ABSTRACT

SUBSTITUENT EFFECTS ON THE TYPE-II PHOTOREACTION OF PHENYL KETONES

By

Allen Edward Kemppainen

Substituent effects on the reactivity towards γ-hydrogen abstraction in the type-II photoelimination of alkyl phenyl ketones were measured for a wide range of substituents on the γ-position. Inductive effects at the γ-carbon were also measured for δ- and ε-substituents and for many of these ketones the solvent effects on the quantum yields were investigated. The data obtained by quenching the excited triplet states with an efficient triplet quencher were treated using the Stern-Volmer relationship to determine triplet lifetimes. In addition the quantum yields and triplet lifetimes for a wide variety of ring substituted alkyl phenyl ketones were determined.

The following results were obtained: (1) The relative reactivities of the type-II photochemical process compare favorably with those determined for hydrogen abstraction by tert-butoxy radicals. (2) A correlation exists between the σ_I of the substituent and the reactivity of the γ-hydrogen towards abstraction by the phenyl ketone triplet. A ρ of -2.0 was found for substituents on the δ-carbon. (3) If ρ for the γ-carbon is taken as -4.4 then contributions from inductive and radical stabilizing effects on the excited state reactivities can be quantitatively separated. (4) It was generally observed that the type-II photoproducts accounted for virtually all of the reaction. A few exceptions were noted

in cases where the substituent was a good photoreducing or otherwise reactive group. (5) No correlation exists between the excited state reactivities and the type-II quantum yields (ϕ_{II}) for the alkyl phenyl ketones tested. (6) Electron withdrawing ring substituents activate the phenyl carbonyl triplet, and electron donating groups deactivate it. However, in most cases the deactivation is much larger than can be accounted for by the inductive effect alone.

The results are consistent with a mechanism which involves a 1,4-biradical intermediate. This can accomodate the lack of correlation between the quantum yields and the excited state reactivities since the type-II quantum yield can be expressed as the product of two probabilities, the quantum yield of biradical formation (ϕ_{BR}) and the probability of product formation from the biradical (ϕ_p).

$$\phi_{II} = \phi_{BR}\phi_p$$

The results with δ-substituents also establish that the reactivities do correlate with σ_I substituent constants. The estimated ρ constant for the γ-carbon indicates that it is highly sensitive to inductive effects. The results obtained for ring substituted alkyl phenyl ketones clearly show that the excited state reactivity is influenced by the inductive effect and the nature of the triplet. The evidence can be interpreted as supporting a thermal equilibrium of reactive n,π* and unreactive π,π* triplet states in which the reaction occurs solely from the n,π* triplet.

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by

Allen Edward Kemppainen

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DEDICATION

The writing of this thesis is dedicated to Dean Tom King, Dean of Students at Michigan State University during my undergraduate years and those of my brother and sisters. During those early years of decision and indecision his influence on me was greater than that of any other person. His friendship, encouragement, and advice were and always will be deeply treasured.

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INTRODUCTION

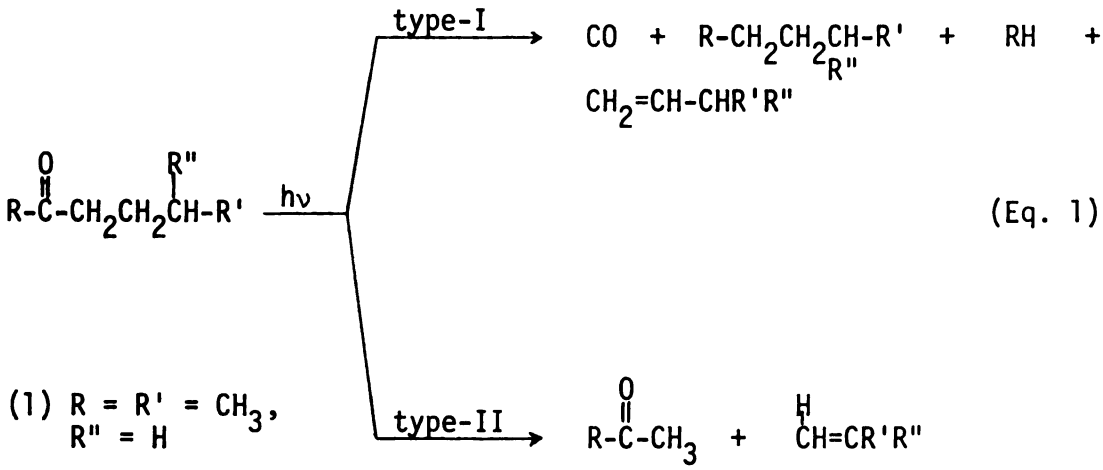
1. Historical Notes.

For at least the last two centuries men of a scientific bent have been very curious about the nature of the interaction of light with matter. To the naturalist the dependence of plant life on sunlight is axiomatic[1]. To the physical scientist, however, the greatest challenge lies in the testing and interpretation of photochemical phenomena. Major credit for the early stages in the formulation of this area should be given to Grothaus and Draper[2] who in the early 1800's developed what is now referred to as the first law of photochemistry: Only the light which is absorbed by a molecule can produce photochemical change. Draper used the term "tithonic rays"[3] to describe a component of light which produced photochemical change in certain compounds, yet, if "ultraviolet rays" were to be substituted in its place, one would find his observations and conclusions to be quite accurate.

2. Discovery of the Type-II Photoelimination.

During the early part of the twentieth century extensive studies were done on the photodecarbonylation of carbonyl compounds[4,5,6]. Much of this work consisted of physical measurements of the kinetics of gas phase reactions and the results are often cited in basic physical chemistry textbooks[7,8]. While conducting such studies on the photolysis of various ketones in the gas phase, Norrish and co-workers discovered that when the ketone or aldehyde contained γ-hydrogens a new type of reaction took place in addition to the decarbonylation[9,10]. Analyses of the product mixtures showed that a cleavage between the carbon-carbon bond which was α-β to the carbonyl took place yielding a lower molecular weight carbonyl compound and an olefin. Norrish classified

them as type-I and type-II reactions (See Equation 1). It was also noted that the latter pathway is preferred. Subsequently it was found that the type-II photoreaction readily occurs in hydrocarbon solvents[11].



(Eq. 1)

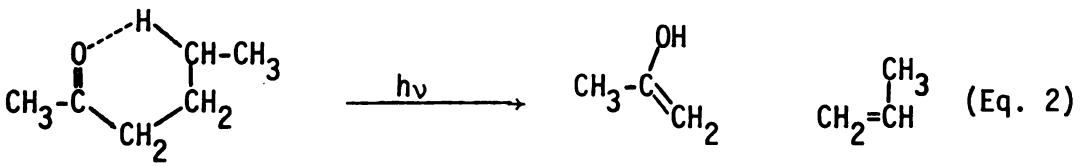
(1) R = R' = CH_3, R" = H

(2) R = $CH_2CH_2CH_3$, R' = R" = H

(3) R = H, R' = R" = CH_3

A number of ketones and aldehydes were irradiated in isooctane and in medicinal paraffin (at 70 to 100°C) and furnished interesting results. The type-II process was found to be relatively unaffected by the solvent or the temperature changes whereas the type-I process, which was entirely suppressed at room temperature, gave high yields at elevated temperatures. Also, the production of small saturated hydrocarbons in the type-I reaction was accompanied by a corresponding unsaturation in the solvent. These facts led to the conclusion that the type-I reaction with ketones involved production of free radicals and the type-II reaction involved some type of concerted mechanism[12]. The case in which the aldehydes photolyzed to give carbon monoxide and the corresponding saturated hydrocarbon with little or no unsaturation in the solvent was considered to be a type-I reaction without production of radicals.

The common differentiation made today is that of the primary process of the excited carbonyl: In the type-I reaction the bond between the carbonyl carbon and the α-carbon is cleaved forming two radicals; in the type-II reaction a γ-hydrogen is abstracted by the excited carbonyl, resulting in the cleavage of the α-β bond. Approximately ten years later Noyes and coworkers[13] restudied the photolysis of methyl butyl ketone in the gas phase and essentially confirmed Norrish's results. A product ratio of 1:1, acetone to propylene, with a quantum yield (ϕ) of about 0.5 was found. Since the quantum yield was relatively unchanged from 25° to 300°C, and considering Norrish's results in hydrocarbon solvents in which the quantum yield was nearly the same, Noyes suggested that possibly a cyclic 6-membered ring-like form of the ketone existed in solution involving hydrogen bonding with the γ-hydrogens, and that this was responsible for the type-II reaction (See Equation 2). A similar argument had been given earlier by Rice and Teller[14] in their treatment of the theory of least motion in elementary free radical reactions. Attempts were made to strengthen this argument using dueterated ketones[15] , the best test being that made by Srinivasan[16] who used



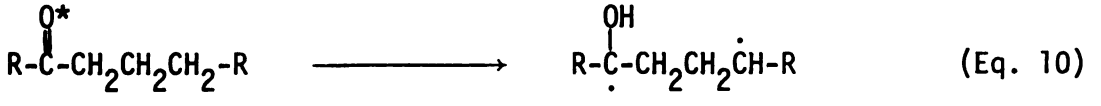
(Eq. 2)

2-hexanone-5,5-d_2 which produced acetone-d_1 as a photolysis product. Some plain acetone which was also formed was attributed to exchange of the enol-intermediate with hydroxy groups bound to the walls of the photolysis cell. 2-Hexanone produced a similar amount of acetone-d_1

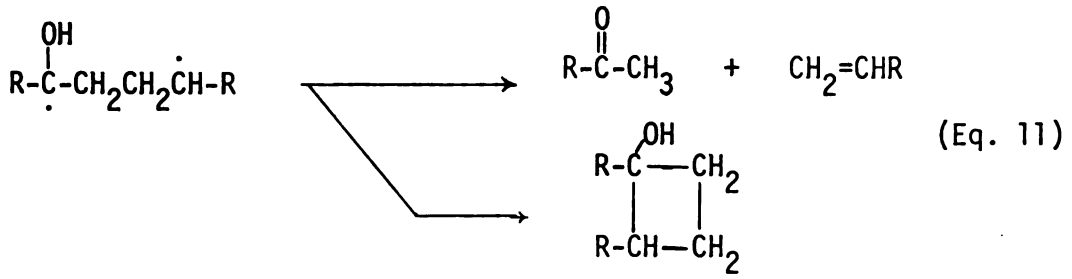
when photolyzed in a cell preconditioned with D_2O vapor. This enol-intermediate, which was first invoked to explain the isotope exchange upon photolysis[15], was later confirmed by actual observation of its infra-red absorption during the gas phase photolysis of 2-pentanone[17]. It was found to be a transient species with a half-life of about 3.3 minutes and the rate of appearance of acetone absorption corresponded to the rate of decay of the enol-species.

3. Later Developments Involving the Type-II Process.

a. Identification of cyclobutanols. By 1960 the type-II photoelimination had begun to lose its status as a side reaction and was being studied in its own right. Yang and Yang[18] had recently identified another photoproduct in the photolysis of 2-pentanone, 2-octanone and 2-nonanone as the cyclobutanol. This was an important clue to the mechanism of the reaction. It was later found that α-methoxy and α-ethoxyacetophenone as well as 1-methoxy-3,3-dimethyl-2-butanone readily formed the oxetanol[19]. LaCount and Griffin[20] later photolyzed valerophenone, γ-phenylbutyrophenone and α-benzyloxyacetophenone, separated the cis and trans isomers of the cyclobutanols by chromatography and identified each by nmr spectroscopy. They found that the trans isomer was preferred in each case. To account for these results a mechanism proceeding through a 1,4-biradical was proposed[18,21] (Equations 10 & 11).



(Eq. 10)



(Eq. 11)

b. Energy transfer and kinetic studies. Classical energy transfer studies had established the fact that direct transfer of excitation occurred in matrix or solution. Terenin and Ermolaev observed that triplet energy from carbonyl compounds was transferred to species which had lower triplet energy levels[22]. The same phenomenon was reported by Bäckström and Sandros[23] for the irradiation of biacetyl. They discovered further[24] that besides being able to quench the phosphorescence of biacetyl with triplet quenchers, they could sensitize its phosphorescence with benzophenone which has a higher triplet energy. Benzophenone is known to convert efficiently to the triplet state since only its phosphorescence emission can be observed. By varying the biacetyl concentration the mean lifetime of the benzophenone triplet was found to be 1.9×10^{-6} second. In studies on the sensitized cis-trans isomerization of piperylene, Hammond and coworkers[25] found that the diene was an efficient quencher of the triplet state of benzophenone and acetophenone. It was also used in later more detailed studies on cis-trans isomerizations[26]. Wagner and Hammond[21] used piperylene to quench the reaction of 2-hexanone and 2-pentanone, and Dougherty[27] used it to quench 2-octanone. Their results were similar: A considerable portion of the reaction was rapidly quenched by addition of small concentrations

of piperylene, after which the quantum yield leveled off to a constant value and seemed unaffected even by very high quencher concentrations. This was good evidence for reaction from two excited states, a quenchable triplet and a non-quenchable singlet. Wagner and Hammond also compared the relative ease of quenching of 2-pentanone and 2-hexanone. They found the latter, with the secondary γ-hydrogens, much more difficult to quench. This was in agreement with previous work by Ausloos[28] and also could be compared to studies by Walling and co-workers[29-32] who found that relative rates of hydrogen abstraction by alkoxy radicals were 4 to 8 times faster from secondary hydrogens than from primary hydrogens. It was also shown that the reactivity of benzophenone triplets towards the C-H bond strength in hydrogen abstractions followed quite closely the reactivity of the alkoxy radicals[33,34]. If any differences were to be noted, the triplet abstraction showed somewhat greater selectivity for the more reactive hydrogens. Wagner and Hammond[35] later performed quenching experiments on butyrophenone and valerophenone. This was the first direct comparison of the two and it was predicted and found that the secondary γ-hydrogens of valerophenone were more reactive (less sensitive to quenching) than the primary hydrogens of butyrophenone. The data was treated by plotting the quantum yield without quencher (ϕ_o) over the quantum yield with quencher (ϕ) versus the quencher concentration [Q], as is described by the Stern-Volmer[23,35] equation (Equation 12).

$$\frac{\phi_o}{\phi} = 1 + k_q[Q]\tau \qquad \text{(Eq. 12)}$$

The classical method of deriving this equation is by using a steady-

state treatment developed by Stern and Volmer over 50 years ago. However, by using a modernistic stochastic formulation, one can arrive at the same relationship[36]. The Stern-Volmer relationship can also be derived by using a simplified treatment based on the definition of the quantum yields of the various processes that take place and the derived mechanism of the reaction[37]. The sum of the quantum yields of all of the processes taking place is defined as unity (Equation 13).

$$\Phi_{total} = \phi_1 + \phi_2 + \phi_3 + \phi_4 + - - + \phi_n = 1 \quad \text{(Eq. 13)}$$

The quantum yield of each individual process of the triplet state can then be expressed as the ratio of the rate of that process to the sum of the rates of all of the processes. For sake of brevity, if the unimolecular rate constant for biradical formation from the triplet is defined as k_r, the unimolecular rate constant for all other deactivating processes as k_d, and the bimolecular quenching rate constant as k_q, then the quantum yield with no quencher present can be expressed as in Equation 14.

$$\phi_o = \frac{k_r}{k_r + k_d} = k_r\tau \quad \text{(Eq. 14)}$$

The quantum yield with quencher added then would become:

$$\phi = \frac{k_r}{k_r + k_d + k_q[Q]} \quad \text{(Eq. 15)}$$

Then dividing Equation 14 by Equation 15 one arrives at the Stern-Volmer relationship (Equation 16).

$$\frac{\phi_o}{\phi} = \frac{k_r/(k_r + k_d)}{k_r/(k_r + k_d + k_q[Q])} = \frac{k_r + k_d + k_q[Q]}{k_r + k_d}$$

$$= \frac{k_r + k_d}{k_r + k_d} + \frac{k_q[Q]}{k_r + k_d} = 1 + \frac{k_q[Q]}{k_r + k_d} \qquad \text{(Eq. 16)}$$

In the special case where k_d is very small, $1/k_r$ can be equated with the average triplet lifetime (τ). The quenching rate constant, k_q, has been calculated using a simplified Debye formula (Equation 17) under the assumption that the rate of quenching is diffusion controlled and thus inversely proportional to the viscosity of the solvent[24]. Although Wagner and Hammond[35] estimated that the rate of quenching was only about

$$k_{diff} = \frac{8RT}{3000\eta} \text{ liters/(mole x sec)} \qquad \text{(Eq. 17)}$$

half that predicted by the Debye equation, the notion that quenching was diffusion controlled was still popularly assumed[38]. The careful work of Wagner and Kochevar[39] has now shown that only in relatively viscous solvents is the quenching rate diffusion controlled, and as the solvent becomes less viscous the deviation from the Debye relationship becomes greater. It was also found that a modified Debye equation (Equation 18) was more representative of the experimentally determined values[39,40].

$$k_{diff} = \frac{8RT}{2000\eta} \text{ liters/(mole x sec)} \qquad \text{(Eq. 18)}$$

c. Characterization of the excited state. The photochemical

behavior of carbonyl compounds is rather obviously related to their excited state(s). In his early work Norrish[9] alluded to an "upper level" of the reacting ketone, however, little was known of its nature at the time. Phosphorescence and fluorescence emissions of carbonyl compounds have been studied for many years[41] and provide critical information in this area. The actual nature of phosphorescence, which was recognized more than a century and a half ago[42], wasn't untangled until the 1940's when the extensive studies of Lewis and co-workers[43] made clear the distinction between fluorescence and phosphorescence: The former resulting from a transition between singlet excited states to singlet ground state and the latter resulting from a spin-forbidden triplet to singlet transition. They also observed the triplet-triplet absorptions[44] in fluorescein which was irradiated sufficiently to promote approximately 80% of the molecules into the triplet state, predicted and observed the extremely weak singlet-triplet absorption bands[45] of a number of compounds which phosphoresced, and suggested that the molecule in the triplet state should have a measurable paramagnetic susceptibility[43]. The concept of a "meta-stable" state, first proposed by Jablonski[46] to account for the longer lifetime phosphorescence, proved to be essentially correct and led to the identification of the triplet state (See Figure 1). Yet the characterization of the triplet state in the photoreactions of carbonyl compounds was not accomplished without difficulties. The hydrogen abstracting species in the photoreduction of benzophenone was first considered to be a "diradical" by Bäckström[47] but as knowledge in this area advanced he redesignated it as the triplet[48]. A controversy developed over whether the type-II cleavage of the dialkyl ketones occurred from the excited singlet or

or triplet state. It was first proposed that 2-hexanone[49], 2-pentanone[50] and a number of alkyl aldehydes and ketones[51] reacted from the excited singlet state. Other evidence strongly suggested that the triplet state was the one involved in going to type-II product[52-54]. Wagner and Hammond[21] later showed that 2-hexanone and 2-pentanone reacted from both the excited singlet and triplet states and determined that early difficulties were due in part to the differences in reactivity of the two ketones. They found that the relative rate of reaction was much greater for the singlet than for the triplet and the reaction of the secondary hydrogens was faster than the primary hydrogens. Another aspect of the excited state arises when the chromophore contains an atom with non-bonding electrons. It is then possible to have either an

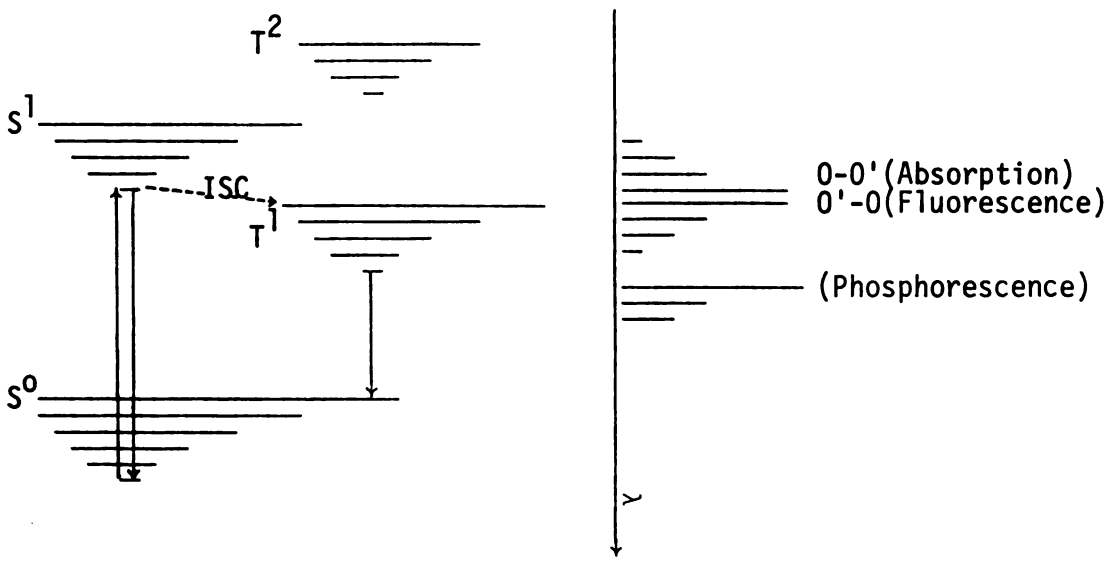
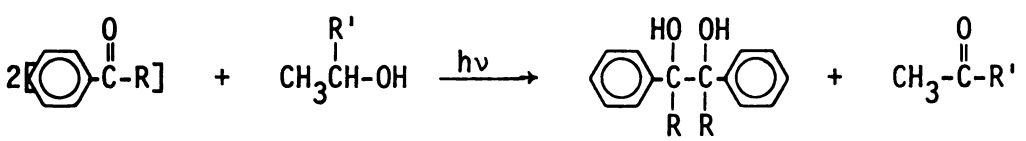


Figure 1. Modified Jablonski Diagram. Diagram is designed to show a case in which the upper singlet (S^1) and the ground state singlet (S^0) have the same internuclear relationships and the 0-0 bands represent the most probable transitions. ISC represents intersystem crossing to the triplet level (T^1), which corresponds to Jablonski's "metastable state." Information taken from Reference 2, pages 274 and 285.

n,π* or a π,π* lowest energy triplet state. This consideration becomes important in explaining the large effects on relative reactivities of a ring substituent on phenyl ketones, yet it is not completely understood. An up to date account has recently been published in a review by Wagner and Hammond[40]. Further discussion on this topic is presented in the section on the effects of ring substituents.

d. Related work in photoreduction. Paralleling the developments in photoeliminations another area of photochemistry of carbonyl compounds, that of photoreduction, developed in a quite independent fashion. Although it had been known that a reaction took place when an alcoholic solution of benzophenone was exposed to sunlight, the products were not known until Ciamician and Silber[55] correctly identified them as the benzpinacol and the corresponding aldehyde or ketone (See Equation 19). Acetophenone was also photolyzed and found to pinacolize,

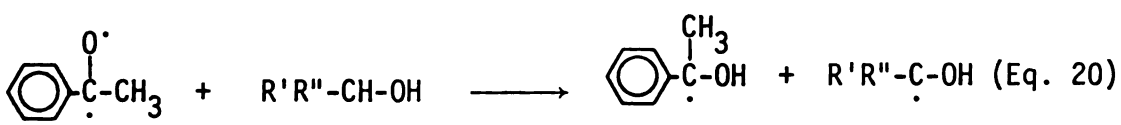


R = CH_3 or 

R' = H or Alkyl

although more slowly than benzophenone. Several alcohols were also tried and it was found that while photoreductions occurred readily in primary and secondary alcohols, only very little reaction took place in tert-butyl alcohol[56]. During the next several years benzophenone was photoreduced in a number of media including hydrocarbons[57], aliphatic acids and ethers[58], and esters[59]. Complex byproducts often resulted

such as resins or addition products. The photoreduction of acetone in a number of alcohols was also studied[60]. Here the principal product appeared to be the 1,2-glycol corresponding to a 1:1 adduct of the acetone and the alcohol, although some isopropyl alcohol and other products, depending on the alcohol used, were noted. The study of the photoreduction of benzophenone was continued by Cohen[61] who used a number of various alcohols as reactants*. His findings corroborate those of earlier works in most cases. He seemed perplexed, however, that cinnamyl alcohol would not photoreduce benzophenone although allyl and benzyl alcohol readily did. Present knowledge of energy transfer would predict that the excited benzophenone would transfer its energy to the styryl group. The investigations[62] continued in this direction until the late 1930's when studies were begun into the mechanism of the photoreduction. Concluding that the hydroxylic hydrogen of the alcohol was not involved in the reaction, Weizmann, Bergmann and Hirshberg[63] claimed that the first step during the irradiation was the activation of the carbonyl to a "diradical form." Splitting of a C-H bond on the alcohol followed, resulting in two radicals which later dimerize (Equation 20). This conclusion was based partly on the results obtained



with optically active 1-phenylethanol. It was found that acetophenone pinacols formed with the optically active alcohols were inactive, and also that the unreacted alcohol retained its original activity.

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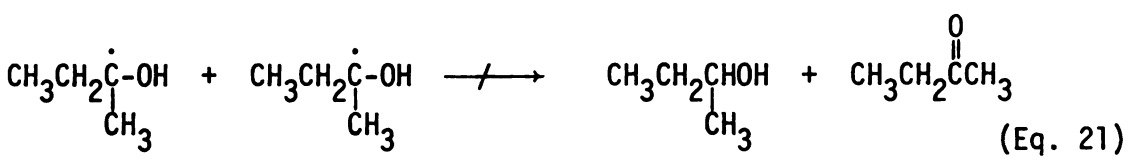
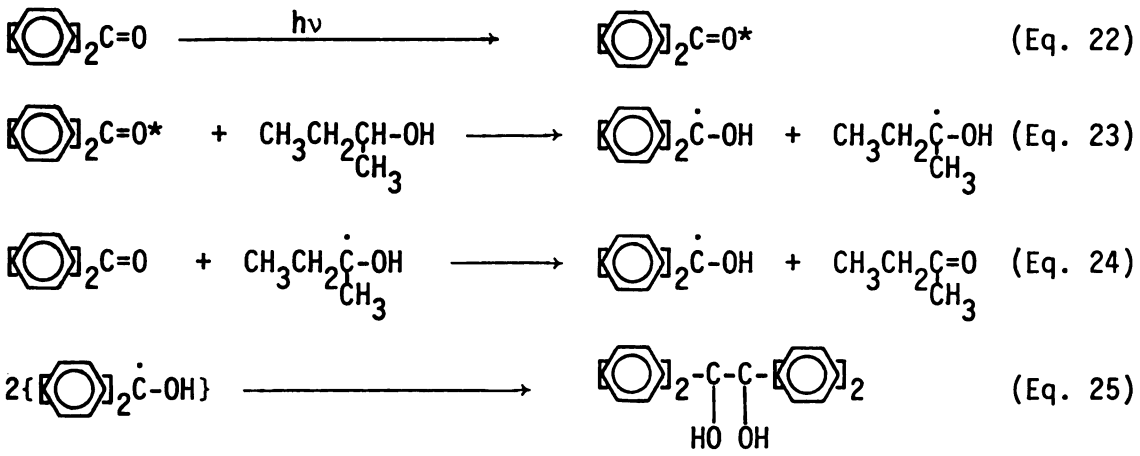
* Among his observations is one that "water is a strong negative catalyst" in the photoreduction of benzophenone.

Bergmann and Hirshberg[64] later reported substituent effects on photoreduction. They noted that ring substituents on benzophenone or acetophenone nearly always impair the reactivity. A naphthyl or biphenyl substituted for a phenyl group in benzophenone stops pinacolization. The same result is seen when a para-methoxy group is placed on the ring of acetophenone, or when a naphthyl is substituted for the phenyl ring. The benzophenone photoreduction was further studied by Pitts and coworkers[65] who found that oxygen dissolved in the photolysis solution inhibits (quenches) the photoreduction. Quantum yields for samples saturated with oxygen, air, and samples degassed on a vacuum line varied from 0.00 to 0.50 to 0.95 respectively. Relatively large concentrations of olefins were also found to inhibit benzpinacol formation. As a result of his and Hammond's[66] work, Pitts concluded that the sole reacting species of benzophenone was the triplet. Further information on the mechanism was obtained by irradiating benzophenone in optically active sec-butyl alcohol. As was found previously with acetophenone[63] the unreacted alcohol retained its original activity. This rules out the disproportionation of the radical species formed (Equation 21) as



(Eq. 21)

well as the reverse of the abstraction step (Equation 23). Also, since the isolated wavelength of 3660A readily produces photoreduction, the initial step has to be excitation of the carbonyl as the alcohol is transparent in this region. Pitts proposed the following mechanism:



(Eq. 22)

(Eq. 23)

(Eq. 24)

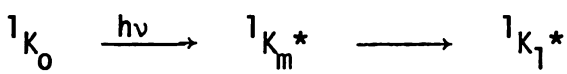
(Eq. 25)

The mechanism of benzophenone photoreduction is still under investigation and some modifications have been proposed to account for a small amount of the mixed pinacol found[67]. Although the notion of hydrogen abstraction by the excited carbonyl was considered quite early in the studies of photoreduction[63], it wasn't until twenty years later that the argument was applied to the type-II photoreaction.

4. Recent Studies on the Effects of Solvents and Substituents on the Type-II Photoreaction.

Since the mid-1960's the type-II photoreaction has generated a considerable amount of interest. Recently aquired data have been invaluable in resolving several of the early problems.

a. Mechanistic implications. Wagner and Hammond[35] proposed the following mechanistic scheme for the steps involved in the type-II process:



(Eq. 26)

$$^1K_1^* \xrightarrow{k_1} \text{PRODUCTS} \qquad \text{(Eq. 27)}$$

$$^1K_1^* \xrightarrow{k_{isc}} {}^3K_n^* \longrightarrow {}^3K_1^* \qquad \text{(Eq. 28)}$$

$$^3K_1^* \xrightarrow{k_3} \text{PRODUCTS} \qquad \text{(Eq. 29)}$$

$$^3K_1^* \xrightarrow{k_d} {}^1K_o \qquad \text{(Eq. 30)}$$

$$^3K_1^* + Q \xrightarrow{k_q} {}^1K_o + Q^* \qquad \text{(Eq. 31)}$$

In the above scheme the ground state ketone is represented by ^1K_o, excited singlet at all possible levels by $^1K_m^*$, and the lowest energy excited singlet by $^1K_1^*$. The triplet ketone at all possible levels of excitation is represented by $^3K_n^*$ and the lowest triplet level by $^3K_1^*$. Non-radiative decay from the excited singlet, which is not included in the scheme, was considered to be negligible. Their results further showed that the quantum yields of valerophenone, butyrophenone, 2-hexanone, and 2-pentanone in no way reflected the differences in reactivities between the ketones with secondary and primary γ-hydrogens. The quantum yields, which ranged from 0.4 to 0.5, also indicated that considerable inefficiency was involved in going to product. As one possibility to account for this a reverse hydrogen transfer was suggested which would provide a radiationless mechanism for return to the ground state of the ketone. Support for this theory comes from Wagner's[68,69] investigations on solvent effects on type-II quantum yields for a number of ketones. Polar, hydrogen bonding solvents raise the ϕ_{dis} to near unity, and since triplet lifetimes don't change much[68] this indicates that the inefficiency in non-polar solvents must be due to the biradical. The results are consistent with a 1,4-biradical intermediate in which the abstracted hydrogen is prevented from returning to

its original location by solvation or hydrogen bonding to the solvent. The original mechanistic scheme can be modified to account for this by replacing Equation 29 with the following:

$$^3K_1 \xrightarrow{k_r} \text{B.R.} \qquad \text{(Eq. 32)}$$

$$\text{B.R.} \xrightarrow{k_p} \text{PRODUCTS} \qquad \text{(Eq. 33)}$$

$$\text{B.R.} \xrightarrow{k_{-r}} {}^1K_0 \qquad \text{(Eq. 34)}$$

Here B.R. represents the biradical intermediate. Kelso[70] recently found that optically active γ-methylhexanophenone racemizes several times faster than it forms type-II products. This verifies that a revertible radical site is formed at the γ-carbon. Results of preliminary investigations further emphasized the discrepancies between triplet state reactivity and quantum yield. It is proposed by Wagner[69] that the type-II quantum yield can be expressed as the product of the following probabilities:

$$\phi_{II} = \phi_{isc}\phi_{BR}\phi_P = \phi_{isc}\left(\frac{k_r}{k_r + k_d}\right)\left(\frac{k_p}{k_p + k_{-r}}\right) \qquad \text{(Eq. 35)}$$

Intersystem crossing quantum yields which have been measured are uniformly near unity for unsubstituted phenyl alkyl ketones[71], pyridyl alkyl ketones[73], and ortho-, meta-, and para-methoxyvalerophenones[74] so ϕ_{isc} is commonly taken as one unless there are indications to the contrary. Wagners proposal[69] on the inhibition of revertible hydrogen transfer in polar solvents provides a key to determining the specific rate constants in Equation 35. Since k_{-r} becomes negligible in polar

solvents ϕ_p becomes 1, and therefore:

$$\phi_{II(alcohol)} \simeq \left(\frac{k_r}{k_r + k_d}\right) = \phi_{BR} \qquad \text{(Eq. 36)}$$

All that is needed to determine k_r is the triplet lifetime, $\tau = 1/(k_r + k_d)$, which when substituted into Equation 36 gives:

$$k_r = (1/\tau)\phi_{II(alcohol)} \qquad \text{(Eq. 37)}$$

Note that in the special case where k_d is very small compared to k_r and $\phi_{II(alcohol)}$ is very close to 1, k_r can be equated to $1/\tau$. Using the above relationship Wagner and Schott[75] have calculated k_r, k_d, and ϕ_p for a number of substituted phenyl alkyl ketones in which ϕ_{BR} is significantly different from 1.

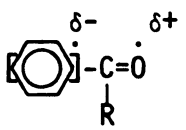
5. Effects of Ring Substituents on Reactivity and Excited State.

As mentioned before substituent effects were first noticed in the studies on benzophenone photoreduction by Bergmann and Hirshberg[64]. Later, studies by Porter and co-workers[76] were also done on the photoreductions of substituted benzophenones. In these cases the quantum yields were considered to be a measure of reactivity towards intermolecular hydrogen abstraction*. Substituents such as fluorine or bromine had little effect on the quantum yield of photoreduction. A phenyl group on one of the rings reduced the quantum yield about one

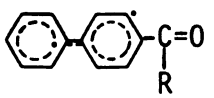
---

* Note that there may be some justification for this in the case of intermolecular hydrogen abstraction since the probability of reverse hydrogen transfer would appear to be much smaller than in the case of intramolecular hydrogen abstraction.

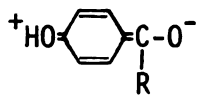
order of magnitude or wiped it out completely. Hammond and co-workers[66] also found that the quantum yields of photoreduction of di-para-methoxy- and di-para-cyanobenzophenone were one fifth and one third respectively of that of benzophenone. Porter explained his results by proposing three possible types of triplet states in the following order of reactivity: $n,\pi^* > \pi,\pi^* > C\text{-}T$ (Charge-Transfer).



n,π*



π,π*



C-T

Benzophenone and the halo-substituted benzophenones then reacted from a lowest n,π^* state which was characterized by an electron deficient oxygen. A phenyl substituent lowered the π,π^* triplet below the n,π^*, so Porter felt that the reaction in these cases must occur from the π,π^* triplet. An inconsistency in his interpretation arises where he considers the lowest triplet state in para-methoxybenzophenone to be π,π^* in nature, yet the quantum yield of photoreduction is about the same as for benzophenone. The unreactive nature of the amino- and hydroxyl- phenyl ketones was attributed to a charge-transfer state, which was stabilized in the polar solvent, isopropanol. When the amino- and hydroxy- benzophenones were irradiated in cyclohexane a small amount of photoreduction took place lending support to the argument.

The first study of the effect of phenyl substituents on the type-II photoreaction was that of Pitts and co-workers[77] in 1966. They photolyzed a number of ortho- and para- substituted butyrophenones at 3130A in alcohol and hydrocarbon solvents. The idea of a charge-transfer

state was discounted in favor of an explanation which considered two effects produced by substitution at the para- position: (1) The substituent could inductively influence the reactivity of the excited carbonyl, and (2) it could alter the electronic structure of the molecule such as to change the nature of the reacting species. High quantum yields were found for para- substituted chloro-, acetoxy-, methyl-, and fluorobutyrophenones which were considered to have an n,π* lowest triplet state. A para-methoxy group lowered the quantum yield somewhat and para-amino-, para-hydroxy-, and para-acetamido- groups completely eliminated the type-II photoproducts. However, all four substituents presumably caused the π,π* triplet to fall below the n,π* triplet in energy, making the excited ketone unreactive. The difficulties in this situation arise from attempting to correlate quantum yield and reactivity. Pitts also quenched the type-II reaction of butyrophenone using piperylene and obtained a linear Stern-Volmer plot. However, this was cited only as evidence that the reaction takes place entirely from the triplet state and no attempt was made to ascertain the triplet lifetime.

