Table I

Compound	Φ_0[a]	$\tau \times 10^7$ sec	$k_r \times 2\,M \times 10^{-4}$ sec^{-1}	$k_{-t} \times 10^{-5}$ sec^{-1}
p-Trifluoromethylacetophenone	0.72	1.31	552.0 ± 1.0[b]	21.0 ± 2.2[b]
Acetophenone	0.35	4.07	86.6 ± 2.2[c]	15.9 ± 0.6[c]
p-Methylacetophenone	0.33	42.3	7.88	1.58
3,4-Dimethylacetophenone	0.069	41.0	1.68 ± 0.18[b]	2.27 ± 0.58[b]

[a] The quantum yield of acetone formation in benzene containing 2 *M* 2-propanol. [b] The value represents the average of two runs. [c] The value represents the average of three runs.

Table II

			$[n,\pi^*]^3$		$[\pi,\pi^*]^3$		τ_{phos}, sec[a]	
Compound	Max, mμ	$[n,\pi^*]^1$ 0–0 band,[b,c] mμ	Emission,[d,e] mμ	Absorption,[b,e] mμ	Emission,[d,e] mμ	Absorption,[b,f] mμ	In EPA	In methylcyclohexane
p-Trifluoromethylacetophenone	333	360	397	384	(383)[g]		0.0007	0.0007
Acetophenone	326	356	386	372	(373)[g]		0.004[h] 0.03	0.003
p-Methylacetophenone	325	352		368	392	386	0.084	0.027
3,4-Dimethylacetophenone	325	352		367	399	392	0.17	0.060

[a] Measured at 77°K. [b] By the phosphorescence excitation method: D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966); the accuracy is estimated to be ±2 mμ. [c] In methylcyclohexane. [d] 0–0 band position; the accuracy is estimated to be ±1 mμ. [e] In EPA. [f] In EPA–EtI. [g] Calculated. [h] The decay is nonexponential; see N. C. Yang and S. L. Murov, *J. Chem. Phys.*, **45**, 4358 (1966).

their radiative lifetimes and chemical reactivities.[1] However, methylated acetophenones exhibit a $[n,\pi^*]^3$ state slightly above the low-lying $[\pi,\pi^*]^3$ state (Table II),[1] and the variation of n,π* character in the $[\pi,\pi^*]^3$ state of these compounds may thus be attributed to the vibronic coupling of the $[\pi,\pi^*]^3$ with the corresponding $[n,\pi^*]^3$ state in addition to the spin–orbital coupling with the $[n,\pi^*]^1$ state.

Since the extent of coupling between two states will depend on the energy gap between them, the coupling will increase as the energy gap decreases. The energy level of an n,π* state will shift to the red slightly when the medium is changed from EPA, a polar one, to methylcyclohexane, a nonpolar one, while the energy level of a $[\pi,\pi^*]^3$ state exhibits little solvent dependence. The energy gaps between the low-lying $[\pi,\pi^*]^3$ state and both the $[n,\pi^*]^3$ and $[n,\pi^*]^1$ states of methylated acetophenones will therefore decrease when the medium is changed from EPA to methylcyclohexane. This medium change should cause an increased mixing of the $[\pi,\pi^*]^3$ state with both the $[n,\pi^*]^3$ and the $[n,\pi^*]^1$ states, and consequently an increased n,π* character of the low-lying $[\pi,\pi^*]^3$ state. This supposition is verified by our experimental observation that the phosphorescence lifetimes of methylated acetophenones are invariably shorter in methylcyclohexane than in EPA.[6] *We conclude, therefore, that the enhanced photochemical reactivity of the low-lying* $[\pi,\pi^*]^3$ *state of methylated acetophenones may be at least in part attributed to the vibronic coupling of the* $[\pi,\pi^*]^3$ *state with the closely spaced* $[n,\pi^*]^3$.

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(6) This was found to be the case also for *m*-methylacetophenone, 3,5-dimethylacetophenone, and 3,4,5-trimethylacetophenone: S. L. Murov, Ph.D. Thesis, University of Chicago, 1966.

(7) The authors wish to thank the National Science Foundation for the support of this work, Professor D. S. McClure and Professor E. C. Lim for some valuable suggestions, and Dr. S. L. Murov for his preliminary investigation, criticism, and stimulation.

(8) NDEA fellow, University of Chicago, 1966–1968.

