measurements over a wide range of temperatures. In view of these errors no speculation based on the difference would appear to be warranted. We note that our data provide $\Delta H°$, $\Delta S°$, $\Delta F°$, and K for formation of the complex. These values are listed in Table I. The thermodynamic quantities are compatible with a loose complex between highly hindered species. A summary of the various rate constants is given in Table II.

The most striking feature of the hydroxylamine–nitroxide exchanges is the temperature dependence of the rate. It is possible to account for this anomalous temperature dependence by a model in which the exchange reaction can proceed by two or more paths with different temperature dependences.

At high temperatures where the rate increases with increasing temperature $k_{\text{OH}}/k_{\text{OD}}$ is greater than 1 and increases with increasing temperature. In the region of anomalous temperature dependence $k_{\text{OH}}/k_{\text{OD}} = 1$. If a two-path model is adopted, the predominant high-temperature path would be one which has a normal isotope effect and the low temperature one with no isotope effect.

Conclusion

Our conclusions appear to be meager relative to the amount of experimental information which has been obtained. The work illustrates the possibility of finding short-lived intermediates by magnetic resonance methods. It demonstrates how complex an apparently simple reaction, the transfer of a hydrogen atom, can be. With further work the conclusions may approach the richness of the experimental information.

Acknowledgments. We wish to thank Drs. A. K. Hoffman and G. Coppinger who kindly supplied some of the samples used in our experiments. This research has been supported by the National Science Foundation under GP 2676 and by the National Institutes of Health under GM 13205.

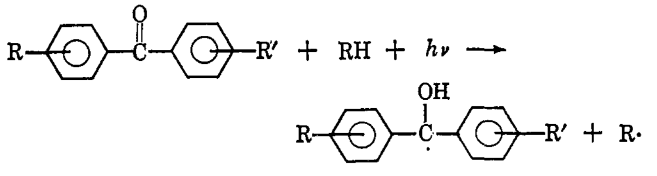
Reactivity of Excited States. Intramolecular Hydrogen Atom Abstraction in Substituted Butyrophenones[1a]

E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr.[1b]

Contribution from the Department of Chemistry, University of California, Riverside, California. *Received December 9, 1965*

Abstract: The quantum efficiency of photocycloelimination of ethylene ("type II process"), ϕ_{II}, from butyrophenone and several *para*-substituted derivatives is highly sensitive to the electron-donating character of the substituent and to the nature of the lowest triplet state. Thus at 3130 A, 25°, and in several solvents, ϕ_{II} drops from 0.42 and 0.39 in butyrophenone and *p*-methylbutyrophenone, respectively, to 0.00 in the *p*-NH_2, *p*-OH, and *p*-C_6H_5 derivatives. Energy-transfer and spectroscopic studies indicate that the photoreaction proceeds from the lowest triplet state of these ketones and that this state is (n,π^*) for reactive and (π,π^*) for unreactive ketones. *p*-Bromo- and *o*-hydroxybutyrophenone do not undergo photocycloelimination. The former eliminates bromine atoms with a quantum yield of 0.25. The latter photoenolizes in a reaction similar to that observed for *o*-hydroxy- and *o*-methylbenzophenone. The photocycloelimination reaction is temperature dependent with an activation energy of about 2 kcal/mole for butyrophenone.

Recent studies concerning the photochemical reactivity of aryl ketones and their ring-substituted derivatives toward *intermolecular* hydrogen atom abstraction, giving ketyl radicals and ultimately pinacol formation, have greatly expanded our knowledge of the effect of substituents on the reactivity and low-lying excited-state structure of these compounds.[2–8]



It is now recognized that the introduction of substituent groups into the aromatic rings of benzophenone, for instance, can drastically alter the *intermolecular* hydrogen atom abstracting ability of the carbonyl group. Two substituent effects have been established, one related to *ortho* substitution and one related to *para* substitution. The *ortho* effect involves formation of a transient six-membered ring followed by transfer of a hydrogen atom from the *ortho* group to the oxygen atom of the carbonyl chromophore, to form what Yang has classified as a photoenol.[7–9] This process is reversible and no net photochemistry results.

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(1) (a) Presented in part at the Symposium on "Structure and Photochemistry of Excited States," 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1964, p7S; and the IVth International Congress on Photobiology, Oxford, July 1964; (b) author to whom inquiries concerning this paper should be sent.

(2) J. N. Pitts, Jr., L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. Vesley, *Photochem. Photobiol.*, 4, 305 (1965).

(3) E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *J. Am. Chem. Soc.*, 85, 2671 (1963).

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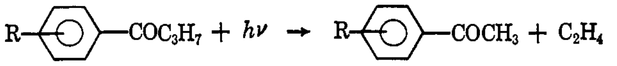
The *para* effect involves the nature of the lowest triplet states of these ketones with ${}^3(n,\pi^*)$ states being generally reactive and ${}^3(\pi,\pi^*)$ states nonreactive.[4-6,10] Similar structural effects have been noted for the photoreactivities of alkyl aryl ketones toward *intermolecular* hydrogen atom abstraction reactions.[11,12] However, the variation of the quantum yield of *intermolecular* hydrogen atom abstraction between *p*-hydroxy- and *p*-methoxy- and *p*-phenyl- and *p*-aminobenzophenones has not been completely explained. Porter and Suppan have proposed that the presence of certain electron-donating substituents results in the lowest-excited triplet being an "intramolecular charge transfer state."[13] As major evidence for the involvement of such states, they cite pronounced solvent effects on the reactivity of *p*-amino- and 4,4′-dimethylaminobenzophenones toward pinacol formation. However, recent investigations of this solvent effect in several laboratories, including our own, suggest that while these ketones, which all agree are unreactive in isopropyl alcohol, may indeed react in cyclohexane, the process does not involve hydrogen atom abstraction leading to pinacol.[14,15] For this as well as spectroscopic considerations, the argument based on participation of "intramolecular charge-transfer states" does not seem compelling.

