

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-workers¹³ and Bäckström and Sandros¹⁴ 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 piperlyenes. Furthermore, no visible phosphorescence 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 dibenzoyl ethylene 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).

(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:

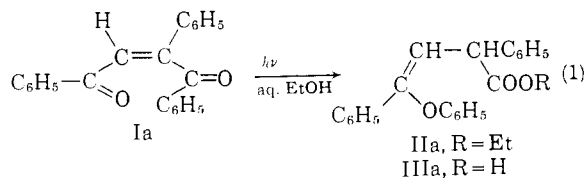
Previously¹⁻³ we have advanced a theoretical treatment describing in electronic detail the mechanisms of photochemical transformations. Parallel to our theoretical studies, we have pursued investigations of an exploratory nature. The following reports a new photochemical reaction of both theoretical and synthetic interest.

(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.

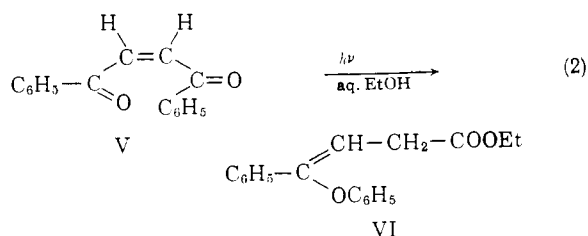
(3) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

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



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-butenic 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 acid⁵ (IV) as expected from structure III.

A second example of this rearrangement was found in the photolysis of dibenzoyl ethylene. Short irradiation of *trans*-dibenzoyl ethylene in aqueous ethanol gave 94% *cis*-dibenzoyl ethylene plus 5% ethyl 4-phenyl-4-phenoxy-3-butenate (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 AX₂ 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.

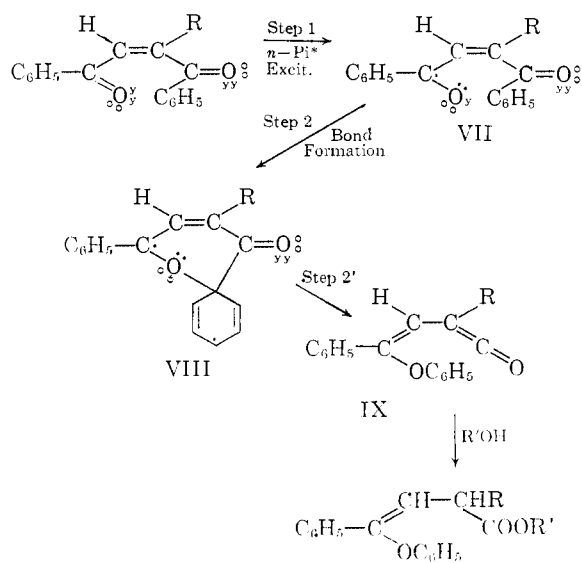
The migration of a phenyl group in a 1,2-dibenzoyl ethylenic moiety from the C-1 carbonyl

(4) Acceptable analyses obtained.

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

carbon atom to the C-2 carbonyl oxygen atom is reasonably formulated as proceeding *via* ketene precursors IX, which then react with ethanol and water to form the observed ester and acid products. Since filters cutting off light below 280 m μ were used in the present studies and the only absorption bands above this wavelength were $n\text{-}\pi^*$, the photochemical reaction clearly originates with the $n\text{-}\pi^*$ excited states of the dibenzoylstyrene and dibenzoyl ethylene reactants.⁶

Application of the mechanistic treatment of $n\text{-}\pi^*$ reactions described earlier¹⁻³ leads to the sequence in Chart I. Here the odd electron-containing p_y oxygen orbital of the excited carbonyl group is envisaged as homolytically attacking the phenyl group of the second benzoyl group. Such a mechanism rationalizes the interesting selectivity in which only one of the two benzoyl phenyl groups of dibenzoylstyrene migrates. In the migration depicted in Chart I both the excited state VII (with $R = \text{C}_6\text{H}_5$) and the bridged intermediate



II, $R = \text{C}_6\text{H}_5$, $R' = \text{Et}$
 III, $R = \text{C}_6\text{H}_5$, $R' = \text{H}$
 VI, $R = \text{H}$, $R' = \text{Et}$

Chart I

VIII will have greater π electron delocalization than their counterparts, in which the second benzoyl group is excited and the alternative second phenyl group migrates.