A simple explanation of the reason for rearrangement of triplet energy levels is that the perturbation of the π-electron cloud of the molecule by the substituents raises the energy of the ground state π-orbitals above the level of the non-bonding orbitals (Figure 2). The

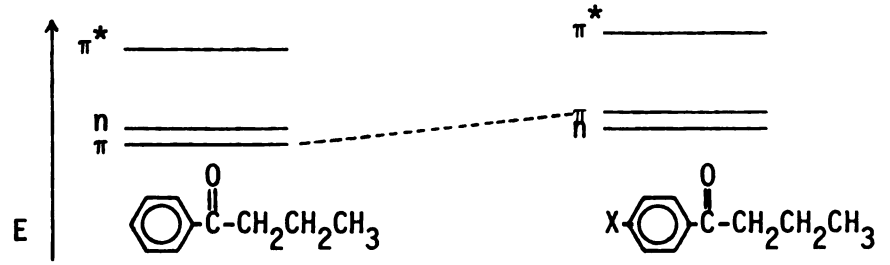


Figure 2. Effect of Ring Substituents on Triplet Energy Levels.

nature of this interchange, which is too complex for discussion here, may also involve the transfer of energy from one level to another by vibronic coupling[78] and/or as recently has been proposed by Wagner[75], thermal equilibrium between the two types of lowest triplet states. It should be pointed out here that a change in environment of the ketone molecule may also cause a switch in the triplet energy levels. Lamola[79] has shown that in a non-polar hydrocarbon glass acetophenone has a lowest n,π^* triplet state. When polar hydrogen bonding solvents are used the lowest energy triplet is π,π^* in nature. Spectroscopic studies by Kearns and Case[80] revealed both n,π^* and π,π^* triplets for several ring substituted acetophenones and indicated that they are quite close in energy. In studies on the photoreduction of substituted acetophenones Yang and co-workers[78,81] have correlated the reactivities of substituted acetophenones with their spectroscopic properties. Trifluoromethylacetophenone and acetophenone which are most reactive have n,π^* lowest triplets while para-methyl- and 3,4-dimethylacetophenone have π,π^* lowest triplets. Yang attributes the reactivity of the ketones with π,π^* lowest triplets to vibronic coupling between the two states[78].

Recently Schott[74] has found that the initial enhancement of ϕ_{II} for para-methoxyvalerophenone in benzene upon addition of tert-butyl alcohol is reversed by continued addition and in high concentrations of alcohol falls below what it was in pure benzene. This is interpreted as the result of an increasing separation between the higher n,π^* and lower π,π^* triplets as the solvent medium becomes more polar. This data is consistent with a small amount of n,π^* triplet as the reacting species in equilibrium with π,π^* triplet. Schott[74] has measured the reactivity of

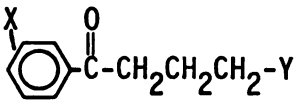
several γ-substituted para-methoxyvalerophenones and found that the relative reactivities are the same as those for the valerophenones with the same γ-substituents. Since a π,π* triplet would not be expected to show the same substituent effects as an electron deficient n,π* triplet, the theory that the reaction occurs from a small concentration of n,π* triplet is strongly supported.

6. Direction of the Research Effort.

a. General contributions to the area of molecular photochemistry. That the interest in molecular photochemistry has sky-rocketed in the last 10 to 12 years can be easily verified by thumbing through the indexes of the basic journals. However, much of what is known is qualitative in nature and very little is known of the processes occurring after excitation of the reacting compound. Thus the necessary task of collecting data, considered by some to be mundane, must be performed to provide a basis for rules and correlations. Hopefully this project will contribute to this basic area of physical photochemistry. Also, an attempt will be made to demonstrate the utility of the type-II photoelimination. In all save one[35] of the investigations which pre-date this work the product yields or quantum yields were the basis of correlations and comparisons. The type-II process has the distinct advantage of measuring the specific rate constant of γ-hydrogen abstraction and of detecting subtle changes in inductive effects on hydrogen abstraction because of its high selectivity.

b. Specific goals. The purpose of this research project was to further investigate the photochemistry of the type-II process in phenyl

alkyl ketones and extend the work of Wagner and Hammond[35] in determining structure-activity relationships. The phenyl alkyl system was chosen because of its versatility in providing numerous possible variations in the basic model:



X = ortho, meta or para substituents.

Y = alkyl, phenyl or heteroatom substituents.

Substituents on the alkyl chain would be chiefly on the γ-position, however, other positions such as β, δ, or ε could also be substituted. Also, since the type-II photoreaction for the phenyl alkyl ketones occurs entirely from the triplet state[35,65] there would be no complication from singlet products which possibly proceed by way of a different mechanism[82]. Following are some of the specific areas to be investigated:

(1) Even from the small number of examples used Wagner and Hammond concluded that the quantum yield was a poor indication of excited state reactivity. Sufficient data could be obtained to prove or disprove this generalization.

(2) The γ-alkyl position will be substituted with a variety of groups to determine the effects on the rate of hydrogen abstraction. Expected effects would be those due to C-H bond strength, steric interactions, stabilization of the radical generated, and inductive effects on the γ-carbon. Since these effects are known for free radical hydrogen abstractions, the results would be a test of a mechanism involving a 1,4-biradical intermediate.

(3) The phenyl ring will be substituted with as large a variety of substituents as is conveniently possible without changing the γ-hydrogens on the alkyl chain. This would measure the changes in reactivity of the triplet carbonyl to abstraction of the γ-hydrogens. Electron donating and withdrawing substituents should produce opposite effects if the nature of the reacting species remains unchanged. Effects of meta-substituents are as of yet uncharacterized as are those of ortho-substituents with only a few exceptions[77,83]. Some substituents which could alter the nature of the lowest triplet state by stabilizing the π,π^* level will also be studied.

(4) Solvent effects on the quantum yields of selected ketones will be studied for information on the efficiency of the biradical intermediate in going to products. This is an important test in that it indicates whether $1/\tau$ is a good representation of k_r. It was previously indicated that if $1/\tau$ is not a good measure of k_r, then k_r can be found by the relationship in Equation 37. There is also the possibility that changing the solvent will affect the nature of the lowest triplet state. Therefore, any changes noted in the reactivity when changing solvents will have to be carefully analyzed.

7. Practical Significance.

The classical, seemingly unavoidable, question of "does your research have any practical significance?" is usually answered in one of two ways: (1) A rather defiant "no" followed by a quick change of subject, or (2) a half-apologetic account of the importance of scientific curiosity. It may surprise some that the type-II photoelimination may

have application of a practical nature or utility other than that of being a scientific curiosity. Following are applications of some importance:

a. Degradation of polymers. The author well remembers being involved in a project to standardize the determination of the thickness of a uv-absorbing coating that was applied to polymer film intended for outdoor use[84]. The polymer film showed progressive degradation upon exposure to sunlight even for moderate lengths of time. Since the mechanism for the degradation was not known the only alternative was to filter out the uv light. A review published recently concludes that the photodegradation of several polymers is due for the most part to the type-II photochemical cleavage[85]. Even in cases where no original carbonyl groups are present, oxidations at some points in the chain during aging or impurities in the monomer could produce them in the polymer in sufficient amounts to cause photochemical degradation.

b. Synthesis of four-membered ring compounds. The ring closure product of the 1,4-biradical occurring during the photolysis of the phenyl alkyl and dialkyl ketones is obtained in yields ranging from poor to good. Even in the cases where the yields are low this is probably the most efficient means of synthesizing this highly strained ring system[18]. The products are in the form of cyclobutanols or oxetanols. Another synthetic possibility is the terminal olefinic product produced in the type-II cleavage. For example, 1-tridecene was formed during the photolysis of pentadecanophenone.

c. Use as a model for determining substituent effects. Although this aspect of the photochemistry of phenyl ketones is to be explored in this project, this may prove to be an important application for the type-II photoreaction in the future.

8. Definition of Terms.

The terms defined below will generally be used throughout the text without further explanation.

a. Reactivity. This term has been used in various ways in the past literature[76,77,86] although several attempts have been made to clearly define its meaning[35,38,87,71]. As used in this work, reactivity refers to the facility with which the excited carbonyl abstracts a γ-hydrogen and is expressed as a rate constant determined by quenching experiments.

b. Non-radiative decay. A means of decay of the excited triplet (of which quenching is an example) which competes with the hydrogen abstraction. Although its nature is not well understood in many cases its rate constant, k_d, can be determined.

c. Quantum yield. Quantum yields are determined by quantitative measurements of product formation or ketone disappearance. The definition of a specific quantum yield is the number of moles of a specific product formed per unit volume divided by the number of Einsteins ($\mathcal{E}$= one mole of photons) absorbed per unit volume by the reacting compound[88]. The specific quantum yields measured in this work are:

ϕ_{II} = The quantum yield of type-II cleavage product. In this work the carbonyl cleavage product was measured.

ϕ_{dis} = Quantum yield of disappearance of parent ketone.

ϕ_{cyc} = Quantum yield of cyclobutanol formation.

Also, the following probabilities are expressed in the notation of quantum yields:

ϕ_{isc} = Quantum yield of intersystem crossing from excited singlet to excited triplet state.

ϕ_{BR} = The probability of formation of 1,4-biradical from the excited triplet state.

ϕ_{p} = Probability of the 1,4-biradical going on to products.

RESULTS

1. General Explanation of Data.

The ketones with the desired substituents were prepared or purchased (See Experimental Section, Part 1, Chemicals) and purified to meet the stated criteria. Benzene, which was used as the solvent, and other compounds used were also carefully purified before use. Solutions of the ketones and an internal standard were irradiated with a medium pressure mercury lamp (3130A) for a predetermined length of time and then analyzed for product formation or ketone disappearance (See Experimental Section, Part 2, Techniques). Some of the specific characteristics of the data are described below.

a. Absolute type-II quantum yields. The type-II quantum yields for the ketones studied were determined by concurrently irradiating degassed solutions of the ketone and an actinometer (usually valerophenone). The quantity actually measured was the appearance of acetophenone product or disappearance of parent ketone. Since the ϕ_{II} for 0.10M valerophenone in benzene has been measured to be 0.33[71], all of the quantum yields reported are relative to valerophenone at this value. The product to standard ratios of the photolyzed ketone and actinometer solutions were measured by gas chromatography (VPC) (See Experimental Section, Part 2).

b. Disappearance and cyclobutanol quantum yields. Disappearance quantum yields (ϕ_{dis}) were determined by measuring a product to standard ratio of the parent ketone before and after photolysis of the sample solution. The concentrations in this case had to be quite accurately known (±0.001M) so that the number of moles of ketone actually disappearing could be accurately calculated. The same general conditions and methods

were used to determine the quantum yield for the presumed cyclobutanols. In this case, however, they were measured by appearance of products in the photolyzed samples and taken as a percentage of the parent ketone in the unphotolyzed solution. (See Experimental Procedures, Part 2)

c. Solvent effects on the quantum yields. The effect of varying the solvent on the type-II quantum yield was determined for several ketones. This was usually done by measuring the type-II quantum yield of the ketone upon gradually increasing the concentration of tert-butyl alcohol. Another method used was to substitute another solvent entirely or to modify the benzene by addition of a fixed amount of a co-solvent.

d. Stern-Volmer quenching slopes. The Stern-Volmer quenching slopes for the ketones studied were obtained by photolyzing them in solutions containing varying amounts of quencher (See Experimental Section, Part 2) and then plotting the ratio of the type-II quantum yield without quencher over the value with quencher versus the quencher concentration. The intercept on the vertical axis should be 1 and the slope represents the value of $k_q\tau$. The quencher most commomly used in this study was 2,5-dimethyl-2,4-hexadiene.

e. Miscellaneous data. Other important data which were needed or desired, such as concentration effects and quantum yields at different percent conversion, are represented graphically. The raw data is contained in Appendix A, Part 5. Results of viscosity measurements on ketone solutions are treated in the section on justification of experimental results.

2. Tabulated Results.

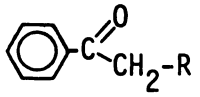
The experimental results obtained from the kinetic studies and quantum yield studies of alkyl-substituted phenyl ketones are tabulated in Table I, those for the ring-substituted phenyl ketones in Table II and the information pertaining to solvent effect studies in Table III.

a. γ-Substituted alkyl pheny ketones. The values presented for ϕ_{II} and k_r in Table I are, with a few exceptions, averages of two or more separate determinations. The variation shown is the actual experimental spread found for the determinations. For example, if two values for ϕ_{II} were measured as 0.34 and 0.36, the ϕ_{II} in the table would be 0.35 ± .01. The k_r values were determined from the least squares analysis (See Appendix B) of Stern-Volmer slopes for each individual run (Appendix A). The ketones with only one quenching run performed on them are: (1) Butyrophenone, γ-methoxy- and γ-phenylbutyrophenone, the values of which agreed closely with previously determined values[71]; (2) pentadecanophenone, of which only sufficient ketone was available for one normal run; and (3) ε-cyano- and ε-chlorohexanophenone and β-phenylbutyrophenone which were not checked because of time limitation. The data for pentadecanophenone seems reasonable based on data for similar ketones. An earlier run with β-phenylbutyrophenone using an excess amount of quencher had indicated that the $k_q\tau$ value was quite low (≈5), so the single repeat run seems to be valid. It would have been desirable to repeat the measurements for ε-cyano- and ε-chlorohexanophenone as the values are quite revealing. The ε-cyanohexanophenone was suspected of having an impurity and after one attempt at further purification the ϕ_{II} for 0.10M ketone increased from 0.24 to 0.28. The quenching slope can then be assumed to be larger

by a like percent. The prepared nonanophenone used in this work showed a sizable impurity (≈20%) in the mass spectrum which was larger by 14 atomic mass units. The octyl bromide used to prepare this ketone showed the same characteristic, as did a commercially obtained sample of nonanophenone. Analysis of the ketone by VPC showed only one sharp peak. It is believed that the impurity is the one higher homolog, decanophenone, and that no change in the photochemistry of nonanophenone occurs by its presence. It is felt that the values in Table I are quite good and should suit the purpose of this study.

The disappearance and cyclobutanol quantum yields were the result of a single run on each compound, the main purpose being a qualitative check to determine whether the type-II process was the major reaction. It is noted that δ-carbomethoxyvalerophenone has no values here as the parent ketone would not come off the VPC column. It is also noted that some of the ketones produce a quencher upon type-II cleavage. The method of handling this was to photolyze the ketone solutions to several different percent conversions and then extrapolate back to zero conversion for ϕ_{II} and $k_q\tau$. This will be explained further in the section on justification of experimental results. Other pertinent information relative to the data is included as referenced notes to the table.

b. Ring substituted alkyl phenyl ketones. The type-II quantum yields and Stern-Volmer quenching slopes for a number of ortho-, meta-, and para-substituted valerophenones are tabulated in Table II. The variation indicated is the actual spread in experimental values and each result is the average of two or more separate determinations. Each

TABLE I. Triplet-State Reactivities and Quantum Yields of Phenyl Ketones: 

Ketone (R =)	$k_q\tau$[a], M^{-1}	k_r[b] [$\times 10^7$ sec^{-1}]	ϕ_{II}	ϕ_{dis}	(ϕ_{cyc})
(Primary Hydrogens)					
$-CH_2CH_3$	568	0.88	0.35±.01[c]	0.45	0.033
$-CH(CH_3)_2$	240±3[c]	2.1	0.36±.01	0.41	0.040
$-C(CH_3)_3$	81±5	6.2	0.19±.005	0.21	0.00
(Secondary Hydrogens)					
$-CH_2CH_2CH_3$	41.0±.05	12.2	0.33±.01	0.43	0.075
$-CH_2CH_2CH_2CH_3$	38±1	13	0.30±.01	0.36	0.076
$-CH_2CH_2CH(CH_3)_2$	27±1	18.5	0.25±.01	0.35	0.074
$-CH_2CH_2C(CH_3)_3$	24±.05	21	0.24±.01	0.34	0.094
$-(CH_2)_6CH_3$	32±3	16	0.25±.01	0.33	0.078
$-(CH_2)_{12}CH_3$	28	18	0.26±.00	0.31	0.025
(Tertiary Hydrogen)					
$-CH_2CH(CH_3)_2$	10.2±.5	49	0.25±.01	0.34	0.020
(Benzyl and Allyl Hydrogen)					
$-CH_2CH_2$- 	12.3 (13.3)[e]	41 (38)[e]	0.50[d]	0.60[d]	0.056[d]
$-CH_2CH_2CH{=}CH_2$	11.3[d]	44	0.26[d]	0.33[d]	0.042[d]

[a] $k_q\tau$ is the Stern-Volmer quenching slope; $k_q = 5 \times 10^9\ M^{-1}sec^{-1}$.

[b] k_r is taken to equal $1/\tau$ for the ketones in this table.

[c] The error cited here is the actual range of values obtained for the ketone in two or more runs. For standard deviations of separate runs see Appendix A.

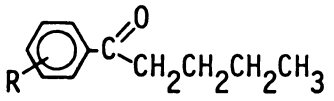
[d] Extrapolated to zero conversion to correct for product quenching.

[e] Corrected value from known percent lowering of ϕ_{II}.

TABLE I., Continued.

(Ketone (R =)	$k_q\tau, M^{-1}$	k_r [$\times 10^7$ sec^{-1}]	ϕ_{II}	ϕ_{dis}	(ϕ_{cyc})
(γ-Heteroatom Substituents)					
$-CH_2CH_2N(CH_3)_2$	0.60±.1	830	0.026±.001	0.058	0.002
$-CH_2CH_2OCH_3$	7.8±.5	64	0.23±.01	0.37	0.089
$-CH_2CH(OCH_3)CH_3$	10.5	48	0.20	0.28	0.046
$-CH_2CH_2OH$	13.0±.8	38.5	0.31±.04	0.42	0.00
$-CH_2CH_2Cl$	180±4	2.8	0.090±.005	0.34	0.003
$-CH_2CH_2COOCH_3$	490[d]	1.02	0.50[d]	0.51[d]	0.00
$-CH_2CH_2CN$	1330[d]	0.38	0.32[d]	0.72[d]	0.00
(δ-Heteroatom Substituents)					
$-CH_2CH_2CH_2CO-$ 	55±3	9.2	0.34±.03	0.34	0.055
$-CH_2CH_2CH_2COOCH_3$	131±3	3.8	0.61±.03	0.79	0.18
$-CH_2CH_2CH_2COOH$	189±2	2.6	0.56±.01	not obtained	
$-CH_2CH_2CH_2Cl$	230±5	2.2	0.58±.02	0.81	0.085
$-CH_2CH_2CH_2CN$	516±14	0.97	0.48±.02	0.57	0.045
(ϵ-Heteroatom Substituents)					
$-CH_2CH_2CH_2CH_2Cl$	88.5	5.7	0.44	0.54	0.012
$-CH_2CH_2CH_2CH_2CN$	74.5 (87)[e]	6.7 (5.7)[e]	0.24 (0.28)[e]	0.35	0.00
(α and β Substituents)					
$-CH($$)CH_3$	5	100	0.0019	0.018	0.000
$-OCH_3$	2.7±.2	185	0.54±.02	0.94	0.31

TABLE II. Triplet-State Reactivities and Quantum Yields of Phenyl Ketones:



Ketone (R =)	$k_q\tau$[a], M^{-1}	$1/\tau$ [$\times 10^7$ sec^{-1}]	ϕ_{II}[b]
ortho-CF_3	38.0 ± .4[c]	13.2	0.20 ± .01
meta-CF_3	15.5 ± .1	32.2	0.23 ± .01
para-CF_3	18 ± 1	28	0.26 ± .01
ortho-F	34.7 ± .3	14.4	0.33 ± .01
meta-F	28 ± 3	18	0.27 ± .01
para-F	34 ± 1	14.7	0.36 ± .00
ortho-Cl	141 ± 9	3.5	0.45 ± .03
meta-Cl	32.0 ± 2.5	15.6	0.33 ± .02
para-Cl	135 ± 3	3.7	0.29 ± .02
meta-CH_3	128 ± 4	3.9	0.34 ± .02
para-CH_3	272 ± 1	1.84	0.39 ± .00

[a] $k_q\tau$ is the Stern-Volmer quenching slope; $k_q = 5 \times 10^9$ $M^{-1}sec^{-1}$.

[b] ϕ_{II} determined by the appearance of the substituted acetophenone.

[c] Error where cited is the actual range of values in two or more runs. For standard deviations of each individual run see Appendix A.

TABLE II., Continued.

Ketone (R =)	$k_q\tau$, M^{-1}	$1/\tau$ [x 10^7 sec^{-1}]	ϕ_{II}
ortho-OCH_3	variable		0.20 ± .06[d]
meta-OCH_3	320 ± 30[d]		0.013 ± .003[d]
para-OCH_3	2250 ± 50	0.22	0.13 ± .01
para-SCH_3	----	----	0.000
para-OH	----	----	<0.002
[Alkyl portion = γ-methylvalerophenone]			
meta-OCH_3	(200)[e]	----	0.030 ± .001
para-OCH_3	865 ± 22	0.58	0.19 ± .02
para- 	----	----	0.0002

[d] These determinations have wide variations and should be regarded as estimates. The $k_q\tau$ values for these ketones were determined graphically and not by least squares analysis.

[e] This value is from one run which is considered to be the most reliable of a series of runs.

individual slope (with a few exceptions) was determined by a least squares computer program on the CDC-6500 (See Appendices A and B). The results which were not subjected to least squares analysis were those for ortho- and meta-methoxyvalerophenone and meta-methoxy-γ-methylvalerophenone. These ketones proved quite difficult to work with and apparently are quite sensitive to a number of variables, some of which are unknown. The values indicated are averages of the most reliable runs and the variation indicates the spread between the values. Also, the para-phenyl- and parahydroxyvalerophenone had such low quantum yields that determining a quenching slope was not practicable. The disappearance and cyclobutanol quantum yield studies are not presented for the ring substituted ketones, due in part to the practical limitation of time and to other difficulties (such as possible alternate photoprocesses) which might occur with these ketones. This aspect will also be treated in the section on indications for further study. Other information pertaining to the table is included as footnotes to Table II.

c. Solvent studies. In the latter stages of this project it became obvious that information available from solvent studies was needed. Although all ketones could not be studied, those with δ-substituents which were of a critical nature in determining inductive effects for substituents, several others which had an unusually low ϕ_{II}, and a number of the more common ketones were studied. Table III contains the data for these runs. In the first portion of the table values of ϕ_{II} with increasing tert-butyl alcohol are shown; the raw data are available in Appendix A, Part 4. The important point here is to show the highest value achieved upon addition of alcohol. One aspect of the data on

TABLE III. Data for Solvent Studies on Selected Ketones.

Ketone, 0.10M in solvent, 0.004M tetradecane standard	Solvent	ϕ_{II}	[ϕ_{II} with t-BuOH] 1.0M	3.0M	5.0M	8.0M	$k_q\tau$ [a]	ϕ_{dis}
Isovalerophenone	Benzene	0.37	0.74	0.82[b]	0.88	0.84	----	----
β,β-Dimethylbutyrophenone	Benzene	0.19	0.35	0.45[b]	0.60	0.76	----	----
γ-Methylvalerophenone	Benzene	0.26	0.58	0.74[b]	0.87	0.87	----	----
Valerophenone	Benzene	0.33	0.74	0.84[b]	1.00[c]		----	----
Hexanophenone	Benzene	0.30	0.68	0.74[b]	0.84	0.86	----	----
γ-Hydroxybutyrophenone	Benzene	0.35	0.51	0.56[b]	0.72	----	----	----
δ-Cyanovalerophenone	Benzene	0.48	0.71	0.63	0.60	0.53	----	----
δ-Chlorovalerophenone	Benzene	0.58	0.67	0.68	0.69	0.53	----	----
δ-Carbomethoxyvalerophenone	Benzene	0.61	0.72	0.77	0.75	0.73	----	----
β-Phenylbutyrophenone	Benzene	0.0019	----	----	----	0.0026	----	----
1,4-Dibenzoylbutane	Benzene	0.34	----	----	----	0.43	----	----
Valerophenone + 0.6M pyridine	Benzene	0.80	----	----	----	----	36	----

[a] $k_q\tau$ is the Stern-Volmer quenching slope, quencher used is 2,5-dimethyl-2,4-hexadiene.

[b] tert-Butyl alcohol concentration 2.0 molar.

[c] tert-Butyl alcohol concentration 6.0 molar.

TABLE III. Continued.

Ketone, 0.10M in solvent, 0.004M tetradecane standard	Solvent	ϕ_{II}	[ϕ_{II} with t-BuOH] 1.0M	3.0M	5.0M	8.0M	$k_q\tau$	ϕ_{dis}
Valerophenone	Methanol	0.92±.04	--	--	--	--	100	1.1
Valerophenone	Acetonitrile	0.85±.04	--	--	--	--	68	0.9
γ-Dimethylaminobutyrophenone	Methanol	0.25±.01	--	--	--	--	4.5±.1	0.28
γ-Dimethylaminobutyrophenone	Acetonitrile	0.05	--	--	--	--	1.5	0.10
γ-Dimethylaminobutyrophenone Hydrochloride	Methanol water	0.009±.001 0.001	--	--	--	--	720	0.070
γ-Dimethylaminobutyrophenone Ethyl Bromide	Methanol	0.0004						
para-Methylvalerophenone[d]	Methanol	0.88	--	--	--	--	2000	----

[d] Pentadecane standard used, naphthalene used as quencher.

solvent effects that is a bit disconcerting is the case of the δ-substituted valerophenones where the ϕ_{II} drops off after reaching a maximum at low alcohol concentration. This could indicate a small quenching impurity in the tert-butyl alcohol or the alcohol itself might possibly be affecting ϕ_{II}. The values are the result of a single run in most cases, some values were checked, however, and this is indicated by a spread in values. Other pertinent information is included as footnotes to the table.

d. Variation of ketone concentration. For sake of consistency all of the photochemical data were determined with 0.10 molar ketone solutions. For the results to be reliable at least 99% of the light should be absorbed by the solution and it was found for several of the ketones that were checked that the absorbance was well over 2 in the vicinity of 3130A. The ϕ_{II} at this concentration is raised somewhat because the ketone increases the polarity of the solvent medium analogous to a polar co-solvent[69]. To compare quantum yields in a non-polar medium they would have to be extrapolated to zero ketone concentration. Results with valerophenone upon addition of ethyl acetate were similar to those with increasing ketone concentration. The ϕ_{II}'s for 0.05M, 0.10M, and 0.20M valerophenone solutions were 0.31, 0.33, and 0.35 respectively[71]. When 0.10M and 0.20M ethyl acetate were added to 0.10M valerophenone the ϕ_{II} was 0.35 and 0.37 respectively. Pentadecanophenone (Figure 3, line B) has a gradual increase in ϕ_{II} with ketone concentration which resembles quite closely that of valerophenone. In the case of ketones with a polar functional group on the alkyl chain additional enhancement should be seen. The δ-benzoyl group clearly does this in the

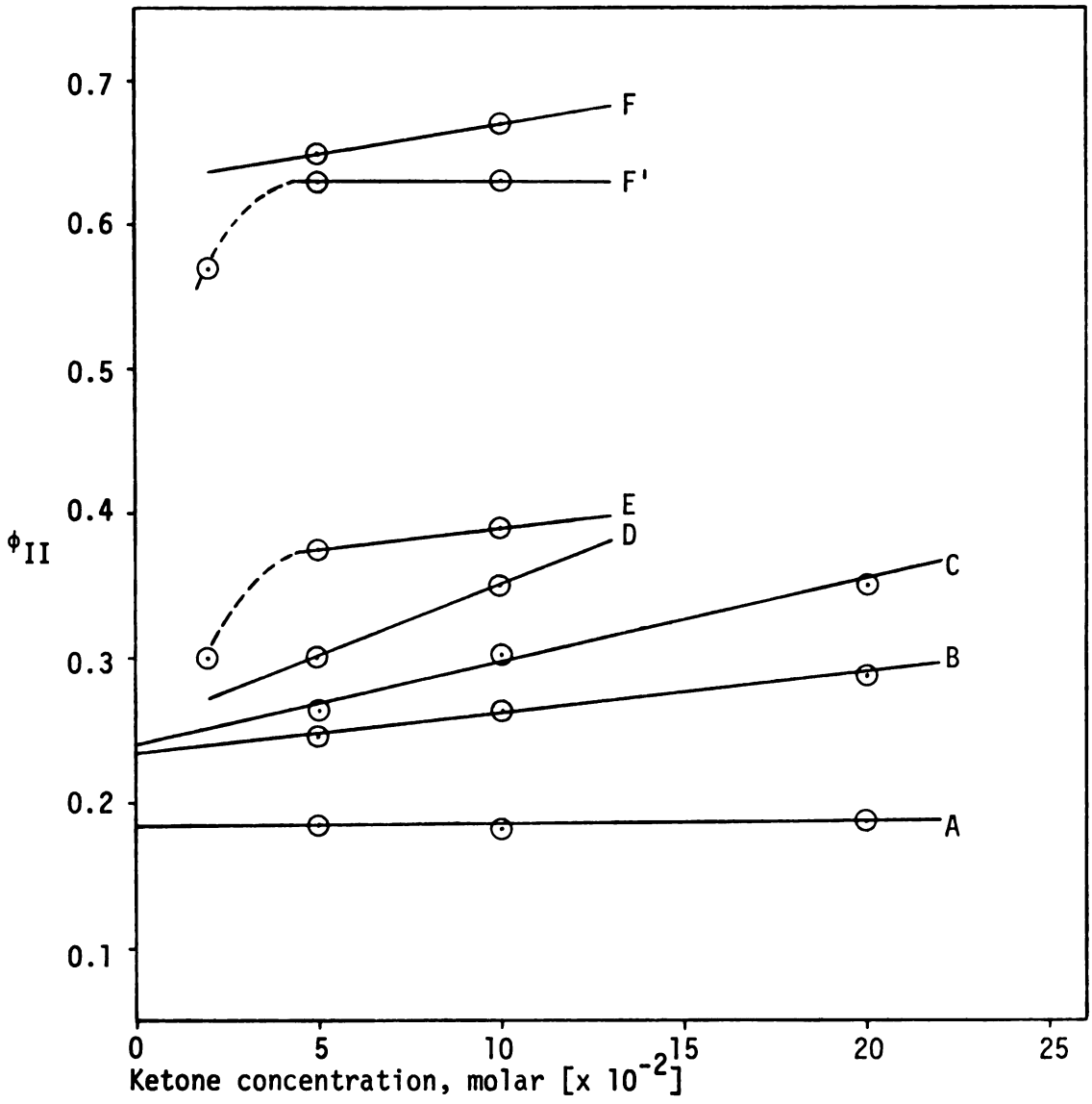


Figure 3. Relationship of Type-II Quantum Yield to Ketone Concentration for Several Ketones. [A] β,β-Dimethylbutyrophenone, [B] Pentadecanophenone, [C] 1,4-Dibenzoylbutane, [D] γ-Hydroxybutyrophenone, [E] γ-Carbomethoxybutyrophenone, and [F] & [F'] δ-Carbomethoxyvalerophenone.

1,4-dibenzoylbutane (C) and in cases where limited data is available: γ-hydroxybutyrophenone (D), γ-carbomethoxybutyrophenone (E), and δ-carbomethoxyvalerophenone (F) and (F') the trend is recognizable. However, the β,β-dimethylbutyrophenone (A), which has reactive primary hydrogens, shows very little increase with concentration. Similar behavior has been

observed for butyrophenone by others[90] so this is accepted as characteristic of these compounds. This test was also used to determine whether quenching impurities were present in the ketone being studied and will be further discussed in the section on justification of data.

3. Justification of Data and Controls Relative to Photochemical Data.

a. Identification of cyclobutanols. The term "presumed cyclobutanols" is used in this study and the symbol (ϕ_{cyc}) is enclosed in brackets because the products here presumed to be the cyclobutanols were not actually separated and identified. There is substantial evidence, however, to support the assumption that the product(s), where claimed, is the cyclobutanol(s). First, it is definitely a photoproduct appearing in significant amounts upon photolysis of most of the ketones (See page 4), and has a retention time slightly less than the parent ketone on a polar VPC column (Figure 15). Also, where cis and trans isomers of the cyclobutanols are expected, two peaks are observed in the VPC analyses (Appendix A, Part 4) in most cases. As mentioned previously the cyclobutanol from butyrophenone and the cis and trans cyclobutanols from valerophenone, γ-phenylbutyrophenone, and α-benzyloxyacetophenone have been separated and each characterized by its nmr spectrum[20]. Recently Turro and Lewis[89] separated and identified the oxetanols of α-methoxyacetophenone and several other α-alkoxyacetophenones by their nmr spectra. In the above cases, therefore, the assumption that the additional photoproduct observed is the cyclobutanol(s) has a strong basis and for the remainder of the ketones the photoproduct(s) analogous to that of the above mentioned examples is assumed to be the cyclobutanol(s). Although many of the ring substituted ketones were observed to have photoproducts which

were very likely the cyclobutanols, none are reported here.

b. Detecting quenching impurities in the ketone. Increasing the concentration of ketone would also increase the concentration of any quenching impurity which is present in the ketone and would therefore decrease the quantum yield. Most of the ketones represented in Figure 3 were tested for quenching impurities and the results indicated that no significant amount of such were present. The ε-cyanohexanophenone which was suspected of having a small amount of quenching impurity did not show as rapid an increase in ϕ_{II} as would be expected for a ketone with a polar functional group on the alkyl chain. The increase with concentration is even slightly less than that for pentadecanophenone, so it is likely that an impurity is offsetting the normal concentration effect.