Actually the use of the benzophenone system to study the excited-state reactivity of ketones has several disadvantages. It is based on a bimolecular abstraction process involving hydrogen atom donation from a solvent molecule. In order to evaluate the physical effects of altering the environment of the ketone, allowance must be made for changes of the C–H bond strength accompanying changes in solvent. In addition, the reactants and products involved are usually high-melting solids which are easily decomposed thermally and not easily analyzed by conventional vpc techniques. The reaction paths and product types are dependent on a variety of factors, such as pH and solvent purity, which must be carefully controlled if the system is to remain well behaved. Spectrophotometric methods of analysis have frequently been employed in dealing with the benzophenone series[13] in order to circumvent the rather difficult and tedious analysis for the substituted benzopinacols. But, these methods involve disappearance of reactant rather than appearance of product, and alterations in reaction paths arising through uncontrolled environmental changes and leading to products other than pinacols cannot be observed.

On the other hand, analogous studies of the effect of structure and environment on the photoreactivity of alkyl aryl ketones toward *intramolecular* hydrogen atom abstraction reactions by the "type II" process avoids these disadvantages. Since the hydrogen atom is abstracted from the alkyl chain of the ketone, the physical environment may be altered drastically and the effects assessed without involving the altered C–H bond strength of the solvent. Also, the products are, in most instances, readily analyzed by gas chromatography, and all reaction products of the ketone may be observed simultaneously.



Finally, the study of alkyl aryl ketones is of general interest because little is known about their photochemistry,[16] and results can be compared with recent investigations of the photocycloelimination reactions and excited states of alkyl ketones.[17]

Experimental Section

Materials. The ketones used were obtained from a variety of sources. Acetophenone, butyrophenone, and several *para*-substituted acetophenones were obtained from Matheson Coleman and Bell. *p*-Chloro- and *o*- and *p*- hydroxybutyrophenone were obtained from Aldrich Chemical. *p*-Bromobutyrophenone was supplied by Columbia, and *p*-aminobutyrophenone was supplied by K and K. 1-Phenylcyclobutanol, α-tetralol, *p*-phenyl-, *p*-acetamido-, and *p*-acetoxybutyrophenone were provided by Dr. J. M. Vernon, while *p*-fluorobutyrophenone was obtained from Dr. P. C. Radlick. All liquid ketones were purified by vapor phase chromatography immediately prior to use. All solid ketones were purified by recrystallization followed by sublimation and zone-refining techniques.

Hydrocarbon solvents were from Matheson Coleman and Bell, and alcohol solvents were obtained from Baker and Adamson. Alcohol solvents were further purified by chemical techniques followed by vacuum distillation on a spinning band column. Hydrocarbon solvents were purified by liquid–solid chromatography on a 20% NaBr–alumina column.[18] Purity was monitored by vapor phase chromatography in all cases.

Liquid-Phase Photolysis. The light source was a PEK Laboratories Inc. 109 super-high-pressure mercury arc filtered with 5 cm of water and suitable JENA UV-IL inteference filters for 3130 and 3660 A. Spectral purity of the light transmitted by this arrangement was determined with a modified Cary 14 spectrophotometer. Lamp intensities were measured by the method of Parker and Hatchard[19] modified by use of ammonium fluoride.[20]

The modified method involves development of 25 ml of irradiated and blank ferrioxalate solution with 3 ml of the acetate buffer, 3 ml of 0.1% phenanthroline solution, and 1 ml of 2 *N* ammonium fluoride solution. This method reduces the development time of the ferrioxalate–phenanthroline complex to within 0.5 hr. All solutions were vacuum degassed prior to irradiation in a quartz cell mounted in a thermostated compartment. Quantum yields are reported for 25° except where noted. Reaction products were separated and quantitatively analyzed by vapor phase chromatography and identified by nmr, infrared, and mass spectrometric methods.

Spectroscopy and Spectrometry. Ultraviolet and visible spectra were recorded on Cary Models 14 and 15 spectrophotometers. Phosphorescence, total emission spectra, and phosphorescence decay times were recorded with equipment constructed in these laboratories.[21] The nmr and epr spectra were obtained with Varian Models A-60 and V-4500 spectrometers, respectively. Infrared spectra were recorded on Perkin-Elmer Models 221 and 137 spectrophotometers.

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(9) E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *J. Am. Chem. Soc.*, 85, 2671 (1963).

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(13) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664, (1965), and earlier references therein.

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(15) Private communication from the laboratory of Professor G. O. Schenck.

(16) See, for instance, J. N. Pitts, Jr., and J. K. S. Wan in "The Carbonyl Group," S. Patai, Ed., John Wiley and Sons, London, 1965.

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(18) We are indebted to Dr. C. G. S. Philips for suggesting this method of solvent purification.

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(21) We are indebted to Professor D. R. Kearns for providing some of these phosphorescence spectra and all singlet–triplet spectra employed in this work.

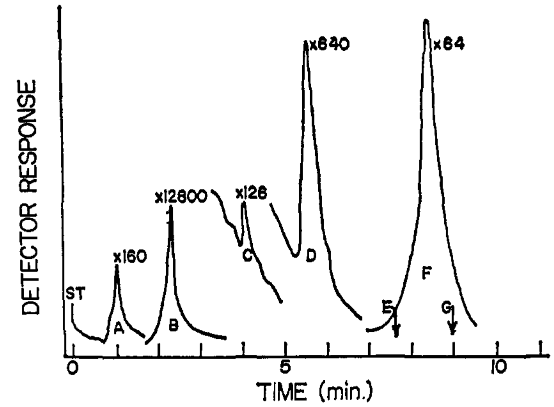
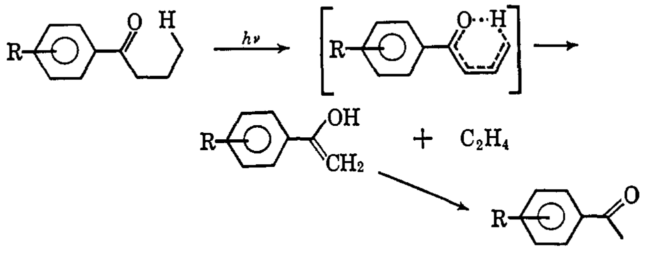


Figure 1. Chromatograph of irradiated butyrophenone–benzene solution on a $^1/_8$-in diameter, 10-ft Carbowax 20M column at 200°: A, benzene; B, acetophenone; C, butyrophenone; D, 1-phenylcyclobutanol; E, α-tetralone; F, unknown compound I; G, α-tetralol.

