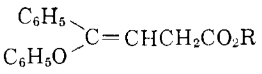
COMMUNICATIONS TO THE EDITOR

PHOTOCHEMISTRY OF DIBENZOYLETHYLENE; A NOVEL PHOTOCHEMICAL REARRANGEMENT AND REDUCTION

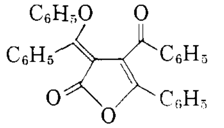
Sir:

When *cis*-dibenzoylethylene (I) is irradiated in the presence of alcohols 1:1 adducts are formed.[1] Methanol, 2-propanol and benzhydrol, which provide IIa, IIb and IIc, respectively, serve as representative examples of alcohols which have been employed. The infrared spectra of the adducts revealed strong carbonyl absorption near 1730 cm.$^{-1}$ which suggested that skeletal rearrangement had occurred and that esters had been formed. This was confirmed by hydrolysis of IIa, IIb and IIc to a common acid, identified as β-benzoylpropionic acid. Phenol was also detected among the hydrolysis products of IIb. That the source of phenol is a phenoxy group occupying a benzyl position in IIb, and presumably IIa and IIc, was demonstrated by ozonolysis which afforded phenyl benzoate. These combined experimental observations are accommodated by enol ether structure II.



$(C_6H_5)(C_6H_5O)C{=}CHCH_2CO_2R$

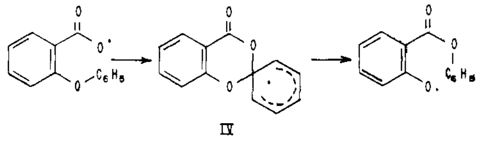
IIa, R = CH_3
b, R = CH_3CHCH_3
c, R = $(C_6H_5)_2CH$



III

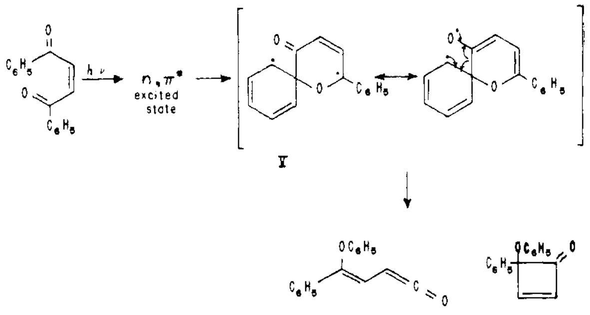
Corroborative evidence for structure II was obtained from the n.m.r. spectrum of IIb. In addition to a complex set of peaks in the aromatic region (τ = 2.4–3.3) there is a triplet centered at τ = 4.00 (vinyl CH), a doublet centered at τ = 6.83 (CH_2CO_2R), as well as the characteristic isopropoxy multiplet centered at τ = 5.08 (OCH) and doublet centered at τ = 8.83 (CH_3). The integrated areas are within experimental error of the expected values.

A striking feature of this presumably intramolecular reaction is the 1,5-phenyl migration to oxygen. Such a process is not without analogy. The related photochemical rearrangement of tetrabenzoylethylene to III has been reported by H. v. Halban and co-workers.[2] This remarkable transformation while complicated by lactonization, also proceeds with phenyl migration to oxygen. It is noteworthy that in this instance geminal benzoyl groups participate in the transfer which is of the 1,4-type. DeTar and Hlynsky[3] have observed that phenyl salicylate is produced from the thermal decomposition of 2-phenoxybenzoyl peroxide. This reaction undoubtedly is homolytic in character and may be formulated as proceeding through the Ar$_1$-6 intermediate IV.[4] The anomalous Hunsdiecker reactions of β,β,β-triarylpropionic acids studied by Wilt and co-workers[5,6] also may involve intramolecular migration of phenyl to oxygen by way of radical intermediates.



IV

It is evident that the n-orbital on oxygen in the n,π^* excited state of ketones is a highly localized site of photochemical reactivity with radical characteristics.[7,8] Thus, an attractive mechanism for the conversion of I to II involves intramolecular attack of the n,π^* excited carbonyl group on the distal aromatic nucleus.[9] Bond formation between the carbonyl oxygen and the aromatic nucleus must be accompanied by extensive electronic reorganization of the carbonyl group (including the promoted electron) and is assumed to give the resonance stabilized, spiro Ar$_1$-6 diradical species V. The formation of II may be rationalized by collapse of V as indicated to a ketene VI or its valence tautomer VII.[10] Subsequent reaction with alcohol leads to II.