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Molecular Structure and Photochemical Reactivity. VIII. Type II Photoelimination of Alkenes from Alkyl Phenyl Ketones. Effects of Varying the Alkyl Group

Sir:

In a system in which two competing photochemical primary processes arise from the same excited state and one process leads to the formation of an unstable species that very rapidly reverts back to the parent molecule, the observed over-all quantum yield of the "stable" product is clearly not a valid measure of the "reactivity" of the precursor excited state. While this point has been made for the type II photoelimination process in two different pairs of ketones with γ-H atoms[1,2] and for a general case in which the unstable chemical intermediate competes with several possible processes,[3] the effects of introducing alkyl substituents on the γ-carbon atom of *n*-butyrophenone illustrate this particularly well. The relative insensitivity of Φ_{II} to γ-alkyl substitution (a small *decrease* is noted) contrasts dramatically with the large *increase* in the rate of the γ-hydrogen atom transfer.[4–6]

The ketones listed in Table I were purified, generally by vapor-phase chromatography, and degassed 0.10 *M* solutions in benzene were irradiated at 3130 Å and 27°, using a merry-go-round apparatus. Yields of acetophenone (1% conversion) were measured by vapor-phase chromatographic analysis. A 0.10 *M* solution of *n*-butyrophenone in benzene was used as actinometer.

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(1) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).

(2) D. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(3) J. N. Pitts, Proceedings of the 13th Conference on Chemistry at the University of Brussels, Oct 1965; published as "Reactivity of the Photoexcited Organic Molecule," Interscience Division of John Wiley & Sons, Inc., New York, N. Y., 1967, p 115. Professor G. S. Hammond made a similar point at this conference.

(4) For review see P. J. Wagner and F. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(5) J. N. Pitts, Jr., 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, No. P142.

(6) Similar conclusions, reached independently, were reported at the 155th National Meeting, of the American Chemical Society San Francisco, Calif., April 1968, by P. J. Wagner and A. E. Kemppainen (Abstracts, No. P113) and are being published.[1]

Table I. Quenching of the Type II Photoelimination for Alkyl Phenyl Ketones (0.10 *M* in Benzene or *n*-Hexane) at 3130 Å by 2,5-Dimethyl-2,4-hexadiene

Ketone	Φ_{II}	$k_q\tau$, M^{-1} A[a]	$k_q\tau$, M^{-1} B[b]	$k_r \times 10^{-6}$ sec^{-1} A[a]
$PhCOCH_2CH_2CH_3$	0.40	755	813	6.6
$PhCOCH_2CH(CH_3)_2$	0.47, 0.44[c]	245	467	20
$PhCOCH_2CH_2CH(CH_3)_2$	0.23[c]	10		500
$PhCOCH_2CH_2CH_2CH_3$	0.31, 0.36[c]	43	67	116
$PhCOCH_2CH_2CH_2CH_2CH_3$	0.31	40	80	125
$PhCOCH_2CH_2CH_2(CH_2)_2CH_3$	0.25	27	67	185
$PhCOCH_2CH_2CH_2(CH_2)_3CH_3$	0.30	27	54	185
$PhCOCH_2CH_2CH_2(CH_2)_4CH_3$	0.29	31	73	161

[a] Column A, in benzene. [b] Column B, in *n*-hexane. [c] Optical bench.

Two ketones were also photolyzed on an optical bench using aqueous ferrioxalate as actinometer.

Quenching studies were carried out in the presence of 2,5-dimethyl-2,4-hexadiene (Q) and the results analyzed using the Stern–Volmer equation

$$\frac{\Phi_{II}{}^{\circ}}{\Phi_{II}} = k_q\tau[Q] + 1$$

where k_q is the rate constant for bimolecular quenching and τ is the actual lifetime of the excited state being quenched in the absence of quencher Q. In this case

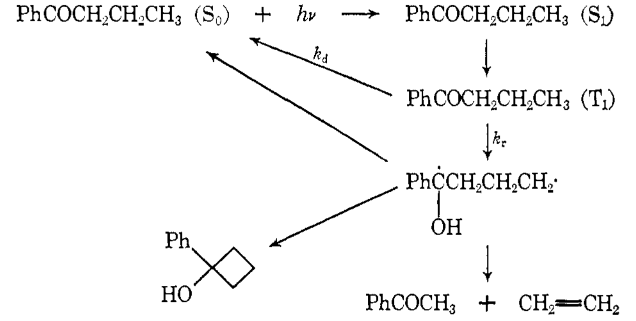
$$\tau = \frac{1}{k_r + k_d}$$

where k_r and k_d are first-order rate constants for the intramolecular hydrogen-abstraction reaction and radiationless deactivation of the triplet state, respectively.

The values of k_r were calculated assuming (i) that k_q is diffusion controlled and equal to 5×10^9 M^{-1} sec^{-1} and (ii) that molecules in the triplet state are produced with 100% quantum efficiency and all undergo the intramolecular hydrogen-abstraction reaction, that is, $\phi_{ISC} = 1.0$ and $k_d = 0$.