Results and Discussion

The major products of the solution phase photolysis of butyrophenone and the ring-substituted derivatives studied here (with the exception of the *o*-hydroxy and *p*-bromo derivatives), at any wavelength above 2800 A and in any hydrocarbon or alcohol solvent, are those resulting from the photocycloelimination ("Norrish type II") reaction, shown in the following scheme.



Quantum yields at 3130 A for the production of acetophenones by this process, ϕ_{II}, in benzene at 25° are given in Table I. Quantum yields of olefin and ketone have been compared and found to be equivalent for several of the ketones and are presumed equivalent for the others. The quantum yields of CO, ethane, propylene, etc., resulting from "type I" radical splits, are less than 0.01 under all conditions employed.

These ketones were found also to undergo photopinacolization reactions in alcohol solvents.

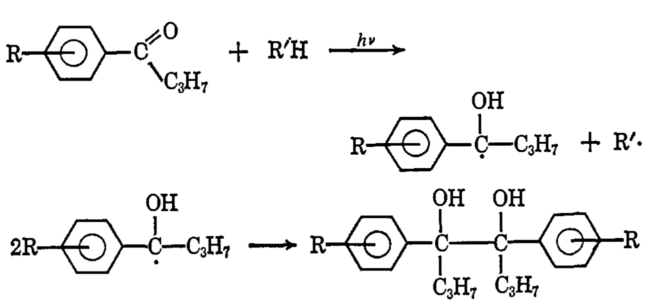


Figure 2. Infrared spectrum of unknown compound I (A) compared with the spectrum of butyrophenone (B) taken in CCl_4.

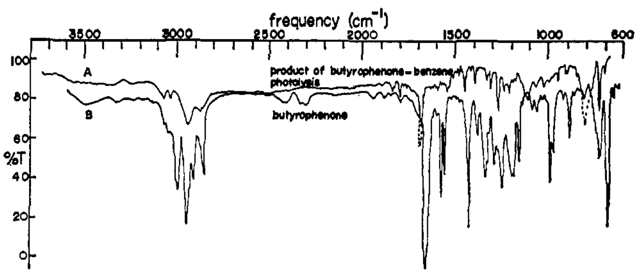
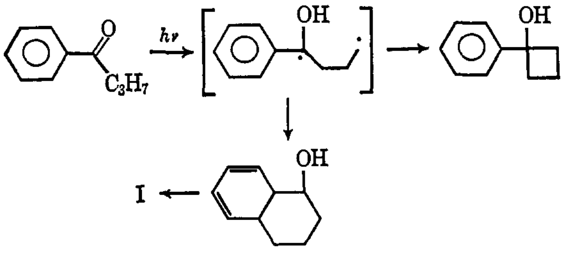


Table I. Quantum Yields of the Type II Processes, ϕ_{II}, in Substituted Butyrophenones in Benzene at 25° and Spectroscopic Properties of these Compounds

Compound	ϕ_{II}	Wave-length mμ[f]	Triplet level, kcal/mole	τ, sec
para Substituted				
p-Chlorobutyrophenone	0.43	395[a]	72.4	0.014[b]
Butyrophenone	0.42	383[c]	74.7	0.002
p-Acetoxybutyrophenone	0.42	385[a]	74.3	0.027
p-Methylbutyrophenone	0.39	388[c]	73.7	0.009[b]
p-Fluorobutyrophenone	0.29	392[a]	72.9	0.004
p-Methoxybutyrophenone	0.10	390[c]	73.3	0.051
p-Acetamidobutyrophenone	0.00	409[a]	69.9	0.058
p-Aminobutyrophenone	0.00	443[c]	64.5	0.084 0.022[d]
p-Hydroxybutyrophenone	0.00	403[c]	71.0	0.084 0.043[d]
p-Phenylbutyrophenone	0.00	...	...	long[b]
p-Bromobutyrophenone[e]	0.00	392[a]	72.9	0.011
ortho Substituted				
o-Hydroxybutyrophenone	0.00	...	...	μsec
o-Methoxybutyrophenone	0.12	390[c]	73.3	0.039
Alkyl-Chain Substituted				
γ-Phenylbutyrophenone	0.49	...	...	...

[a] Employing singlet–triplet spectra. [b] In 2-pentene. [c] In 4:1 ethanol–methanol at −190°. [d] In glacial acetic acid. [e] *p*-Bromobutyrophenone reacts *via* bromine atom elimination. [f] Of 0–0 phosphorescence band.

The quantum yield of butyrophenone pinacol from the butyrophenone–isopropyl alcohol photolysis, ϕ_{pinacol}, was less than 0.03. Quantum yields of pinacol were not determined for the other butyrophenones, but ϕ_{pinacol} was less than 0.01 in each case. Only two other products were detected in the butyrophenone photolysis, 1-phenylcyclobutanol and an as yet unidentified product having a vpc retention time similar to α-tetralone (bicyclo[4.4.0]decadienone) on Carbowax 20M and Silicone SE-30 columns and an infrared spectrum indicating the presence of a carbonyl group and an *ortho*-disubstituted benzene group. Figure 1 illustrates the chromatogram of unknown product (I) compared with retention times of α-tetralone and α-tetralol. Figures 2 and 3 illustrate the infrared and ultraviolet spectrum of I, respectively, compared with those of butyrophenone. The following general scheme is compatible with this evidence.



