product/Standard Ratio ^a	Acetophenone Concentration	ϕ_{II}
.050	.750	.00392	.296
.078	.760	.00397	.300
.100	.770	.00402	.304

^a.00298 M C₁₆ Internal Standard COLUMN 1 - 125°C
Incident Radiation .0132 Einstein/ℓ.

Table 29. Photolysis of 3,4-Dimethylvalerophenone

Ketone Concentration	Product/Standard Ratio ^a	Acetophenone Concentration	ϕ_{II}
.05	.622	.00672	.354
.08	.570	.00615	.324
.10	.550	.00594	.314
.17	.367	.00396	.208

^a.00619 M C₁₆ Internal Standard COLUMN 1 - 129°C
Incident Radiation .0190 Einstein/l.

D. Miscellaneous Data

Table 30. Data for Cyclobutanol Ratios

Compound	Cyclobutanol/ Acetophenone Area Ratio	VPC Response Factor	% Cyclobutanol to Acetophenone
3,4 DMVP	.237	.82	18 ± 2 ^b
3,5 DMVP	.214	.82	16 ± 2.5 ^b
MMVP	.662	.74	14 ± 1.5 ^b
MMBP	.110	.80	8.8 ± 1.5 ^c
PMBP	.110	.80	8.8 ± 1.5 ^c
3,4 DMBP	.094	.82	7.7 ± 1.5 ^c
3,5 DMBP	.126	.82	10.3 ± 1.5 ^c

^aKetones were irradiated to 20-40%, depending on whether the retention time of the cyclobutanol was similar to that of the parent ketone's;

^bError cited was taken as ±10%, due to larger differences in area ratios and slopes;

^cError cited was ~±15% due to the same reasons as in subscript b.

Table 31. Standard-Product Molar Response Ratios

Standard/Product	Area/mole (Standard) Area/mole (Product)
Tetradecane/Acetophenone	2.0 ^a
Pentadecane/ <u>p</u> -Methylacetophenone	1.95 ^a
Pentadecane/ <u>m</u> -Methylacetophenone	1.95 ^a
Pentadecane/3,5-Dimethylacetophenone	1.70 ^a
Hexadecane/3,4-Dimethylacetophenone	1.75 ^a

^a ± 5%

Table 32. Experimental Data for Determining Disappearance Quantum Yields

Ketone	Ketone	Ketone/Standard Ratio Before (h ν)	Ketone/Standard Ratio After (h ν)
<u>p</u> -methylbutyrophenone		4.98	5.39
<u>m</u> -methylbutyrophenone		4.69	4.65
3,4-dimethylbutyrophenone		5.08	4.95
3,5-dimethylbutyrophenone		5.60	5.61
<u>m</u> -methylvalerophenone		7.16	6.68
3,4-dimethylvalerophenone		6.41	6.70
<u>p</u> -methylvalerophenone		6.21	6.23
3,5-dimethylvalerophenone		5.37	5.30