Another important observation is that the good linearity of the lines A, B, and C indicates that within an experimental range of a percent or two all of the light is being absorbed by the ketone solution. What happens when this is no longer true is seen in the cases of γ-carbomethoxybutyrophenone (E) and δ-carbomethoxyvalerophenone (F') at the 0.02M ketone concentrations. The apparent quantum yield is below the extrapolated line since only 85-90% of the 3130A light is absorbed.

c. Does the type-II quantum yield vary significantly with percent conversion? With respect to the measurement of the amount of products formed upon photolysis of the ketone solutions, it was assumed that for conversions of low percentage (up to 8%) the ϕ_{II} would remain constant throughout the duration of the run. This assumption is especially critical since the quantum yields of all ketones were determined relative to

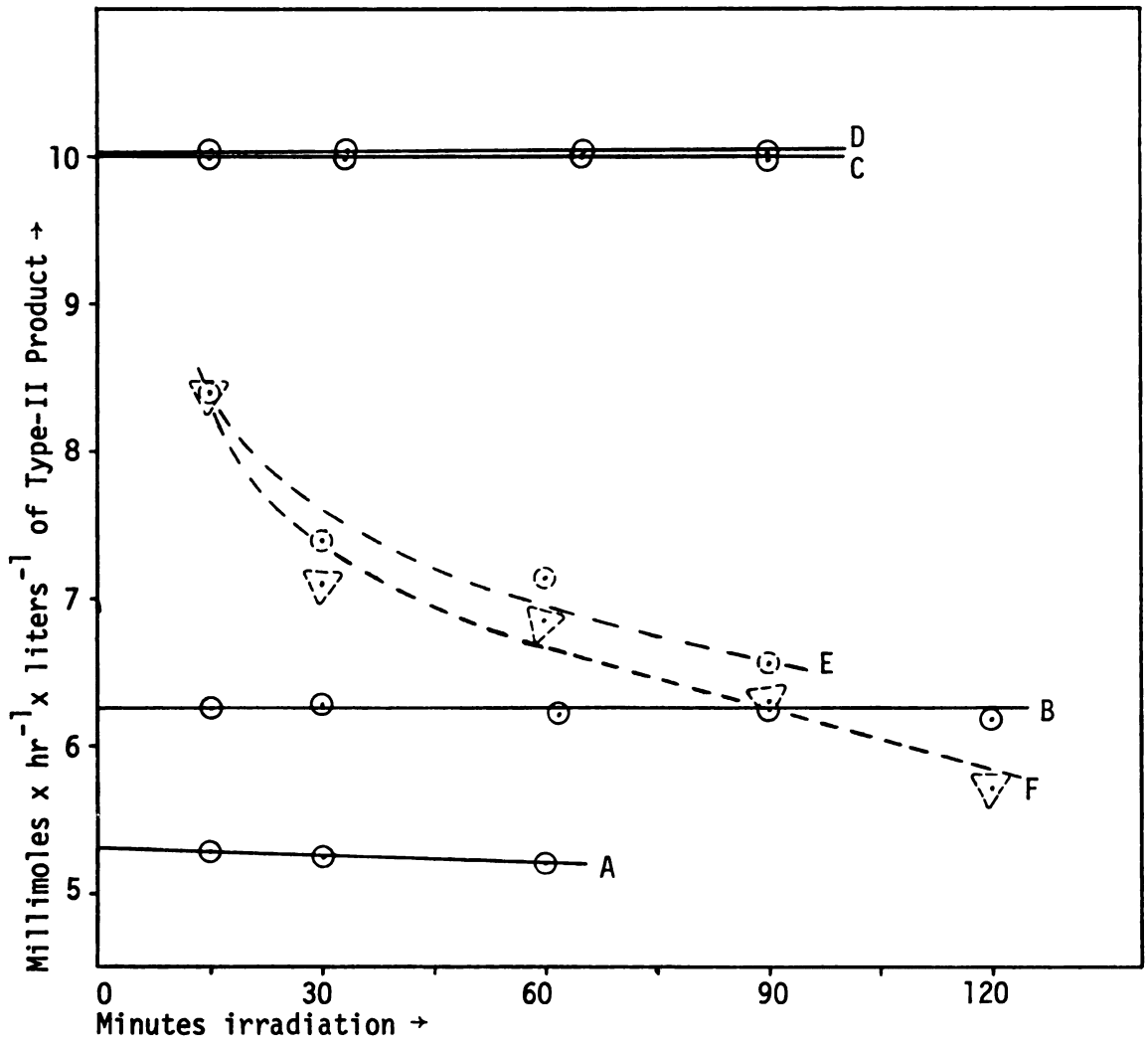


Figure 4. Product Formation Per Unit Time versus Irradiation Time. [A] & [B] 0.10M Valerophenone, [C] 0.10M & [D] 0.05M δ-Carbomethoxyvalerophenone, [E] 0.10M & [F] 0.05M γ-Carbomethoxybutyrophenone.

valerophenone by simultaneous irradiation. The only practical means of checking this would be to irradiate the ketone solution for increasing lengths of time and measure the product yield per unit time. This was done in the early stages of this work for several ketones. Here another assumption, a technical one, that the output of the mercury lamp would not vary significantly for short irradiation periods was made. For longer periods of irradiation of 10 or 20 hours the output noticeably drops

off due to mineral deposits in the cooling jacket of the lamp. Because of its importance as an actinometer valerophenone was tested several times; two typical runs are shown in Figure 4, lines (A) and (B). The millimoles of product per hour per liter is very consistent at various percent conversions, which in the case of (B) is in excess of 12%. The very slight fading noticed is undoubtedly due to slightly decreasing lamp output. The δ-carbomethoxyvalerophenone, whether 0.05M or 0.10M, had a very consistent rate of product formation out to 15% conversion for the 0.10M ketone (C) and 30% conversion for the 0.05M ketone (D). Also, the photolysis of valerophenone has been carried out to over 75% conversion with no apparent decrease in ϕ_{II}[90]. The relationships shown in Figure 4, (A), (B), (C), and (D) could have occurred only if the assumptions made were good ones, so for low percent conversions the ϕ_{II} is considered to be constant. This is not so if a quencher happens to be produced in the photolysis, as can be seen for γ-carbomethoxybutyrophenone (E) and (F). In cases where product-quenching occurs a separate treatment is used.

d. The problem of product-quenching. Four of the ketones listed in Table 1 produce an olefin fragment which acts as a quencher; these are γ-cyano-, γ-vinyl-, γ-carbomethoxy-, and γ-phenylbutyrophenone. As more product is produced the type-II quantum yield is progressively decreased, as illustrated for γ-carbomethoxybutyrophenone in Figure 4, (E) and (F). This "added" quencher decreases the $k_q\tau$ value in a quenching run because the "unquenched" samples actually are quenched. In order to have a more accurate value for $k_q\tau$ the γ-cyano-, γ-vinyl-, and γ-carbomethoxybutyrophenone were photolyzed to several different percent conversions each

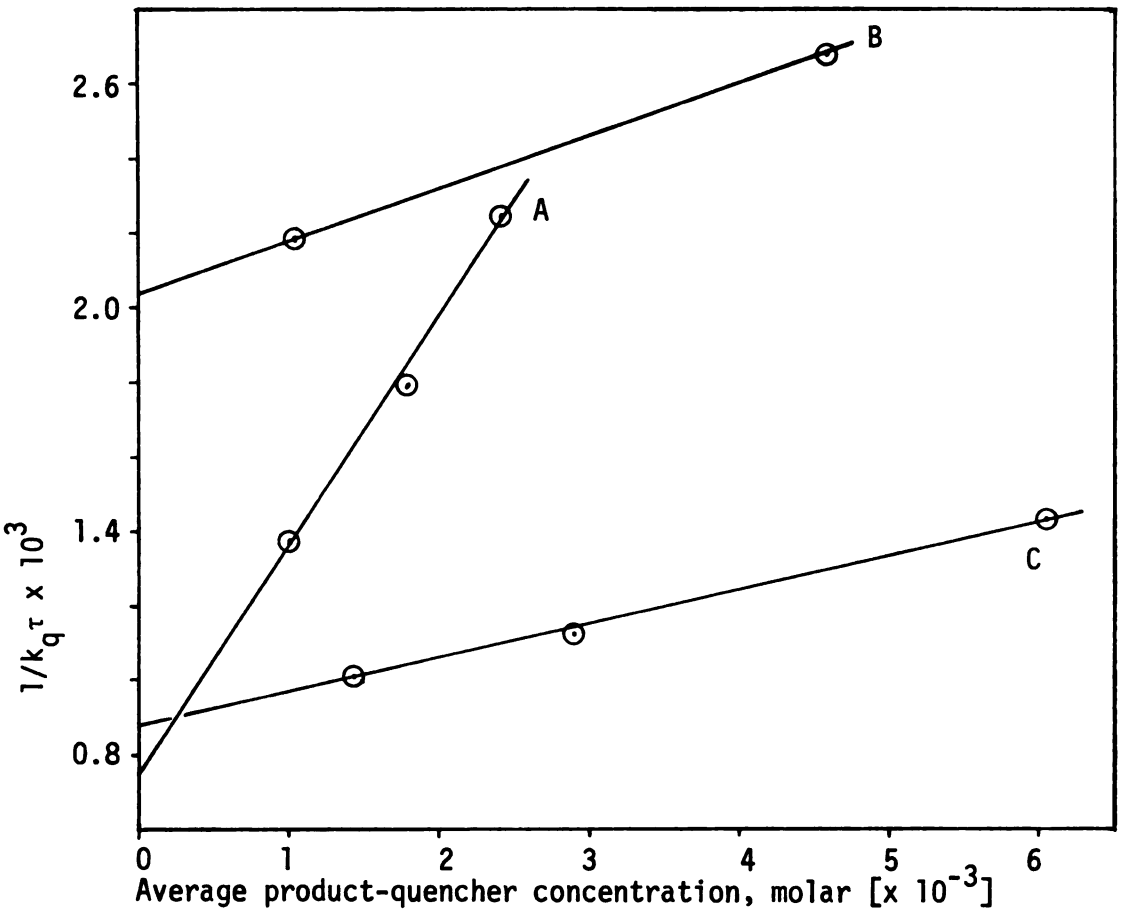


Figure 5. $1/k_q\tau$ versus Average Quencher Concentration. [A] γ-Cyanobutyrophenone, [B] γ-Carbomethoxybutyrophenone, and [C] γ-Vinylbutyrophenone (vertical scale expanded by a factor of 100).

and the reciprocal $k_q\tau$ values were plotted against one half of the product concentration (See Figure 5). The intercept at zero product concentration is taken as the best estimate of the actual $k_q\tau$. The method for finding ϕ_{II} is to plot $1/\phi_{II}$ versus the average quencher concentration (one half of the product concentration). The intercepts were determined graphically using the known data points (See Figure 6). Only one $k_q\tau$ value, at 5.6% conversion, was found for γ-phenylbutyrophenone. From the plot of $1/\phi_{II}$ versus one half the product concentration ϕ_{II} at 5.6%

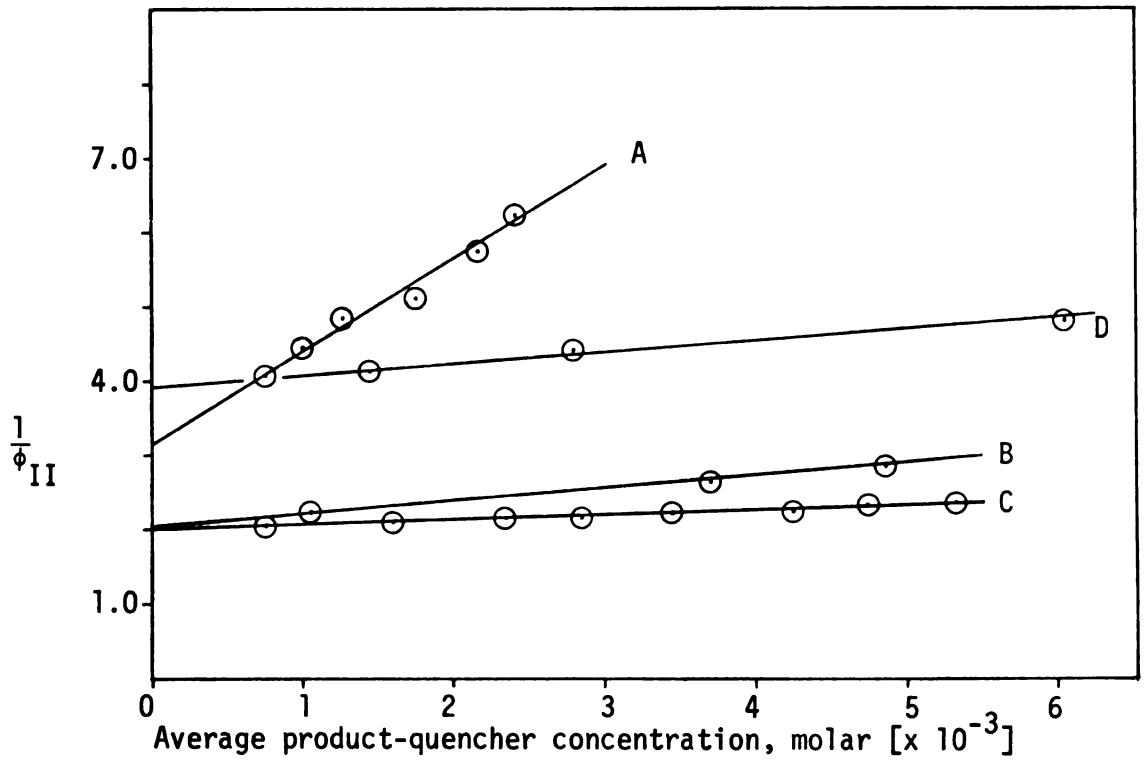


Figure 6. $1/\phi_{II}$ versus Average Quencher Concentration. [A] γ-Cyanobutyrophenone, [B] γ-Carbomethoxybutyrophenone, [C] γ-Phenylbutyrophenone, and [D] γ-Vinylbutyrophenone.

conversion is found to be 0.46. By multiplying by the same proportion needed to arrive at the extrapolated ϕ_{II} of 0.50, $k_q\tau$ would then be 13.3 at zero conversion. From the Stern-Volmer relationship (Equation 16) it is seen that $1/\phi_{II}$ is a linear function of k_q $[Q]/\phi_{o_{II}}$ with an intercept of $1/\phi_{o_{II}}$. Since $k_q\tau$ is directly related to $1/\phi_{II}$ it should also have a linear plot versus the average product concentration with an intercept of $1/k_q\tau_o$ (Figure 5). When extrapolated back to zero average product-quencher concentration the best values for the $k_q\tau$'s were found to be: γ-vinylbutyrophenone = 11.3; γ-carbomethoxybutyrophenone = 490; γ-cyanobutyrophenone = 1330. Further discussion on product quenching appears in the Discussion Section, Part 7, Indications for Further Research.

The disappearance quantum yields for these ketones are estimated by extending the plot in Figure 6. The average quencher concentration was taken as one half the ketone which disappeared (less the contribution from cyclobutanols). Then ϕ_{II} was found for this average quencher concentration and a ratio of extrapolated ϕ_{II} to product-quenched ϕ_{II} was found. The extrapolated value for ϕ_{dis} was then found by the following:

$$\phi_{dis}(Extrp) = \frac{\phi_{II}(Extrp)}{\phi_{II}(Exp)} \times \phi_{dis}(Exp) \qquad \text{(Eq. 38)}$$

Cyclobutanol quantum yields, where shown, were found in the same manner.

e. Solution viscosity. For the ketones with secondary hydrogens in Table I it is noted that as the chain length increases the $k_q\tau$ value decreases. This could be caused by a change in τ, or perhaps a change in k_q. If the solution viscosity significantly increased with some ketones k_q may be noticeably affected, since from the Debye equation (Equation 17) it is seen that k_q is inversely proportional to the viscosity coefficient η. Tests were made with pure benzene, 0.10M valerophenone and 0.004M tetradecane in benzene, and 0.10M pentadecanophenone and 0.004M tetradecane in benzene, the latter having the longest alkyl chain as well as the highest molecular weight of the ketones measured. An Ostwald viscometer was used and the liquid flow was timed with a stopwatch. The comparative times are reported as they are proportional to the viscosity coefficient[91]. Although η for the pentadecanophenone solution is larger by about 4.7% this cannot account for the decrease in $k_q\tau$ which is about 32% lower than that of valerophenone. Based on the comparison in Table IV changes in the viscosities of the sample solutions due to

TABLE IV. Viscosity Measurements for Benzene, Valerophenone, and Pentadecanophenone.

Sample Solution	Average time of 4 determinations
Pure benzene	2 min 47.8 sec
0.10M Valerophenone, 0.004M tetradecane in benzene	2 min 52.3 sec
0.10M Pentadecanophenone, 0.004M tetradecane in benzene	3 min 00.3 sec

the various ketones are considered to have a relatively minor effect on the reactivity measurements.

DISCUSSION

1. Quantum Yields of Side-Chain Substituted Ketones.

As was previously mentioned the quantum yields of product formation or ketone disappearance are the only measureable quantities and all relationships are derived from them. Table I lists the quantum yields found for the ketones with alkyl substituents. For virtually all of these ketones ϕ_{II} is determined by the behavior of the biradical, as shall be shown in the discussion of solvent effects.

a. ϕ_{dis}, a test for material balance. With only a few of the ketones studied has it been previously shown that the type-II reaction accounts for practically all of the products. In order to establish whether ϕ_{II} (plus cyclobutanols) is quantitative an independent determination was made of the quantum yield of disappearance. The quantum yield of cyclobutanol formation (ϕ_{cyc}) was also determined independent of ϕ_{II}. The condition required is:

$$\phi_{dis} = \phi_{II} + (\phi_{cyc}) \qquad \text{(Eq. 39)}$$

The ketones in Table I with hydrocarbon side-chain substituents all fulfill this condition quite well. Small discrepancies are seen for butyrophenone and γ-methylvalerophenone where the ϕ_{dis} appears larger than can be accounted for by experimental error (±4% reliability, See Experimental Section). Intermolecular hydrogen abstraction may be competing in the case of butyrophenone as photoreduction products have been reported by others[77]. This is probably not the case for γ-methylvalerophenone, however, as the tertiary hydrogen reacts about 60 times faster than the primary hydrogens of butyrophenone. It is possible that a coupling product may be formed here since both radical sites are quite stable, but

until more is known about the biradical lifetimes much of their behavior will be a matter of speculation. The low apparent (ϕ_{cyc}) for pentadecanophenone compared to the other ketones with secondary hydrogens also deserves comment. It is difficult to attribute this to any steric effect since nonanophenone has a (ϕ_{cyc}) three times larger. Also, only one peak was apparent in the VPC analysis for the cyclobutanol (Appendix A, Part 3), but this may be an analytical shortcoming. At the temperatures required for parent ketone analysis nonanophenone also appeared to have only one cyclobutanol peak, but at lower temperature two overlapping peaks could be seen.

Several of the ketones in the second half of Table I which have heteroatom substituents do not show good material balance. For example, the ϕ_{II} accounts for only 50% of the disappearance for γ-dimethylaminobutyrophenone, 75% for γ-hydroxybutyrophenone, and less than 30% for γ-chlorobutyrophenone. The difference for γ-dimethylaminobutyrophenone can be rationalized as due to intermolecular photoreduction. Amines are known to photoreduce triplet carbonyl species[92] and valerophenone has been found to have a ϕ_{dis} of 0.64 with 0.80M triethylamine present in benzene[72]. Small but significant amounts of photoreduction may also explain the difference for γ-hydroxybutyrophenone since there effectively is 0.10 molar secondary alcohol present in the solution. A few percent competing intermolecular hydrogen abstraction could account for this discrepancy. Special note is given to the fact that γ-, δ-, and ε-chloro- substituted ketones all do not satisfy Equation 39. It is tempting to attach some special significance to the chlorine in these cases. When γ-chlorobutyrophenone was photolyzed in benzene an additional photoproduct was produced in good yield which had approximately twice the

retention time on the VPC as the parent ketone. The degassed solutions turned yellow during irradiation but became colorless upon exposure to air. Although no conclusions can be drawn at this point, the observations suggest that a higher molecular weight photoproduct, possibly a dimer, is also formed and that it apparently is air sensitive. If this can be attributed to the presence of an alkyl chloride substituent, it would seem logical to assume that the δ- and ε-chloro-ketones would be similarly affected but to a lesser degree since the chlorines are further from the reaction site. This situation deserves further study to determine whether chlorine substituents do in fact play some role in the photoreaction.

For the β-phenylbutyrophenone ϕ_{II} is an order of magnitude smaller than ϕ_{dis} but even in the latter case the quantum yield is extremely small. Such small quantum yields require long irradiation periods and it would not be surprising if small amounts of photoreduction were to take place in the solution. The importance of ϕ_{dis} here is that it verifies the unreactive nature of this ketone. Possible reasons for this will be forwarded later on in the discussion. Finally, the γ-cyanobutyrophenone also falls into this category, however, the comparison must be treated cautiously. In this case the efficient quencher, acrylonitrile, is produced during the reaction and the extrapolated slope (≃1300) indicates that the reaction is very sensitive to quenching. In order for the extrapolated ϕ_{dis} to be accurate no processes competing with ϕ_{II} can occur, or if they do, they must be quenched with the same efficiency as the type-II process. Since there is no basis for making this assumption the material balance for γ-cyanobutyrophenone cannot be evaluated. The

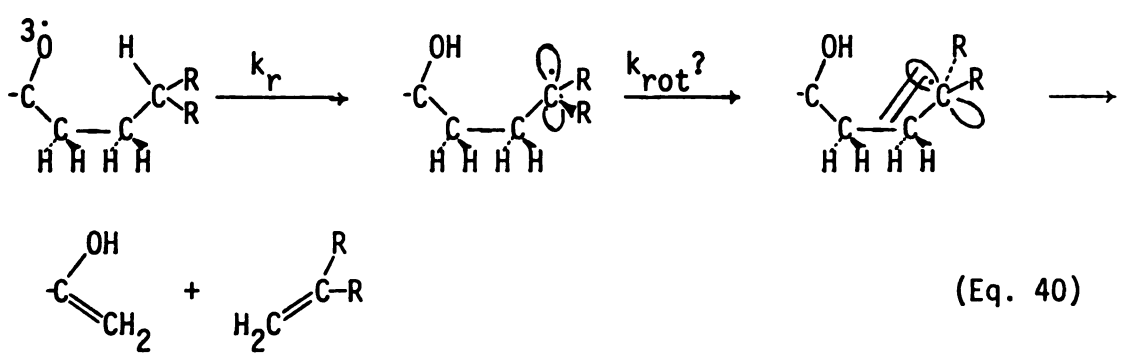
other ketones which have product quenching are much more reactive and therefore any differences in product quenching between ϕ_{II} and ϕ_{dis} would be smaller. This supposition agrees with the data. An overall view of the results of ϕ_{dis} shows that the type-II reaction accounts for virtually all of the photoreaction except in special cases where good hydrogen donating substituents are present, and apparently where reactive heteroatom substituents, such as chlorine, are present.

b. A search for steric effects on ϕ_{II}. After noting the considerable variations of ϕ_{II} caused by substituent groups on the γ-carbon, it became necessary to establish whether or not steric factors were involved. The usual low efficiency of these ketones can be attributed to revertible hydrogen transfer, however, the dimethylamino group on the γ-carbon lowered ϕ_{II} by an order of magnitude to 0.025. It seemed possible here that the substituent may have reached a critical size which interfered with hydrogen abstraction. To test this possibility ketones with alkyl groups of increasing size on the γ-position, yet all having secondary γ-hydrogens of the same reactivity, were measured. The results from this test (See Table I) are summarized below:

γ-Substituent:	$-CH_3$	$-CH_2CH_3$	$-(CH_2)_6CH_3$	$-(CH_2)_{12}CH_3$	$-CH(CH_3)_2$	$-C(CH_3)_3$
ϕ_{II}:	0.33	0.30	0.25	0.26	0.25	0.24

The tendency of ϕ_{II} is to decrease, however, the effect is seen to be gradual. The isopropyl group, which is about the same size as the dimethylamino group, causes no drastic reduction in ϕ_{II}, and neither does the tert-butyl group. It would also appear that for long straight-alkyl

chains ϕ_{II} reaches a minimum of about 0.25. It is apparent from this that little steric hindrance from the γ-substituent is involved, or at least the critical size has not been reached. It can also be inferred that the geometry required for type-II cleavage is quite close to that achieved in the psuedo 6-membered ring formed upon hydrogen abstraction. If a substantial amount of rotation or movement of the alkyl side chain through the solvent cage were required it would seem that going from a methyl to a tert-butyl group would produce a larger effect on ϕ_{II} than the approximate 25% drop observed. The trend noted as the size of the group increases can be rationalized. It was proposed by Wagner[71] that an optimum geometry for type-II cleavage of the biradical would be one in which the carbon atoms would be coplanar and in which maximum overlap between the p-orbitals of the biradical and the breaking α-β bond is present. As the biradical is formed it would tend to be pushed out of coplanarity by the eclipsing interactions of the hydrogens on the α and β carbons. This argument has also been used by Lewis and Hilliard[93] in their work on cyclization versus cleavage of substituted butyrophenones. Another source of poor overlap is possible in the case of large alkyl substituents on the γ-carbon. There may be sufficient interaction between such a group and the phenyl or hydroxyl group to skew the p-orbital

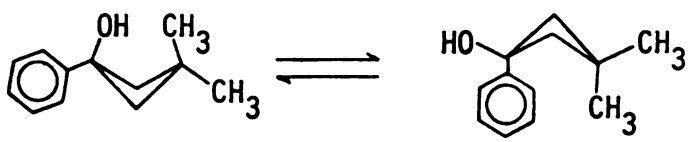


(Eq. 40)

slightly out of the plane of the carbon atoms. Both situations would

necessitate slight rotation to attain optimum overlap for type-II cleavage and this ability to rotate may be affected by increasing substituent size on the γ-carbon. The effect of increased eclipsing interactions is quite evident with two β-methyl groups as the ϕ_{II} for β,β-dimethylbutyrophenone drops to 0.19.

c. Steric effects on (ϕ_{cyc}). The fact that β,β-dimethylbutyrophenone yields a negligible amount of cyclobutanol can be attributed to a steric effect on the formation of the cyclobutane ring. The two methyl groups on the β-carbon would end up on the 3-position of the ring and would interfere with either the hydroxyl or phenyl group (Equation 41).



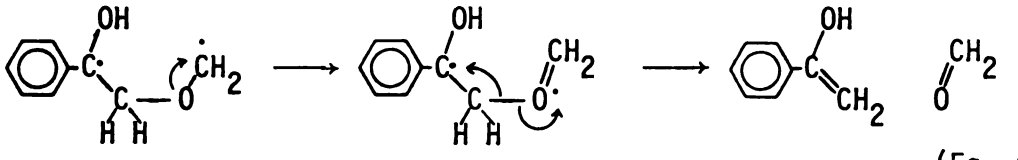
(Eq. 41)

This effect was independently found by Lewis and Hilliard[93].

It was surprising that no cyclobutanol could be detected for the γ-hydroxybutyrophenone since there would seem to be no steric problems. A unique characteristic of this cyclobutanol is that it is a 1,2-glycol and it is possible that its formation involves unusual interactions. It is also possible that the glycol either decomposes during VPC analysis or is held up for an unusually long time on the column. No cyclobutanols were observed for γ-carbomethoxy-, γ-cyano-, or ε-cyano-ketones, however, this may be due to analytical conditions so their absence is not conclusive.

The large enhancement of (ϕ_{cyc}) for α-methoxyacetophenone is almost certainly due to relief of ring strain by having an oxygen as one of the atoms in the oxetane ring. Turro and Lewis[89] found large ϕ_{cyc}'s for

several α-alkoxyacetophenones which they studied. Also, the high ϕ_{II} for this compound may result from a faster mode of type-II cleavage (Equation 42).



(Eq. 42)

d. Solvent effects on ϕ_{II}. ϕ_{II} can be influenced by either competitive decay of the triplet (quenching, for example) or by return of the biradical to form the ground state ketone. If the biradical is intercepted for some reason, ϕ_{II} would be lowered but ϕ_{dis} or k_r would not be affected. The proposed modification of the original mechanism added the steps:

$$^3K_1 \xrightarrow{k_r} [\text{Biradical}] \xrightarrow[k_{-r} \rightarrow {}^1K_0]{} \text{Product} \qquad \text{(Eq. 43)}$$

Considering the expression for the type-II quantum yield, $\phi_{II} = \phi_{BR}\phi_p$, the importance of Wagner's[69] proposal becomes obvious. When the maximum ϕ_{II} is found in alcohol solvents it can be assumed that all the biradical is going on to product, so $\phi_p \simeq 1$. This allows ϕ_{BR} to be determined by Equation 36 and k_r can be found by Equation 37. In Table I the k_r values were assumed to equal $1/\tau$. For this to be true ϕ_{II} in alcohol should be near unity to insure that the large majority of triplet is proceeding to biradical. Table V summarizes the results from Table III for those ketones which were tested. Taking (ϕ_{cyc}) in benzene into consideration and using a "rule of thumb" that a combination of ϕ_{II}(alcohol)

TABLE V. Maximum ϕ_{II} in Alcohol Sovents.

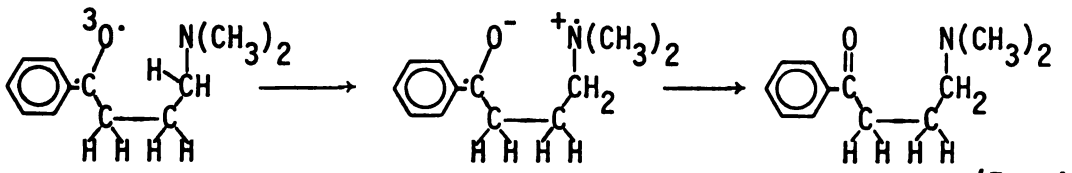
Ketone	Maximum ϕ_{II} in Alcohol	(ϕ_{cyc}) from Table I	Adjusted $k_r \times 10^7$ sec^{-1}
Isovalerophenone	0.88	0.04	none
β,β-Dimethylbutyrophenone	0.76	0.00	none[a]
Hexanophenone	0.86	0.08	none
Valerophenone	1.00	0.08	none
γ-Methylvalerophenone	0.87	0.02	none
γ-Hydroxybutyrophenone	0.72	0.00	none[a]
δ-Cyanovalerophenone	0.71	0.05	0.74
δ-Chlorovalerophenone	0.69	0.09	1.7
δ-Carbomethoxyvalerophenone	0.72	0.18	none
1,4-Dibenzoylbutane	0.43	0.06	4.5
γ-Dimethylaminobutyrophenone	0.25	0.002	208

[a] ϕ_{II}(alcohol) appears to extrapolate to higher values for these ketones (See Results Section).

plus (ϕ_{cyc}) less than 0.90 requires correction according to the relationship in Equation 37, an adjusted k_r can be calculated. The δ-substituents were specifically measured because of their usefulness in determining the inductive effects on the reactivity of the γ-hydrogens. Except for the 1,4-dibenzoylbutane fairly significant increases in ϕ_{II} were noted in alcohol, however, it is not certain that the maximum had been reached in all cases (See Results Section on solvent effects). The solvent effect on $k_q\tau$ will be treated later on in the discussion on that topic.

e. ϕ_{II} of δ-substituted ketones. With the exception again of the 1,4-dibenzoylbutane, the ϕ_{II} of the δ-substituted valerophenones is noticeably higher than those with plain hydrocarbon side chains. This increase by roughly a factor of 2 could conceivably be due in part to intramolecular hydrogen bonding which would assist in overcoming some of the eclipsing interactions. This explanation is weakened somewhat by fact that chloro and cyano groups are poor hydrogen bonders. Another possibility is that the inductive effect of the substitutent tends to polarize the radical center and retard the revertible hydrogen transfer. The 1,4-dibenzoylbutane behaves anomalously as can be seen by ϕ_{II} and ϕ_{dis}. The low value of 0.43 for ϕ_{II} in alcohol indicates that another mode of decay of the triplet is occurring with roughly equal efficiency as the hydrogen abstraction. The cause of this is not understood, however, it is possible that an energy transfer through space occurs to the other benzoyl group with reduction in the efficiency of γ-hydrogen abstraction.

f. Competitive triplet deactivation. Two ketones with very small ϕ_{II}'s deserve to be considered separately. γ-Dimethylaminobutyrophenone (ϕ_{II} = 0.025) and β-phenylbutyrophenone (ϕ_{II} = 0.002) both were quenched only slightly with diene and thus assumed to have quite reactive γ-hydrogens. In a separate study[72] evidence was found to support a charge-transfer intermediate which competes with γ-hydrogen abstraction for the triplet by a 20:1 ratio (Equation 44). The 10-fold increase in ϕ_{II} when γ-dimethylaminobutyrophenone was photolyzed in methanol may in part be attributed to hydrogen bonding of the solvent to the nitrogen making the charge transfer more difficult. The β-phenylbutyrophenone is highly



(Eq. 44)

deactivated with a ϕ_{II} in alcohol of only 0.0026. The overwhelming majority of triplet decays in preference to abstracting a γ-hydrogen. Kelso[94] has found that β,γ-diphenylbutyrophenone has a ϕ_{II} in benzene of 0.11 and a ϕ_{II}(alcohol) of 0.19. These are low compared to γ-phenylbutyrophenone which has a ϕ_{II} in benzene of 0.50 and a ϕ_{II}(alcohol) of 0.90. An excimer-complex with overlap of the keto- and β-phenyl rings is cited as a possible mode of triplet decay in this case.

2. Substituent Effects on the γ-Position.

a. Variations with C-H bond strength. One of the first results obtained was the confirmation of the predicted order of reactivity of the γ-hydrogen towards abstraction by the carbonyl triplet. It was found to parallel the already well established series according to the strength of the C-H bond being broken[95]. Table VI compares the relative reactivities for the different types of C-H bonds tested in this investigation with previous work using other hydrogen abstracting species. The ratios shown for the reactivity towards benzophenone triplet were calculated from values determined using toluene as the standard (=1). Also, some difficulty was reported in obtaining a reliable tertiary to primary reactivity ratio. If the ratio, (16:8), for two types of secondary hydrogens towards intermolecular hydrogen abstraction at 40°C are good values (there is no reason to assume they are not), then a similar ratio applied to the case of

TABLE VI. Comparison of Relative Reactivities of Carbonyl Triplet Species and tert-Butoxy Radicals.

	Triplet Species (22°C)				tert-Butoxy Radicals per-H		
	Phenyl Ketone			Benzophenone[a]	Intermolecular[b]		Intramolecular[c]
Bond Type	$k_r \times 10^7$ sec^{-1}	Per Mole	Per Hyd.	per Hyd.	(40°C)	(20°C)	(40°C)
1° C-H	0.88[d]	1	1	1	1	1	1
2° C-H	12.2	14	21	---	8	9	9
(2° C-H)	---	--	--	50[e]	16[e]	--	--
3° C-H	49	56	168	300	44	53	47

[a] Reference 34. Hydrogen donors were 2,3-dimethylbutane and n-butane except for (e) which was cyclohexane.

[b] Reference 29. Same conditions as in Reference 34.

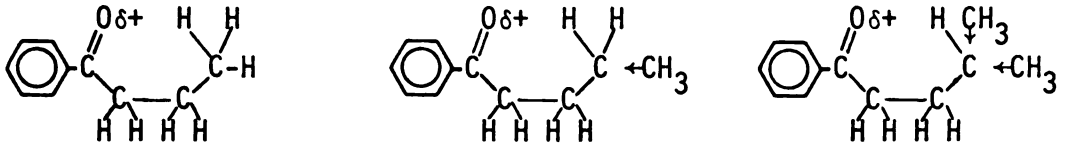
[c] Reference 32. Long chain tert-butoxy radicals were used for intramolecular hydrogen abstraction.

[d] This k_r obtained for butyrophenone may be slightly high. Earlier values obtained were 0.75 x 10^7 sec^{-1} by Wagner[71] and 0.67 x 10^7 sec^{-1} by Pitts[100].