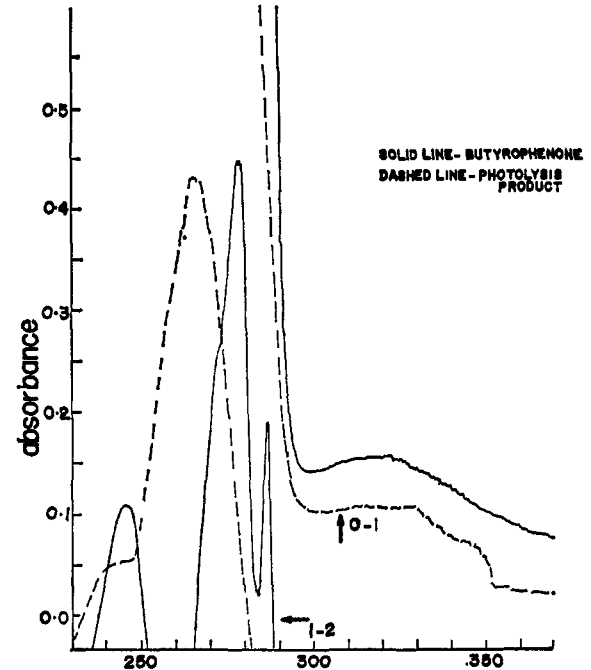


Figure 3. Ultraviolet spectrum of unknown compound I (dashed line) compared with the spectrum of butyrophenone (solid line) taken in cyclohexane.

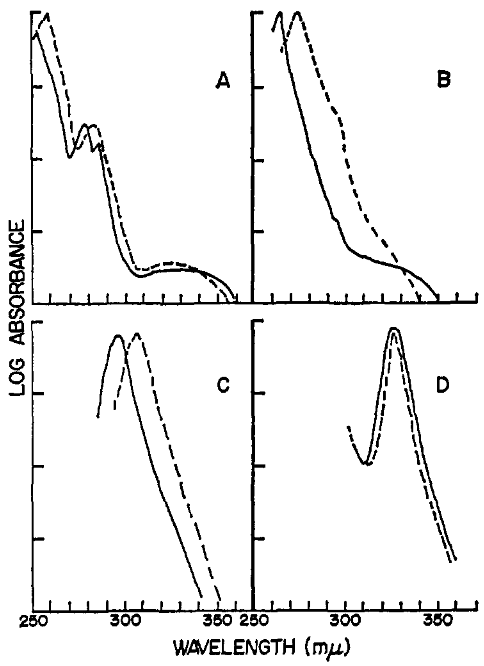


Figure 4. Ultraviolet absorption of some butyrophenones in hexane (solid line) and isopropyl alcohol (dashed line): A, butyrophenone; B, *p*-methoxybutyrophenone; C, *p*-aminobutyrophenone; D, *o*-hydroxybutyrophenone.

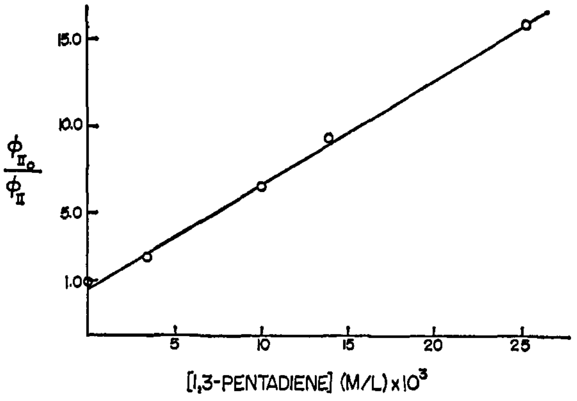


Figure 5. Stern–Volmer plot for quenching of the photocycloelimination reaction of butyrophenone by 1,3-pentadiene.

No quantum yield determinations were made for substituted butyrophenones except that the sum of the quantum yields for processes other than the "type II" were less than 0.01 under all conditions employed.

Butyrophenone, *p*-methyl-, *p*-fluoro-, *p*-chloro-, *p*-acetoxy-, *p*-acetamido-, and *p*-phenylbutyrophenone display a low-intensity absorption band ($\epsilon < 100$) in the 3000–3500 A region which undergoes the characteristic n,π* blue shift in polar solvents. The n,π* band of *p*-methoxybutyrophenone is observed as a small shoulder on its π,π* band at about 3000 A. This n,π* band is almost completely hidden beneath the π,π* band in polar solvents. The n,π* band of both *p*-amino- and *p*-hydroxybutyrophenone are shifted beneath the π,π* band for these compounds which now occurs at about 3500 and 3200 A respectively. This is shown in Figure 4. It is interesting that ϕ_{II} for *p*-methoxybutyrophenone is identical for solutions in both polar and nonpolar solvents although in one case (irradiation at 3130 A) excitation apparently involves a $\pi \rightarrow \pi^*$ transition, whereas in the other case it is an $n \rightarrow \pi^*$ transition.

The substituent effects in the butyrophenone system were similar but not identical with those observed for the benzophenones: an *ortho* effect, primarily involving photoenolization, and a *para* effect in which the substituent influenced the excited state(s) involved in the photochemical reaction. The *para* effect, in turn, seems to be the result of at least two factors: the electron-donating ability of the substituent, which is primarily responsible for variations of reactivity among "reactive" ketones; and the nature of the lowest triplet, which primarily determines whether or not the ketone will be reactive at all.

