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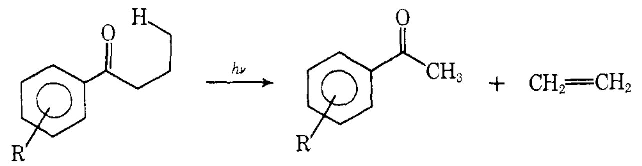
Molecular Structure and Photochemical Reactivity. IX. Photolytic and Radiolytic Type II Elimination Reaction of *n*-Butyrophenones. Effects of *meta* Substituents

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.

phorescence emission. When the 0–0 phosphorescence band was not well defined, E_T was estimated from the onset of the emission band.

As noted earlier, for convenience, substituted *n*-butyrophenones may be divided into two general groups classified as "reactive" ($\Phi_{II} \sim 0.1–0.4$) and "unreactive" ($\Phi_{II} \sim 0–0.1$).[2,3] It is generally held that "reactive" and "unreactive" compounds possess lowest triplet states which are predominantly ${}^3(n,\pi^*)$ or ${}^3(\pi,\pi^*)$ in character, respectively.[3] The *o*-, *m*-, and *p*-fluoro-*n*-butyrophenones are typical of those belonging to the "reactive" group. Methyl- and chloro-substituted compounds behave similarly. However, as seen in Table I, acetoxy and methoxy derivatives cannot be readily classified.

The Φ_{II} values for *o*- and *p*-acetoxy-*n*-butyrophenones are normal, but their phosphorescence lifetimes (τ_p) are considerably longer than those usually found for (n,π^*) triplet states. The *o*- and *p*-methoxy derivatives have lower Φ_{II} values, but τ_p is also longer than expected. The most significant result, however, is the striking decrease in Φ_{II} when acetoxy or methoxy substituents are in the position *meta* to the carbonyl group. This decrease is also accompanied by a considerable increase in τ_p, which suggests that the lowest triplet states for the *meta* derivatives are (π,π^*) states. Furthermore, the low-intensity $n \rightarrow \pi^*$ absorption, characteristic of "reactive" butyrophenones, is absent in the uv spectra of the *m*-acetoxy and *m*-methoxy compounds.

Wagner and Kemppainen[5] have found similar substituent effects for the type II cleavage of alkenes from methoxy-substituted *n*-valerophenone and γ-methylvalerophenone.

The variations in Φ_{II} are closely related to variations in G_{II}. The results emphasize the close relationship between this photochemical or radiochemical processes in solution. This can be rationalized in the following terms. In the radiolysis experiments almost all the incident energy was absorbed by the benzene solvent. Thus singlet and triplet excited states of benzene are produced initially.[8] These subsequently transfer electronic energy to the butyrophenone, producing ultimately the lowest triplet state of butyrophenone, the acknowledged precursor to the type II process.

Our results indicate that the triplet states of acetoxy- and methoxy-*n*-butyrophenones, responsible for phosphorescence and possibly the type II reaction, have greater (π,π^*) character than those of the normal "reactive" compounds, particularly when these substituents are in the position *meta* to the carbonyl group. However, as recently pointed out,[9] the phosphorescence emission of alkyl phenyl ketones in a matrix at 77°K has been found to consist of *both* a short- and a long-lived component.

Thus it appears that the energy separation of (n,π^*) and (π,π^*) triplet states may be quite small in certain solvents. However, the observation of short- and long-lived emissions may be caused by a matrix effect. In the case of the derivatives discussed above, although the type II reaction proceeds from a (n,π^*) triplet state, the (π,π^*) triplet state (or a mixed triplet state) may have similar energy so that phosphorescence from both states is observed. The lack of correlation between Φ_{II} and the rate constant for hydrogen abstraction in the excited state has already been pointed out,[10] and therefore the anomalous values of Φ_{II} for the *m*-methoxy and *m*-acetoxy derivatives should be cautiously interpreted, until quenching and phosphorescence data are available.

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[8] J. M. King and G. S. Hammond, *J. Am. Chem. Soc.*, in press.

[9] N. C. Yang and S. Murov, *J. Chem. Phys.*, 45, 4358 (1966); A. A. Lamola, *ibid.*, 47, 4810 (1967); R. D. Rauh and P. A. Leermakers, *J. Am. Chem. Soc.*, 90, 2246 (1968); J. N. Pitts, Jr., 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, No. P142.

[10] J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *J. Am. Chem. Soc.*, 90, 5900 (1968); P. J. Wagner and A. E. Kemppainen, *ibid.*, 90, 5896 (1968).

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Oxidation Reactions of Manganese(III) Acetate. II. Formation of γ-Lactones from Olefins and Acetic Acid[1]

Sir:

The oxidation of organic compounds by Mn(III) complexes in aqueous solution has been extensively studied, and most of the results have been successfully interpreted in terms of inner-sphere one-electron-transfer processes.[2] The nonaqueous chemistry has been less extensively explored,[3] and the reactions previously reported have been interpreted as resulting from inner-[3a] or outer-sphere[3b] one-electron-transfer steps. We have found that solutions prepared by dissolving manganese(III) acetate dihydrate in glacial acetic acid react with alkanes, alkenes, and aromatic compounds to give a variety of products which are best explained as resulting from interaction of the substrate with an electrophilic species derived from solvent acetic acid or from acetate groups coordinated with the metal. In the present communication we report the formation of γ-lactones from olefins.

An example is the formation of γ-methyl-γ-phenylbutyrolactone (**2**) from α-methylstyrene (eq 1). A mixture of 360 ml of acetic acid, 180 ml of acetic anhydride, 45 g of α-methylstyrene, and 80 g of $Mn(OAc)_3 \cdot 2H_2O$[4] was heated to reflux (45 min) until the

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[1] Previous article in this series: H. Finkbeiner and J. B. Bush, Jr., paper presented at the Faraday Society Discussion, "Homogeneous Catalysis with Special Reference to Hydrogenation and Oxidation," University of Liverpool, Liverpool, England, Sept 1968.

[2] Reviewed by W. A. Waters and J. S. Littler in "Oxidations in Organic Chemistry," Part A, K. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 186.

[3] See, for example, (a) R. van Helden and E. C. Kooyman, *Rec. Trav. Chim.*, 80, 57 (1961); (b) P. J. Andrulis, M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, 88, 5473 (1966).

[4] The $Mn(OAc)_3 \cdot 2H_2O$ was prepared by heating a mixture of 500 ml of acetic acid and 48 g of $Mn(OAc)_2 \cdot 4H_2O$ to reflux for 20 min, then slowly adding 8.0 g of $KMnO_4$. After refluxing for an additional 30 min, the mixture was cooled to room temperature and 85 ml of water