[e] Values are for cyclohexane, see Reference 29.

benzophenone would give a relative reactivity ratio of 1:25 for the primary to penultimate secondary hydrogen. The analogy is not perfect but it is good. The relative reactivities found for the type-II intramolecular hydrogen abstraction are in the same direction as those reported for

intra- and intermolecular hydrogen abstraction by the tert-butoxy radical, and they exhibit an increasing selectivity of 3° > 2° > 1° as was reported for the case of benzophenone triplet hydrogen abstraction. One of the underlying reasons for the differences in reactivity of the various types of hydrogen can be looked at as due to the inductive effect of the methyl groups on the C-H bond undergoing attack by an electron deficient species. When substitution is made at a position one carbon re-



Increasing reactivity

moved from the carbon undergoing hydrogen abstraction the effect is diminished. A graphic comparison of the $k_q\tau$ values found for a number of phenyl alkyl ketones is shown in Figure 7. The Stern-Volmer slopes form distinguishable groups for the ketones with primary hydrogens [A], [B], and [C]; secondary hydrogens [D] through [J]; and tertiary hydrogen [M]. The effects of β-methyl groups on the k_r for primary hydrogens can be seen by the ratios 1 : 2.4 : 7.1 for butyrophenone, isovalerophenone, and β,β-dimethylbutyrophenone respectively. When statistical correction is made for the number of hydrogens the ratios are 1 : 1.2 : 2.4. The analogous case for secondary hydrogens would be valerophenone, hexanophenone (1 δ-CH_3), and δ-methylhexanophenone (2 δ-CH_3's) for which the relative reactivity ratios are 1 : 1.06 : 1.5. Although the difference is small it does appear that the inductive effect influences the less reactive primary hydrogens to a greater extent than it does the secondary hydrogens. The changes in k_r on increasing alkyl substitution are

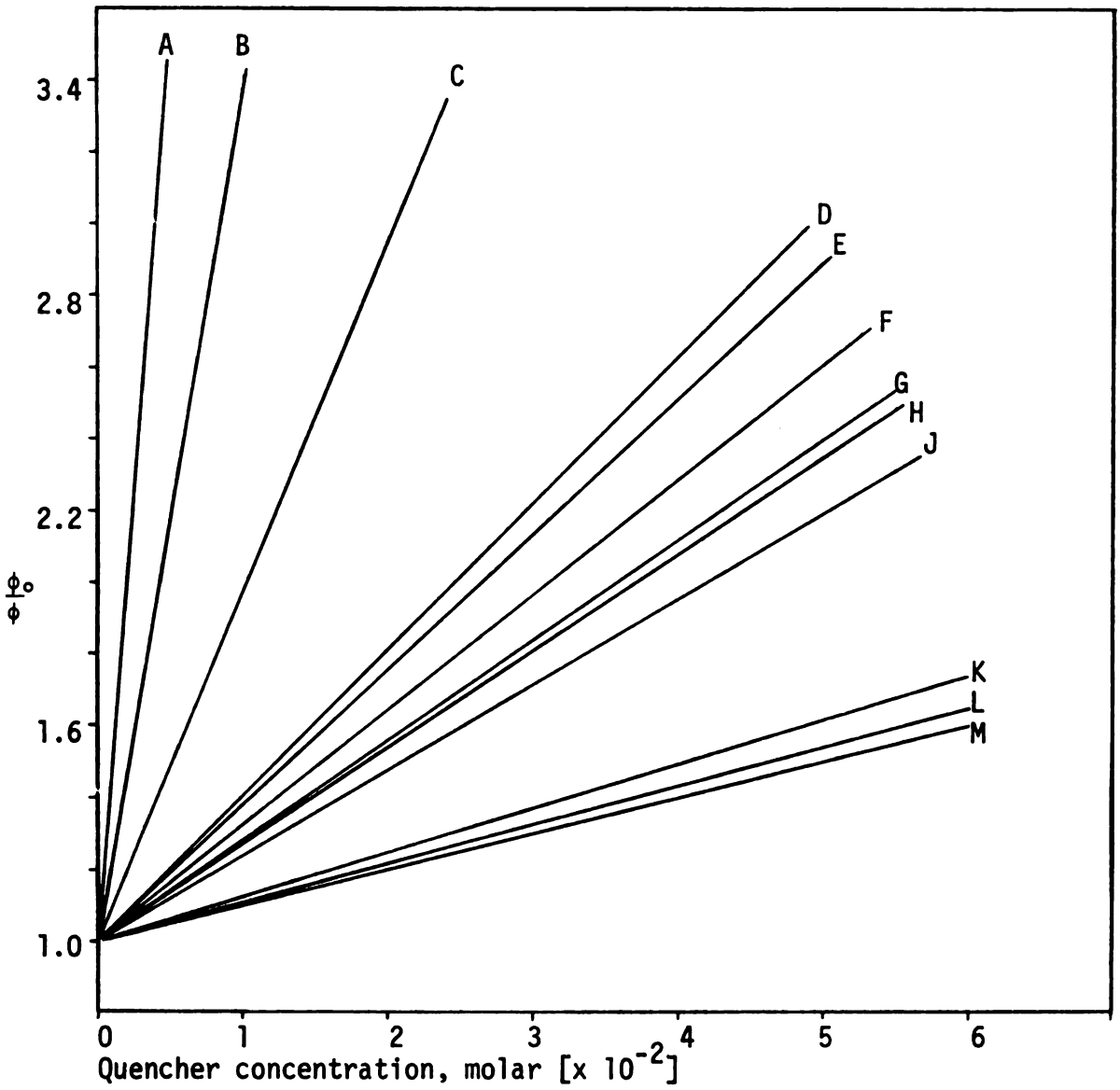


Figure 7. Stern-Volmer Quenching Slopes of Alkyl Phenyl Ketones. [A] Butyrophenone, [B] Isovalerophenone, [C] β,β-Dimethylbutyrophenone, [D] Valerophenone, [E] Hexanophenone, [F] Nonanophenone, [G] Pentadecanophenone, [H] δ-Methylhexanophenone, [J] δ,δ-Dimethylhexanophenone, [K] γ-Phenylbutyrophenone, [L] γ-Vinylbutyrophenone, and [M] γ-Methylvalerophenone.

indeed rather small for the secondary hydrogens but a trend is apparent in the reactivities which qualitatively is the order of inductive ability of the alkyl groups[96]:

$$-CH_3 < -CH_2CH_3 < -C_8H_{18} < -C_{14}H_{30} < -\underset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3 < -\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

No such comparison is available for the more reactive tertiary hydrogen [M] but any effect of substitution on the adjacent carbons would probably be small. Its reactivity is seen to be quite similar to hydrogens next to a radical stabilizing group [K] or [L]. Radical stabilization at the tertiary center most likely plays some role in the increased reactivity of the tertiary hydrogen.

b. Nonalkyl side chain substituents. When unsaturated groups, heteroatoms, or groups containing heteroatoms are substituted at the γ-position the effects are more complex. Some of the substituents affect the reactivity of the hydrogen being abstracted by both inductive and radical stabilizing effects. Work by Walling and co-workers[30,32,97] with tert-butoxy radicals shows the influence of a heteroatom substituent on the relative amounts of hydrogen abstraction as one progresses down the carbon chain from the substituent (Table VII). Substituent effects on the relative reactivities towards abstraction by benzophenone triplet have been looked at for a number of hydrogen donor compounds of which only one, benzyl hydrogen, can be compared to the present work. The results vary considerably. Padwa found a ratio of 4.6 : 1 for the relative reactivity per hydrogen for the α-hydrogens of ethylbenzene compared to toluene[98]. When this is compared to Walling's data[34] the relative reactivity per hydrogen for secondary α-benzyl hydrogen is 460 times larger than for primary alkyl hydrogen. The two sets of data are not consistent, however, as Padwa found a relative reactivity per hydrogen of tertiary hydrogen to toluene of 1.26 : 1, while Walling obtained a 3 : 1 ratio. Padwa[98] also has shown that the triplet states of propiophenone and acetophenone are similar to benzophenone triplet in their reactivity

TABLE VII. Substituent Effects on Hydrogen Abstraction by tert-Butoxy Radicals.

Substituent (H-donor)	Relative Reactivity per Hydrogen[a] at 40°C (Carbons numbered from substituent) C_1-H	C_2-H	C_3-H	C_4-H
Chloro[b] ($CH_3CH_2CH_2CH_2Cl$)	5.1	4.6	10.2	2.4[d]
Cyano[b] ($CH_3CH_2CH_2CN$)	0.67	1.3	0.67[d]	
Phenyl[c],0°C (CH_3CH_2- )	45			
Vinyl[c] ($CH_3CH_2CH{=}CH_2$)	61			
Alkoxy[c],0°C (CH_3CH_2OEt)	78			
Alkyl[c], 0°C (CH_3CH_2-R)	13			

[a] Compared to the primary hydrogens of 2,3-dimethylbutane.

[b] See Reference 30.

[c] See Reference 97. Ratios at 0°C are slightly higher than at 40°C.

[d] These values only are for the primary hydrogens at the end of the chain, other results are for secondary hydrogens.

towards a number of types of hydrogen[98]. Table VIII contains analogous values found for the type-II intramolecular hydrogen abstraction. When the effects on the reactivities by the first six substituents are compared to those found for hydrogen abstraction by tert-butoxy radicals in Table VII the similarities are striking. The ratios for the chloro and cyano substituents are nearly equal for the two methods, and for the other four substituents they are larger by a factor of about 1.4 for the type-II process. Also, the relative reactivities progressing down the side chain are almost identical for the cases where data are available.

TABLE VIII. Effects on the Type-II Intramolecular Hydrogen Abstraction of Side-Chain Substituents on Alkyl Phenyl Ketones.

	Relative Reactivity per Hydrogen at 22°C (Carbons numbered from substituent)			
Substituent [Side-chain position]	C_1-H [γ]	C_2-H [δ]	C_3-H [ε]	C_5-H
Chloro	4.8	3.8	9.7	
Cyano	0.65	1.65	[9.7][a]	
Phenyl	65			
Vinyl	75			
Methoxy	104			
Alkyl	21	22	---	27
Carbomethoxy	1.7	6.5		
Carboxy	---	4.4		
Benzoyl	---	15.7		
Hydroxy	66			
Dimethylamino	1420			

[a] This position cannot be compared to the tert-butoxy radical abstraction for which butyronitrile having C_3 primary hydrogens was used.

These results strongly suggest that the mechanism for the type-II photochamical reaction involves a hydrogen abstraction by a species similar to tert-butoxy radicals. It is also apparent that this step is influenced by inductive and radical stabilizing effects. The remainder of Table VIII lists the effects of substituents for which no data was found for comparison. An interesting observation is that the type-II process can discern between the subtle differences of a carboxylic acid and a

carboxylate ester. It should also be pointed out that all of the compounds in Tables VII and VIII involve secondary hydrogen (except where indicated) which in part accounts for the good comparisons. Existing data for radical abstraction of primary hydrogen which was sought for comparison is poor and incomplete.

Of major concern in the work with tert-butoxy radicals and benzophenone triplets were the difficulties in obtaining reliable relative reactivities. Since they had to be determined by product yields several inherent difficulties arose. The product yields depend on two steps in the cited cases: (1) Abstraction of hydrogen from donor compound by the tert-butoxy radical or benzophenone triplet, and (2) abstraction of a chlorine from a chlorine donor by the alkyl radical to give product. Although yields were high the process for benzophenone was shown not to be quantitative and in some cases significant multiple substitution was noted[34]. This causes problems in determining large ratios accurately where minute amounts of one product is formed. The reaction with tert-alkoxy radicals is complicated by β-scission of the radicals[31] and also by secondary reactions with the products[97]. In comparison the type-II process is relatively clean with very little secondary reaction. Being an intramolecular process many of the variables are removed and the entire system can be kept constant except for the substituent.

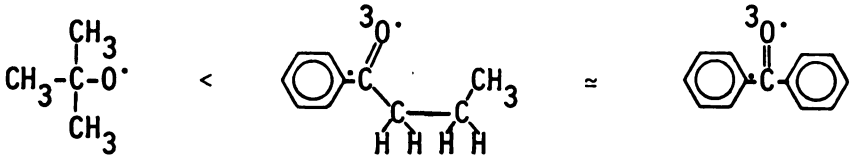
c. Comments on relative selectivities. The notion of selectivity of a radical towards abstraction of hydrogen has been rationalized by invoking their relative reactivities[95], thus for the halogens:

Increasing selectivity →

F· Cl· Br· I·

← Increasing reactivity

In comparing the present work with that of tert-butoxy radicals and benzophenone triplets, the following order is indicated for selectivity:



Qualitatively this should be the inverse order of their reactivities.

d. Quantitative relationships. Some correlations between photochemical reactivities and substituent effects have been attempted. A respectable Hammett plot was obtained for the relative reactivities of substituted toluenes towards benzophenone triplet[34]. A similar attempt with the type-II photoreaction of para-substituted butyrophenones was not as successful because the σ+ values were plotted against ϕ_{II} rather than the reactivity[77]. It is obvious from the k_r values in Table I that the γ-position is affected by both inductive and radical stabilizing effects and that no reasonable correlations are possible. In order to eliminate the effect of radical stabilization the δ-substituted ketones were measured. A Hammett plot of the log of the relative reactivities (using $k_r \times 10^{-7}$) versus the σ_I values[99] for the substituents one methylene group away from the reaction center is shown in Figure 8. In obtaining the best slope for this plot the corrected k_r values for δ-chloro- and δ-cyanovalerophenone were used (Table V). The correction improves the correlation for δ-chlorovalerophenone but the value for δ-cyanovalerophenone is shifted slightly from the best line. The reaction constant

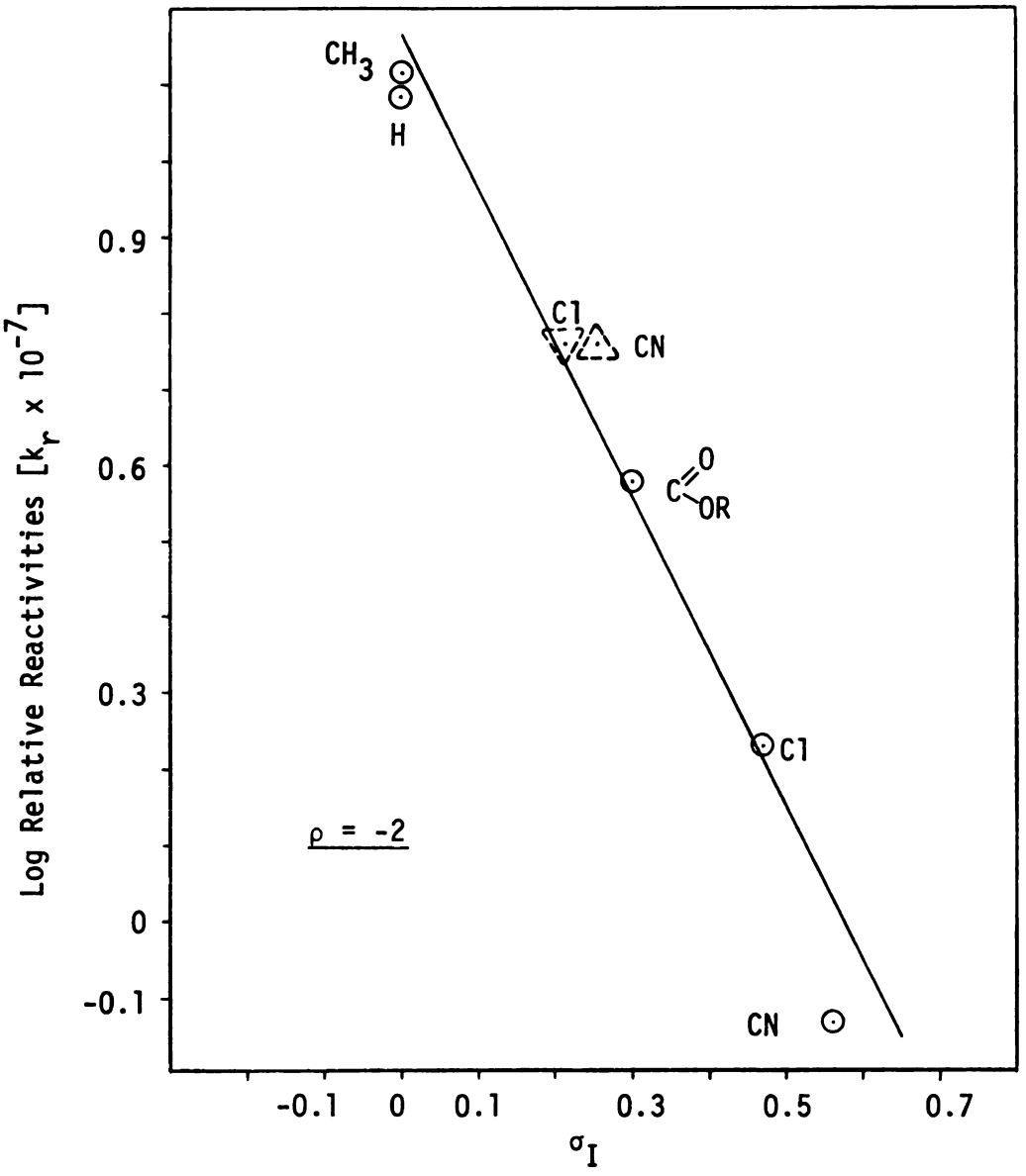


Figure 8. Hammett Plot for δ- and ε-Substituted Alkyl Phenyl Ketones. Corrected k_r values used for δ-chloro and δ-cyano ketones. ⊙= δ-substituents; △= ε-substituents.

(ρ) found from the slope is -2 for the δ-carbon. This relationship was further tested by measuring the k_r for ε-chloro- and ε-cyanohexanophenone to see whether they would correlate with a σ_I calculated by the following equation (Equation 45) for an additional interposed methylene

$$\sigma_I(X\text{-}CH_2\text{-}) = 0.45\sigma_I(X\text{-})^{99} \qquad \text{(Eq. 45)}$$

group. Excellent agreement was found for the ε-chlorohexanophenone and a fairly good one in the case of ε-cyanohexanophenone considering the known direction of the error (See Results Section). Equation 45 can also be used to calculate ρ for the γ-position since the effective σ_I would be 1/0.45 times greater, or conversely, the ρ would be larger by the same factor if σ were held constant. The ρ for the γ-position is calculated to be -4.4, a large negative value, indicating it is very sensitive to substitution and the reaction is enhanced by electron donating substituents. Knowledge of ρ for the γ-position now allows a calculation of the expected reactivity for each of the γ-substituents. It should be possible by comparing the expected and experimental reactivities to determine the contribution of radical stabilization to the overall reactivity. This data is compared in Table IX. The data admittedly could stand a bit of polish, however, the results are still highly informative. Compared to a methyl group the carboxylate ester group shows little additional stabilization of the radical and the phenyl and cyano groups are about equal in their effects. A surprising factor is the apparent high stabilizing ability of the substituents with nonbonding electrons. The order, in fact, seems to be that of their basicities:

$$-OCH_3 > -OH > -Cl$$

The γ-dimethylamino group is omitted from the table because of uncertainty over the actual k_r value. Although ϕ_{II} for γ-dimethylaminobutyrophenone has been determined to be 0.25 in methanol (Table III), it is felt that hydrogen bonding by the solvent to the amino group may be a

TABLE IX. Comparison of Experimental Reactivities to Calculated Reactivities from σ_I and Experimental ρ Value.

γ-Substituent	σ_I	$\sigma\rho$[a]	Relative[b] Reactivity	Relative[c] Experimental Reactivity	Apparent Stabilization Factor
Methyl	0.00	0.00	1.00	1.00	1.00
Phenyl	0.10	-0.44	0.36	3.1	8.6
Methoxy	0.25	-1.10	0.080	5.00	62
Hydroxy	0.25	-1.10	0.080	3.16	40
Carbomethoxy	0.30	-1.32	0.048	0.081	1.7
Chloro	0.47	-2.07	0.0085	0.23	27
Cyano	0.56	-2.46	0.0035	0.031	8.9

[a] $\sigma\rho$ = log(Expected Relative Reactivity); ρ= -4.4.

[b] Due to inductive effect only, found from $\sigma\rho$.

[c] Relative to valerophenone taken as 1.

significant factor. The complications introduced by this occurrence are (1) a change in the inductive effect of the dimethylamino group, (2) a decrease in the ability of the triplet to decay via charge transfer, and (3) a probable decrease in the radical stabilizing ability of the dimethylamino group. The degree of influence of each of these three factors is not known. If the comparison in Table IX is applied to the dimethylamino group (σ_I = 0.10) using the value of ϕ_{II}(alcohol) = 0.25 in Equation 37, then the "apparent stabilization factor" is 47. This value is in the vicinity of those of other substituents with nonbonding electrons.

An unresolved problem also exists for the γ-chlorobutyrophenone as the ϕ_{II} can account for less than one third of the ϕ_{dis}. Whether this has an effect on the apparent k_r is not yet known but it should be recalled that its behavior is quite similar to that of hydrogen abstraction by tertiary alkoxy radicals. The σ_I for the benzoyl group is not commonly found in reference texts, however, that for the acetyl group is listed as 0.28[99]. Using Equation 37 the k_r for 1,4-dibenzoylbutane is found to be 4.5×10^7 sec^{-1}. Finding the antilog of this value on the Hammett plot in Figure 8 yields a σ_I for the benzoyl group of 0.26. It would also be possible using this method to determine the inductive effect of a double bond by making δ-vinylvalerophenone and measuring its relative reactivity. This quantitative treatment has provided, probably for the first time, a means of separating out the inductive and radical stabilizing effects on hydrogen abstraction.

3. Support for a Biradical Mechanism.

Probably the strongest argument for the intermediacy of a 1,4-biradical in the type-II photochemical process has been the lack of evidence to the contrary. The current work by Kelso[70] with the optically active ketone provides the best direct evidence since racemization of the optically active γ-carbon in recovered parent ketone can only be explained by the occurrence of an sp^2 center at this position. The present work provides strong evidence for reinforcement of this mechanistic route. First it can be pointed out that the substituent effects on the relative reactivities of the type-II photoreaction closely resemble those for hydrogen by alkoxy radicals. In order for the type-II reactivities to exhibit such similar behavior the step involved must also be one of

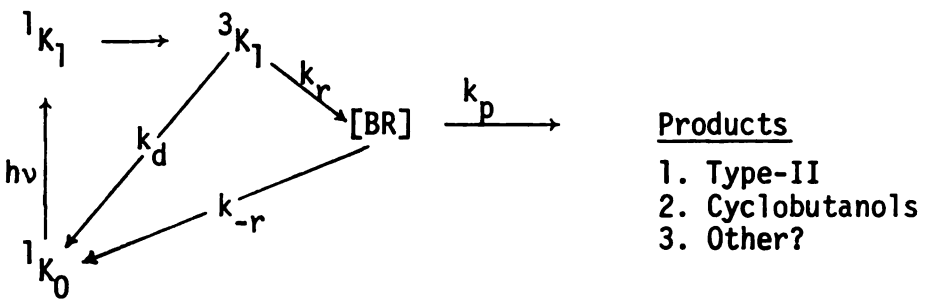


Figure 9. Schematic Representation of the Mechanism of the Photochemical Processes in the Type-II Photoreaction.

hydrogen abstraction leading to a biradical. This comparison was made for several substituent groups of alkyl and heteroatom make-up and the relative reactivities were always found to be in good agreement (See Tables VI and VII). A second indication supporting a biradical intermediate, as was pointed out by Wagner[69], is that as a hydrogen bonding cosolvent is added in increasing increments the initial effect is to increase ϕ_{II}. The opportunity for hydrogen bonding to solvent impedes the hydrogen from reverting to the radical site and effectively increases the radical lifetime. This results in larger ϕ_{II}'s which is found experimentally for a number of ketones studied (Table III). A third reason, which often tends to be underestimated, is that including the biradical step into the mechanism allows a logical explanation of the experimental observations that quantum yields and reactivities do not correlate. From the schematic representation of the mechanism in Figure 9 several important relationships can be traced. The quantum yield of biradical formation from the triplet is dependent on the relative values of k_r and k_d. Thus k_r may vary considerably yet ϕ_{BR} could be large providing k_d is small in comparison to k_r. It can also be seen that

observed quantum yields from the biradical will depend on relative values of k_p and k_{-r}, so even highly reactive ketones could have low quantum yields. The relative amounts of ϕ_{II} and ϕ_{cyc} may also vary and there may be competition from other processes such as δ-hydrogen abstraction, coupling, photoreduction, etc. If the biradical step were to be omitted from the scheme all changes in k_r would have to be accompanied by corresponding changes in k_d to account for the quantum yields. This explanation is less than satisfactory as it would require large variations in k_d for ketones with the same phenyl ketone chromophore structure. From the large number of ketones studied the observed behavior best fits a biradical mechanism.

4. Additional Solvent Effects.

a. Changes in $k_q\tau$. Besides the effect on ϕ_{II} which was discussed in a previous section other differences are noted in Table III. The measured slope changes with solvent, an effect which can usually be attributed to changes in k_q[39]. Comparison to a more commonly used ketone such as valerophenone is helpful when interpreting data for those ketones which for solubility problems must be run in methanol. Table X lists the $k_q\tau$'s for valerophenone, γ-dimethylaminobutyrophenone, and γ-dimethylaminobutyrophenone hydrochloride in three solvents. The $k_q\tau$ for valerophenone goes up in methanol by a factor of 2.5, but for γ-dimethylaminobutyrophenone it increases about 7.5 times. The increases in acetonitrile, about 1.7 and 2.5 times respectively, are not quite as far apart. An explanation for the result in methanol is that the reactivity of the γ-hydrogens of γ-dimethylaminobutyrophenone is being affected by hydrogen bonding of solvent to the amine nitrogen. By converting the

TABLE X. Effect of Solvents on $k_q\tau$.

Ketone	$k_q\tau$ in Benzene	$k_q\tau$ in Acetonitrile	$k_q\tau$ in Methanol	ϕ_{II} in Methanol
Valerophenone	41	68	100	1.00
γ-Dimethylaminobutyrophenone	0.6	1.5	4.5	0.25
γ-Dimethylaminobutyrophenone Hydrochloride	---	---	720	0.009

γ-dimethylaminobutyrophenone to the hydrochloride salt the γ-hydrogens are strongly deactivated as evidenced by a quenching slope of 720 with a ϕ_{II}(alcohol) of 0.009. For γ-dimethylaminobutyrophenone hydrochloride both disappearance and type-II quantum yields show that the process is extremely inefficient. γ-Dimethylaminobutyrophenone ethyl bromide was even less efficient with a ϕ_{II} of 0.0004 in methanol. The reason for such low efficiency is not yet understood, especially when considering that the opportunity for charge-transfer is eliminated (Equation 34). In control experiments neither 0.08M KBr nor 0.08M $(CH_3)_3NC_2H_5Br$ had any effect on the quantum yield of valerophenone in methanol. Neither should the size of the γ-substituents produce any serious steric problems. A possibility to account for the low ϕ_{II}'s could be that establishing a full positive charge next to the γ-carbon introduces serious repulsive interactions with the triplet carbonyl, or that deactivation in these cases is so strong that other means of triplet decay overwhelm γ-hydrogen abstraction. Also, since photoreduction appears to occur in preference to γ-hydrogen abstraction in these cases, it is possible that small amounts of quenching products in the methanol may have a devastating effect on $k_q\tau$ and ϕ_{II}. A more careful look at the behavior of these

ketones is needed, however, the results do give an indication of the deactivating properties of the quaternary amine group.

An interesting result was obtained when the benzene solvent was modified by making it 0.60 molar with pyridine. The ϕ_{II} increased to 0.80, which is as high or higher than with equimolar tert-butyl alcohol, but $k_q\tau$ was unaffected (Table III). This is in good agreement with the proposal[69] that the inefficiency in the type-II process in benzene is due to the biradical.

b. An estimation of biradical lifetime. It was previously mentioned that knowedge of the biradical lifetime in solution would be of help in explaining some of the photochemical behavior of the phenyl alkyl ketones. One obvious benefit in having a reliable measure of biradical lifetime would be that of determining whether anomolous behavior such as extremely low quantum yields due to the biradical. Perhaps a relative measure of this lifetime can be acheived by a kinetic treatment of the dependence of ϕ_{II} on small increments of alcohol added to the benzene solution. The biradical can be visualized as being affected as in Figure 10. In order to adapt the data to a Stern-Volmer type diagram each

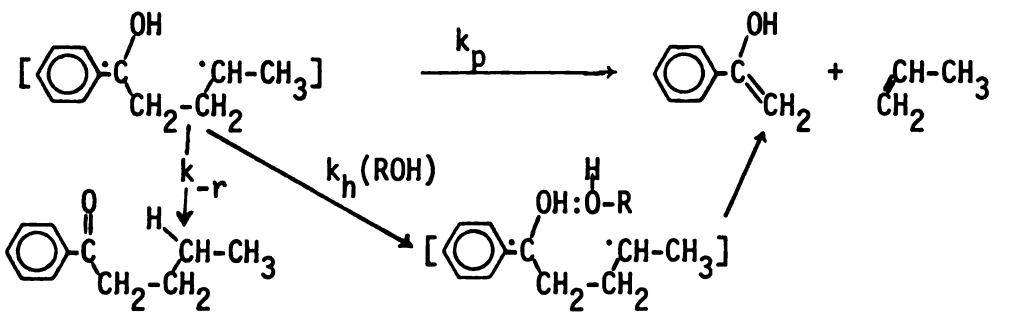


Figure 10. Hydrogen Bonding to the Biradical Intermediate in Alcohol Solvents.

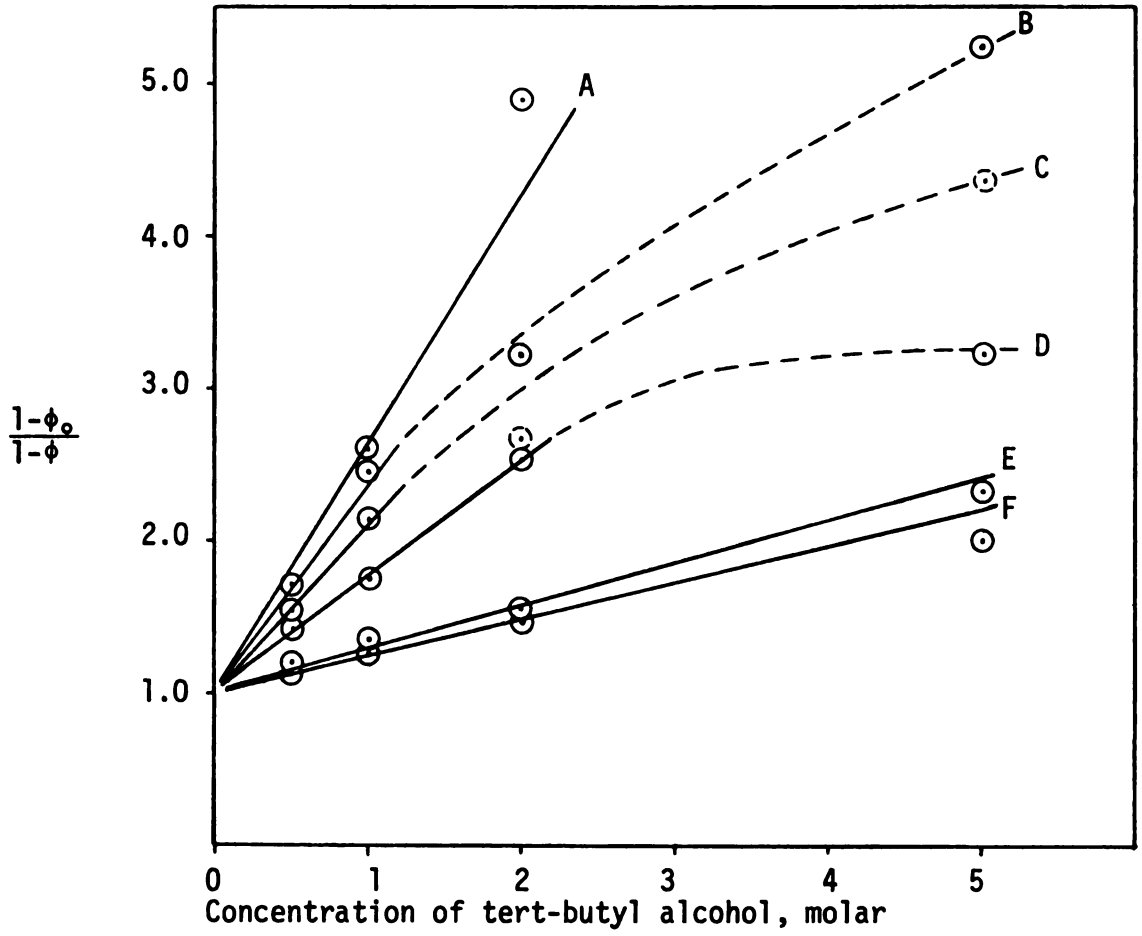


Figure 11. Stern-Volmer Type Treatment of Increasing Quantum Yields upon Addition of Alcohol Cosolvent. [A] Valerophenone, [B] Isovalerophenone, [C] Hexanophenone, [D] γ-Methylvalerophenone, [E] γ-Hydroxybutyrophenone, and [F] β,β-Dimethylbutyrophenone.

side of the equation in the normal treatment is subtracted from one.

$$1-\phi_o = 1 - \frac{k_p}{k_p + k_{-r}} = \frac{k_{-r}}{k_p + k_{-r}} \qquad \text{(Eq. 46)}$$

$$1-\phi_A = 1 - \frac{k_p + k_h(ROH)}{k_p + k_h(ROH) + k_{-r}} = \frac{k_{-r}}{k_p + k_h(ROH) + k_{-r}} \qquad \text{(Eq. 47)}$$

Then dividing $1-\phi_o$ by $1-\phi_A$ the expression becomes:

$$\frac{1-\phi_o}{1-\phi_A} = 1 + \frac{k_h(ROH)}{k_p + k_{-r}} = 1 + k_h(ROH)\beta \qquad \text{(Eq. 48)}$$

TABLE XI. Comparison of Initial Slopes [$k_h\beta$] with Type-II Quantum Yields.

Ketone	Initial $k_h\beta$	Relative[a] Ratio	ϕ_{II}
Valerophenone	1.6	6.4	0.33
Isovalerophenone	1.45	5.8	0.36
Hexanophenone	1.15	4.6	0.30
γ-Methylvalerophenone	0.75	3.0	0.25
β,β-Dimethylbutyrophenone	0.25	1.0	0.19
γ-Hydroxybutyrophenone	0.33	1.3	0.35

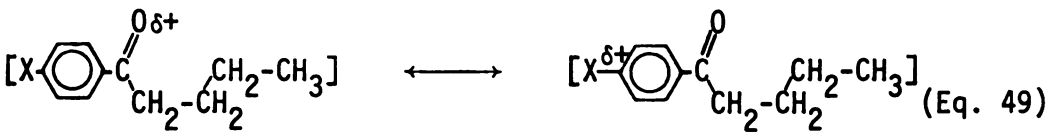
[a] The smallest $k_h\beta$ was merely taken as 1 for an easier comparison.

Here $\beta = 1/(k_p + k_{-r})$ which is proportional to the average biradical lifetime in solution, and k_h would be the effective rate of hydrogen bond formation. By plotting Equation 48 a value for $k_h\beta$ is found from the initial slope. As long as all other factors remain constant $k_h\beta$ should not change very much and the slope would represent a relative average lifetime of the biradical. In Figure 11 data for several ketones were plotted in this manner and the results are summarized in Table XI. With the exception of γ-hydroxybutyrophenone the trend of longer relative biradical lifetimes to larger ϕ_{II} is fair. In the case of γ-hydroxybutyrophenone it is possible that intramolecular hydrogen bonding interferes with k_h and alters the $k_b\beta$. The data could be improved by using smaller alcohol concentrations to determine the initial slope. This would give a more linear and accurate relationship of ϕ_{II} to increasing

alcohol concentration.

5. Effects of Ring Substituents on Triplet Reactivities.

A major area of investigation was the effect of ring substituents on the reactivity of the triplet towards γ-hydrogen abstraction. The behavior was first investigated for the methoxy and methyl groups, both electron donating in nature to the phenyl ring. As seen in Table II the $1/\tau$ decreases considerably for these compounds indicating that the reactivity has decreased. The effect is in the right direction for the concept of an electron deficient reactive n,π* triplet being deactivated by electron donating ring substituents (Equation 49). It was predicted that



(Eq. 49)

electron withdrawing groups on the ring would increase the reactivity of the triplet. This was verified for the trifluoromethylvalerophenones, especially for the meta and para isomers (Table II). These results parallel those found by Wagner and Capen[73] for the n-butyl pyridyl ketones in which the n,π* triplet is acitvated by the inductive effect of the nitrogen in the ring. A closer examination of the data for the ketones measured in Table II indicates that a simple inductive effect does not account for the observations.

a. Change in the nature of the triplet. If the $1/\tau$'s for the methoxy and methyl substituted valerophenones are compared to those for the trifluoromethylvalerophenones and valerophenone, it appears that the values in the former cases are much too large. A good indication that the inductive effect does not account entirely for their behavior can be seen

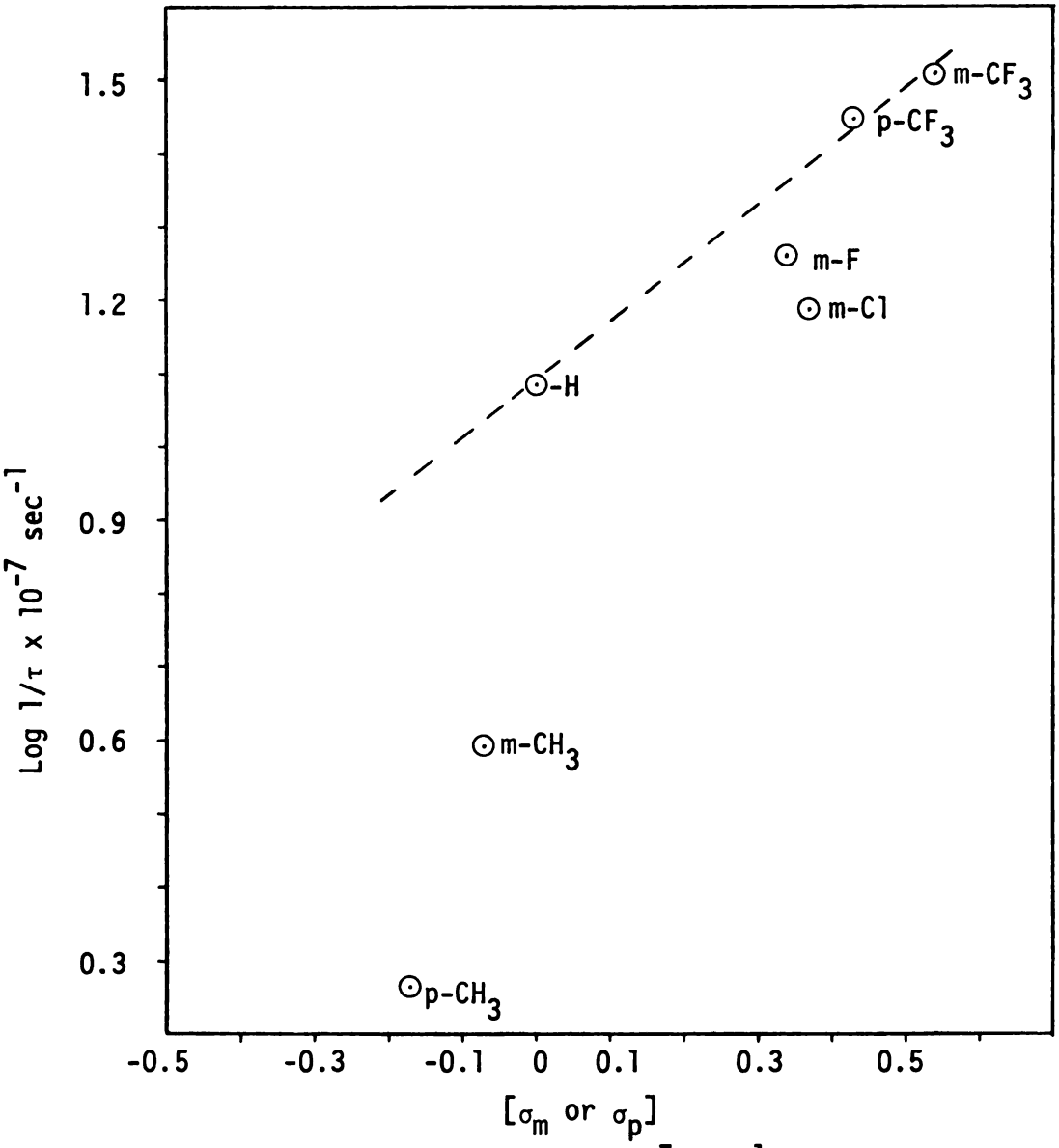


Figure 12. Log of the $1/\tau \times 10^{-7}$ sec^{-1} of Ring Substituted Phenyl Ketones versus σ_m or σ_p.

in Figure 12 in which σ_m or σ_p are plotted against the log of the $1/\tau$ values for several substituents. A poor relationship exists between the various substituents. If the meta- and para-trifluoromethyl substituents are assumed to have only an inductive effect and their log $1/\tau \times 10^{-7}$ values are taken to be on a line with that of valerophenone, then the

values for the meta- and para-methyl substituents plotted against σ_m and σ_p fall far below the line (Figure 12). Meta- and para-methoxy substituents have an even larger deviation. This behavior is explained by the rearrangement of triplet energy levels[40,76,77] under the influence of the substituent so that the nonreactive π,π^* triplet is lower in energy than the n,π^* triplet. The photoreaction which then occurs may do so from an equilibrium concentration of n,π^* triplet. According to Yang's[78,81] results it would be expected that para-methoxy-, para-methyl-, and possibly para-chloro-, and para-fluorovalerophenone would have π,π^* lowest energy triplets. The analogous meta and ortho substituted ketones may also have π,π^* lowest triplet states, however, less is known about these compounds and much of their character must be inferred from comparison to the para substituted ketones. From the data in Table II it is seen that para-methoxy-, para-methyl-, and para-chlorovalerophenones are strongly deactivated, the behavior associated with a π,π^* triplet. The fluoro substituents are interesting in that they have almost no effect on the reactivity or the ϕ_{II}. Pitts and co-workers[100] reported the same effect on fluoro substituted butyrophenones. There seems to be only a small inductive effect operating with very little, if any, effect on the nature of the triplet. This may be characteristic of the nature of fluorine substituents on an unsaturated system; to influence the sigma bonds of the molecule without affecting the π-system[101]. The high reactivity of the ring substituted fluoro-valerophenones indicates that the lowest triplet state must be n,π^* in nature.

b. The effects of meta substituents. An interesting observation of the $1/\tau$ values is that all of the meta substituted ketones have greater reactivities, or alternatively, are not deactivated as much as the

TABLE XII. Summary of $1/\tau$ [x 10^7] sec^{-1} from Table II for Ring Substituents on Valerophenone.