Further examples of this rearrangement as well as related mechanistic studies will be described in our full paper on the subject.

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(6) In any event, the $n\text{-}\pi^*$ state will be the lowest energy singlet. The same energy relationship of the triplet $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ states is probable but not certain.

(7) (a) Postdoctoral Research Associate 1961-62; (b) NIH Pre-doctoral Fellow; (c) Undergraduate research student. Support of this research by fellowships and research grant RG-7487 of the National Institutes of Health of the Public Health Service is gratefully acknowledged.

HOMOLYTIC PHENYLATION OF BENZENE, NAPHTHALENE AND ANTHRACENE IN THE PRESENCE OF COPPER SALTS. CORRELATION OF PARTIAL RATE FACTORS WITH LOCALIZATION ENERGIES¹

Sir:

Previous correlations of theoretical indices with reactivity data for homolytic aromatic substitution have been limited to alkyl and trichloromethyl "affinities" of arenes.^{2,3} Although the linearity of these relationships suggests validity, adequate test of theory requires knowledge of rates or relative rates of formation of specific compounds.

Previous publications,^{4,5} which established that arylarene is a major product of Meerwein reactions with both anthracene and benzene, provided a basis for the present investigation, *vide infra*. Thus phenylation was accomplished in aqueous acetone solution of arene or arenes, benzenediazonium chloride and cuprous and cupric chlorides, Table I. The reactivity of anthracene was also measured relative to naphthalene and is in excellent agreement with the value based on benzene, Table I, Runs 13-16. While both the orientation and reactivity data for anthracene are new, the phenylation of naphthalene has been studied previously using other methods of arylation and with conflicting results.⁶ Since some of the analytical methods used earlier are now obsolete, we repeated the work of Huisgen and Grashey⁷ and found that N-nitrosoacetanilide gives essentially the same orientation and reactivity data as the Meerwein reaction, Table I, Runs 25-28.

The partial rate factors for the 9-, 1- and 2-positions in anthracene and the 1- and 2-positions in naphthalene, calculated from the experimentally determined quantities in Table I, are 660, 55, 7.0, 22, and 3.2, respectively. A plot of the logarithms of these partial rate factors against the appropriate differences in radical localization energies⁸ is linear with a slope corresponding to $\beta = -7.9$ kcal. (Fig. 1). Correlation of all positions in these arenes reinforces earlier evidence that the direction of radical attack is essentially perpendicular to the nodal plane⁹ and enhances the prospects of using this β -value to predict partial rate factors, *etc.*, for homolytic phenylation of other polycyclic arenes.

Recent studies of the mechanism of the reaction of aryl peroxides with benzene by DeTar and Long¹⁰ and by Eliel, *et al.*,¹¹ have demonstrated that dimerization and other side-reactions of

(1) Financial support from the Aeronautical Research Laboratory, Wright-Patterson Air Force Base and the assistance of M. Fryd are gratefully acknowledged.

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chap. 11.

(3) Although free radical arylation has been studied extensively, polar factors in the usual substrates, derivatives of benzene, have frustrated attempts at theoretical interpretation; G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, Chap. 2.

(4) S. C. Dickerman, L. B. Levy and A. W. Schwartz, *Chem. and Ind.*, 360 (1958).

(5) S. C. Dickerman and K. Weiss, *J. Org. Chem.*, **22**, 1071 (1957).

(6) A review of the subject and a new determination of the total rate factor appeared recently; D. I. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 3112 (1961).

(7) R. Huisgen and R. Grashey, *Ann.*, **607**, 46 (1957).

(8) Ref. 2, p. 336.

(9) H. Weingarten, *J. Org. Chem.*, **26**, 730 (1961).