The given values agree reasonably well with those of Wagner.[7]

The variations in Φ_{II} are such that the large decrease in τ, observed on alkyl substitution of the γ-carbon atom in *n*-butyrophenone, cannot be attributed to large increases in k_d. The value of τ decreases by a factor of 80 while Φ_{II} decreases by a factor of only 2. This indicates that the decrease in τ is not caused by an increase in k_d. The lower lifetimes must therefore be a direct consequence of increasing hydrogen abstraction rate. The effect of solvents on Φ_{II} provides evidence supporting $k_d \ll k_r$.



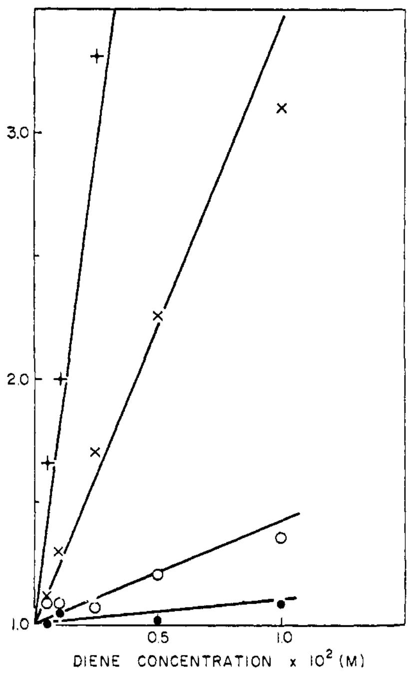


Figure 1. Dependence of Φ_{II} on 2,5-dimethyl-2,4-hexadiene concentration for *n*-butyrophenone (+) (two points not shown), isovalerophenone (×), *n*-valerophenone (○), and γ-methylvalerophenone (●).

Wagner has demonstrated that Φ_{II} is considerably increased when alkyl phenyl ketones are photolyzed in *t*-butyl alcohol rather than benzene.[8,9] We have confirmed this in the case of *n*-butyrophenone and also shown that the quantum yield of ethylene from photolysis of 2-pentanone is 2.1 times greater in *t*-butyl alcohol than in benzene.[10] Since the quantum yields for ketone disappearance are close to unity in *t*-butyl alcohol, Wagner believes that the hydroxyl proton in the postulated biradical intermediate forms a hydrogen bond with the solvent of sufficient stability to hinder its transfer back to the γ-carbon atom. In nonpolar solvents this retransfer process provides an effective route for radiationless deactivation, and Φ_{II} values are consequently lower than in polar solvents. Leermakers[11] has also recently published a detailed study of solvent effects in the type II process of *n*-butyrophenone. His results further support that $k_d \ll k_r$ in polar and nonpolar solvents.

Yang has obtained evidence for a biradical intermediate in the photolysis of 2-hexanone and deuterated 2-hexanones.[2]

Increasing the number of carbon atoms in the unbranched *n*-alkyl group from C_4 to C_{14} has little effect on Φ_{II} for the alkyl phenyl ketones examined. The values of Φ_{II} for the ketones from *n*-nonanophenone to myristophenone are all equal to 0.31 ± 0.02. The available values of $k_q\tau$ also indicate that increasing chain length has little influence on the lifetime of the triplet state. In each case, a secondary hydrogen atom is abstracted and increasing chain length should not unduly alter its environment so that k_r should be constant.

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(7) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **90**, 5896 (1968).

(8) P. J. Wagner, *Tetrahedron Letters*, 1753 (1967).

(9) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5898 (1967).

(10) R. Simonaitis and J. N. Pitts, Jr., unpublished results.

(11) R. D. Rauh and P. Leermakers, *J. Am. Chem. Soc.*, **90**, 2246 (1968).

As the hydrogen atom being abstracted from the γ-carbon atom is varied from a primary to a tertiary hydrogen, a striking increase in k_r is observed. The rate of intramolecular hydrogen atom abstraction in the triplet state is thus highly dependent on the strength of the C–H bond being broken. If the biradical intermediate is produced with 100% efficiency, as Wagner suggests, Φ_{II} will be determined largely by the relative rates at which it reacts to give acetophenone and an alkene or transfers the hydroxyl hydrogen back to the γ carbon yielding the initial ketone. As the γ-hydrogen atom abstracted was varied from primary through tertiary, k_r *increased* as expected, but the observed *decrease* in Φ_{II} is not easily rationalized.

A detailed study of the intramolecular hydrogen abstraction reaction and of the triplet states of phenyl alkyl ketones is in progress to explain these observations.