Substituent	ortho	meta	para
Trifluoromethyl	13.2	32.2	28
Fluoro	14.4	18	14.7
Chloro	3.5	15.6	3.7
Methyl	---	3.9	1.84
Methoxy	---	(1.6)[a]	0.22
Methoxy; γ-Methyl	---	(2.5)[a]	0.58

Valerophenone = 12.2.

[a] Estimated values, See Table II.

corresponding para or ortho substituted ketones. Two possible reasons can be given for this: (1) A more effective inductive ability from the meta position, or (2) a decreased ability of a meta substituent to effect an interchange in lowest triplet levels. Both effects may operate to varying degrees. Also, the ortho substituted ketones may not be accomodated by this explanation. A qualitative explanation of the data in Table XII is as follows: For the trifluoromethyl and fluoro substituents the triplet energy levels are relatively unaffected and the substituents activate the excited state, the trifluoromethyl groups more so than the fluoro and the meta substituents slightly more than the para. The ortho trifluoromethyl group appears to be anamolous in this situation as it behaves as if it were less activating than its para isomer by a factor of two. For the chloro ketones the meta substituent exerts a small

activating inductive effect but the ortho and para isomers appear to be deactivating the triplet significantly, possibly causing a shift in the nature of the triplet. The meta- and para-methyl groups even further deactivate the triplet, the para more so than the meta, and the meta- and para-methoxy substituents greatly deactivate the triplet towards γ-hydrogen abstraction. This is probably due to the nature of the triplet in the latter cases as para-methyl and para-methoxy substituents are believed to cause the lowest triplet to shift to π,π^*[78].

c. Qualification of "reactivity". The behavior of the ring substituted ketones has been compared using $1/\tau$ as a measure of reactivity. Data needed for determining the actual values of k_r are lacking for most of the ketones in Table II. Wagner and Schott[75] have found that for para-methoxy- and para-chlorovalerophenone and para-methoxy-γ-methylvalerophenone the ϕ_{dis}'s in alcohol are 0.26, 0.80, and 0.67 respectively. Para-methylvalerophenone was found to have a ϕ_{II} of 0.88 in methanol in which case k_r can be approximated by $1/\tau$. For the others k_r must be calculated using Equation 37. An inspection of the ϕ_{II}'s in Table II reveals that except for the methoxy substituents not much change occurs for those ketones considered so far. The trifluoromethyl ketones have ϕ_{II}'s which are lower by about 20-40%, and the ortho-chlorovalerophenone has a ϕ_{II} about 30% higher, but the rest vary only slightly from valerophenone. If the assumption is made that the probability for cleavage of the alkyl chain from the biradical does not change much, the implication is that the ratio of reverse hydrogen transfer also stays about the same when the ring is substituted. If this were the case the $1/\tau$ values for trifluoromethyl, fluoro, chloro, and methyl substituted valerophenones would be

good measures of their k_r's. For para- and meta-methoxy substituents, however, ϕ_{II}'s of 0.13 and 0.013 indicate that other processes must be competing with γ-hydrogen abstraction, especially for the meta substituent. Using the assumption just mentioned and the relation for valerophenone in Equation 50 from which ϕ_{br} can be found to be 0.33, values of

$$\phi_{II} = \phi_{br}\phi_p = 0.33 \qquad \text{(Eq. 50)}$$

$$\phi_{II}(\text{alcohol}) = 1 = \phi_{br} \qquad \text{(Eq. 51)}$$

k_r and k_d for meta- and paramethoxyvalerophenone can be estimated.

$$\phi_{II} = \frac{k_r}{k_r + k_d} \times 0.33 \; ; \quad k_r = \frac{\phi_{II}}{0.33 \times \tau} \qquad \text{(Eq. 52)}$$

Likewise, since γ-methylvalerophenone has a ϕ_{II} of 0.25 and a ϕ_{II}(alcohol) of 0.87, the relationship for meta- and para-methoxy-γ-methylvalerophenone would be:

$$\phi_{II} = \frac{k_r}{k_r + k_d} \times 0.25 \; ; \quad k_r = \frac{\phi_{II}}{0.25 \times \tau} \qquad \text{(Eq. 53)}$$

Using the values found for τ, where $1/\tau = k_r + k_d$, and substituting into Equations 52 and 53 gives the results shown in Table XIII. It is interesting that for those ketones measured the ϕ_{br} found this way is somewhat higher in value, but not drastically different, from ϕ_{BR} measured from ϕ_{II} in alcohol solvents. These results probably give a significant comparison of k_d's for meta- and para-methoxy ketones, which in the case of the meta-methoxy substituents are an order of magnitude larger than for the para-methoxy ketones. The k_r's for the meta- and para-methoxy substituents are seen to slightly different in each case. These results must of course be treated cautiously as the assumption made for ϕ_p may

TABLE XIII. Estimation of k_r and k_d for Several Ring Substituted Alkyl Phenyl Ketones.

Substituted Valerophenone	$[\phi_{br}]$	$\phi_{II}(alc)$	k_r $[x10^7]sec^{-1}$	k_d $[x10^7]sec^{-1}$
para-Methyl	1.2	0.88	1.84	---
meta-Methoxy	0.039	---	0.062	1.538
para-Methoxy	0.39	0.26	0.086	0.134
meta-Methoxy; γ-Methyl	0.12	---	0.30	2.2
para-Methoxy; γ-Methyl	0.76	0.67	0.44	0.14

not always be true (as can be seen for several ketones in Table II with ϕ_{II}'s larger than 0.33). Also, ϕ_{br} was determined from the ϕ_{II} values which makes no allowance for cyclobutanols. Results from solvent studies would be a great help in interpreting the data.

d. Powerful deactivating substituents. Three of the ring substituted ketones in Table II, para-thiomethoxy- and para-hydroxyvalerophenone and para-phenyl-γ-methylvalerophenone were found to be extremely unreactive. The ϕ_{II} and ϕ_{dis} for para-thiomethoxyvalerophenone were both found to be zero indicating that no triplet is reacting. The possibility that the methyl phenyl sulfide is quenching the reaction can be eliminated on the basis of investigations which show that phenyl ketones with a sulfur in the alkyl chain readily indergo the type-II photoreaction[102]. Also, alkyl sulfides have been found to be inefficient quenchers[103]. In previous examples where the quantum yields were on the order of 0.01 or less low ϕ_{BR}'s were found indicating that k_r was very low or that k_d was

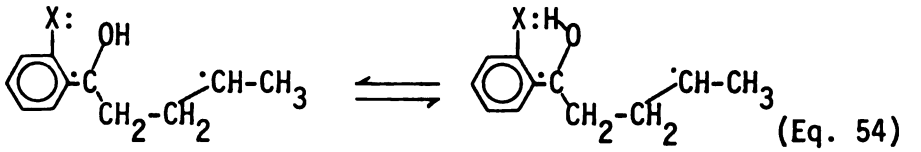
larger than usual. This must also be the situation for the three ketones in question. The very low ϕ_{II}'s indicate that the triplet states are π,π^* in nature. In terms of an equilibrium concentration the equilibrium would be displaced far towards the π,π^* triplet in these cases. Good supporting evidence for a π,π^* triplet in para-phenyl-γ-methyl- and para-thiomethoxyvalerophenone also comes from phosphorescence studies[71] which show the characteristic long lifetimes of the π,π^* triplets[79].

These results could also be consistent with Porter's[76] concept of a charge-transfer triplet. The quantum yields for these ketones are summarized in Table XIV. There is a certain logic to the argument that a correlation exists between the reactivity and the ability to stabilize a charge separation in these ketones. A difficulty may arize in the definition and connotation of the term "charge-transfer." Perhaps the ability to support a charge separation (charge-transfer?) greatly affects the rate of nonradiative decay[81] leading to the low observed quantum yields.

TABLE XIV. Type-II Quantum Yields for Highly Deactivated Phenyl Alkyl Ketones.

Substituted Valerophenones	ϕ_{II}	ϕ_{dis}	Solvent
para-Thiomethoxy	0.00	0.00	benzene
para-Hydroxy	0.002	----	benzene
para-Methoxy	0.13	----	benzene
(Unsubstituted)	0.33	0.43	benzene

e. Ortho substituents. The ortho-chloro and ortho-methoxy substituents on valerophenone are seen to increase the ϕ_{II}'s significantly (Table II). An explanation for this is difficult at this stage. There is the possibility that intramolecular "solvation" can occur with the biradical and thereby increase ϕ_p (Equation 54). The fact that the ortho-chloro- and ortho-methoxyvalerophenone, which may hydrogen bond with



(Eq. 54)

their nonbonding electrons, have higher ϕ_{II}'s than the meta and para isomers supports this. Ortho-trifluoromethylvalerophenone, which would not be expected to hydrogen bond, has a lower ϕ_{II} than its meta or para isomers. Ortho-fluorovalerophenone presents an ambiguous situation since its ϕ_{II} is smaller than its para but larger than its meta isomer.

The ortho-trifluoromethyl group has already been mentioned as decreasing the apparent reactivity of the ketone triplet when it would be expected to activate it by induction. Wagner and Capen[73] found the same relative effect with the 2-pyridyl butyl ketone. It may be that electrostatic or field effects occur involving the excited carbonyl in these cases; the nature of these effects is not known. A clue to the importance of intramolecular solvation of the biradical may be found by studying the relative effects of added increments of a hydrogen bonding cosolvent on ϕ_{II} of the ortho, meta, and para isomers of the ketones in question. The ortho-methoxyvalerophenone deserves special mention because of its variable behavior. Attempts to obtain a reliable measure of τ were hampered by large fluctuations in results from seemingly consistent

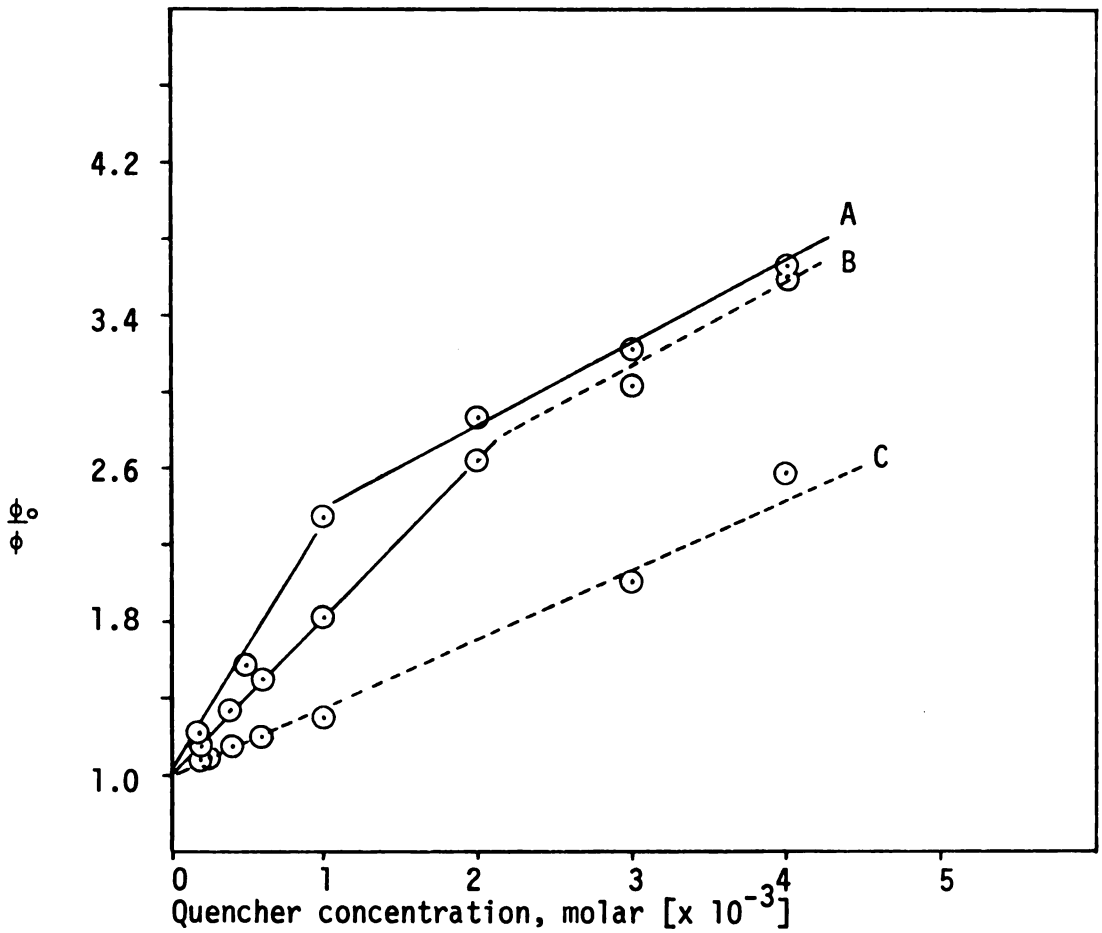


Figure 13. Stern-Volmer Quenching Slopes for ortho-Methoxyvalerophenone. [A] & [C], two similar runs photolyzed at 3130A; [B] photolyzed at 3660A.

techniques. The Stern-Volmer plots for the quenching runs in three instances are shown in Figure 13. Some of the runs exhibited high ϕ_{II}'s ($\simeq$0.25) and had a curved or "bent" graph as in line A of Figure 13. In a kinetic analysis, which is beyond the scope of this work, Wagner[104] demonstrated that the case of two reacting excited states, one being more reactive (less easily quenched) would behave in such a fashion. Yang[105] has also found similar behavior in the quenching of photocycloaddition reactions and attributes the behavior to two reacting excited states.

Wagner's and Hammond's[35] original work on quenching of dialkyl ketones which react from both the singlet and triplet excited states also have similar plots. The difference in the case of ortho-methoxyvalerophenone is that both excited states would be triplets. A quenching run was also performed on ortho-methoxyvalerophenone at 3660A (line B, Figure 13) with the result that the slope was linear out to a higher quenching ratio. The indication is that the relative amounts of the two excited states is sensitive to the energy of the light absorbed. Some of the runs had considerably lower $k_q\tau$'s as in line C, Figure 13, and at times some scatter in the points. It is quite obvious that this ketone is extremely sensitive to other variables, possibly the efficiency of degassing, efficiency of the filtration of the light source, small amounts of contaminants in the solvent, etc. Further study with these precautions in mind is warrented.

6. Summary

a. Conclusions. From the data presented in this work several conclusions of basic importance concerning the type-II photoreaction can be made.

(1) The mechanism of the type-II photochemical reaction must involve a 1,4-biradical intermediate. Evidence for this is seen in the similarity of the substituent effects on the relative reactivities towards hydrogen abstraction for the phenyl ketone triplets and tert-alkoxy radicals. Additional support comes from the observed solvent effects on the quantum yields and the fact that the quantum yields show no correlation to the measured reactivities.

(2) It has been established that the reactivity towards γ-hydrogen

abstraction correlates with σ_I substituent constants. Using the technique of determining the inductive effect of a substituent when removed by one methylene group from the reaction center, a reaction constant, ρ, can be calculated for the γ-carbon. This made possible a unique determination: The separation of the inductive and radical stabilizing effects of substituents on the reactivity towards γ-hydrogen abstraction.

(3) Substituents on the ring of alkyl phenyl ketones affect the triplet state reactivity in two principal ways, by induction and by altering the nature of the excited triplet. The latter effect is manifested by changes of much greater magnitude than the former. The large range of reactivities found for the various ring substituted valerophenones is consistent with the concept of a thermal equilibrium between n,π^* and π,π^* excited triplet states.

b. Significant observations.

(1) The type-II quantum yield (including cyclobutanols) was found to account quantitatively for the reaction products of alkyl phenyl ketones substituted on the alkyl chain except in cases where the substituent is a good photoreducing, or otherwise reactive, group.

(2) The steric effects at the γ-position on ϕ_{II} are very small over a fairly large range of substituent sizes. There is evidence, however, that a moderate effect on ϕ_{II} may occur from the eclipsing repulsions of α and β hydrogens or substituents in the planar transition state necessary for type-II cleavage.

(3) The formation of cyclobutanols is very sensitive to substituents which would sterically interfere on the cyclobutane ring.

(4) Intramolecular solvation of the biradical may account for

increased ϕ_{II}'s in certain alkyl phenyl ketones which are substituted beyond the γ-carbon or on the ortho ring position with polar substituents.

(5) The ϕ_{II} can be drastically affected by special avenues of triplet decay, such as charge-transfer and excimer-complex formation.

(6) The overall utility of the type-II photoreaction and its many advantages over other techniques makes it a valuable tool in physical organic chemistry. In the area of measuring substituent effects on reactivity, the type-II process measures the specific rate constant for hydrogen abstraction whereas the other methods depend on analyses of product yields. In determining σ_I substituent constants the type-II process has the advantage of its high selectivity, being able to discriminate between subtle changes in the substituent. The remainder of the substrate does not change for the various substituents. Also, from the known effects of hydrogen bonding solvents on the biradical, a method of measuring the average lifetime of the biradical is proposed. The results of this work show that the type-II photoreaction can be used in a variety of ways to obtain basic structure-activity relationships.

7. Indications for Further Research.

At times it would seem that finding the answer to one question would generate two or three more. Several of the unresolved problems which are substantial enough to be an interesting research project are mentioned here.

a. Photolysis of γ-chlorobutyrophenone. The additional photoproduct which was consistently observed in the γ-chlorobutyrophenone solutions deserves to be isolated and identified. This would provide information on the process competing with the type-II photoreaction. It might

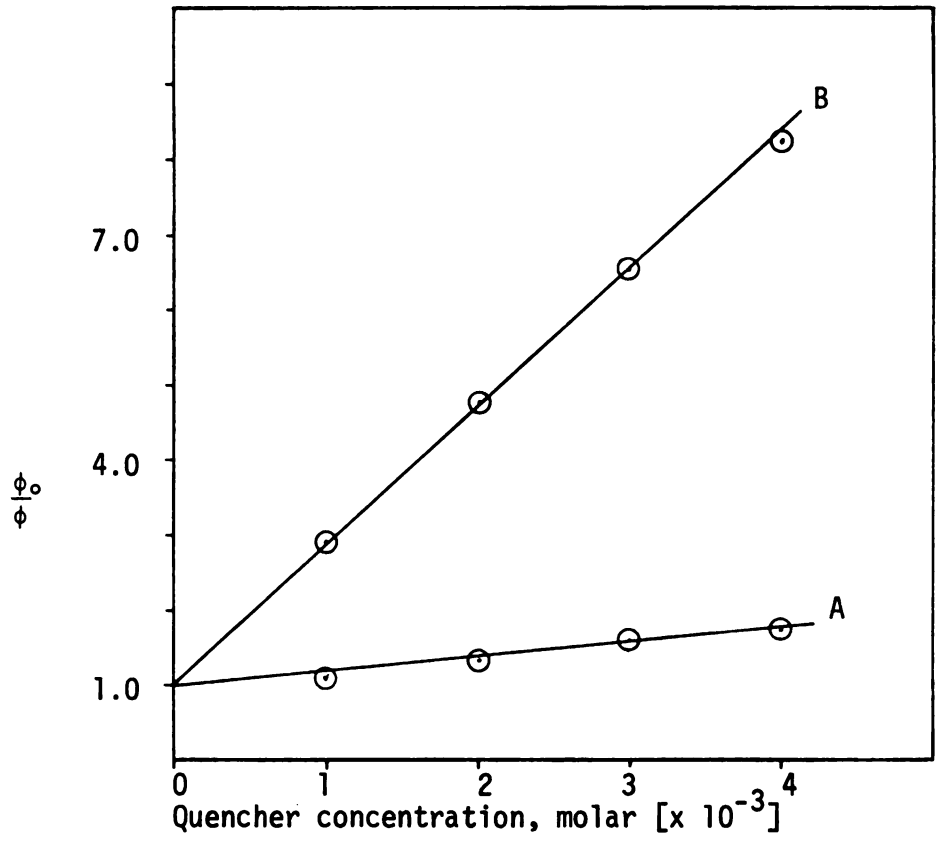


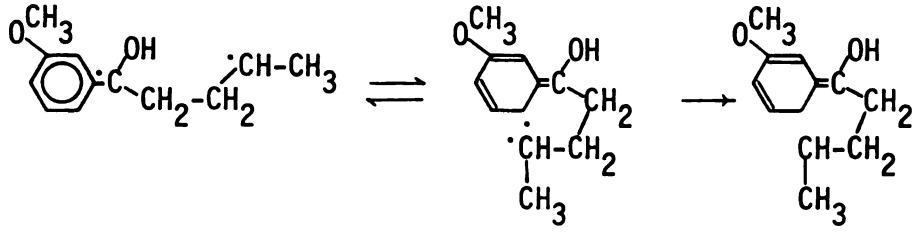
Figure 14. Stern-Volmer Quenching Slopes for meta-Methoxyvalerophenone. [A] Type-II product, [B] presumed cyclobutanols.

also be determined whether the triplet or biradical is responsible for the low ϕ_{II}.

b. Studies on the cyclobutanols for meta-methoxyvalerophenone.

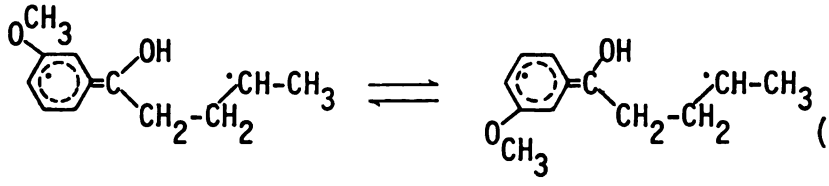
When a sample of meta-methoxyvalerophenone (which was very pure so that no interfering peaks occurred in the VPC analysis) was photolyzed, the products presumed to be the cyclobutanols were found to have about three times the quantum yield and were quenched about ten times faster (Figure 14) than the meta-methoxyacetophenone (Appendix A, Part 2). This behavior was not noted for any of the other ketones, however, the

meta-methoxy- -methylvalerophenone which may behave similarly contains large interfering impurities. It is possible that these products are not cyclobutanols but some other compounds such as ring adducts (Equation 55).



(Eq. 55)

In order to test this the photoproducts must be isolated and identified. The difference in sensitivity implies that the two photoproducts occur from different excited states. It might be noted that if the excited state of the ketone has some double bond character between the carbonyl carbon and the phenyl ring, then two forms of the 1,4-biradical can be drawn. This may be of significance as one form may favor the formation



(Eq. 56)

of cyclobutanols and/or be quenched at a different rate.

c. Wavelength studies. The results of the photolysis of ortho-methoxyvalerophenone indicate that this ketone is sensitive to the wavelength of the irradiating light. This is interesting because in this case the reaction may be occurring from two excited triplet states which are close enough in energy to be affected by changes in the wavelength of irradiating light. This should be investigated further as it would provide information on the nature of the reacting excited states.

d. The biphenyl ketone. The results with para-phenyl-γ-methylvalerophenone cannot be explained in the same terms as those for the alkyl phenyl ketones. The ϕ_{II} has been postulated as being extremely low because of the π,π* nature of the triplet. However, when an attempt was made to quench the small amount of reaction using 2,5-dimethyl-2,4-hexadiene the ϕ_{II} increased. At 0.01 molar quencher the quantum yield was four times larger. Also, 0.10 molar benzophenone or 0.05 molar triphenylene decreased the quantum yield slightly. When the biphenyl ketone was photolyzed in 1.0 molar tert-butyl alcohol the ϕ_{II} decreased, and in 8.0 molar tert-butyl alcohol a white precipitate was formed. It should also be mentioned that when the solutions in the sample tubes were held next to a mercury lamp which was filtered for 3660A light they seemed to fluoresce intensely. This may be a clue to its behavior as the triplet may be decaying rapidly by phosphorescence. Measurements of the phosphorescence quantum yield would be helpful in explaining this behavior.

e. The $k_q\tau$'s from product quenching. The ketones with carbonyl or unsaturated groups on the γ-carbon produce their own quencher during the type-II process and this required special treatment to arrive at $k_q\tau$ (See Results Section). A kinetic relationship has been worked out by Wagner and Kelso[70], and independently by Zweig and co-workers[123], which indicates that if the reciprocal of the quantum yield is plotted against the average quencher concentration (one half the percent conversion minus the cyclobutanols), the slope divided by the intercept should equal the $k_q\tau$ (Equation 57).

$$\frac{\phi-\phi_o}{[Q]/2} \times \frac{1}{\phi_o} = k_q\tau \qquad \text{(Eq. 57)}$$

TABLE XV. Comparison of $k_q\tau$ Values from Product Quenching and Diene Quenching.

Substituted Butyrophenone	$k_q\tau$ [Product quenching]	$k_q\tau$ [Diene quenching]
γ-Vinyl	42	11
γ-Phenyl	33	13
γ-Cyano	403	934
γ-Carbomethoxy	79	470

When this calculation was carried out the agreement with the $k_q\tau$ found by quenching with diene was not very good (Table XV). The most surprising result is that for γ-vinylbutyrophenone, which produces butadiene. It would be expected to have about the same value as the $k_q\tau$ for added diene quenching. The cases of the other quenching products cannot be directly compared as the relative effectiveness of quenching compared to the diene is not known (except for methyl methacrylate which was found to be about 10% as efficient as the diene)[71]. The product-quenching for the γ-carbomethoxybutyrophenone does show less quenching by a factor of 5, which is a fair comparison. It may be that a portion of the quenching is neglected in the common treatment, and that is the triplet quenching of the excited acetophenone (product) which may receive energy by energy transfer or absorption. This would cause a drop in the ϕ_{II} due to the carbonyl product in addition to that due to the olefin product. Studies to detect and characterize this effect would be important and probably help in the explanation of the discrepancies of product quenching.

EXPERIMENTAL

PART ONE. CHEMICALS

1. Preparation and Purification of the Phenyl Ketones used in Photolyses.

a. Methods of preparation. Several methods of preparation were used depending on the availability of the starting materials and the desirable characteristics of the reaction. The general methods are listed below with the ketones prepared by that method. The reagents used are given with the source in parentheses; special preparative procedures or conditions are treated in more detail. The physical properties for the prepared ketones are listed in Table XVI. The structure for each ketone was verified by its infra-red spectrum, and in most cases also by its nmr and/or mass spectrum (See Appendix C). The purchased ketones were purified according to the listed methods, the physical properties and suppliers are listed in Table XVII.

Method I. The alkyl Grignard[106] was prepared and benzonitrile or a substituted benzonitrile was added to it. In a typical preparation 0.10 moles of the alkyl Grignard was prepared from the alkyl bromide and magnesium turnings in dry ether and 0.095 moles of the nitrile was added dropwise. After a short reflux period the product was worked up by using approximately three times the stoiciometric amount of hydrochloric acid over ice cubes to insure the formation of the imine salt. The cold aqueous layer was quickly separated and placed on a steam bath for 1 to 2 hours to hydrolyze the imine salt. The resulting ketone was extracted with ether and dried over anhydrous magnesium sulfate, the ether then was removed and the ketone purified. An advantage to this method is

that the bulk of the organic impurities are eliminated in the first ether layer after formation of the imine salt. The following ketones were prepared by this method:

δ-Methylhexanophenone. Made from benzonitrile (Eastman Organic Chemicals) and 4-methyl-1-bromopentane (bp = 95-98°C at 146mm Hg). The latter was made from 4-methyl-1-pentanol (Chemical Samples Co.) and phosphorous tribromide.

δ,δ-Dimethylhexanophenone. Made from benzonitrile and 4,4-dimethyl-1-bromopentane (bp = 111-113°C at 160mm Hg). The latter was prepared from 4,4-dimethyl-1-pentene (Chemical Samples Co.) by oxidative borohydration* and reaction with phosphorous tribromide as follows:

$$(CH_3)_3CCH_2CH{=}CH_2 \xrightarrow[H_2O_2,\ OH^-]{BH_3\cdot THF} (CH_3)_3CCH_2CH_2CH_2OH \xrightarrow{PBr_3} (CH_3)_3C(CH_2)_3Br$$

Nonanophenone. Made from benzonitrile and repurified student-prepared octyl bromide. The octyl alcohol (Matheson Coleman & Bell) used to prepare the octyl bromide contains a significant amount of what appears to be nonyl alcohol.

γ-Methoxybutyrophenone. Made from benzonitrile and 3-methoxy-1-bromopropane which was prepared from 3-methoxy-1-propanol (Pfaltz and Bauer).

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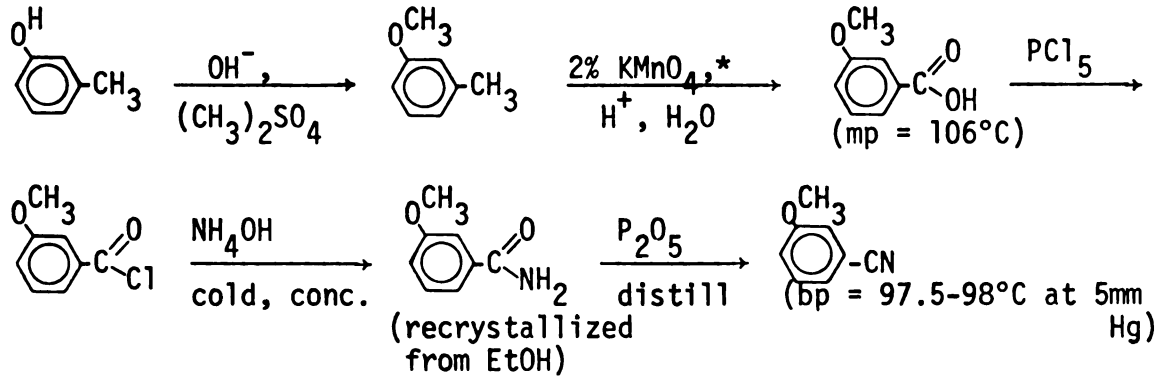
* The author is indebted to Prof. Michael W. Rathke, Michigan State University, for his assistance in the procedure for this step in the preparation.

meta-Methoxyvalerophenone. Made from 1-bromobutane (Matheson Coleman & Bell) and meta-methoxybenzonitrile which was prepared from meta-cresol (Aldrich Chemical Co.) by the following well known procedures:



*(See A. Oppenheim and S. Pfaff, Berichte, 885 (1875)).

meta- and ortho-Chlorovalerophenone. Made from 1-bromobutane and the meta- and ortho-chlorobenzonitriles (Aldrich).

meta- and ortho-Fluorovalerophenone. Made from 1-bromobutane and the meta- and ortho-fluorobenzonitriles (Columbia Organic Chemicals).

ortho-, meta-, and para-Trifluoromethylvalerophenones. Made from 1-bromobutane and the ortho-, meta-, and para-trifluoromethylbenzonitriles (Pierce Chemical Co.).

meta-Methylvalerophenone. Made from 1-bromobutane and meta-tolunitrile (Eastman).

γ-Methoxyvalerophenone. Made from benzonitrile and 1-bromo-3-methoxybutane which was made from 3-methoxy-1-butanol (Matheson Coleman & Bell) and phosphorous tribromide.

γ-Vinylbutyrophenone. Made from 5-bromo-1-pentene (Chemical Samples Co.) and benzonitrile.

Method II. Phenyl magnesium bromide was prepared[107,108] and the aliphatic nitrile or substituted nitrile was added to it. The stoichiometric amounts and work-up procedure were the same as in Method I. The resulting yields were generally lower when this method was used and a biphenyl coupling by-product was formed in some cases. Most of this was eliminated in the ether layer during work-up but any that carried over had to be carefully removed by recrystallization. The following ketones were made by Method II:

γ-Methylvalerophenone. Made from 4-methylvaleronitrile (K & K Laboratories) and bromobenzene (Fisher Scientific Co.).

γ-Chlorobutyrophenone. Made from 4-chlorobutyronitrile (Aldrich) and bromobenzene.

γ-Dimethylaminobutyrophenone. Made from 4-dimethylaminobutyronitrile (Columbia) and bromobenzene.

δ-Chlorovalerophenone. Made from 5-chlorovaleronitrile (Aldrich) and bromobenzene.

meta-Methoxyvalerophenone. Made from meta-bromoanisole (Eastman) and valeronitrile (K & K Labs). Several impurities were present in the ketone made by this method.

ortho-Methoxyvalerophenone. Made from ortho-bromoanisole (Eastman) and valeronitrile.

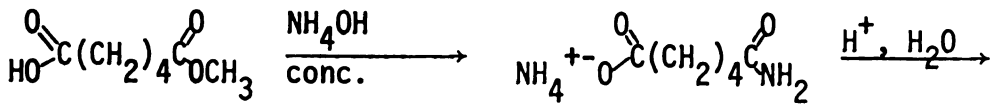
meta- and para-methoxy-γ-methylvalerophenone. Made from meta- and para-bromoanisole (Eastman) and 4-methylvaleronitrile (K & K Labs).

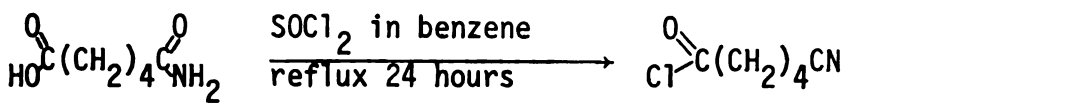
para-Thiomethoxyvalerophenone. Made from 4-bromothioanisole (Aldrich) and valeronitrile.