The photoreaction of I with 2-propanol takes an alternate course in the presence of photosensitizers such as benzophenone. Under these conditions the primary process is photoreduction of I to dibenzoylethane (complete characterization of the reaction

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(1) A variety of light sources have been employed; however, superior results were obtained with a General Electric Sun Lamp (275W). Pyrex vessels were utilized and all solutions were degassed. In general benzene was used as a solvent; however, other solvents have been employed without significantly altering the reaction course. The yield of IIb (m.p. 53.5–54.5°) was 55% after irradiation for 60 hours.

(2) H. Schmid, M. Hochweber and H. von Halban, *Helv. Chim. Acta*, **30**, 1135 (1947), and earlier papers. The mechanism of this reaction is currently under study in our laboratories.

(3) D. F. DeTar and A. Hlynsky, *J. Am. Chem. Soc.*, **77**, 4411 (1955).

(4) R. Heck and S. Winstein, *ibid.*, **79**, 3105 (1957).

(5) J. W. Wilt and J. L. Finnerty, *J. Org. Chem.*, **26**, 2173 (1961).

(6) J. W. Wilt and D. D. Oathoudt, *ibid.*, **23**, 218 (1958).

(7) M. Kasha in "Comparative Effects of Radiation," ed. by M. Burton, J. S. Kirby-Smith and J. L. Magee, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 85.

(8) H. E. Zimmerman, 17th National Organic Symposium of the Amer. Chem. Soc., June, 1961, Bloomington, Indiana, Abstracts, p. 31.

(9) That the n,π^* excited state is the active species in this reaction seems a valid assumption since Pyrex vessels were employed and hence light above 300 mμ. The typical hypsochromic shift was observed for the band in this region of the spectrum of I when solvent polarity was increased. *Cf.* H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(10) E. F. Jenny and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 2005 (1956).

products is in progress). This transformation is reminiscent of the reduction of *p*-quinones to hydroquinones,[11] and may be effected with such poor hydrogen donors as cyclohexane. The reduction is essentially quantitative when tri-*n*-butylstannane, a much better donor, is employed.[12] No reduction is observed, even with tri-*n*-butylstannane, in the absence of a photosensitizer.

Hammond and co-workers[13] and Bäckström and Sandros[14] recently demonstrated that excitation of benzophenone in solution is followed by quantitative intersystem crossing. Thus, the chemically significant excited state of benzophenone is a triplet and sensitization almost certainly involves energy transfer from the triplet state with production of the triplet state of the acceptor.[13] Consequently it is inviting to identify the photosensitized reduction of I with a triplet state.

It is noteworthy, however, that I is inefficient in photosensitizing the *cis–trans* isomerization of the piperylenes. Furthermore, no visible phosphorescent emission was observed for I in methylcyclohexane:isopentane glass (5:1) at 77° K.[15] Thus, it would appear that inter-system crossing is an inefficient process with dibenzoylethylene and that the phenyl migration reaction probably proceeds by way of the singlet state. Reaction by way of such a short lived species is not unexpected in view of the intramolecular character of the process. It should be emphasized, however, that the assignments of excited states in this preliminary report must be considered provisional in the absence of definitive spectroscopic data.

Acknowledgment.—We gratefully acknowledge support of this work by the Army Research Office (Durham).

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[11] A. Schönberg and A. Mustafa, *Chem. Reviews*, **40**, 181 (1947).

[12] G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

[13] G. S. Hammond, P. A. Leermakers and N. J. Turro, *ibid.*, **83**, 2395, 2396 (1961), and earlier papers.

[14] H. L. J. Bäckström and K. Sandros, *J. Chem. Phys.*, **23**, 2197 (1955).

[15] G. S. Hammond and W. Herkstroeter, private communication.