"Reactive" ketones appear to undergo the photocyclo elimination process from their lowest triplet state. This is supported by oxygen- and naphthalene-quenching experiments. ϕ_{II} for butyrophenone was found to drop from 0.42 to about 0.20 in solutions which were 10^{-3} *M* in either oxygen, naphthalene, or 1,3-pentadiene. Furthermore, energy-transfer experiments with 1,3-pentadiene quenching excited butyrophenone resulted in linear Stern–Volmer plots of $^1/\phi_{II}$ *vs.*[1,3-pentadiene] to at least $^1/\phi_{II} = 40$, indicating that the low-lying excited singlet states of this ketone play no dominant role (see Figure 5). This conclusion is also supported by the fact that *intermolecular* hydrogen atom abstraction by acetophenone occurs exclusively *via* the triplet state.[11]

It would then appear that the alkyl aryl ketones generally react from the lowest triplet state as do the aryl ketones in hydrogen atom abstraction reactions. This is in contrast to recent results on the photocycloelimination reaction of alkyl ketones in which it was reported that the first excited singlet state may be of varying importance. Thus, it appears that 2-hexanone

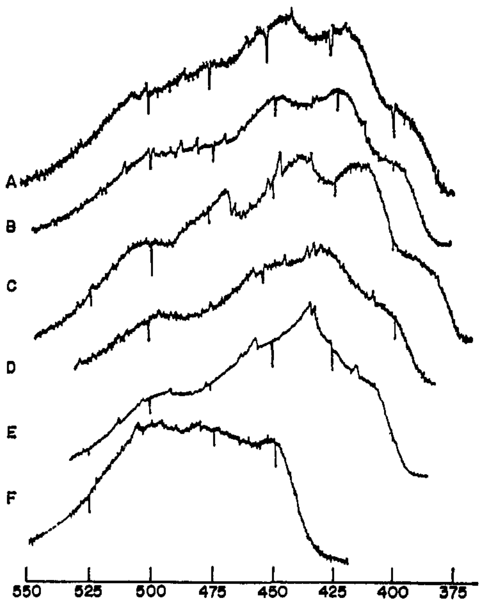


Figure 6. Phosphorescence spectra of some butyrophenone derivatives in 2:1 ethanol-methanol glass at −190°: A, butyrophenone; B, *p*-methylbutyrophenone; C, *p*-fluorobutyrophenone; D, *p*-methoxybutyrophenone; E, *p*-hydroxybutyrophenone; F, *p*-aminobutyrophenone.

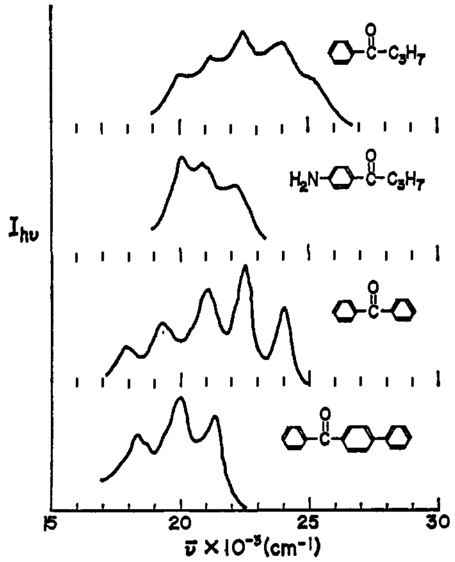


Figure 7. Phosphorescence spectra of some butyro- and benzophenones.

undergoes the "type II" process extensively from an excited singlet state, whereas 2-pentanone undergoes this process almost exclusively from the triplet state.[17]

Table I also gives the position of the 0–0 phosphorescence bands and the corresponding triplet energy levels and first-order phosphorescence decay times, τ, of the butyrophenones in 1:2 methanol–ethanol glass at −190°.

Phosphorescence spectra obtained in methanol–ethanol glass at −190° are shown for some of the butyrophenones in Figure 6.

It is evident that the triplet states of the nonreactive compounds lie at lower energies than do those of the reactive ones; furthermore, they have much longer radiative lifetimes in the rigid matrices (*e.g.*, 0.002 sec for butyrophenone *vs.* 0.084 for *p*-aminobutyrophenone). This behavior is similar to that observed in the benzophenones series. Figure 7 contrasts the phosphorescence spectra of selected butyrophenones and benzophenones. These results suggest that the lowest lying triplets of butyrophenone, *p*-methyl-, *p*-methoxy-, *p*-acetoxy-, *p*-fluoro-, *p*-chloro-, and *p*-bromobutyrophenone are $^3(n,\pi^*)$, but they are $^3(\pi,\pi^*)$ states in *p*-amino-, *p*-acetamido-, *p*-hydroxy-, and *p*-phenylbutyrophenone. Thus, nonreactivity of the latter ketones seems to be due to the π,π^* nature of their triplet state. As mentioned earlier, similar conclusions have been reached concerning the spectroscopy[22] and *intermolecular* hydrogen atom abstraction reactions of *para*-substituted benzophenones.[4–6]

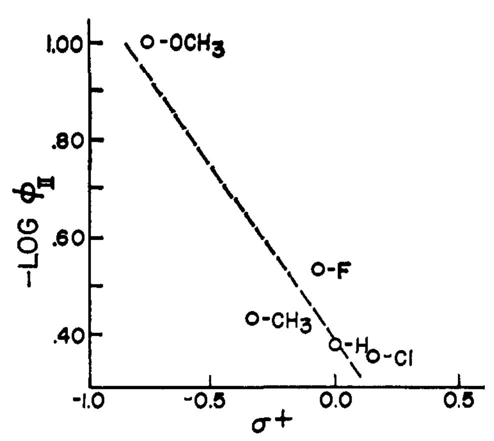


Figure 8. Plot of $-\log \phi_{II}$ *vs.* Hammett σ^+ constant for some *para*-substituted butyrophenones.

In general, the quantum yields for *para*-substituted compounds decrease with increasing electron-donating ability of the substituent, dropping from 0.42 in butyrophenone to 0.10 in *p*-methoxybutyrophenone. This is evident in Figure 8, a plot of $\log \phi_{II}$ *vs.* the Hammett σ^+ constant, in which the trend toward higher quantum yield with increasing σ^+ value is pronounced. Assuming that the excited states of butyrophenone are similar to those of formaldehyde, specifically that a reduction of electronic charge occurs on the carbonyl oxygen atom during an n,π^* transition,[23] the $\log \phi_{II}$ *vs.* σ^+ relation indicates that electron-donating substituents reduce the reactivity of the excited carbonyl group by increasing the negative charge on the oxygen atom, thus reducing its affinity for the γ-hydrogen atom.