ε-Chlorohexanophenone. Made from bromobenzene and 6-chlorocapronitrile (Columbia).

Method III. The cadmium reagent was prepared from the corresponding Grignard reagent and anhydrous cadmium chloride[109]. In a typical preparation 0.10 moles of the Grignard reagent was prepared and anhydrous cadmium chloride (0.105 moles for phenyl Grignards and 0.055 moles for alkyl Grignards) was added. The ether solvent was replaced with benzene and the acid chloride was then added dropwise after which the solution was refluxed for 1 to 2 hours. Work-up proceded by pouring the reaction mixture into ice water and acidifying with 10% sulfuric acid solution. The ketone was then extracted, dried and purified. The following ketones were prepared by Method III:

δ-Cyanovalerophenone. Made from bromobenzene and 5-cyanovaleryl chloride. The latter was prepared from adipic acid monomethyl ester (Aldrich) as follows:





(N.E. found = 140±5) (bp = 132-133°C at 10mm Hg)

para-Methoxyvalerophenone. Made from 1-bromobutane and para-anisoyl chloride which was made from para-anisic acid (Aldrich) and phosphorous pentachloride.

meta-Methoxyvalerophenone. Made from 1-bromobutane and meta-anisoyl chloride prepared as shown in Method I.

meta- and para-methoxy-γ-methylvalerophenones. Made from 3-methyl-1-bromobutane (Aldrich) and the meta- and para-anisoyl chlorides as above.

Method IV. The corresponding aliphatic acid chloride was dissolved in a large excess (10 to 15 fold) of pure benzene and 1.1 moles of anhydrous aluminum chloride per mole of acid chloride was added[110]. The reaction mixture was protected with a drying tube and allowed to stir overnight in the hood. The ketone was obtained by pouring the mixture into ice water, acidifying to clear the solution, and extracting with ether. The following ketones were made by method IV:

γ-Methylvalerophenone. Made from 4-methylvaleryl chloride (Eastman) and benzene (Fisher).

β,β-Dimethylbutyrophenone. Made from tert-butyl acetyl chloride (Aldrich) and benzene.

para-Phenyl-γ-methylvalerophenone. Made from 4-methylvaleryl chloride and biphenyl (Eastman) in benzene solution.

Method V. Occasionally the alkyl substituents on the phenyl ketone can be altered. If the carbonyl group must be protected the ketal is made and the required operation performed on the ketal (for example, substitution[111] or reduction[112]). The following ketones were made by substitution or alteration of the alkyl group on the phenyl ketone:

γ-Hydroxybutyrophenone. Student-prepared β-benzoyl propionic acid, made from succinic anhydride (Fisher) and benzene via the Friedel-Crafts reaction, was repurified by recrystallization from chloroform and converted to the ethyl ester (bp = 158°C at 8mm Hg). The ketal of ethyl β-benzoylpropionate was made by refluxing with ethylene glycol (Fisher) and a trace of benzene sulfonic acid in a benzene solution. The water was removed via a Dean-Stark trap, the ketal-ester was isolated, and the ester was reduced with lithium aluminum hydride in ether. The procedure followed was that of Ward[112]; the only changes were that the work-up of the reduced ketal was accomplished with a dilute sodium bisulfate solution and the hydrolysis of the ketal with a 1% sulfuric acid solution.

γ-Cyanobutyrophenone. The ketal of γ-chlorobutyrophenone (prepared by Method II) was prepared as in the case of ethyl β-benzoylpropionate and reacted with sodium cyanide in dimethylsulfoxide (Matheson

Coleman & Bell) at 85-90°C[111]. The reaction mixture was then diluted with an equal volume of water and the ketone extracted with pentane.

ε-Cyanohexanophenone. Made from ε-chlorohexanophenone (prepared by Method II) by reacting with sodium cyanide in dimethyl sulfoxide.

γ-Dimethylaminobutyrophenone hydrochloride. A solution of γ-dimethylaminobutyrophenone (made by method II) in benzene was vigorously stirred while a slow stream of anhydrous hydrogen chloride was passed over the surface of the solution. The crystals were filtered off and purified.

γ-Dimethylaminobutyrophenone ethyl bromide. A solution of γ-dimethylaminobutyrophenone and a 3 to 4 fold excess of ethyl bromide in pentane was allowed to sit, with occasional swirling, for 4 days. The crystals were filtered off and purified.

Method VI. In two cases the alkyl ester was prepared by reacting the corresponding acid with diazomethane. The diazomethane was prepared from N-methyl-N-nitrosourea and base[113] and was added to an ether solution of the acid until decolorization no longer took place. The ketones prepared this way were γ-carbomethoxybutyrophenone from 4-benzoylbutyric acid, and γ-carbomethoxyvalerophenone from 5-benzoylvaleric acid (both acids from Aldrich).

b. Methods of purification. Purification of the ketones often proved to be the most difficult step. The method which most

TABLE XVI. Physical Data for Synthesized Ketones.

Ketone Formula/ Molecular Weight*	Physical Properties	Method of Preparation. % Yield	Method of Purification.
β,β-Dimethylbutyrophenone $C_{12}H_{16}O$ 176.259	bp = 127-128°C at 21mm Hg 107-108°C at 8mm Hg	Method IV 83%	Distillation, column chromatography, and redistillation.
γ-Methylvalerophenone $C_{12}H_{16}O$ 176.259	bp = 122°C at 9.5mm Hg 94-95°C at 4mm Hg mp = -0.5°C	Method II 34-86% Method IV 86%	Distillation, recrystallization first from methanol and then from pentane, and redistillation.
δ-Methylhexanophenone $C_{13}H_{18}O$ 190.286	bp = 136-137°C at 8.5mm Hg	Method I 46%	Distillation.
δ,δ-Dimethylhexanophenone $C_{14}H_{20}O$ 204.313	bp = 140-142°C at 8.5mm Hg 141°C at 7.5mm Hg	Method I 40%	Distillation, column chromatography, and redistillation.
Nonanophenone $C_{15}H_{22}O$ 218.340	bp = 145-147°C at 5mm Hg 140-141°C at 3mm Hg	Method I 37%	Recrystallized from methanol, column chromatographed and redistilled.
γ-Hydroxybutyrophenone $C_{10}H_{12}O_2$ 164.196	mp = 28-30°C	Method V 50%	Recrystallized from carbon tetrachloride.

* The molecular weights were calculated from the latest table of atomic weights adopted by the IUPAC. See Chem & Engr News, 48, #4, p. 39 (January 26, 1970).

Ketone Formula/ Molecular Weight	Physical Properties	Method of Preparation. %Yield	Method of Purification
γ-Methoxybutyrophenone $C_{11}H_{14}O_2$ 178.223	bp = 103-104°C at 1.1mm Hg	Method I 20%	Distillation.
γ-Chlorobutyrophenone $C_{10}H_{11}OCl$ 182.650	bp = 122-128°C at 5mm Hg 110-111°C at 2.5mm Hg	Method II 36%	Distillation.
γ-Vinylbutyrophenone $C_{12}H_{14}O$ 174.235	bp = 127-127.5°C at 8mm Hg	Method I Prepared by Dr. P. J. Wagner 56%	Distillation.
γ-Methoxyvalerophenone $C_{12}H_{16}O_2$ 192.258	bp =	Method I Prepared by Dr. P. J. Wagner.	Distillation.
γ-Dimethylaminobutyrophenone $C_{12}H_{17}ON$ 191.274	bp = 132-133°C at 6mm Hg 117°C at 3mm Hg	Method II 50-56%	Distillation. Small impurity remains, less than 0.01%.
γ-Dimethylaminobutyrophenone Hydrochloride $C_{12}H_{18}NOCl$ 227.735		Added HCl to ketone in benzene.	Recrystallized from absolute ethanol.
γ-Dimethylaminobutyrophenone Ethyl Bromide $C_{14}H_{22}ONBr$ 300.240		Added ethyl bromide to ketone in pentane. 94%	Rinsed with pentane during filtration.

Ketone Formula/ Molecular Weight	Physical Properties	Method of Preparation. % Yield	Method of Purification
γ-Carbomethoxybutyrophenone $C_{12}H_{14}O_3$ 206.233	bp = 137-137.5°C at 2mm Hg mp = 18-19°C	Method VI 90%	Distillation.
γ-Cyanobutyrophenone $C_{11}H_{11}ON$ 173.215	bp = 139-142°C at 2mm Hg mp = 39°C	Method V 49%	Distillation, recrystallization from ethanol-petroleum ether mixture.
δ-Chlorovalerophenone $C_{11}H_{13}OCl$ 196.669	mp = 49-51°C	Method II Made by Dr. P. J. Wagner.	Recrystallization from hexane. Purified by Dr. P. J. Wagner.
δ-Cyanovalerophenone $C_{12}H_{13}ON$ 187.234	mp = 69-71°C	Method III 24%	Recrystallization first from ethanol-petroleum ether mixture, then from carbon tetrachloride and sublimed.
δ-Carbomethoxyvalerophenone $C_{13}H_{16}O_3$ 220.268	mp = 35-36°C	Method VI 93%	Recrystallization from pentane-ether mixture; then ligroine.
ε-Chlorohexanophenone $C_{12}H_{15}OCl$ 210.704	mp = 31-31.5°C	Method II 38%	Recrystallization from hexane (twice) and then from pentane.
ε-Cyanohexanophenone $C_{13}H_{15}ON$ 201.261	bp = 162-167°C at 2mm Hg mp = 33.5-34°C	Method V 53%	Distillation on short-path column and recrystallization (attempted) from hexane.

Ketone Formula/ Molecular Weight	Physical Properties	Method of Preparation. % Yield	Method of Purification
p-Methoxyvalerophenone $C_{12}H_{16}O_2$ 192.258	bp = 143°C at 6mm Hg	Method III 33% approx.	Distillation, and recrystallization from pentane and methanol.
m-Methoxyvalerophenone $C_{12}H_{16}O_2$ 192.258	bp = 134-135°C at 6mm Hg 131-132°C at 4.5mm Hg	Method I 31% Method II 27% Method III 24-74%	Method I product - distillation only. Recrystallization from pentane and methanol; chromatography; redistillation for others.
o-Methoxyvalerophenone $C_{12}H_{16}O_2$ 192.258	bp = 142°C at 7mm Hg	Method II 74%	Recrystallization from pentane and methanol, chromatography and redistillation.
p-Methoxy-γ-methylvalerophenone $C_{13}H_{18}O_2$ 206.285	bp = 163°C at 3.5mm Hg 160-164°C at 4mm Hg	Method II 30% Method III 20%	Distillation, recrystallization from pentane and methanol, and redistillation.
m-Methoxy-γ-methylvalerophenone $C_{13}H_{18}O_2$ 206.285	bp = 130-131°C at 2.5mm Hg 140-142°C at 4mm Hg	Method II 64% Method III 30% approx.	Distillation. (Attempt by preparative chromatography) Impurity present.
o-Chlorovalerophenone $C_{11}H_{13}OCl$ 196.669	bp = 116-118°C at 6mm Hg	Method I 52%	Distillation.

Ketone Formula/ Molecular Weight	Physical Properties	Method of Preparation. % Yield	Method of Purification
m-Chlorovalerophenone $C_{11}H_{13}OCl$ 196.669	mp = 38-39°C	Method I Made by E. Harris as a senior project.	Recrystallization from hexane.
o-Fluorovalerophenone $C_{11}H_{13}OF$ 180.214	bp = 108°C at 10mm Hg	Method I Made by Dr. P. J. Wagner.	Distillation. Purified by Dr. P. J. Wagner.
m-Fluorovalerophenone $C_{11}H_{13}OF$ 180.214	bp = 113-114°C at 10mm Hg	Method I Made by Dr. P. J. Wagner.	Distillation. Purified by Dr. P. J. Wagner.
o-Trifluoromethylvalerophenone $C_{12}H_{13}OF_3$ 230.221	bp = 121-122°C at 11mm Hg	Method I Made by Dr. P. J. Wagner.	Distillation. Purified by Dr. P. J. Wagner.
m-Trifluoromethylvalerophenone $C_{12}H_{13}OF_3$ 230.221	bp = 116-117°C at 11mm Hg	Method I Made by Dr. P. J. Wagner.	Distillation. Purified by Dr. P. J. Wagner.
p-Trifluoromethylvalerophenone $C_{12}H_{13}OF_3$ 230.221	bp = 115-116°C at 10mm Hg mp = 34-35°C	Method I Made by Dr. P. J. Wagner.	Distillation. Purified by Dr. P. J. Wagner.

Ketone Formula/ Molecular Weight	Physical Properties	Method of Preparation. % Yield	Method of Purification
m-Methylvalerophenone $C_{12}H_{16}O$ 176.259	bp = 129°C at 10mm Hg	Method I 46%	Distillation.
p-Thiomethoxyvalerophenone $C_{12}H_{16}OS$ 208.32	bp = 163-165°C at 3mm Hg mp = 49-51°C	Method II 21%	Distillation and recrystallization from pentane.
p-Phenyl-γ-methylvalerophenone $C_{18}H_{20}O$ 252.357	bp = 189-194°C at 3mm Hg mp = 71-72°C	Method IV 19%	Distillation and recrystallization from absolute ethanol.

TABLE XVII. Purification of Purchased Ketones.

Ketone Formula/ Molecular Weight	Supplier	Physical Properties	Method of Purification
Butyrophenone $C_{10}H_{12}O$ 148.197	Aldrich Chemical Company	bp = 99°C at 9.5mm Hg	Recrystallization from pentane and methanol; chromatography and distillation.
Valerophenone $C_{11}H_{14}O$ 162.224	Eastman Organic Chemicals	bp = 108-109°C at 10.5 mm Hg	Recrystallization from pentane and methanol; chromatography and distillation.
Isovalerophenone $C_{11}H_{14}O$ 162.224	Eastman Organic Chemicals	bp = 100-100.2°C at 6mm Hg	Distillation.
Hexanophenone $C_{12}H_{16}O$ 176.259	Aldrich Chemical Company	mp = 25.5-26°C	Recrystallization from hexane.
Pentadecanophenone $C_{21}H_{34}O$ 302.494	Eastman Organic Chemicals	mp = 28-29°C	No purification because of high purity and small amount of sample.
γ-Phenylbutyrophenone $C_{16}H_{16}O$ 224.303	Aldrich Chemical Company	mp = 54.5-55°C	Recrystallized several times from hexane.
5-Benzoylvaleric Acid $C_{12}H_{14}O_3$ 206.233	Aldrich Chemical Company	mp = 77.5-79°C	Recrystallization from distilled water.

Ketone

Formula/ Molecular Weight	Supplier	Physical Properties	Method of Purification
1,4-Dibenzoylbutane $C_{18}H_{18}O_2$ 266.340	Aldrich Chemical Company	mp = 106-107°C	Recrystallization from absolute ethanol-petroleum ether mixture.
α-Methoxyacetophenone $C_9H_{14}O_2$ 150.177	Aldrich Chemical Company	bp = 89-90°C at 2.5mm Hg	Distillation.
β-Phenylbutyrophenone $C_{16}H_{16}O$ 224.303	Aldrich Chemical Company	mp = 71.5-72.5°C	Recrystallization from absolute ethanol-petroleum ether mixture.
p-Chlorovalerophenone $C_{11}H_{13}OCl$ 196.669	Columbia Organic Chemicals	mp = 31-31.5°C	Recrystallization from hexane.
p-Fluorovalerophenone $C_{11}H_{13}OF$ 180.214	Pfaltz and Bauer	mp = 26-26.5°C	Recrystallization from hexane.
p-Methylvalerophenone $C_{12}H_{16}O$ 176.259	Pfaltz and Bauer	mp = 19-20°C	Recrystallization from hexane.
p-Hydroxyvalerophenone $C_{11}H_{14}O_2$ 178.223	Eastman Organic Chemicals	mp = 64-65°C	Recrystallization from absolute ethanol-petroleum ether mixture.

efficiently improved the product was used. Quite frequently several methods were used to purify one ketone.

Method A. Distillation at reduced pressure was the most commonly used purification step. Reduced pressure was necessary for the compounds in this general class because of their high boiling points. The usual range of pressure used was 5 to 20 mm Hg. Distillations were made through a 25 cm vacuum jacketed vigreaux column or a 12 cm microware vacuum jacketed vigreaux column, depending on the amount of crude ketone available. The acceptable product cut was usually taken when the thermometer reading at the top of the column came within 3 degrees of the thermometer reading at the bottom of the column.

Method B. Recrystallization was found to be a very effective means of removing small amounts of impurities and producing a very pure product. Both polar and non-polar, and sometimes mixed solvents were used. The last traces of solvent was removed in a vacuum dessicator. Most common solvents used were: pentane, hexane, methanol, absolute ethanol, distilled water, carbon tetrachloride, petroleum ether, and petroleum ether-ethanol mixtures.

Method C. Some liquid ketones were passed neat through a small column of alumina while close watch was maintained so that any colored bands formed did not pass through into the product. In some cases this seemed to be the only way that small amounts of colored impurities could be removed from the ketone (i.e. valerophenone). A neutral alumina of fairly high activity was used. (If the activity was in doubt the

alumina was dried for several days at 120°C to insure activity. It is felt that this treatment also removes small amounts of moisture from the ketone.

Method D. Sublimation was used on occasion when other methods could not purify the ketone to desired stadards and when the physical properties of the ketone allowed for efficient sublimation. A vacuum sublimation was used at a pressure of about 0.01mm Hg with gradual warming until sublimation took place. The collection tube was generally cooled with a dry ice-isopropyl alcohol mixture.

c. Criteria of purity. It is very important that the ketones used are of the utmost purity since in some cases even the smallest amount of quencher (0.0001 molar) changes the photochemical behavior. Also, small amounts of polar impurities such as water or alcohols may affect the data. Besides the usual physical characteristics of small melting or boiling ranges and a colorless or white appearance, all ketones were checked closely using vapor phase chromatography. Only a few ketones had impurities amounting to 0.10% or more of the peak area of the product ketone. Assuming the impurities were of approximately the same molecular weight as the ketones, the final 0.10 molar solution would have 0.0001 molar impurity present. Most of the ketones were very pure having barely detectable impurities or amounts less than 0.01%. As a final check, if an impurity was suspected to be causing quenching and lowering of the quantum yield, a photolysis run was made at varying concentrations of ketone. If no decrease in product with increasing ketone concentration was noted, it was assumed that no quencher was

present in the ketone.

2. Purification of Solvents and Other Compounds.

The purity of the solvents is a very critical consideration in relation to the photochemical behavior of the ketones to be photolyzed in them. It would be possible for some impurity to be a triplet quencher, a light absorber, or a species more polar than the solvent itself, all of which would alter the values obtained in the experimental runs. This is especially true where the ketone is of low reactivity and therefore more subject to quenching, etc. The solvents, quenchers, and standards used were all purified by some means and an evaluation of their purity made. Methods of purification of the compounds used are listed below.

a. Benzene. Benzene was the solvent of choice for the photolysis of the phenyl ketones. It is transparent in the region of absorption studied, it is quite non-reactive photochemically in this region, the hydrogens are not easily abstracted, and it is fairly easy to purify to a high degree. Thiophene free, 99 mole % benzene supplied by Fisher Scientific Co. was further purified by stirring over concentrated sulfuric acid (5% by volume) for several days. The sulfuric acid layer was then removed via a separatory funnel and another portion added and stirring was continued for a like period of time. This was repeated 3 or 4 times or until the sulfuric acid no longer turned yellow after stirring. The benzene was then stirred over a dilute (1M) KOH solution (≈10% by volume) for one day and then dried over 4 mesh calcium chloride for a day. The benzene was finally distilled from P_2O_5 (about 10 gr/liter of benzene) through a 45 cm column packed with glass helices. A reflux

ratio of 10:1 or larger was maintained at the distilling head and approximately 10% of the benzene was discarded as the forerun and 10% remained in the pot. The boiling point was 79.8±0.2°C, uncorrected. The benzene treated in this manner seemed quite satisfactory, no discoloration occurred even on extended irradiations. On injection into the VPC under normal conditions a small impurity precedes the benzene peak on the VPC chart and a very small one, which is also apparent on the manufacturers VPC strip, comes off on the tail of the benzene. These are apparently inert and in no way interfere with the analysis.

b. Methanol. Methanol supplied by Fisher Scientific Co. was further purified by adding approximately 1 gram of magnesium shavings per liter of methanol and distilling through a 45 cm glass helice packed column. A reflux ratio of 10:1 or greater was maintained at the distilling head and a middle fraction of approximately 60% was collected. The boiling point was 64.5±0.2°C, uncorrected. The methanol purified as above was stored in a clean, dry bottle and kept tightly capped. For reliable results it was found that the methanol should be purified on the day it is to be used, or at least not more than one or two days prior to use. Methanol stored for more than a week was found to be unsatisfactory.

c. tert-Butyl alcohol. The tert-butyl alcohol used was supplied by the J. T. Baker Co. and further purified by treatment with clean, freshly cut metallic sodium, about one gram per liter of alcohol. The sodium did not react until refluxing temperature was reached, indicating that the alcohol was quite dry. The tert-butyl alcohol was distilled through a 45 cm glass helice packed column at a reflux ratio of 10:1 or larger,

and a middle fraction of about 60% was taken for use and stored in a tightly capped bottle. The boiling point was 82.0±0.2°C, uncorrected.

d. Acetonitrile. Acetonitrile supplied by Fisher Scientific Co. was further purified by D. J. Buchek[114] by distillation from potassium permanganate. Distillation was done through a 45 cm glass helice packed column and approximately 10% was discarded as forerun and 10% remained in the pot. The boiling point was 81.5±0.2°C, uncorrected.

e. 2,5-Dimethyl-2,4-hexadiene. This most commonly used quencher was obtained from Aldrich Chemical Co. and was purified by first distilling through a 25 cm vigreaux column, collecting a 60% middle fraction with a boiling range of 40.0 to 40.5°C at 20mm Hg. The collected material was then recrystallized from itself by cooling until partially frozen and decanting the unfrozen portion of the liquid. The recrystallization was repeated. The impurities in the commercial diene were found to be significantly reduced by the above procedure. The 2,5-dimethyl-2,4-hexadiene from another supplier, Chemical Samples Co., was found to be of somewhat better purity than that obtained from Aldrich. Upon standing on the shelf near the freezing compartment in the refrigerator, large crystals would sublime to the top of the bottle. These crystals were scraped out and used on occasion without further purification.

f. Piperylene. Commercially obtained piperylene from Aldrich Chemical Co. which was merely distilled as a means of purification was found to cause a reddish-brown color in benzene solutions upon extended irradiation. By passing the piperylene through a 5 inch layer of

neutral alumina and then redistilling, extended irradiations could be made without discoloration. Distillation was made through a 25 cm vigreaux column and a 60% middle fraction was collected for use.

g. Internal standards. The internal standards used were all high molecular weight alkanes which were further purified by stirring over concentrated sulfuric acid until the acid would no longer discolor. The alkane was then rinsed with a dilute base solution, dried over calcium chloride and distilled at a reduced pressure. In the cases where the alkanes are solids at room temperature, the final pruification was by recrystallization from absolute ethanol. The standards used in this project were all purified by Prof. P. J. Wagner and are listed below.

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 = 35-35.5°C

h. Pyridine. The commercial pyridine supplied by Fisher Scientific Co. was distilled through a 25 cm vigreaux column and a middle fraction of about 60% was collected for use. The boiling range was 114.5±0.5°C, uncorrected.

i. Ethyl acetate. The ethyl acetate was distilled as above, and a middle fraction (60%) boiling at 77±0.2°C was collected for use.

PART TWO. TECHNIQUES

1. Preparation of Photolysis Samples.

a. Photolysis solutions. Stock solutions of the ketones were prepared by weighing out the required amount into a volumetric flask, then pipetting into the flask the predetermined amount of an internal standard solution and then filling to volume with solvent. Individual flasks for the quenching runs were made up by pipetting an equivalent amount of the stock ketone-standard solution into numbered volumetric flasks, adding the required amount of a standard quencher solution and filling to volume with solvent. The solutions were then injected into pyrex photolysis tubes using a 5 ml hypodermic syringe with a 4 inch needle, filling each tube uniformly with 2.8 ml. The photolysis tubes were prepared from selected culture tubes by heating the neck of the tube to the softening point and drawing it out approximately 4 inches.

When solvent effects were measured the same procedure was followed except that increments of a standard tert-butyl alcohol solution were added instead of quencher. In some cases quenching runs were made in solvents other than benzene. The procedure was the same except for substitution of the solvent.

b. Degassing procedure. The ketone solutions were degassed using a process similar to that used in earlier studies[35,115]. The sample tubes were attached to a vacuum line over No. 00 one-hole rubber stoppers on individual stopcocks. The solutions were frozen in liquid nitrogen and a vacuum of 1×10^{-3} mm of mercury (or less) was applied for

several minutes. The samples were then allowed to thaw and the cycle was repeated. After the third freezing and evacuation the tubes were sealed off with a gas-oxygen torch.

c. A typical run. The procedures for making up the solutions and the photolysis samples are illustrated in the following run performed on hexanophenone.

(1) A 0.10M stock tetradecane standard solution was made up by weighing out 0.9920 gr of tetradecane into a 50 ml volumetric flask and filling to volume with benzene.

(2) A stock 0.10M quencher solution was made up by weighing out 2.7550 gr of 2,5-dimethyl-2,4-hexadiene into a 250 ml volumetric flask and filling to volume with benzene.

(3) A stock 10.0M tert-butyl alcohol solution was made by weighing out 18.531 gr of tert-butyl alcohol into a 25 ml volumetric flask and filling to volume with benzene.

(4) The stock ketone solution was made by weighing 2.2033 gr of hexanophenone into a 25 ml volumetric flask and pipetting in 5 ml of stock 0.10M tetradecane standard solution.

(5) Individual sample flasks were made up by pipetting 2 ml of the stock ketone-standard solution into a 10 ml volumetric flask, adding the desired amount of quencher solution or alcohol solution, and filling to

volume with benzene. The run was labeled as follows:

Quenching run [0.10M hexanophenone, 0.004M tetradecane standard].

Flask #	Quencher added	Quencher Concentration
X - 1	0	0
X - 1'	0	0
X - 2	1 ml	0.010M
X - 3	2 ml	0.020M
X - 4	3 ml	0.030M
X - 5	4 ml	0.040M

Solvent study [0.10M hexanophenone, 0.004M tetradecane standard].

Flask #	tert-Butyl alcohol added	tert-Butyl alcohol Concentration
X - 6	0.5 ml	0.5M
X - 7	1.0 ml	1.0M
X - 8	2.0 ml	2.0M
X - 9	5.0 ml	5.0M
X - 10	8.0 ml	8.0M

The solutions were then placed in photolysis tubes for degassing as previously described. For the analyses see Appendix A, Part 1, Hexanophenone, Run 2, and Appendix A, Part 4, Hexanophenone.

2. Photolysis Procedure.

The sample tubes were irradiated in a merry-go-round apparatus specially designed to give each tube an equivalent amount of light, and to allow for filtration of the light for a specific mercury emission band. The apparatus is described in detail by Moses, Liu, and Monroe[116]. The light source used was a Hanovia medium pressure 450 watt mercury lamp which was held in a water cooled quartz probe. The probe was inserted into a cylindrical pyrex tube containing a filter solution and of a diameter to allow a one centimeter pathlength through the filter solution.

All photolyses were done at 3130A (unless another wavelength is specified) using a 0.002 molar potassium chromate; 1% potassium carbonate filter solution[116,117]. The samples were generally photolyzed until from 3 to 6% of the original ketone (0.10M solution) was converted to product. Occasionally the conversion was outside of these limits if the conditions warranted it (such as extremely high or low quantum yields), and occasionally actinometer tubes were photolyzed to 8 or 10% conversion, but only after determining that the quantum yield was not affected by doing so (See section on justification of results).

3. Procedure for Estimation of Ketone Disappearance and Cyclobutanols.

The procedure for determining the quantum yields of ketone disappearance and cyclobutanol formation follows quite closely that already described with some minor changes. The ketone-standard solution was made up and a 2.8 ml sample was degassed, sealed, and photolyzed as before. Then the original ketone disappearance was measured as a ratio of ketone to standard. The proposed cyclobutanols were measured as a product to standard ratio. The standard had to be carefully chosen so it would not interfere with either the parent or product ketones or the cyclobutanols. Analyses were done by gas chromatography with varying of the conditions for maximum efficiency in separation of the components. The principal differences in procedure followed from that of Section 1 were: (1) The stock solutions were made up by weighing out the ketone and internal standard to a minimum accuracy of ±0.0005 grams. This was necessary because actual moles of disappearance had to be determined from the percent disappearance of the parent ketone. Also, the presumed cyclobutanol(s) formed were measured as a percent appearance of cyclobutanol compared to

original ketone, assuming that the detector sensitivity towards the cyclobutanol was the same as for the parent ketone. It is felt that any actual difference here would not be very large. (2) Photolyses were carried out to 10 to 25% conversion in order to achieve a more measureable difference in the parent ketone peaks with VPC. This causes no serious problems except in cases where the ketone produces a quencher upon photolysis. (3) The analysis of these samples had to be carried out at somewhat more extreme conditions in order to get reasonable experimental accuracy. Although the parent ketone should not be affected by these higher temperatures (Appendix A, Part 3), there is some possibility that the cyclobutanols may be decomposed. (4) In a few cases no cyclobutanol(s) was seen in the VPC analysis and it was thought possible that it may be coincident with the parent ketone. In such cases another analysis was made using a column of slightly higher polarity (5% QF-1 and 1.5% Carbowax 20M). This column was checked using a photolyzed valerophenone solution and was found to hold up the cyclobutanols longer relative to the parent ketone than the standard column of 5% QF-1 and 1% Carbowax 20M. If no cyclobutanol(s) was seen using both columns it was assumed none was present.

4. Analysis Procedure.

a. Instruments. All of the analyses for product formation and ketone disappearance were obtained by gas chromatography. The instruments used all had flame ionization detectors and in general had similar characteristics. Response to the standard-product mixtures used were found to be the same on the three instruments employed. Each of the instruments was prepared for on-column injection of the samples so that high

injection port temperatures for "flashing" the samples were not needed. Nitrogen or helium was used as a carrier gas and flow rates were adjusted to manufacturers recommendations. The data was quantitatively recorded on strip chart recorders equipped with DISC area integrators. The samples were injected with a Hamilton microliter syringe (#7101) using two or three 0.3 to 0.5 microliter shots per sample. The syringe was rinsed 20 times with clean solvent before analyzing another sample.

b. Conditions. The analytical conditions providing the optimum time per single analysis (about 3 to 5 minutes) and the greatest sensitivity to the samples being analyzed were adopted. The following conditions are arranged in sets and will be referred to as such elsewhere. Since the most common standard-product combination is tetradecane-acetophenone, the conditions used for its analysis are referred to as standard sets of conditions (Std Set). Special conditions denote changes to analyze other standard-product combinations (e.g. octadecane-meta-methoxyacetophenone). The sets of conditions are given in Table XVIII with special conditions in Table XIX.

c. VPC trace. An exact copy of a VPC trace of the analysis of hexanophenone is shown in Figure 15.

5. Area-Mole Response Ratios for Internal Standards.

The use of a photochemically inert internal standard in the photolysis solution permits the normalization of the injection sample sizes. The error involved in attempting to use the exact amount in each VPC injection is thereby eliminated. For quantitative work or when using an

TABLE XVIII. Analytical Conditions.

	Standard Set I	Standard Set II	Standard Set III
Instrument:	Varian Aerograph Series 200 (Dual Column)	Varian Aerograph Series 1200	Aerograph Hi-Fi Model 600-C
Column:	12 ft x 1/8th inch aluminum	12 ft x 1/8th inch aluminum	6 ft x 1/8th inch aluminum
Column Packing:	4% QF-1 & 1% Carbowax 20M on 60/80 Chromosorb G	4% QF-1 & 1% Carbowax 20M on 60/80 Chromosorb G	4% QF-1 & 1% Carbowax 20M on 60/80 Chromosorb G
Carrier Gas:	Helium	Nitrogen, pre-purified	Nitrogen, pre-purified
Flow rates,			
Carrier Gas:	25 ml/min	30 ml/min	20 ml/min
Hydrogen:	25 ml/min	30 ml/min	20 ml/min
Flame Air Source:	Aquarium pump	Compressed air tank	Aquarium pump
Temperatures,			
Oven:	110-115°C	105-110°C	105-110°C
Injector Port:	135-140°C	130-135°C	Approx. 150°C
Detector:	170-180°C	170-180°C	
Settings,			
Range:	1	1	10
Attenuation:	2,4, or 8	2,4, or 8	2,4, or 8

TABLE XIX. Special Analytical Conditions.

Special Set	Same as:	Except for:
Ia	Standard Set I	Oven Temperature = 120-125°C
Ib	Standard Set I	Oven Temperature = 130°C
Ic	Standard Set I	Oven Temperature = 140°C
Id	Standard Set I	Oven Temperature = 150°C
Ie	Standard Set I	Oven Temperature = 155°C
If	Standard Set I	Oven Temperature = 170°C
Ig	Standard Set I	Oven Temperature = 175°C
Ih	Standard Set I	Column: 8 ft x 1/8th inch aluminum Column packing: 4% QF-1 & 1.5% Carbowax 20M on 60/80 Chromosorb G.
IIa	Standard Set II	Oven Temperature = 120°C
IIb	Standard Set II	Oven Temperature = 125-130°C
IIc	Standard Set II	Oven Temperature = 135°C
IId	Standard Set II	Oven Temperature = 140°C
IIIa	Standard Set III	Oven Temperature = 140-145°C
IIIb	Standard Set III	Oven Temperature = 165°C
IIIc	Standard Set III	Column: 6 ft x 1/8th inch stainless steel Column packing: 5% SE-30 on 60/80 Chromosorb W Oven Temperature = 195°C Injector Port Temperature = 220°C[a]
IIId	Special Set IIIc	Oven Temperature = 210°C
IIIe	Special Set IIIc	Oven Temperature = 170°C
IIIf	Special Set IIIc	Oven Temperature = 185°C
IIIg	Standard Set III	Column: 10 ft x 1/8th inch aluminum Column packing: 10% Carbowax TPA on 60/80 Chromosorb W Oven Temperature = 200°C Injection Port Temperature = 250°C[a]

[a] These are approximate temperatures since there is no direct temperature measurement on the Hi-Fi 600-C.

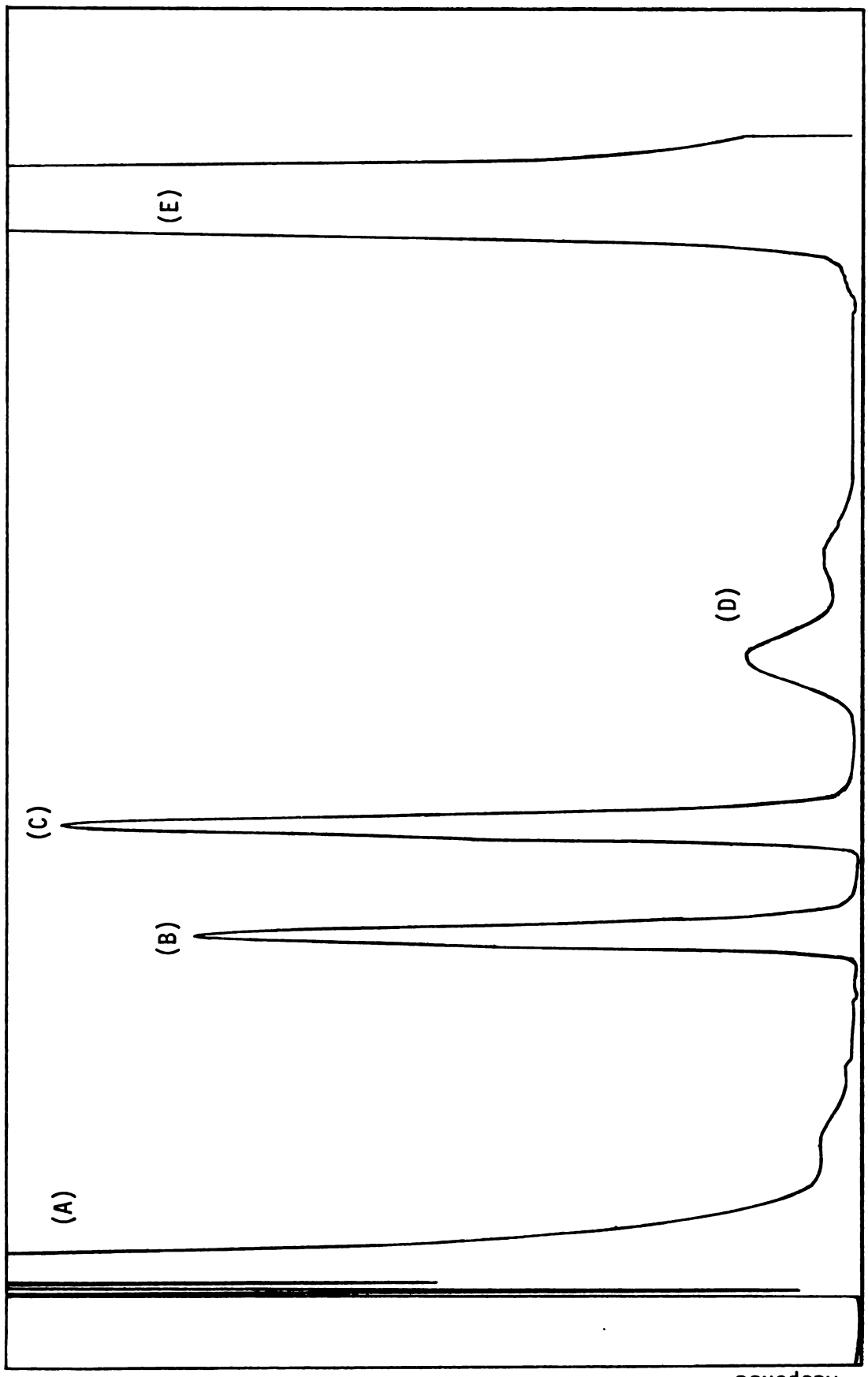


Figure 15. VPC Chart for Analysis of Hexanophenone. (A) Benzene, (B) Tetradecane, (C) Acetophenone, (D) trans and cis Cyclobutanols, and (E) Hexanophenone.

actinometer which produces a product different from the ketone under investigation it is necessary to know the response ratio per mole for the standard-product combinations. These ratios have been determined as area/mole (Std) to area/mole (Prod) for a number of standard-product combinations by weighing out the appropriate amounts of each and diluting with benzene; then making 6 or more determinations of product/standard ratios by VPC. The average value of the ratios and the molar concentrations of the standard and product were then used to calculate the molar response ratios (Table XX).