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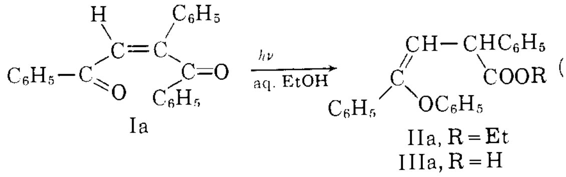
MECHANISTIC ORGANIC PHOTOCHEMISTRY. V.[1] PHENYL MIGRATION IN A NEW PHOTOCHEMICAL REACTION

Sir:

Previously[1-3] we have advanced a theoretical treatment describing in electronic detail the mechanisms of photochemical transformations. Parallel to our theoretical studies, we have pursued investigations of an exploratory nature. The following reports a new photochemical reaction of both theoretical and synthetic interest.

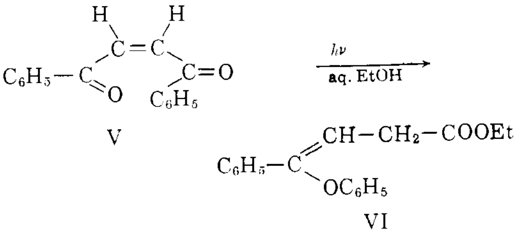
Irradiation of *cis*-1,2-dibenzoylstyrene (Ia) in 95% ethanol was found to give ethyl 2,4-diphenyl-4-phenoxy-3-butenoate (II) (yields in three runs, 39, 30, 64%). Also isolated were lesser quantities of 2,4-diphenyl-4-phenoxy-3-butenoic acid (stereoisomer IIIa, m.p. 141–142°; 13, 1, 23%), *trans*-dibenzoylstyrene (Ib) (12, 15, 16%), and recovered *cis*-dibenzoylstyrene (Ia) (7, 22, 0%).



(1)

The structure of II was elucidated by elemental analysis,[4] infrared, ultraviolet, n.m.r. and degradation. Most critically, the n.m.r. contained doublets centering at 3.74 and 5.29 τ (J = 10 cps., areas 1:1) attributed to an isolated AB system, triplet at 8.99 τ and quartet at 5.99 τ (J = 7 cps., areas 3:2) ascribable to ester ethoxyl, and aryl absorption at 2.4–3.4 τ (area 20). Saponification of II gave stereoisomeric 2,4-diphenyl-4-phenoxy-3-butenoic acids, IIIa, m.p. 141–142°, and IIIb, m.p. 126.0–127.5°. Except for the absence of the ethoxyl hydrogen peaks, the n.m.r. spectra were similar to that of the ester precursor; the doublets of IIIa appeared at 3.64 and 5.06 τ while those of IIIb were at 4.21 and 5.50 τ. Acidic hydrolysis of IIIa and IIIb afforded in each case both phenol and 2-phenyl-3-benzoylpropionic acid[5] (IV) as expected from structure III.

A second example of this rearrangement was found in the photolysis of dibenzoylethylene. Short irradiation of *trans*-dibenzoylethylene in aqueous ethanol gave 94% *cis*-dibenzoylethylene plus 5% ethyl 4-phenyl-4-phenoxy-3-butenoate (VI). Product VI was obtained in 36% yield on longer irradiation. Structure VI was based on similar evidence to that for II, including hydrolysis to phenol and 3-benzoylpropionic acid. In this case, however, the n.m.r. spectrum possessed typical AX_2 absorption, a vinyl triplet at 4.00 τ and methylene doublet at 6.78 τ (J = 7 cps., areas 1:2). The ethyl methylene quadruplet at 5.90 τ and methyl triplet at 8.80 τ (J = 7 cps., areas 2:3) were unexceptional. The aryl absorption at 2.4–3.4 τ had a total relative area of 10.



(2)

The migration of a phenyl group in a 1,2-dibenzoylethylenic moiety from the C-1 carbonyl

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[1] Paper IV of this series: H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, in press (1962).

[2] H. E. Zimmerman, 17th National Organic Symposium of the Amer. Chem. Soc., June, 1961, Bloomington, Indiana, Abstracts, p. 31.

[3] H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

[4] Acceptable analyses obtained.

[5] Y. Akhnookh, W. I. Awad and F. G. Baddar, *J. Chem. Soc.*, 1013 (1959).