A plot of $\log \phi_{II}$ *vs.* σ^+ values[24] does result in a better behaved relationship than that of $\log \phi_{II}$ *vs.* σ values[25] which would be expected under normal conditions when *para* substituents are conjugated with the electron-withdrawing carbonyl. These relationships are admittedly crude and should not be expected to be otherwise for several reasons. We are not dealing with ground-state reactivities, σ^+ constants are not determined for the compounds to which the hydrogen atom or ion is transferred and hence are not strictly applicable here, and σ^+ constant values vary depending

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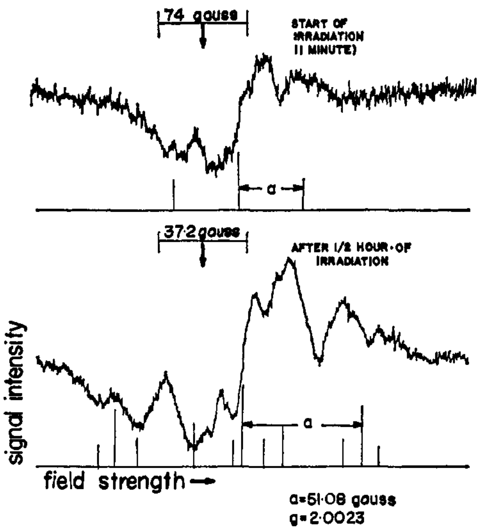


Figure 9. Epr spectrum of product of low-temperature (−180°) photolysis of *p*-bromobutyrophenone in IPA after 1 min of irradiation (upper curve) and after 0.5 hr of irradiation (lower curve).

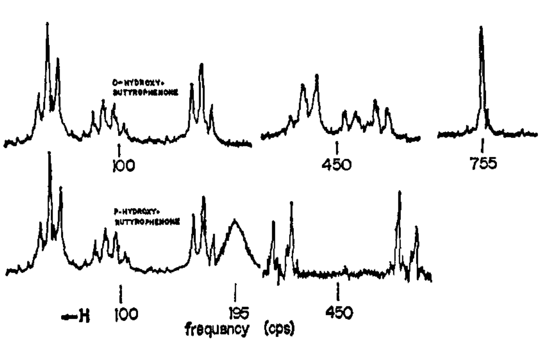


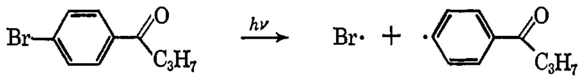
Figure 10. Comparison of nmr spectra of *o*- and *p*-hydroxybutyrophenone. The broad hydroxyl proton resonance at 195 cps for *p*-hydroxybutyrophenone contrasts with the sharp resonance at 755 cps (low field) for *o*-hydroxybutyrophenone.

on reactions and compound type. Finally, since the σ^+ constant, strictly speaking, applies to rate constants, a plot of the log of the lifetime of the triplet state *vs.* σ^+ would be expected to result in a better fit; we are currently engaged in investigating this aspect of the problem.

ϕ_{II} does not vary significantly when, in place of benzene, the irradiation is carried out in cyclohexane, methylcyclohexane, or in isopropyl alcohol. These results contrast with those of Porter and Suppan who reported pronounced solvent effects on the hydrogen atom abstraction reactivity of *para*-substituted benzophenones.[13] However, recently Walling and Gibian[14] stated they did not observe a great increase in this reactivity for 4,4′-dimethylaminobenzophenone in going from isopropyl alcohol to cyclohexane. Furthermore, unpublished data from Professor Schenck's[15] and our own laboratory indicate that no pinacol is formed when *p*-aminobenzophenone is irradiated in cyclohexane.

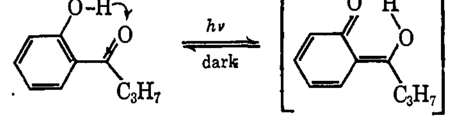
Finally, our results with *p*-phenyl- and *p*-methoxybutyrophenone and the spectroscopic data available to us on the butyrophenone system lead us to believe that so-called "charge-transfer states" are not involved in the photochemistry of the butyrophenones, and that our results may be satisfactorily explained on the basis of conventional n,π* and π,π* states having varying "charge-transfer" character, as outlined above.

The major products of the *p*-bromobutyrophenone–benzene photolysis are butyrophenone, HBr, and some butyrophenones unsaturated at the alkyl chain. Butyrophenone is formed with a quantum yield of 0.25. A 0.1 *M* solution of *p*-bromobutyrophenone in IPA glass at −190° was irradiated with light from a Hanovia utility lamp, filtered with Pyrex, while the sample was in the resonance cavity of an epr spectrometer. An epr signal at g = 2.0023 was detected. The three-line spectrum developed immediately after irradiation began and developed hyperfine structure after 0.5 hr of irradiation. This is shown in Figure 9. Upon warming and refreezing the sample, the epr band disappeared. The splitting of 52 gauss correlates with that observed for phenyl radicals.[26] We attribute our spectrum to the radical of butyrophenone formed in the bromine elimination reaction.



This reaction has not been reported previously, although the photolysis of bromobenzene below 2800 A producing bromine and phenyl radicals has been reported.[27] The ultraviolet absorption of bromobenzene terminates at 2800 A (o.d. = 0.008). *p*-Bromobutyrophenone was photolyzed at 3130 A where this ketone has a "normal" n,π* absorption band. Thus, the question arises as to how energy is transferred from the carbonyl group to a dissociative mode of the C–Br bond on the phenyl ring. Since this reaction also occurs in an IPA glass at −190°, it is suggested that energy is transferred by intersystem crossing or internal conversion (*i.e.*, intramolecular energy transfer), and *intermolecular* processes are not necessarily involved.

o-Hydroxybutyrophenone exhibits a very strong absorption band in the ultraviolet with a maximum at 3260 A. This band exhibits no wavelength shift on changing solvent from hydrocarbon to alcohol (Figure 4). The nmr spectrum (Figure 10) has a very sharp hydroxyl proton resonance at low field (τ −3.4). The infrared hydroxyl absorption occurs at about 3100 cm^{-1} in CCl_4 solution and does not shift on dilution (Figure 11). These facts together with the unreactivity of the *o*-hydroxy compound indicate that the hydroxyl proton is strongly coupled with the carbonyl chromophore in the ground state, and a photoenolization process may occur on excitation.