Illustrating the use of the molar response (MR) ratios the quantum yield for a ketone with a different standard-product combination from the actinometer is calculated from a series of ratios as follows:

$$\phi_{II} = \frac{\frac{Prod}{Std}\,[Ketone]}{\frac{Prod}{Std}\,[Act]} \times \frac{Std\ conc[Ket]}{Std\ conc[Act]} \times \frac{MR\ ratio\ [Ket]}{MR\ ratio\ [Act]} \times \phi_{II}[Act]$$

6. Controls in Experimental Procedures.

a. Degassing procedures. A pressure of 1×10^{-3} mm Hg was considered adequate for degassing all of the ketone solutions. Under optimum conditions 1×10^{-4} mm Hg could be obtained. The adequacy of the former pressure for reducing the dissolved oxygen to a non-interfering level has been demonstrated for the case of ketones with extremely long triplet lifetimes[118].

b. Volumetric glassware. All volumetric pipets and flasks used in making up solutions and dilutions were class-A volumetric ware. The

TABLE XX. Standard-Product Molar Response Ratios.

Standard/Product	Area/mole(Std) / Area/mole(Prod)	Analytical Conditions
Tetradecane/Acetophenone	2.0	Std Set II
Tetradecane/m-Trifluoromethyl-acetophenone	1.85[a]	Std Set III
Tetradecane/m-Fluoroacetophenone	2.0[b]	Std Set I
Pentadecane/m-Methylacetophenone	2.0	Special Set IIa
Pentadecane/p-Methylacetophenone	2.0	Special Set IIa
Hexadecane/p-Chloroacetophenone	2.3[c]	Special Set IIb
Hexadecane/m-Chloroacetophenone	2.3	Special Set IIb
Hexadecane/Acetophenone	2.3	Std Set I
Heptadecane/m-Methoxyacetophenone	2.3[d]	Special Set IIb
Octadecane/p-Methoxyacetophenone	2.4[e]	Special Set IIIa or Special Set IId
Octadecane/p-Chloroacetophenone	2.1	Special Set IIc
Eicosane/p-Phenylacetophenone	1.5	Special Set IIIc

[a] Also used for ortho- & para-trifluoromethylacetophenone determinations.

[b] Used also for ortho- and para-fluoroacetophenone determinations.

[c] Used also for ortho-chloroacetophenone determination.

[d] Used also for ortho-methoxyacetophenone determination.

[e] Used also for meta-methoxyacetophenone determination.

least accurate piece of volumetric equipment was the 5 ml hypodermic syringe used to inject 2.8 mls of solution into the photolysis tubes. Here the consistency is dependent on technique.

c. Photolysis tubes. Corning brand pyrex 13 x 100 mm straight lip culture tubes were used for all determinations. In early tests Exax brand tubes were tried, however, the results were erratic. One problem is that Exax glass transmits only about 60% of the light at 3130A. The pyrex tubes were culled to exclude any with outside diameters not within the 13 to 13.1 mm range. Also the lip was carefully examined for any deformity which would preclude a good seal with the rubber stoppers on the vacuum line. The following paragraph describes the cleaning of the tubes.

d. Cleaning of glassware. Since very small amounts of impurities in the solution could affect the photochemical behavior of the ketones in some cases, all of the glassware used was subjected to a ritualistic cleaning. First it was soaked in a commercial glass cleaner solution over a steam bath for a day or two, then rinsed with hot tap water 4 times, with distilled water 3 times, and allowed to drain dry upside down. When completely dry the glassware was placed in an oven at 120°C for 1 or 2 days. There was some concern that silicone stopcock grease may be contaminating the solutions and quenching the photoreaction of the ketones. Silicone grease was tested and found not to be a quencher. (See Table XXI)

e. Accuracy and reliability. It is interesting to estimate the

TABLE XXI. Effect of Silicone Stopcock Grease on Photolysis of Valerophenone.

Valerophenone, 0.10M in benzene, 0.004M tetradecane standard.	Prod/Std Ratio
Actinometer tubes (no silicone grease)	6.80
Contains 0.20 gr/10 mls of silicone grease	6.64

maximum possible error, excluding gross accidental errors, and compare this to the general spread of the data. A qualitative method for estimating the maximum error is to total the percent uncertainties of each inidvidual operation[119]. This was done as follows for a "normal" run which is typical of practically all the ketones studied. Each operation for which the tolerances are known is listed.

(1) Uncertainty in standard concentration (e.g. tetradecane)

		%[120]
(a)	Weighing on Sartorius substitution balance, approximately 0.5000±0.0005 grams	0.10
(b)	Class A volumetric flask, 25 ml, stock sol'n.	0.12
(c)	Class A 2 ml pipet, to ketone solution	0.30
(d)	Class A 10 ml volumetric flask	0.20
(e)	Class A 2 ml pipet, to sample flask	0.30
(f)	Class A 10 ml volumetric flask	0.20

(2) Uncertainty in ketone concentration (Not critical for ϕ_{II})

(3) Uncertainty in filling photolysis tubes, 5 ml hypodermic syringe, 2.8±0.02 mls 0.70

(4) Uncertainty in light absorption (greater than 99.9% absorption for 1 cm cell) for selected photolysis tubes, outside diameter 1.305±0.005 cm 0.10

(5) Uncertainty in area of irradiation ports of merry-go-round apparatus (machined to 0.0001 inch tolerance) 0.00

(6) Uncertainty in VPC analysis, based on range of Prod/Std ratios for a large number of determinations	2.0*
Total uncertainty in results (%)	4.0

When the actinometer is subjected to essentially the same treatment as above and also considered, the maximum possible error is 8%. The spread in the values of ϕ_{II} in Tables I and II generally fall into the 3 to 4% range and the percent deviation, if it were calculated, would even be less. In the quenched samples, which involve two more pipeting operations, all but a few of the individual slopes have a standard deviation of less than 5% of the value of the slope. This comparison shows that the technique is sufficiently good to cause much of the uncertainty to cancel out. This could be especially true in comparing actinometer and sample tubes. Reliability of the measurements appears to be on the order of ±4%, except in the cases of the ortho- and meta-methoxyvalerophenones which are apparently subject to very subtle variations.

* This was the maximum deviation from the average that was acceptable, analyses were repeated until satisfactory in cases where deviations were larger. In the qreat majority of the analyses two or three consecutive injections varied by less than 1%.

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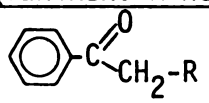
APPENDICES

APPENDIX A. PART 1. EXPERIMENTAL QUENCHING RUNS FOR DETERMINING STERN-VOLMER DIAGRAMS FOR KETONES: 

R = CH_2CH_3

Butyrophenone, 0.10M in benzene, 0.004M tetradecane standard[a].

Run No. 1

Quencher[b] Conc. (M)	Prod/Std[c] Ratio	$\frac{\phi_o}{\phi}$
0	0.831	1.00
0.001	0.523	1.59
0.002	0.388	2.14
0.003	0.336	(2.48)[g]
0.004	0.254	3.28
Act[d]	0.82	

L Sq Slope (σ)[e] = 568 (3)
Intercept (σ) = 1.01 (.01)

Anal Cond Std Set I[f]

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.797	
Act	0.740	

Anal Cond Std Set I

The following conditions apply to all quenching runs unless specifically restated:

[a] An internal standard is used for analytical purposes, standard is named in heading. See Experimental Procedures.

[b] The quencher used is 2,5-dimethyl-2,4-hexadiene unless otherwise specified.

[c] The product to standard ratios given are averages of two or more actual measurements. See Experimental Procedures.

[d] All actinometers are 0.10M valerophenone, 0.004M tetradecane in benzene unless otherwise indicated. ϕ_{II} is taken to be 0.33.

[e] The least squares slope, intercept, and standard deviations were calculated on the CDC-6500 computer at the MSU computer center. See Appendix B for computer program used.

[f] Analytical conditions are tabulated in the Experimental Section.

[g] This point omitted because it deviated by twice the standard deviation.

R = $CH(CH_3)_2$

Isovalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.23	1.00
0.002	0.817	1.50
0.004	0.625	1.99
0.006	0.495	2.53
0.008	0.424	2.91
Act	none	
0	0.565	
Act[a]	0.536	

L Sq Slope (σ) = 243 (5)
Intercept (σ) = 1.02 (.02)

Anal Cond Std Set II

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.868	1.00
0.002	0.579	1.49
0.004	0.452	1.91
0.006	0.340	2.54
0.008	0.303	2.85
0	0.862	
Act	0.758	

L Sq Slope (σ) = 237 (9)
Intercept (σ) = 1.01 (.05)

Anal Cond Std Set I

R = $C(CH_3)_3$

β,β-Dimethylbutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.587	1.00
0.010	0.330	1.81
0.020	0.229	2.62
0.030	0.165	3.62
0	0.609	
Act	1.05	

L Sq Slope (σ) = 86.7 (2.3)
Intercept (σ) = 0.96 (.04)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.942	1.00
0.010	0.589	1.60
0.020	0.388	2.42
0.030	0.298	3.16
0.040	0.234	4.02
0	0.938	
Act	1.68	

L Sq Slope (σ) = 76.0 (1.9)
Intercept (σ) = 0.92 (.05)

Anal Cond Std Set I

---

[a] This actinometer only is 0.10M butyrophenone and 0.004M tetradecane in benzene; ϕ_{II} = 0.35.

R = $CH_2CH_2CH_3$

Valerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.99	1.00
0.010	0.729	1.36
0.020	0.557	1.77
0.030	0.443	2.24
0.040	0.382	2.59
0	1.052	
Act	none	

L Sq Slope (σ) = 40.5 (.7)
Intercept (σ) = 0.98 (.02)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.833	1.00
0.010	0.604	1.40
0.020	0.465	1.81
0.030	0.375	2.25
0.040	0.318	2.65
0	0.853	
Act	none	

L Sq Slope (σ) = 41.5 (.3)
Intercept (σ) = 0.99 (.01)

Anal Cond Std Set I

R = $CH_2CH_2CH_2CH_3$

Hexanophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.76	1.00
0.010	1.245	1.40
0.020	0.970	1.80
0.030	0.813	2.14
0.040	0.670	2.60
0	1.71	
Act	1.88	

L Sq Slope (σ) = 39.4 (.71)
Intercept (σ) = 1.00 (.02)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.886	1.00
0.010	0.648	1.39
0.020	0.539	1.67
0.030	0.422	2.13
0.040	0.361	2.49
0	0.911	
Act	0.99	

L Sq Slope (σ) = 37.2 (1.1)
Intercept (σ) = 0.99 (.03)

Anal Cond Std Set I

R = $CH_2CH_2CH(CH_3)_2$

δ-Methylhexanophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.44	1.00
0.010	1.08	1.32
0.020	0.917	1.55
0.030	0.779	1.83
0.040	0.672	2.12
0	1.41	
Act	1.88	

L Sq Slope (σ) = 27.5 (0.5)
Intercept (σ) = 1.01 (.01)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.20	1.00
0.010	0.953	1.25
0.020	0.779	1.52
0.030	0.654	1.82
0.040	0.592	2.01
0	1.18	
Act	1.63	

L Sq Slope (σ) = 25.9 (0.7)
Intercept (σ) = 1.00 (.01)

Anal Cond Std Set I

R = $CH_2CH_2C(CH_3)_3$

δ,δ-Dimethylhexanophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.34	1.00
0.010	1.08	1.24
0.020	0.912	1.47
0.030	0.785	1.71
0.040	0.680	1.97
0	1.34	
Act	1.88	

L Sq Slope (σ) = 24.1 (0.2)
Intercept (σ) = 1.00 (.005)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.893	1.00
0.010	0.695	1.27
0.020	0.590	1.50
0.030	0.510	1.74
0	0.878	
Act	1.19	

L Sq Slope (σ) = 24.5 (0.4)
Intercept (σ) = 1.01 (.01)

Anal Cond Std Set I

R = $(CH_2)_6CH_3$

Nonanophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.48	1.00
0.010	1.17	1.265
0.020	0.912	1.60
0.030	0.754	1.93
0.040	0.687	2.13
0	1.44	
Act	1.88	

L Sq Slope (σ) = 29.3 (1.0)
Intercept (σ) = 1.00 (.006)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.753	1.00
0.010	0.553	1.36
0.020	0.448	1.68
0.040	0.320	2.36
0	0.751	
Act	1.05	

L Sq Slope (σ) = 33.8 (0.3)
Intercept (σ) = 1.01 (.01)

Anal Cond Std Set I

R = $(CH_2)_{12}CH_3$

Pentadecanophenone, 0.10M in benzene, 0.004M tetradecane standard.

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.69	1.00
0.020	1.06	1.56
0.040	0.783	2.11
0.060	0.630	2.62
0.080	0.508	3.24
0	1.61	
Act	2.07	

L Sq Slope (σ) = 27.7 (0.3)
Intercept (σ) = 1.00 (.02)

Anal Cond Std Set I

R = $CH_2CH(CH_3)_2$

γ-Methylvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	3.73	1.00
0.020	2.95	1.19
0.060	2.16	1.62
0.080	1.89	1.86
0	3.27	
Act[a]	4.85	

L Sq Slope (σ) = 10.75 (.2)
Intercept (σ) = 0.99 (.02)

Anal Cond Std Set III

---

[a] This actinometer only was 0.10M butyrophenone, 0.004M tetradecane standard, ϕ_{II} = 0.35.

R = $CH_2CH(CH_3)_2$

γ-Methylvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.762	1.00
0.020	0.616	1.24
0.040	0.557	1.37
0.060	0.478	1.59
Act	0.991	
0	0.367	
Act	0.463	

L Sq Slope (σ) = 9.5 (0.5)
Intercept (σ) = 1.02 (.02)

Anal Cond Std Set III

Run No. 3[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.241	1.00
0.020	0.196	1.22
0.040	0.173	1.38
0.060	0.149	1.61
0.080	0.130	1.84
0	0.236	
Act[b]	0.646	

L Sq Slope (σ) = 10.35 (0.3)
Intercept (σ) = 1.00 (.01)

Anal Cond Std Set III

R = CH_2CH_2-C6H5

γ-Phenylbutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.731	1.00
0.020	0.600	1.21
0.040	0.497	1.46
0.060	0.418	1.74
0	0.722	
Act	0.516	

L Sq Slope (σ) = 12.3 (.4)
Intercept (σ) = 0.98 (.015)

Anal Cond Std Set I

ϕ_{II} versus per cent conversion.

Prod/Std Ratio	% Conv.	Act	ϕ_{II}
0.215	1.72	0.144	0.492
0.395	3.16	0.275	0.474
0.585	4.68	0.416	0.464
0.722	5.77	0.516	0.462
0.872	6.97	0.644	0.448
1.07	8.55	0.795	0.444
1.18	9.45	0.904	0.431
1.38	11.1	1.08	0.422

Anal Cond Std Set I

---

[a] Standard concentration was 0.008M for this run.

[b] This actinometer only was 0.10M butyrophenone, 0.004M tetradecane standard, ϕ_{II} = 0.35.

R = $CH_2CH_2CH{=}CH_2$

γ-Vinylbutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1 (2.91% conv.)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.352	1.00
0.010	0.333	1.10
0.020	0.305	1.20
0.030	0.279	1.31
0.040	0.263	1.39
0	0.376	
Act	0.490	

L Sq Slope (σ) = 9.9 (.2)
Intercept (σ) = 1.00 (.00)

Anal Cond Std Set I

Run No. 2 (5.82% conv.)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.729	1.00
0.010	0.645	1.12
0.020	0.622	1.17
0.030	0.581	1.25
0.040	0.527	1.38
0	0.724	
Act	1.05	

L Sq Slope (σ) = 8.9 (.6)
Intercept (σ) = 1.01 (.01)

Anal Cond Std Set I

Run No. 3 (12.1% conv.)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.52	1.00
0.010	1.40	1.08
0.020	1.37	1.10
0.030	1.26	1.20
0.040	1.17	1.29
0	1.50	
Act	2.40	

L Sq Slope (σ) = 7.0 (.6)
Intercept (σ) = 0.99 (.01)

Anal Cond Std Set I

R = $CH_2CH_2N(CH_3)_2$

γ-Dimethylaminobutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.310	1.00
0.20	0.276	1.12
0.60	0.241	1.29
1.00	0.191	1.62
Act	3.69	

L Sq Slope (σ) = 0.60 (.04)
Intercept (σ) = 0.99 (.03)

Anal Cond Std Set II

Run No. 2[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.446	1.00
0.40	0.358	1.24
0.80	0.298	1.49
1.20	0.259	1.72
0	0.442	
Act	5.66	

L Sq Slope (σ) = 0.60 (.005)
Intercept (σ) = 1.00 (.003)

Anal Cond Std Set II

Run No. 3[b]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.831	1.00
0.20	0.762	1.08
0.40	0.606	1.35
0.80	0.534	1.55
1.20	0.444	1.85
0	0.806	
Act	5.66	

L Sq Slope (σ) = 0.71 (.04)
Intercept (σ) = 0.99 (.03)

Anal Cond Std Set II

Run No. 4[c]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.428	1.00
1.00	0.282	1.53
0	0.434	
Act	5.63	

Slope = 0.53

Anal Cond Std Set II

---

[a] The quencher used in this run was piperylene.

[b] The internal standard in this run was 0.002M hexadecane. An impurity in the high concentration of 2,5-dimethyl-2,4-hexadiene interfered with the dteradecane during analysis.

[c] This run had a single quenched sample using biphenyl as a quencher.

R = $CH_2CH_2OCH_3$

γ-Methoxybutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.737	1.00
0.020	0.585	1.23
0.040	0.554	1.30
0.060	0.458	1.59
0.080	0.438	1.65
0	0.706	
Act	1.01	

L Sq Slope (σ) = 8.3 (.75)
Intercept (σ) = 1.02 (.04)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.814	1.00
0.020	0.664	1.19
0.040	0.609	1.30
0.060	0.543	1.45
0.080	0.491	1.61
0	0.840	
Act	1.19	

L Sq Slope (σ) = 7.4 (.24)
Intercept (σ) = 1.01 (.01)

Anal Cond Std Set I

R = $CH_2CH(OCH_3)CH_3$

γ-Methoxyvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.842	1.00
0.020	0.711	1.19
0.040	0.600	1.41
0.060	0.537	1.58
0.080	0.455	1.86
0	0.852	
Act	1.44	

L Sq Slope (σ) = 10.5 (.4)
Intercept (σ) = 0.99 (.02)

Anal Cond Std Set I

R = CH_2CH_2OH

γ-Hydroxybutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.33	1.00
0.010	1.15	1.15
0.020	1.00	1.32
0.030	0.94	1.41
0.040	0.85	1.56
0	1.31	
Act	1.24	

L Sq Slope (σ) = 13.8 (.5)
Intercept (σ) = 1.01 (.01)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.295	1.00
0.020	1.055	1.25
0.030	0.957	1.38
0.040	0.886	1.49
0.050	0.824	1.61
0	1.335	
Act	1.63	

L Sq Slope (σ) = 12.2 (.1)
Intercept (σ) = 1.00 (.004)

Anal Cond Std Set I

R = CH_2CH_2Cl

γ-Chlorobutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.252	1.00
0.002	0.183	1.34
0.004	0.142	1.72
0.006	0.119	2.05
0	0.237	
Act[a]	1.01	

L Sq Slope (σ) = 176.5 (2.3)
Intercept (σ) = 1.00 (.01)

Anal Cond Std Set III

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.278	1.00
0.002	0.210	1.30
0.004	0.154	1.76
0.006	0.133	2.04
0.008	0.114	2.38
0.008	0.108	2.52
0	0.266	
Act[a]	1.01	

L Sq Slope (σ) = 183 (7)
Intercept (σ) = 0.98 (.04)

Anal Cond Std Set III

---

[a] These actinometers only are 0.10M butyrophenone, 0.004M tetradecane in benzene; ϕ_{II} = 0.35.

R = $CH_2CH_2COOCH_3$

γ-Carbomethoxybutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1 (9.2% conv.)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.15	1.00
0.002	0.680	1.69
0.004	0.478	2.40
0.006	0.366	3.14
0.008	0.289	3.98
0.008	0.290	3.96
0	1.15	
0	1.16	
Act	0.97	

L Sq Slope (σ) = 373 (5)
Intercept (σ) = 0.96 (.03)

Anal Cond Std Set III

Run No. 2[a] (2.10% conv.)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.05	1.00
0.001	0.721	1.46
0.002	0.569	1.85
0.003	0.466	2.25
0.004	0.362	2.90
0	1.05	
Act	0.78	

L Sq Slope (σ) = 459 (21)
Intercept (σ) = 0.97 (.05)

Anal Cond Std Set III

Run No. 3[b]

ϕ_{II} versus per cent conversion

Prod/Std Ratio	% Conv.	Act	ϕ_{II}
2.10	4.20	0.777	0.444
3.55	7.10	1.57	0.375
7.12	14.24	3.19	0.369
9.48	18.96	4.69	0.334
11.39	22.78	6.17	0.305

Anal Cond Std Set III

Run No. 4[a]

ϕ_{II} versus per cent conversion

Prod/Std Ratio	% Conv.	Act	ϕ_{II}
1.05	2.10	0.777	0.444
1.85	3.70	1.57	0.389
3.70	7.40	3.19	0.384
4.92	9.84	4.69	0.347

Anal Cond Std Set III

---

[a] Tetradecane concentration 0.001M.

[b] Ketone concentration 0.050M and tetradecane concentration 0.0005M.

R = CH_2CH_2CN

γ-Cyanobutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1 (3.6% conv.)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.437	1.00
0.001	0.305	1.46
0.002	0.203	2.19
0.003	0.190	2.35
0.004	0.152	2.93
0.008	0.081	5.50
0	0.440	
0	0.457	
Act	1.01	

L Sq Slope (σ) = 558 (25)
Intercept (σ) = 0.90 (.10)

Anal Cond Std Set I

Run No. 2 (4.84% conv.)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.598	1.00
0.001	0.418	1.44
0.002	0.340	1.78
0.003	0.260	2.32
0.004	0.216	2.79
0	0.608	
Act	1.25	

L Sq Slope (σ) = 446 (14)
Intercept (σ) = 0.97 (.03)

Anal Cond Std Set I

Run No. 3 (2.02% conv.)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.252	1.00
0.001	0.150	1.68
0.002	0.105	2.40
0.003	0.078	3.20
Act	0.373	

L Sq Slope (σ) = 732 (14)
Intercept (σ) = 0.97 (.03)

Anal Cond Std Set I

Run No. 4

ϕ_{II} versus per cent conversion

Prod/Std Ratio	% Conv.	Act	ϕ_{II}
0.187	1.50	0.252	0.245
0.317	2.53	0.505	0.207
0.437	3.50	0.736	0.196
0.538	4.30	1.02	0.174
Run No. 1[a]			0.145
Run No. 2			0.159
Run No. 3			0.223

Anal Cond Std Set I

---

[a] The actinometer value in this run is suspected of being slightly large.

R = $CH_2CH_2CH_2CO$- 

1,4-Dibenzoylbutane, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.35	1.00
0.010	0.739	1.81
0.020	0.673	1.99
0.030	0.522	2.57
0.040	0.417	3.20
0	1.33	
Act	1.28	
0	1.50[a]	
Act	1.60	

L Sq Slope (σ) = 51.6 (3.8)
Intercept (σ) = 1.08 (.09)

Anal Conc Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.21	1.00
0.010	0.860	1.40
0.020	0.606	1.98
0.030	0.463	2.59
0.040	0.367	3.30
0	1.19	
Act	1.08	

L Sq Slope (σ) = 57.9 (2.5)
Intercept (σ) = 0.90 (.06)

Anal Conc Std Set I

R = $CH_2CH_2CH_2COOCH_3$

δ-Carbomethoxyvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.87	1.00
0.002	1.49	1.26
0.004	1.27	1.48
0.006	1.03	1.825
0.008	0.921	2.04
0.008	0.947	1.99
0	1.89	
0	1.88	
Act	0.97	

L Sq Slope (σ) = 128.5 (4.2)
Intercept (σ) =1.00 (.01)

Anal Cond Std Set III

Run No. 2[b]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.25	1.00
0.001	1.15	1.09
0.002	1.04	1.21
0.003	0.93	1.35
0.004	0.81	1.54
Act	0.659	

L Sq Slope (σ) = 134 (8)
Intercept (σ) = 0.97 (.02)

Anal Cond Std Set III

---

[a] Separate determination.

[b] Tetradecane concentration 0.001M, irradiated 15 minutes.

R = $CH_2CH_2CH_2COOH$

δ-Carboxyvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.528	1.00
0.002	0.375	1.39
0.004	0.305	1.71
0.006	0.258	2.02
0.008	0.206	2.53
0.008	0.207	2.51
0	0.514	
Act[b]	0.646	

L Sq Slope (σ) = 187 (6)
Intercept (σ) = 0.99 (.03)

Anal Cond Std Set III

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.55	1.00
0.002	1.88	1.36
0.004	1.44	1.78
0.006	1.21	2.12
0.008	1.01	2.53
0	2.57	
Act	1.50	

L Sq Slope (σ) = 191 (2)
Intercept (σ) = 0.99 (.01)

Anal Cond Std Set I

R = $CH_2CH_2CH_2Cl$

δ-Chlorovalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	3.44	1.00
0.010	1.12	3.07
0.020	0.627	5.48
0.030	0.428	8.04
0.040	0.316	(10.90)
0	3.43	
Act	1.98	

L Sq Slope (σ) = 229 (5)
Intercept (σ) = 0.99 (.02)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.52	1.00
0.002	1.75	1.44
0.004	1.35	1.87
0.006	1.06	2.38
0.008	0.90	2.80
0	2.61	
Act	1.44	

L Sq Slope (σ) = 227 (3)
Intercept (σ) = 0.99 (.01)

Anal Cond Std Set I

---

[a] Tetradecane concentration of 0.008M.

[b] This actinometer only was butyrophenone, 0.10M in benzene, 0.004M tetradecane standard, ϕ_{II} = 0.35.

R = $CH_2CH_2CH_2CN$

δ-Cyanovalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.785	1.00
0.010	0.274	6.50
0.020	0.153	11.6
0	1.765	
Act	1.25	

L Sq Slope (σ) = 530 (7)
Intercept (σ) = 1.07 (.09)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.69	1.00
0.001	1.15	1.47
0.002	0.905	1.87
0.003	0.678	2.49
0.004	0.563	3.00
0	1.70	
Act	1.23	

L Sq Slope (σ) = 502 (16)
Intercept (σ) = 0.96 (.04)

Anal Cond Std Set I

R = $CH_2CH_2CH_2CH_2Cl$

ε-Chlorohexanophenone, 0.10M in benzene, 0.004M tetradecane standard.

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.02	1.00
0.002	1.71	1.17
0.004	1.47	1.35
0.006	1.29	1.54
0.008	1.17	1.70
0	1.96	
Act	1.50	

L Sq Slope (σ) = 88.5 (1)
Intercept (σ) = 1.00 (.005)

Anal Cond Std Set I

R = $CH_2CH_2CH_2CH_2CN$

ε-Cyanohexanophenone, 0.10M in benzene, 0.004M tetradecane standard.

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.13	1.00
0.002	0.963	1.15
0.004	0.848	1.31
0.006	0.753	1.48
0.008	0.704	1.58
0	1.09	
Act	1.50	

L Sq Slope (σ) = 74.5 (2.6)
Intercept (σ) = 1.01 (.01)

Anal Cond Std Set I

R = CH-  -CH_3

β-Phenylbutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1 (Irradiated 36 hrs)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.188	1.00
0.10	0.118	1.55
0.20	0.0917	2.00
0.30	0.0759	2.42
0.30	0.0729	2.52
0.40	0.0593	3.08
Act	0.89/hour	

L Sq Slope (σ) = 5.04 (.15)
Intercept (σ) = 1.00 (.04)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.162	
Act	11.7	

Anal Cond Std Set I

R = OCH_3

α-Methoxyacetophenone, 0.10M in benzene, 0.001M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	5.27	1.00
0.040	4.65	1.133
0.080	4.02	1.31
0.120	3.81	1.38
0.160[b]	3.56	1.48
Act	0.794	

L Sq Slope (σ) = 3.02 (.2)
Intercept (σ) = 1.02 (.02)

Anal Cond Std Set III

Run No. 2[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.881	1.00
0.040	0.763	1.166
0.080	0.716	1.24
0.120	0.667	1.333
0.160	0.640	1.39
0	0.897	
Act[b]	0.685	

L Sq Slope (σ) = 2.38 (.21)
Intercept (σ) = 1.04 (.02)

Anal Cond Std Set III

---

[a] Tetradecane standard concentration 0.005M.

[b] Actinometers are 0.10M butyrophenone, 0.004M tetradecane standard in benzene; ϕ_{II} = 0.35.

R = OCH_3

α-Methoxyacetophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 3 (Irradiated 1 hr)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.715	1.00
0.020	0.660	1.07
0.040	0.606	1.17
0.060	0.569	1.24
0.080	0.559	1.27
0.10	0.525	1.35
0.20	0.470	1.51
0.30	0.402	1.76
0.40	0.338	2.09
0	0.698	
Act[a]	0.433	

Anal Cond Std Set III

Run No. 4 (Irradiated 2 hrs)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.38	1.00
0.020	1.19	1.13
0.040	1.09	1.23
0.060	1.02	1.32
0.080	1.00	1.34
0.10	0.942	1.42
0.20	0.792	1.69
0.30	0.716	1.87
0.40	0.622	2.15
0	0.130	
Act	none	

Anal Cond Std Set III

Run No. 5 (Irradiated 3 hrs)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.02	1.00
0.020	1.64	1.20
0.040	1.67	1.18
0.060	1.50	1.31
0.080	1.32	1.49
0.10	1.29	1.53
0.20	1.17	1.68
0.30	1.04	1.89
0.40	0.926	2.13
0	1.91	
Act	none	

Anal Cond Std Set III

Initial (0.020 to 0.080M quencher) and Final (0.10 to 0.40M quencher) Slopes at various Irradiation Times.

	L Sq Slope	Intercept
(1 hour)	(σ)	(σ)
Initial:	3.55 (.26)	1.01(.01)
Final:	2.59 (.13)	1.02(.03)
(2 hours)		
Initial:	4.35 (.45)	1.03(.02)
Final:	2.75 (.18)	1.08(.04)
(3 hours)		
Initial:	5.45 (.75)	1.02(.04)
Final:	2.62 (.28)	1.12(.07)

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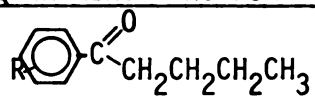
[a] Butyrophenone actinometer, 0.10M in benzene, 0.004M tetradecane standard; $\phi_{II} = 0.35$.

APPENDIX A. PART 2. EXPERIMENTAL QUENCHING RUNS FOR DETERMINING STERN-VOLMER DIAGRAMS FOR KETONES: 

R = o-CF_3

ortho-Trifluoromethylvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\Phi_o}{\Phi}$
0	0.556	1.00
0.020	0.297	1.86
0.040	0.215	2.58
0.060	0.172	3.22
0.080	0.136	4.08
0	0.554	
Act	0.89	

L Sq Slope (σ) = 37.6 (.8)
Intercept (σ) = 1.04 (.04)

Anal Cond Std Set II

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\Phi_o}{\Phi}$
0	0.859	1.00
0.020	0.463	1.85
0.040	0.328	2.61
0.060	0.255	2.61
0.080	0.210	4.08
0	0.854	
Act	1.29	

L Sq Slope (σ) = 38.4 (.5)
Intercept (σ) = 1.05 (.03)

Anal Cond Std Set II

R = m-CF_3

meta-Trifluoromethylvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\Phi_o}{\Phi}$
0	0.637	1.00
0.020	0.500	1.28
0.040	0.396	1.61
0.060	0.330	1.93
0.080	0.286	2.23
0	0.638	
Act	0.89	

L Sq Slope (σ) = 15.6 (.2)
Intercept (σ) = 0.99 (.01)

Anal Cond Std Set II

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\Phi_o}{\Phi}$
0	1.03	1.00
0.020	0.79	1.29
0.040	0.64	1.59
0.060	0.547	1.87
0.080	0.452	2.26
0	1.00	
Act	1.29	

L Sq Slope (σ) = 15.5 (.4)
Intercept (σ) = 0.98 (.02)

Anal Cond Std Set II

R = p-CF_3

para-Trifluoromethylvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.724	1.00
0.020	0.546	1.315
0.040	0.436	1.66
0.060	0.356	2.02
0.080	0.306	2.35
0	0.712	
Act	0.89	

L Sq Slope (σ) = 17.0 (.2)
Intercept (σ) = 0.99 (.01)

Anal Cond Std Set II

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.08	1.00
0.020	0.797	1.36
0.040	0.634	1.71
0.060	0.513	2.11
0.080	0.427	2.53
0	1.09	
Act	1.23	

L Sq Slope (σ) = 19.0 (.3)
Intercept (σ) = 0.98 (.02)

Anal Cond Std Set I

R = o-F

ortho-Fluorovalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.40	1.00
0.002	1.27	1.07
0.004	1.20	1.13
0.008	1.06	1.28
0	1.33	
Act	1.32	

L Sq Slope (σ) = 34.9 (.7)
Intercept (σ) = 1.00 (.00)

Anal Cond Special Set Ih

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.37	1.00
0.010	1.02	1.34
0.020	0.82	1.67
0.030	0.650	2.10
0.040	0.585	2.34
0	1.38	
Act	1.37	

L Sq Slope (σ) = 34.4 (1.1)
Intercept (σ) = 1.00 (.03)

Anal Cond Special Set Ih

R = m-F

meta-Fluorovalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.12	1.00
0.010	0.848	1.32
0.040	0.538	2.08
0	1.12	
Act	1.32	

L Sq Slope (σ) = 26.6 (.8)
Intercept (σ) = 1.02 (.02)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.07	1.00
0.010	0.828	1.29
0.020	0.677	1.58
0.030	0.544	1.97
0.040	0.492	2.17
0	1.06	
Act	1.37	

L Sq Slope (σ) = 30.2 (1.1)
Intercept (σ) = 1.00 (.03)

Anal Cond Std Set I

R = p-F

para-Fluorovalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.15	1.00
0.002	1.06	1.08
0.004	1.00	1.15
0.008	0.91	1.27
0	1.16	
Act	1.32	

L Sq Slope (σ) = 33.4 (1.2)
Intercept (σ) = 1.01 (.05)

Anal Cond Std Set I

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.02	1.00
0.010	0.754	1.37
0.020	0.592	1.74
0.030	0.523	1.97
0.040	0.422	2.44
0	1.03	
Act	1.23	

L Sq Slope (σ) = 34.8 (1.4)
Intercept (σ) = 1.01 (.03)

Anal Cond Std Set I

R = o-Cl

ortho-Chlorovalerophenone, 0.10M in benzene, 0.002M octadecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.11	1.00
0.002	1.66	1.27
0.004	1.32	1.60
0.006	1.13	1.87
0.008	0.96	2.20
0	2.10	
Act	0.792	

L Sq Slope (σ) = 150 (2)
Intercept (σ) = 0.99 (.01)

Anal Cond Special Set IIc

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	3.47	1.00
0.002	2.69	1.34
0.004	2.25	1.54
0.006	1.94	1.79
0.008	1.66	2.09
Act	1.46	

L Sq Slope (σ) = 132 (5)
Intercept (σ) = 1.03 (.02)

Anal Cond Special Set IIc

Run No. 3[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.00	1.00
0.002	0.768	1.30
0.004	0.620	1.61
0.006	0.536	1.87
0.008	0.466	2.15
0	1.00	
Act	0.78	

L Sq Slope (σ) = 144 (2)
Intercept (σ) = 1.01 (.01)

Anal Cond Special Set IIb

---

[a] Standard used in this run was 0.004M hexadecane.