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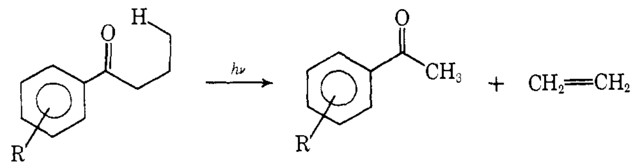
Molecular Structure and Photochemical Reactivity. IX. Photolytic and Radiolytic Type II Elimination Reaction of *n*-Butyrophenones. Effects of *meta* Substituents

Sir:

Quantum yields for photoreduction of substituted acetophenones in 2-propanol have recently been published by Yang and co-workers.[1] They observed that introduction of methyl and methoxy substituents in the *meta* and *para* positions lowers the quantum yield, particularly when the substituent is in the *meta* position to the carbonyl group.

The investigation of the effects of substituents on the photochemical reactions of alkyl phenyl ketones can be simplified if the solvent does *not* react and if bimolecular reactions of radicals arising from the ketone or the solvent can be avoided. The type II photoelimination of ethylene from *n*-butyrophenones is an intramolecular reaction and well suited for examination of substituent effects.[2,3] Pitts and co-workers[2,3a,b] have already



shown that the quantum yield of acetophenone (Φ_{II}) in this reaction is highly dependent upon the substituent present. Introduction of electron-donating substituents such as *p*-OH and *p*-NH_2 lowers Φ_{II} to zero in benzene. Spectroscopic studies indicate that the lowest triplet state in these compounds has mainly the character of a $^3(\pi,\pi^*)$ state, whereas the lowest triplet state of *n*-butyrophenone is mainly $^3(n,\pi^*)$ type.

We wish to report some novel substituent effects on the type II process of *n*-butyrophenones when these compounds are exposed to uv or γ radiation.

The *n*-butyrophenones listed in Table I were synthesized by standard procedures[6] or purchased and were purified by vapor-phase chromatography. Degassed 0.1 *M* solutions in benzene contained in 1-cm cells with optically flat windows were irradiated at 3130 Å and 25°. Alternatively they were placed in the cavity of a 15,000-Ci ^{60}Co γ-radiation source and irradiated to receive a constant total dose of 2×10^{19} eV/g. Acetophenone yields were measured by vapor-phase chromatographic analysis. Quantum yields of acetophenone (Φ_{II}) were obtained by actinometry using aqueous potassium ferrioxalate[4] and radiolysis *G* values for acetophenone (G_{II}) by dosimetry with ferrous ammonium sulfate[7] solution.

Table I. Quantum Yields and Radiolysis *G* Values for the Type II Process, Triplet Energies, and Phosphorescence Lifetimes for Substituted *n*-Butyrophenones

Substituent	Φ_{II}	G_{II}, molecules/ 100 eV	E_T, kcal mol^{-1}	τ_p, msec
H	0.40	1.57	74.7	5
o-F	0.32	1.30	74.5	3
m-F	0.38	1.27	72.5	8
p-F	0.28	0.93	73.7	4
o-OCH_3	0.12	0.18	73.3	39
m-OCH_3	0.005	0.00	70.9	370
p-OCH_3	0.10	0.21	73.3	51
o-OAc	0.37	1.28	72.2	43
m-OAc	0.08	0.44	72.4	490
p-OAc	0.42	1.47	74.3	27
o-Cl	0.27	1.37	72.2	11
m-Cl	0.34		72.2	35
p-Cl	0.41		72.4	45
m-CH_3	0.42	1.25	71.1	40
p-CH_3	0.39	1.26	73.7	9

Phosphorescence spectra of the butyrophenones were also recorded for solutions in EPA at 77°K. Triplet energies (E_T) were calculated from the 0–0 phosphorescence band frequencies, and phosphorescence lifetimes by analysis of the curves for decay of total phos-

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[1] N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Am. Chem. Soc.*, **89**, 5466 (1967).

[2] See discussion by J. N. Pitts, Jr., Proceedings of the 13th Conference on Chemistry, Brussels, Oct 1965; published as "Reactivity of the Photoexcited Organic Molecule," Interscience Division of John Wiley & Sons, Inc., New York, N. Y., 1967, p 115.

[3] (a) J. N. Pitts, L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. F. Vesley, IVth International Congress of Photobiology, Oxford, July 1964; published as "Recent Progress in Photobiology," E. J. Bowen, Ed., Blackwells, 1965, p 23; *J. Photochem. Photobiol.*, 4, 305 (1965); (b) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 2652 (1966); (c) for a detailed review of this see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968); see also ref 4 (pp 352, 353) and 5.

[4] See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966.

[5] P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **90**, 5898 (1968).

[6] J. C. Mani and J. N. Pitts, Jr., unpublished results.

[7] (a) A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, Inc., New York, N. Y., 1960; (b) J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964.