^a Error is probably ±10%

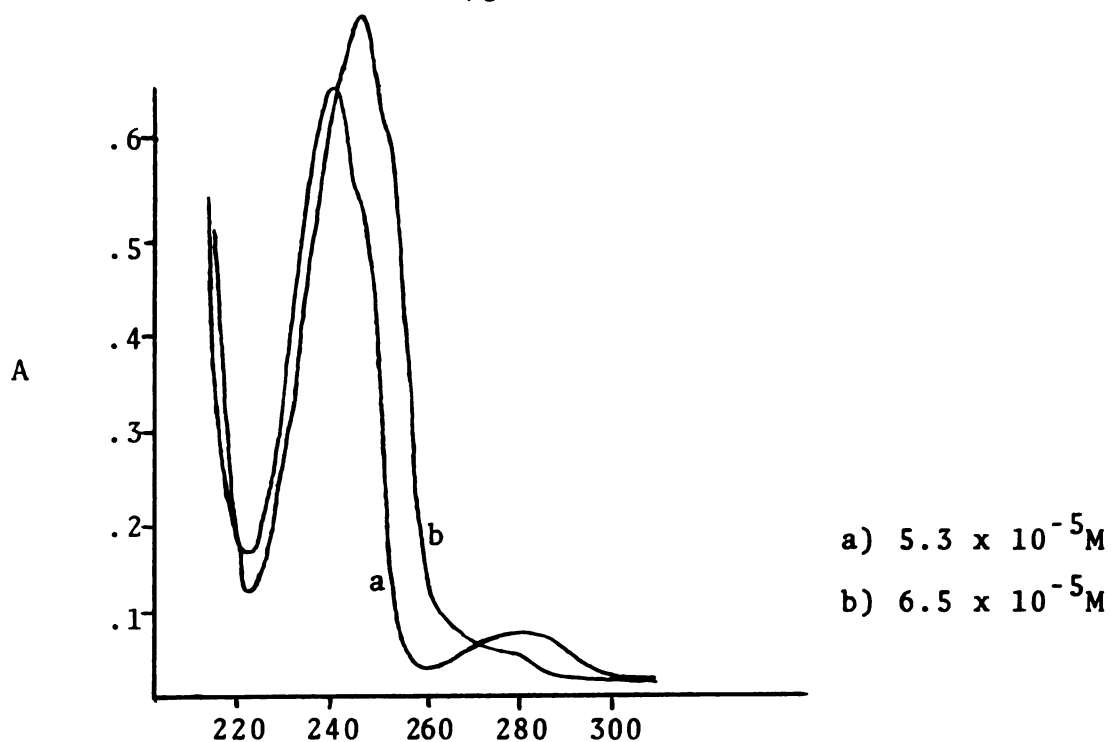


Figure 15. Absorbion spectra for a) m-methylbutyrophenone,
 b) p-methylbutyrophenone.
 Methylated valerophenones produced identical spectra.

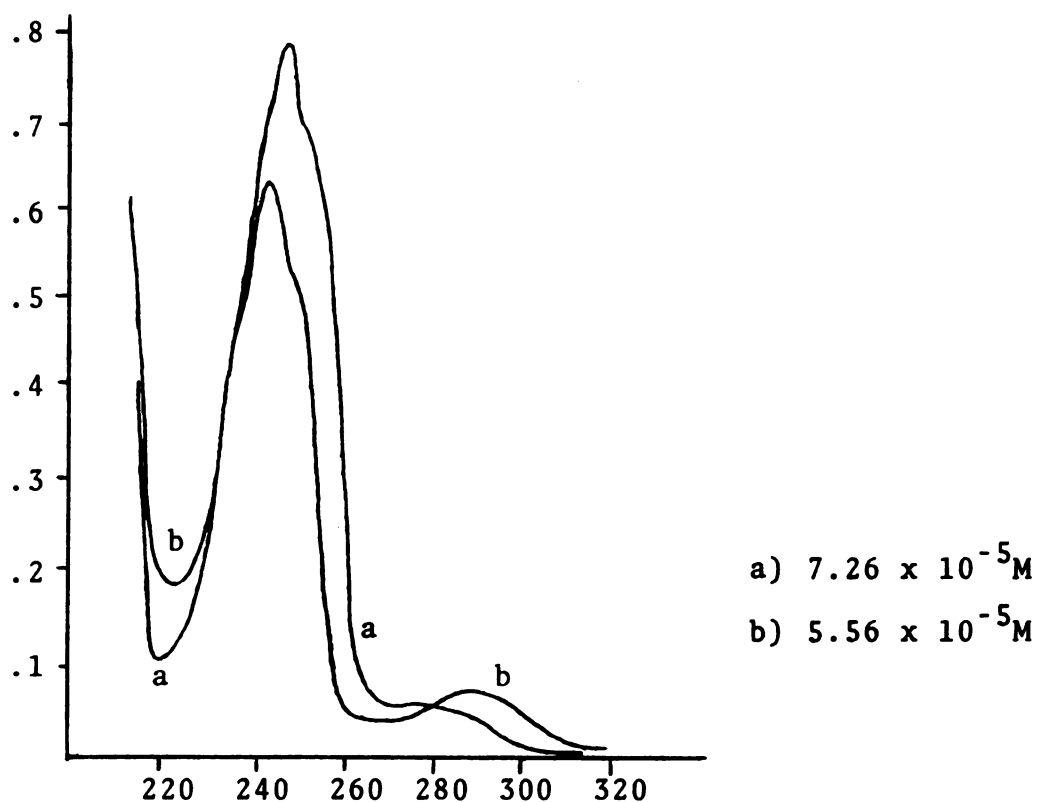


Figure 16. Absorbion spectra for a) 3,4-dimethylbutyrophenone,
 b) 3,5-dimethylbutyrophenone.
 Methylated valerophenones produced identical spectra.

B I B L I O G R A P H Y

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