This type of reaction occurs in *o*-methyl-[7] and *o*-hydroxybenzophenone.[5,8] As is the case with *o*-methoxybenzophenone,[8] *o*-methoxybutyrophenone is reactive; ϕ_{II} = 0.12, the same as for *p*-methoxybutyrophenone.

o-Hydroxybutyrophenone differs from the other compounds also in that it emits a very fast green phos-

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[26] K. Morokuma, S. Ohnishi, T. Masuda, and K. Fukui, *Bull. Chem. Soc. Japan*, 36, 1228 (1963).

[27] S. Ohnishi, T. Tanei, and I. Nieta, *J. Chem. Phys.*, 37, 2402 (1962).

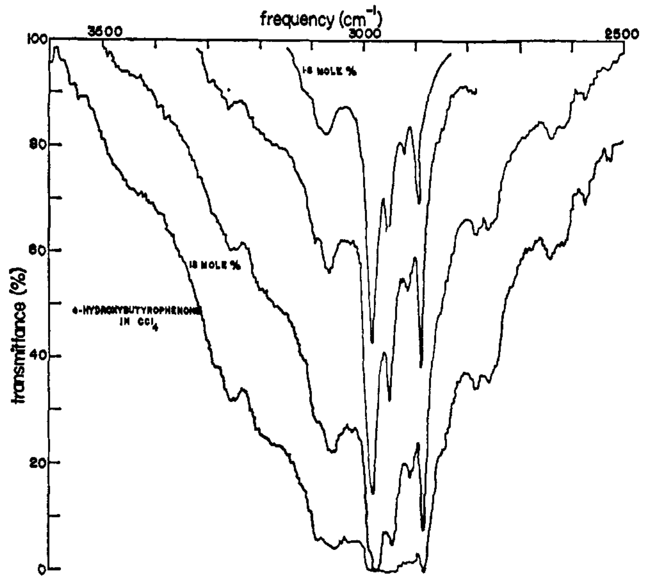

Figure 11. Infrared spectrum of *o*-hydroxybutyrophenone in CCl_4 in the region 2500 to 3500 cm^{-1}. Concentration is given in mole per cent of ketone.

phorescence in methanol–ethanol glass at $-190°$, its first-order decay time being less than 10 μsec. Unfortunately, the total emission spectrum of the compound is almost featureless, unlike those of the other ketones, and it was not possible to calculate a frequency value for the splitting of vibronic levels of the ground-state species from the spectrum. Calculation of this frequency from the phosphorescence spectra of the other substituted butyrophenones indicated that it was essentially identical with that of the infrared active carbonyl stretching frequency. This was also true for *p*-bromobutyrophenone.

The phosphorescence decay times in rigid glass at $-190°$, listed in Table I, must be considerably longer than those of the corresponding ketones in liquid solution at room temperature since the fluid solutions do not phosphoresce. It seems likely that the observed decrease in triplet lifetime may be the result of triplet quenching by impurities such as residual oxygen.

The results of Livingston and Ware on the rates of decay of triplet anthracene in liquid solutions indicate that quenching processes in solutions of low viscosity are diffusion controlled. They find that the activation energy of triplet quenching corresponds to the activation energy of diffusion, $\Delta E\mu$, in low-viscosity hydrocarbon and alcohol solutions.[28] They point out that extremely low concentrations of oxygen may be responsible for this and that ordinary degassing techniques may not be efficient enough to reduce the concentration to tolerable limits. A calculation of $\Delta E\mu$ for benzene solutions in the range of 20 to 70° results in a value of about 2.2 kcal/mole.[29]

The photocycloelimination process in butyrophenone and *p*-methoxybutyrophenone is severely attenuated below 0°, as with 2-pentanone.[30] This suggests a slight activation energy for the "type II" process.

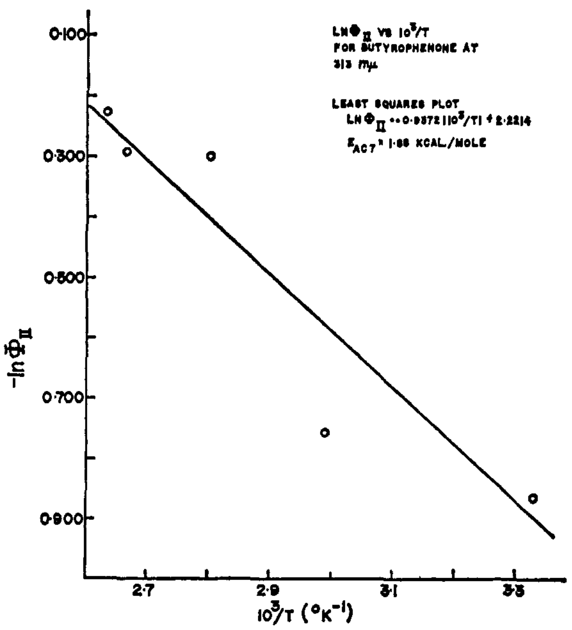

Figure 12. Plot of $-\ln \phi_{II}$ *vs.* $1/T$ for the photolysis of butyrophenone in liquid benzene solution at 313 mμ.