R = m-Cl

meta-Chlorovalerophenone, 0.10M in benzene, 0.002M octadecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.02	1.00
0.002	1.89	1.07
0.004	1.74	1.16
0.006	1.66	1.22
0.008	1.59	1.27
0	2.02	
Act	1.46	

L Sq Slope (σ) = 34.5 (1.6)
Intercept (σ) = 1.01 (.01)

Anal Cond Special Set IIc

Run No. 2[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.519	1.00
0.004	0.467	1.14
0.008	0.425	1.25
0.012	0.387	1.37
0.016	0.358	1.48
0	0.542	
Act	0.78	

L Sq Slope (σ) = 29.8 (.6)
Intercept (σ) = 1.01 (.01)

Anal Cond Special Set IIb

R = p-Cl

para-Chlorovalerophenone, 0.10M in benzene, 0.002M octadecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.27	1.00
0.002	1.80	1.26
0.004	1.47	1.54
0.006	1.24	1.83
0.008	1.08	2.10
Act	1.46	

L Sq Slope (σ) = 138 (1)
Intercept (σ) = 0.99 (.01)

Anal Cond Special Set IIc

Run No. 2[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.636	1.00
0.002	0.499	1.26
0.004	0.415	1.53
0.006	0.351	1.79
0	0.619	
Act	0.78	

L Sq Slope (σ) = 132 (1)
Intercept (σ) = 1.00 (.002)

Anal Cond Special Set IIb

---

[a] Standard used in these runs was 0.004M hexadecane.

R = m-CH_3

meta-Methylvalerophenone, 0.10M in benzene, 0.004M pentadecane standard.

Run No. 1[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.795	1.00
0.002	0.659	1.20
0.004	0.551	1.44
0.006	0.505	1.59
0.008	0.440	1.80
0	0.788	
Act	1.04	

L Sq Slope (σ) = 99.5 (2.7)
Intercept (σ) = 1.01 (.01)

Anal Cond Special Set IIa

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.43	1.00
0.002	1.13	1.25
0.004	0.934	1.51
0.006	0.810	1.74
0.008	0.704	2.00
0	1.39	
Act	1.41	

L Sq Slope (σ) = 124 (1)
Intercept (σ) = 1.00 (.005)

Anal Cond Special Set Ia

Run No. 3[b]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.435	1.00
0.002	1.09	1.33
0.004	0.936	1.55
0.006	0.802	1.81
0.008	0.698	2.08
0	1.455	
Act	1.27	

L Sq Slope (σ) = 132 (3)
Intercept (σ) = 1.03 (.02)

Anal Cond Special Set Ia

Run No. 4

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.20	1.00
0.010	0.505	2.30
0.020	0.324	3.58
0	1.13	
Act	1.27	

L Sq Slope (σ) = 129 (1)
Intercept (σ) = 1.00 (.00)

Anal Cond Special Set Ia

---

[a] The slope and quantum yield in this run are suspected of being slightly low.

[b] The quantum yield in this run is much too high, possibly due to an erroneous quencher concentration. This would not negate the quenching study.

R = p-CH_3

para-Methylvalerophenone, 0.10M in benzene, 0.004M pentadecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.11	1.00
0.002	0.722	1.55
0.004	0.545	2.06
0.006	0.432	2.60
0.008	0.350	3.20
0	1.12	
Act	1.04	

L Sq Slope (σ) = 273 (3)
Intercept (σ) = 0.99 (.02)

Anal Cond Special Set IIa

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.52	1.00
0.001	1.19	1.26
0.002	0.971	1.55
0.003	0.822	1.83
0.004	0.725	2.07
0	1.48	
Act	1.41	

L Sq Slope (σ) = 271 (4)
Intercept (σ) = 1.00 (.01)

Anal Cond Special Set IIa

R = p-  ; γ-CH_3

para-Phenyl-γ-methylvalerophenone, 0.10M in benzene, 0.001M eicosane standard.

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.249	1.00
0.005	0.884	0.275
0.010	1.00	0.243
0.020	0.09	0.223
0	0.238	
Act	81.3	
1.0M t-BuOH	0.200	
(0.05M ketone, 0.002M std)		
0	0.113	
0	0.118	
(0.025M ketone, 0.001M std)		
0	0.214	
0.10M Bzph	0.186	
0.05M Trph	0.201	
Act	81.3	
0	0.114	
0.10M Bzph	0.097	
0.05M Trph	0.094	
Act	35.9	

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
(0.0125M ketone, 0.0005M std)		
0	0.393	
0	0.439	
0.10M Bzph[a]	0.350	
0.10M Bzph[b]	0.340	
0.05M Trph[a]	0.346	
0.05M Trph	0.361	
Act	81.3	

Anal Cond Special Set IIIc

---

[a] Benzophenone

[b] Triphenylene

R = p-OCH_3

para-Methoxyvalerophenone, 0.10M in benzene, 0.002M octadecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.49	1.00
0.0005	1.15	2.14
0.0010	0.805	3.06
0.0015	0.564	4.32
0.0020	0.483	5.68
0	2.43	
Act	3.85	

L Sq Slope (σ) = 2308 (71)
Intercept (σ) = 0.93 (.09)

Anal Cond Special Set IId

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	4.16	1.00
0.0002	2.81	1.47
0.0004	2.14	1.93
0.0006	1.82	2.27
0.0008	1.48	2.79
0	4.10	
Act	6.50	

L Sq Slope (σ) = 2190 (55)
Intercept (σ) = 1.02 (.03)

Anal Cond Special Set Ie

R = p-OCH_3; γ-CH_3

para-Methoxy-γ-methylvalerophenone, 0.10M in benzene, 0.002M octadecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	4.35	1.00
0.001	2.29	1.90
0.002	1.61	2.70
0.003	1.29	3.37
0.004	0.97	4.48
0	4.35	
Act	3.85	

L Sq Slope (σ) = 843 (28)
Intercept (σ) = 1.00 (.07)

Anal Cond Special Set IId

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.08	1.00
0.001	1.086	1.92
0.002	0.741	2.81
0.003	0.569	3.66
Act	2.47	

L Sq Slope (σ) = 887 (8)
Intercept (σ) = 1.02 (.02)

Anal Cond Special Set Ie

R = m-OCH_3

meta-Methoxyvalerophenone, 0.10M in benzene, 0.002M heptadecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.770	1.00
0.0005	0.652	1.18
0.0010	0.569	1.35
0.0015	0.514	1.49
0.0020	0.485	1.58
0	0.765	
Act	8.81	

Anal Cond Special Set IIb

Run No. 2

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.416	1.00
0.0004	0.369	1.13
0.0030	0.227	1.83
0	0.684	1.00[a]
0.0004	0.682	1.01[a]
0.0030	0.370	1.87[a]
Act	none	

Anal Cond Special Set IIb

Run No. 3

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.798	1.00
0.001	0.735	1.06
0.002	0.532	1.47
0.003	0.380	2.05
0.004	0.313	2.49
0	0.761	
Act	14.7	

Anal Cond Special Set Ib

Run No. 4[b]

Quencher Conc. (M)	Prod/Std[c] Ratio	$\frac{\phi_o}{\phi}$
0	0.516	1.00
0.001	0.484	1.07
0.002	0.398	1.30
0.003	0.323	1.60
0.004	0.303	1.71
0	0.519	
Act	15.8	

Anal Cond Special Set Ib

---

[a] Ketone prepared via cadmium reagent method, other cases ketone prepared via Grignard reagent.

[b] Quantum yield is too low in this run, probably due to contaminated stock standard solution.

[c] Cyclobutanol areas were also measured for this run, the values for the six samples are in order: (Prod/Std), (ϕ_o/ϕ); (1.56), (1.00); (0.535), (2.91); (0.328), (4.76); (0.238), (6.56); (0.19), (8.28); (1.69), (1.00).

R = o-OCH_3

ortho-Methoxyvalerophenone, 0.10M in benzene, 0.004M heptadecane standard.

Run No. 1

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.43	1.00
0.001	1.14	2.13
0.002	1.00	2.43
0.003	0.90	2.70
0.004	0.83	2.94
0	2.43	
Act	3.54	

Anal Cond Special Set IIb

Run No. 2[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.96	1.00
0.001	1.23	2.36
0.002	1.01	2.87
0.003	0.894	3.24
0.004	0.793	3.66
0	2.83	
0.0005	1.85	1.57
0.0002	2.40	1.21
Act	1.99	

Anal Cond Special Set IIb

Run No. 3[a]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.21	1.00
0.0002	2.02	1.10
0.0004	1.72	1.29
0.0006	1.70	1.31
0.002	1.00	2.21
0.003	0.91	2.43
0.004	0.69	3.20
0	3.62[b]	
Act	2.65	

Anal Cond Special Set Ib

Run No. 4[a,c]

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.42	1.00
0.0002	2.02	1.15
0.0004	1.74	1.34
0.0006	1.50	1.55
0.001	1.28	1.82
0.002	0.88	2.65
0.003	0.77	3.03
0.004	0.64	3.64
0	2.25	
Act	none	

Anal Cond Special Set Ib

---

[a] Standard concentration of 0.002M.

[b] This value for unquenched ketone gave ϕ_{II} of 0.25.

[c] This series irradiated at 3660A.

R = o-OCH_3

ortho-Methoxyvalerophenone, 0.10M in benzene, 0.004M heptadecane standard.

Run No. 5

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.722	1.00
0.0002	0.671	1.076
0.0004	0.627	1.15
0.0006	0.602	1.20
0.001	0.557	1.296
0.002	0.370	1.95
0.003	0.359	2.01
0.004	0.270	2.59
Act	1.48	

Anal Cond Special Set Ib

Run No. 6

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	2.20	1.00
0.0002	1.90	1.16
0.0004	1.82	1.21
0.0006	1.65	1.33
0.001	1.75	1.26?
0.002	1.57	1.40
0.003	1.54	1.43
0.004	1.47	1.56
0	2.19	
Act	3.82	

Anal Cond Special Set Ib

R = p-SCH_3

para-Thiomethoxyvalerophenone, 0.10M in benzene, 0.002M octadecane standard.

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.00	----
Act	1.92 (Irrad. 3 hrs)	

Anal Cond Special Set IId

R = OH

para-Hydroxyvalerophenone, 0.10M in benzene, 0.001M heptadecane standard.

Relative area for 0.5 microliters:
Irrad. ketone sol'n = 2
0.05M product sol'n = 275
Act (Prod/Std) ratio = 12.1

Anal Cond Special Set IIIg

R = m-OCH_3; γ-CH_3

meta-Methoxy-γ-methylvalerophenone, 0.10M in benzene, 0.002M heptadecane standard.

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.54	1.00
0.0005	1.37	1.12
0.0010	1.30	1.18
0.0015	1.18	1.30
0.0020	1.10	1.39
0	1.52	
Act	8.81	
0	1.14	
Act	7.54	

Anal Cond Special Set IIb

APPENDIX A. PART 3. EXPERIMENTAL DATA FOR DETERMINING DISAPPEARANCE AND CYCLOBUTANOL QUANTUM YIELDS.

Ketone	Conc.(M)	Std 0.02	Ketone/Std Ratio: Before	After (hν)	Act	Cyclobutanols:[a] Prod/Std	#	Anal Cond
Butyrophenone	0.108	C_{17}	3.02	1.66	4.44	0.091	1	Special Set Ib
Valerophenone	0.0987	C_{18}	2.77	1.69	3.70	0.187	2	Special Set Id
γ-Hydroxybutyrophenone	0.100	C_{17}	1.96	1.07	3.70	none		Std Set I
Isovalerophenone	0.119	C_{18}	3.14	1.98	3.70	0.14	2	Special Set Ic
β,β-Dimethylbutyrophenone	0.0995	C_{16}	3.26	2.50	3.70	none		Special Set Ib
γ-Methylvalerophenone	0.112	C_{16}	3.53	2.36	3.70	0.066	1	Special Set Ib
Hexanophenone	0.111	C_{16}	3.40	2.20	3.70	0.25	2	Special Set Ib
α-Methoxyacetophenone	0.105	C_{16}	1.93	1.18	1.64	0.246	1	Special Set Ib
γ-Methoxybutyrophenone	0.109	C_{16}	2.69	1.71	4.44	0.237	2	Special Set Ib
Nonanophenone	0.098	C_{17}	3.59	2.20	4.69	0.323	2[b]	Special Set Ie
γ-Phenylbutyrophenone	0.0865	C_{17}	3.76	2.29	3.20	0.136	2[b]	Special Set If
β-Phenylbutyrophenone	0.0845	C_{17}	3.61	3.52	4.69	none		Special Set If
1,4-Dibenzoylbutane	0.0845	C_{17}	4.00	2.66	3.20	0.218	2	Special Set IIId
δ-Methylhexanophenone	0.0975	C_{16}	3.32	2.12	4.17	0.255	2	Special Set Ic

[a] The (#) stands for the number of presumed cyclobutanols observed on the VPC trace during analysis.

[b] At higher temperatures there appeared to be only one peak on the VPC chart, however, at lower temperatures (120°C) two overlapping peaks, corresponding to cis and trans isomers could be seen.

APPENDIX A. PART 3. CONTINUED

Ketone	Conc.(M)	Std 0.02M	Ketone/Std Ratio: Before	After (hν)	Act	Cyclobutanols: Prod/Std	#	Anal Cond
δ,δ-Dimethylhexanophenone	0.0863	C_{17}	2.93	1.63	4.69	0.363	2	Special Set Id
γ-Methoxyvalerophenone	0.104	C_{17}	2.88	1.98	4.69	0.146	1	Special Set Id
γ-Dimethylaminobutyrophenone	0.100	C_{18}	3.28	2.49	17.22	0.023	1	Special Set IIIb
γ-Chlorobutyrophenone	0.1036	C_{17}	1.90	1.26	4.17	0.062	1	Special Set Id
γ-Cyanobutyrophenone	0.1083	C_{17}	2.91	2.45	4.17	none		Special Set Id
Pentadecanophenone	0.0886	C_{18}	4.32	2.98	3.70	0.11	1	Special Set IIId
δ-Carboxyvalerophenone	(no determination)							
γ-Carbomethoxybutyrophenone	0.1058	C_{18}	2.55	1.96	3.70	none		Special Set IIIe
δ-Chlorovalerophenone	0.1032	C_{18}	1.91	0.57	3.70	0.14	2	Special Set IIIe
δ-Carbomethoxyvalerophenone	0.1118	C_{18}	2.93	1.08	3.70	0.48	1	Special Set Ig
δ-Cyanovalerophenone	0.1020	C_{18}	2.55	1.88	3.70	0.10	2	Special Set Ig
ε-Chlorohexanophenone	0.100	C_{18}	2.70	1.50	3.40	0.027	1	Special Set IIIf
ε-Cyanohexanophenone	0.100	C_{18}	2.39	1.69	3.40	none		Special Set IIIf
γ-Vinylbutyrophenone	0.100	C_{17}	3.04	2.59	2.40	0.058	2	Special Set Ic
p-Thiomethoxyvalerophenone	0.100	C_{18}[a]	33.0 33.0	33.1 32.0	1.92 ≃ 14	none		Special Set IId

[a] Standard concentration = 0.002M.

APPENDIX A. PART 4. SOLVENT STUDIES ON THE PHOTOCHEMICAL BEHAVIOR OF SUBSTITUTED PHENYL KETONES.

Isovalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH[a] Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	0.868	0.376
0.50	1.46	0.635
1.00	1.71	0.744
2.00	1.88	0.816
5.00	2.03	0.881
8.00	1.93	0.836
0	0.862	
Act[b]	0.758	

Anal Cond Std Set I

β,β-Dimethylbutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	0.445	0.195
0.50	0.646	0.285
1.00	0.806	0.352
2.00	1.02	0.445
5.00	1.37	0.598
8.00	1.73	0.755
0	0.449	
Act	0.758	

Anal Cond Std Set I

γ-Methylvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	0.883	0.26
0.50	1.61	0.48
1.00	1.93	0.576
2.00	2.47	0.735
5.00	2.92	0.87
8.00	2.92	0.87
0	0.862	
Act	1.10	

Anal Cond Std Set I

Valerophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	0.99	0.33
0.50	1.77	0.585
1.00	2.19	0.742
2.00	2.48	0.840
6.00	3.02	1.00
Act	none	

Anal Cond Std Set I

---

[a] Tert-butyl alcohol was added in increments to the benzene solutions.

[b] Actinometers are 0.10M valerophenone, 0.004M tetradecane standard in benzene unless otherwise indicated.

Hexanophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	0.886	0.30
0.50	1.64	0.547
1.00	2.02	0.675
2.00	2.21	0.738
5.00	2.53	0.840
8.00	2.56	0.856
0	0.911	
Act	0.99	

Anal Cond Std Set I

γ-Hydroxybutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	1.33	0.35
0.50	1.70	0.45
1.00	1.93	0.51
2.00	2.11	0.56
5.00	2.70	0.72
0	1.31	
Act	1.24	

Anal Cond Std Set I

δ-Chlorovalerophenone, 0.10M benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	1.51	0.60
1.00	1.68	0.67
3.00	1.70	0.68
5.00	1.72	0.69
8.00	1.33	0.53
0	1.53	
Act	0.829	

Anal Cond Std Set II

δ-Cyanovalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	1.27	0.50
1.00	1.79	0.71
3.00	1.53	0.61
3.00	1.60	0.64
5.00	1.50	0.60
8.00	1.34	0.53
0	1.28	
Act	0.829	

Anal Cond Std Set II

δ-Carbomethoxyvalerophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	1.44	0.58
1.00	1.82	0.72
3.00	1.94	0.77
5.00	1.88	0.75
8.00	1.84	0.73
0	1.46	
Act	0.829	

Anal Cond Std Set II

β-Phenylbutyrophenone, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	0.044	
8.0	0.0604	
Act	none	

Anal Cond Std Set I

Valerophenone, 0.10M in solvent, 0.004M tetradecane standard.

Run No. 1 (benzene solvent plus 0.60M pyridine added)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.12	1.00
0.010	0.840	1.32
0.020	0.655	1.69
0.030	0.535	2.07
0.040	0.432	2.56
0	1.10	
Act	0.460	

Anal Cond Std Set I

Run No. 2 (benzene solvent)

EtAc[a] Conc. (M)	Prod/Std Ratio	ϕ_{II}
0	0.916	0.33
0	0.912	0.33
0.10	0.971	0.35
0.10	0.982	0.35
0.20	1.038	0.375
0.20	1.021	0.37

Anal Cond Std Set I

Run No. 3 (methanol solvent)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.64	1.00
0.020	0.618	2.59
0.040	0.315	5.08
0.060	0.208	7.68
0	1.56	
Act	none	
0	1.96	
Act	0.70	
0	1.42	
Act	0.486	
0	1.48	
Act	0.554	

Anal Cond Std Set I

Run No. 4 (acetonitrile solvent)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.40	1.00
0.020	0.621	2.26
0.040	0.382	3.67
0.040	0.378	3.71
0.060	0.274	5.10
0.060	0.275	5.09
0	1.40	
Act	none	
0	2.12	
Act	0.785	
0	1.16	
Act	0.478	

Anal Cond Std Set I

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[a] Ethyl acetate used in solvent study.

γ-Dimethylaminobutyrophenone, 0.10M in solvent, 0.004M tetradecane standard.

Run No. 1 (methanol solvent)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	1.12	1.00
0.10	0.844	1.33
0.20	0.60	1.87
0.30	0.497	2.26
0.40	0.386	2.90
Act	1.56	

Anal Cond Std Set I

Run No. 2 (acetonitrile solvent)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.552	1.00
0.10	0.465	1.165
0.20	0.417	1.30
0.30	0.375	1.445
0.40	0.337	1.61
0	0.542	
Act	3.70	

Anal Cond Std Set I

γ-Dimethylaminobutyrophenone Hydrochloride, 0.10M in solvent, 0.004M tetradecane standard (except where indicated).

Run No. 1 (methanol solvent)

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.253	1.00
0.001	0.140	1.78
0.005	0.056	4.5
0	0.245	
0	0.248	
Act	9.59	

Anal Cond Std Set I[a]

Run No. 2[b] (water solvent, no standard used).

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.13	
Act	33.5	

Anal Cond Std Set I[a]

---

[a] The amine hydrochlorides were analyzed by regenerating the amine by adding a small amount of fine potassium carbonate, shaking for one minute, and analyzing the sample within ten minutes.

[b] The product to standard ratio was estimated by taking accurate 0.5 microliter shots of the sample and the actinometer.

Disappearance of γ-Dimethylaminobutyrophenone, 0.10M in given solvent, 0.020M octadecane standard.

Solvent	(Prod/Std Ratio) Before	After (hν)	Moles disapp'd	Moles Act	ϕ_{dis}
methanol	3.04	2.40	0.021	0.074	0.28
acetonitrile	3.77	3.49	0.0074	0.074	0.10
[γ-Dimethylaminobutyrophenone hydrochloride, same conditions as above]					
methanol	2.62	1.11	0.058	0.812	0.071
water	2.30	2.29	0.00	0.812	0.00

Anal Cond Special Set IIIb

---

para-Methylvalerophenone, 0.10M in methanol, 0.004M pentadecane standard.

Quencher[a] Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.740	1.00
0.0002	0.525	1.40
0.0004	0.419	1.75
0.0010	0.240	3.06
0.0020	0.133	5.52
0	0.727	
Act	1.19	

Anal Cond Special Set Ia

1,4-Dibenzoylbutane, 0.10M in benzene, 0.004M tetradecane standard.

t-BuOH Conc. (M)	Prod/Std Ratio	ϕ_{II}
8.0	2.16	0.43
Act	1.66	

Anal Cond Std Set II

γ-Dimethylaminobutyrophenone Ethyl Bromide, 0.10M in methanol, 0.004M tetradecane standard.

Quencher Conc. (M)	Prod/Std Ratio	$\frac{\phi_o}{\phi}$
0	0.014	
Act	12.5	
0	0.024	
Act	19.9	

Anal Cond Std Set II

---

[a] Naphthalene used as quencher.

APPENDIX A. PART 5. MISCELLANEOUS DATA ON QUANTUM YIELDS.

a. Type-II Quantum Yields versus Ketone Concentration.

Ketone, in benzene solvent, tetradecane standard.	Std Conc.	[Prod/Std Ratios] 0.02M	0.05M	0.10M	0.20M	Act
β,β-Dimethylbutyrophenone	0.004	----	0.92	0.90	0.92	1.64
Pentadecanophenone	0.004	----	1.22	1.31	1.43	1.64
1,4-Dibenzoylbutane	0.004	----	1.31	1.50	1.74	1.64
γ-Hydroxybutyrophenone	0.004	----	2.26[a]	1.33	----	1.24
ε-Cyanohexanophenone	0.004	----	1.36	1.40	1.52	1.66
δ-Carbomethoxyvalerophenone	0.001	2.47	5.48[b]	2.74	----	1.44[d]
γ-Carbomethoxybutyrophenone	0.001	1.60[c]	3.56[b]	1.85	----	1.57[d]

b. Type-II Quantum Yield versus Irradiation Time (Conversion)[e].

Ketone, 0.10M in benzene, 0.001M tetradecane standard.	Prod/Std Ratios for Irradiation Times: 15 min	30 min	62 min	90 min	120 min
γ-Carbomethoxybutyrophenone (··f)	1.05 (2.10)	1.85 (3.55)	3.70 (7.12)	4.92 (9.48)	---- (11.39)
Valerophenone	0.78	1.57	3.19	4.69	6.17
	15 min	33 min	65 min	90 min	
δ-Carbomethoxyvalerophenone (··f)	1.25 (2.57)	2.74 (5.49)	5.50 (11.26)	7.46 (15.6)	
Valerophenone	0.659	1.44	2.78		

[a] Standard concentration 0.002M.

[b] Standard concentration 0.0005M. [c] Standard concentration 0.0012M.

[d] These actinometers also 0.001M in standard; others are 0.004M.

[e] Other measurements of ϕ_{II} versus conversion are included in the data with γ-phenyl, γ-vinyl, γ-cyano, and γ-carbomethoxybutyrophenone.

[f] Ketone 0.05M and standard 0.0005M, to correct to 0.001M standard divide by 2.

c. Viscosity Measurements[a] on Solvent and Solutions.

Run No.	Purified Benzene	Valerophenone, 0.10M in benzene, 0.004M C_{14} Std	Pentadecanophenone, 0.10M in benzene, 0.004M C_{14} Std
1	2 min 49.0 sec	2 min 51.6 sec	3 min 01.0 sec
2	2 48.7	2 52.0	3 00.0
3	2 48.5	2 52.9	3 00.1
4	2 48.7	2 52.7	3 00.0
Ave	2 48.7	2 52.3	3 00.3

d. Effects of Miscellaneous Materials on the Type-II Quantum Yield.

Valerophenone, 0.10M in methanol, 0.004M tetradecane standard.

Material added:	Prod/Std Ratio
none	1.465
none	1.50
0.080M KBr	1.47
0.020M $Et_4N^+Br^-$	1.48
0.040M "	1.51
0.080M "	1.49
0.20M Et_3N	0.756
0.40M "	0.486
0.80M "	0.258

[a] Measurements were made with an Ostwald viscometer at 25°C.

APPENDIX B. COMPUTER PROGRAM FOR DETERMINING LEAST SQUARES SLOPES OF STERN-VOLMER DIAGRAMS.[a]

This Fortran IV program[121] is a straightforward determination of the least squares values[122] of Stern-Volmer slopes. One useful feature of the program is that the line is not constrained to going through one for the unquenched sample so the experimental intercept and its standard deviation can be used for diagnostic purposes. Instead, the value 1.0 at zero quencher concentration is used as one point on the line, giving it 20 to 25% weight in most cases. The data per sample is limited to one card of 16 five-place columns (4 digits plus decimal). Calculations were done on the CDC-6500 computer at Michigan State University.

```
      Program Kemp(Input, Output, Tape60=Input, Tape61=Output)
C     Ref L. G. Parratt Probability and Exp Errors in Science, p129
      Dimension Phi(16), Quen(16), Ident(10)
C     Read Number of Pairs of Data Points on Card
    1 Read (60,2) IN
    2 Format (I5)
      IF (IN.GT.100) Go to 99
      Read (60,3) Ident
      Write (61,33) Ident
    3 Format (10A8)
   33 Format (10A8)
      Read (60,6)((Phi(I),Quen(I)), I=1, IN)
    6 Format (16F5.3)
C     Compute Sums of Phi(I), Quen(I), and of Products
      SUMXX=0.0
      SUMY=0.0
      SUMX=0.0
      SUMXY=0.0
      SUM=0.0
```

---

[a] This program was designed by Dr. Ellister MacDonald, post-doctoral fellow at Michigan State University, 1969-1971.

APPENDIX B. Continued.

```
      Do 10 I=1,IN
      SUMXX=SUMXX+Quen(I)*Quen(I)
      SUMXY=SUMXY+Phi(I)*Quen(I)
      SUMY=SUMY+Phi(I)
      SUMX=SUMX+Quen(I)
      SUM=SUM+1.0
   10 Continue
C     Now Compute Average X and Y
      AVY=SUMY/SUM
      AVX=SUMX/SUM
C     Now Form Deviations in X and Y
      DiffY=0.0
      DiffX=0.0
      DFSQX=0.0
      DD=0.0
      Do 11 K=1,IN
      DiffY=Phi(K)-AVY
      DiffX=Quen(K)-AVX
      DD=DD+DiffY*DiffX
      DFSQX=DFSQX+((Quen(K)-AVX)**2)
   11 Continue
C     Now Form A and B
      A=(AVY*SUMXX-AVX*SUMXY)/DFSQX
      B=DD/DFSQX
C     Now Form E.S.D ≠ S on Y
      SOMY=0
      Do 12 L=1,IN
      Z=Phi(L)-A-B*Quen(L)
      SOMY=SOMY+Z*Z
C     Print Deviations From L.S.Line
      Write(61,44) Phi(L), Quen(L), Z
   44 Format(2F8.4,F7.3)
   12 Continue
      SY=SQRT(SOMY/SUM)
C     Now Compute E.S.D of A
      SIMX=0.0
      SIMXX=0.0
      Do 13 M=1,IN
      SIMX=Quen(M)*Quen(M)+SIMX
   13 Continue
      SIMXX=SUM*SIMX-(SUMX*SUMX)
      SAA=SQRT(SIMX/SIMXX)
      SA=SAA*SY
C     Now Compute E.S.D of B
      SBB=SQRT(SUM/SIMXX)
      SB=SBB*SY
      Write(61,14) A, SA, B, SB
   14 Format(2(2F10.6,4X))
      Go to 1
   99 Call Exit
      END
```

APPENDIX C. IDENTIFYING SPECTRAL CHARACTERISTICS OF PREPARED KETONES.

Ketone Key	IR Spectrum[a] Phenyl ketone carbonyl stretch Substituted phenyl bands Other bands labeled VS = very strong etc.	nmr Spectrum[b] S = singlet D = doublet T = triplet M = multiplet Q = quintet 5_p = 5 protons	Mass[c] Spectrum parent peak m/e⁻
β,β-Dimethylbutyrophenone	1685 cm^{-1} VS 1600 1450 }S	5_pM at 2.16 & 2.65τ 2_pS at 7.23τ 9_pS at 8.96τ	176
γ-Methylvalerophenone	1685 cm^{-1} VS 1600 1450 }S	5_pM at 2.15 & 2.66τ 2_pT at 7.16τ 3_pM at 8.41τ 6_pD at 9.10τ	176
δ-Methylhexanophenone	1685 cm^{-1} VS 1600 1450 }S	5_pM at 2.18 & 2.67τ 2_pT at 7.18τ 5_pM at 8.1-8.9τ 6_pD at 9.11τ	190
δ,δ-Dimethylhexanophenone	1685 cm^{-1} VS 1600 1450 }S	5_pM at 2.18 & 2.65τ 2_pT at 7.19τ 4_pM at 8.2-8.9τ 9_pS at 9.1τ	204
Nonanophenone	1685 cm^{-1} VS 1600 1450 }S		218 + (232≃20%)

[a] Taken on a Perkin Elmer 237B Infrared Spectrometer. Substituted phenyl bands were generally doublets of which the strongest band is indicated. Assignments were made according to chart in Reference 124.

[b] Taken on a Varian A-60 nmr spectrometer.

[c] The author is indebted to Mrs. R. L. Guile for the mass spectra taken on a Hitachi-Perkin Elmer RMU-6 Mass Spectrometer.

APPENDIX C. (Continued)

Ketone	IR Spectrum	nmr Spectrum	Mass Spectrum
γ-Hydroxybutyrophenone	1685 cm^{-1} VS 1600 }S 1450 3300-3500 VS (O-H)	5_pM at 2.16 & 2.7τ 1_pS at 6.02τ 2_pT at 6.42τ 2_pM at 7.02τ 2_pM at 8.14τ	164
γ-Methoxybutyrophenone	1685 cm^{-1} VS 1600 }S 1450 1120 VS ($C-OCH_3$)		178
γ-Chlorobutyrophenone	1680 cm^{-1} VS 1600 }S 1450	5_pM at 2.16 & 2.60τ 2_pT at 6.42τ 2_pT at 6.95τ 2_pQ at 7.88τ	182
γ-Dimethylaminobutyrophenone	1685 cm^{-1} VS 1595 }S 1445 2770 VS (NCH_2-H)		191
γ-Carbomethoxybutyrophenone	1685 cm^{-1} VS 1600 }S 1450 1735 VS ($-\overset{O}{\overset{\|}{C}}-OCH_3$)		206
γ-Cyanobutyrophenone	1685 cm^{-1} VS 1600 }S 1450 2240 M (CN)		173

APPENDIX C. (Continued)

Ketone	IR Spectrum	nmr Spectrum	Mass Spectrum
γ-Methoxyvalerophenone	1685 cm^{-1} VS 1600 1450 }S 1130 S (C-OCH_3)		192
γ-Vinylbutyrophenone	1685 cm^{-1} VS 1600 1450 }S 1640 M (C=C)	5_pM at 2.1 & 2.6τ 1_pM at 3.8-4.45τ 2_pM at 4.8-5.1τ 2_pT at 7.08τ 4_pM at 7.8-8.3τ	174
δ-Chlorovalerophenone	1685 cm^{-1} VS 1595 1445 }S	5_pM at 2.14 & 2.60τ 2_pT at 6.50τ 2_pT at 7.08τ 4_pM at 8.18τ	197
δ-Cyanovalerophenone	1690 cm^{-1} VS 1600 1450 }S 2240 M (CN)		187
δ-Carbomethoxyvalero-phenone	1685 cm^{-1} VS 1600 1450 }S 1735 VS (CH_3OC=O)		220
ε-Chlorohexanophenone	1685 cm^{-1} VS 1595 1445 }S		210
ε-Cyanohexanophenone	1685 cm^{-1} VS 1600 1450 }S 2240 M (CN)		201

APPENDIX C. (Continued)

Ketone	IR Spectrum	nmr Spectrum	Mass Spectrum
p-Methoxyvalero-phenone	1680 cm^{-1} VS 1600 VS 1510,1460 } S 1420 1260 VS (Φ-OCH_3)		
m-Methoxyvalero-phenone	1680 cm^{-1} VS 1600 VS 1480,1470 } S 1420 1265 VS (Φ-OCH_3)		
o-Methoxyvalero-phenone	1680 cm^{-1} VS 1600,1490 } S 1470,1440 1250-1280 VS (Φ-OCH_3)		
p-Methoxy-γ-methyl-valerophenone	1680 cm^{-1} VS 1600 VS 1505,1455 } S 1415 1260 VS (Φ-OCH_3)		
m-Methoxy-γ-methyl-valerophenone	1680 cm^{-1} VS 1600,1490 } S 1480,1430 1250-1290 VS (Φ-OCH_3)		
m-Chlorovalerophenone	1685 cm^{-1} VS 1570 } S 1420		196

APPENDIX C. (Continued)

Ketone	IR Spectrum	nmr Spectrum	Mass Spectrum
o-Chlorovalerophenone	1700 cm^{-1} VS 1590 1430 }S		196
m-Fluorovalerophenone	1685 cm^{-1} VS 1590 1440 }VS 1260 VS (Φ-F)		180
o-Fluorovalerophenone	1685 cm^{-1} VS 1610 1480,1450 }VS 1210 VS (Φ-F)		180
p-Trifluoromethyl-valerophenone	1695 cm^{-1} VS 1580 W 1410 S 1130,1165 VS (CF_3)		230
m-Trifluoromethyl-valerophenone	1695 cm^{-1} VS 1610 1440 }S 1130,1160 VS (CF_3)		230
o-Trifluoromethyl-valerophenone	1710 cm^{-1} VS 1580 1450 }S 1125,1160 VS (CF_3)		230
m-Methylvalerophenone	1685 cm^{-1} VS 1600 1465 }S		

APPENDIX C. (Continued)

Ketone	IR Spectrum	nmr Spectrum	Mass Spectrum
p-Thiomethoxyvalero-phenone	1680 cm^{-1} VS 1590 VS 1465,1435 }M 1400		
p-Phenyl-γ-methyl-valerophenone	1680 cm^{-1} VS 1605 VS		
Valerophenone (for comparison)	1690 cm^{-1} VS 1600 }S 1450	5_pM at 2.13 & 2.63τ 2_pT at 7.16τ 4_pM at 8.1-8.9τ 3_pT at 9.1τ	162