In order to determine this, vacuum-degassed solutions of 0.1 *M* butyrophenone in benzene were irradiated at 3130 A and at temperatures ranging from 25 to 117°. Employing the steady-state treatment, the results, plotted in Figure 12, show an activation energy for the process of about 2 kcal/mole. This value is less than that of the activation energy for hydrogen atom abstraction reactions by radicals (11 kcal/mole $< \Delta E_{act} <$ 4 kcal/mole) and may represent the energy necessary to arrive at the six-membered cyclic transition state. It is also comparable with the activation energy of "ketonization" of enol–acetone formed in the photolysis of 2-pentanone.[31]

When 0.1 *M* solutions of the unreactive butyrophenones in IPA glass at $-190°$ are irradiated at 3000–4000 A, "low-field" epr resonances, similar to those of the nonreactive *para*-substituted benzophenones,[6] appear at about $g = 4$ (1400 guass). All signals disappeared rapidly in the dark; the resonance decay times agreed with the phosphorescence decay times. Signal intensities follow the same order as the integrated absorption extinction coefficient for these compounds in the 3000–4000 A region. These results are given in Table II. The resonances shift position and reduce in

Table II. Epr Resonances Observed for Some Butyrophenone Derivatives at $-190°$

Compound	Solvent	Band position, gauss	Band width, gauss
Butyrophenone	IPA	1413 (weak)[a]	27.89
p-Methoxybutyrophenone	IPA	1362 (strong)	17.71
p-Aminobutyrophenone	IPA	1392 (strong)	17.71
	Acetic acid	1405 (weak)	20.08
p-Hydroxybutyrophenone	IPA	1362 (strong)	18.58
	Acetic acid	1407 (weak)	34.01

[a] Resonance intensity shown in parentheses.

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(28) R. Livingston and D. R. Ware, *J. Chem. Phys.*, **39**, 2593 (1963).

(29) See "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, pp 2258–2264, for viscosity values.

(30) R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).

(31) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **86**, 3602 (1964).

intensity in glacial acetic acid solutions. It is not known how much of this effect is due to change in dielectric constant with change of solvents.

Weaks resonances are also observed for the reactive butyrophenones at about $g = 4$. n,π^* triplets have not been observed previously by epr techniques. This has been attributed to large zero-field splittings resulting from magnetic dipole interactions between the electrons in the "localized" n,π^* state. Thus the n,π^* epr spectrum is expected to lie outside the frequency limits that are ordinarily observed. Also, the short lifetimes and attendant low steady-state concentrations of n,π^* triplets preclude convenient observation of these resonances. We are continuing our investigation into this matter.

We are also studying structural effects at the γ position of the alkyl chain. Thus γ-phenylbutyrophenone has a large ϕ_{II}, 0.49. It is interesting that the major peak in the mass spectrum of this compound is at m/e 120 and arises from the electron-impact-induced rearrangement analogous to the photochemical "type II" split.[32] These results seem to reflect the different lability of primary and secondary hydrogen atoms on carbon chains as well as the presence of the γ-phenyl group. Walling and Gibian also found that the triplet state of benzophenone is extremely sensitive to C–H bond strength.[14] They further find that benzophenone is unreactive toward acetic acid. This indicates, as implied above, that the triplet's reactivity is based on its ability to attract the σ electron enveloping the hydrogen atom.

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(32) For a discussion of possible correlations between photoelectron- and γ-ray-initiated intramolecular processes and earlier references, see J. N. Pitts, Jr., J. K. Foote, and J. K. S. Wan, *Photochem. Photobiol.*, **4**, 323 (1964); see also D. J. Coyle, *J. Phys. Chem.*, 67, 1800 (1963).

Triplet States in Radiation Chemistry. Radiochemical *cis–trans* Isomerization

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Abstract: Radiation-induced *cis–trans* isomerization of three pairs of olefins has been studied by determination of both initial rates of isomerization and the composition of radiostationary states. The data correlate strikingly well with data obtained in sensitized photoisomerization reactions of the same substrates. Consequently, we infer that isomerization involves formation and decay of excited triplet states of the olefins. The sum of the *G* values for the *trans* → *cis* and *cis* → *trans* reactions is taken as the value of *G* for formation of olefin triplets. Except in very concentrated solutions most of the excitation must be first absorbed by the solvent and then transferred to the solute. The highest yield of triplets measured in benzene was 9.9, and a value of 20 was estimated in an experiment in which pure *cis*-stilbene was irradiated. The very high *G* values for triplets are attributed to the fact that reactive energy acceptors can compete effectively with triplet–triplet annihilation reactions in regions of high excitation density within spurs.

Benzene and aromatic compounds in general are relatively stable toward degradation by ionizing radiation. This stability may be attributed to the availability of electronic excited states having little probability of dissociation. It has been suggested[3–5] that at least part of the yield of biphenyl, partially reduced biphenyls, and hydrogen in the radiolysis of benzene may arise from bimolecular reactions of electronically excited states within spurs. Recently, correlations have been made between triplet-state photochemical reactions and radiolyses.[6] Our interest was aroused by the question of the nature, role, and yield of excited states in radiation chemistry. We were particularly interested in comparing chemical phenomena observed with radiation-produced excited states to those observed in photochemistry.

No data are available that give a convincing value for the total yield of any excited state of benzene though several attempts have been made. Cherniak, Collinson, and Dainton[3] have estimated *G* (100-ev yield) for excited benzene to be 1.35 from $FeCl_3$ radical-scavenging experiments in which an excited state was invoked to explain the shape of the $G(-FeCl_3)$ *vs.* $FeCl_3$ concentration curve. Recent work of Nosworthy[7] and of Fischer, Lehman, and Stein[8] on the *cis–trans* isomerization of the maleate–fumarate and stilbene pairs, respectively, gives a value of 1.0–1.1 for the yield of benzene triplets. The extensive work of Cundall and Griffiths[9] has led to

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(1) National Science Foundation Postdoctoral Fellow, 1964–1965.

(2) National Institutes of Health Postdoctoral Fellow, 1965–1966.

(3) E. A. Cherniak, E. Collinson, and S. S. Dainton, *Trans. Faraday Soc.*, 60, 1408 (1964).

(4) J. Y. Yang, J. D. Strong, and J. G. Burr, *J. Phys. Chem.*, **69**, 1157 (1965).

(5) W. G. Burns, *Trans. Faraday Soc.*, 58, 961 (1962).

(6) See, for example, P. Dunion and C. N. Trumbore, *J. Am. Chem. Soc.*, 87, 4211 (1965), and references therein.

(7) J. Nosworthy, *Trans. Faraday Soc.*, **61**, 1138 (1965).

(8) E. Fischer, H. P. Lehman, and G. Stein, *Chem. Commun.* 583 (1965). We thank Professor Stein for a preprint of this work.