hydroboration of the two olefinic bonds of diallylphenylphosphine by phenylborane. The n.m.r. spectrum was in complete agreement with the assigned structure. The boron resonance was recorded at +23 p.p.m. relative to trimethyl borate as reference. The p.m.r. spectrum gave a peak area for aromatic protons of 10.0 and for aliphatic protons of 12.5. The aromatic protons gave a complex pattern of peaks bounded by τ 3.13 and 3.31 and centered at 3.2. The aliphatic protons gave a complex pattern with peaks centered at τ 8.39, 9.04, and 9.61. The spectrum was obtained from a carbon tetrachloride solution of the compound using acetaldehyde as the external standard. Unlike analogous diallylamines, only one product was isolated from this reaction.[4] In the case of the nitrogen analogs, monocyclic 1,2-azaborolidines were also isolated, apparently having been formed by intramolecular reduction of an allylic carbon–nitrogen bond. The fact that the monocyclic product does not form in the phosphorus case suggests that the boron–phosphorus bond is not as stable as the boron–nitrogen bond. This is in accord with the dissociation energies for complexes of trimethylamine and trimethylphosphine with trimethylborane, which have been found to be 17.6 kcal./mole and 16.5 kcal./mole, respectively.[5,6]

The compound was found to be unusually thermally stable. Thermal gravimetric analysis of the compound revealed that it retained 95% of its original weight at 350° and 30% of its original weight at 500°.

Acknowledgments.—We are grateful to the National Lead Foundation for support of this research in the form of a fellowship. We are also grateful to Dr. Wallace S. Brey, Jr., of this department, for determination and interpretation of the n.m.r. spectra, and to Dr. P. E. Slade of Chemstrand Research Center for the thermal gravimetric analysis.

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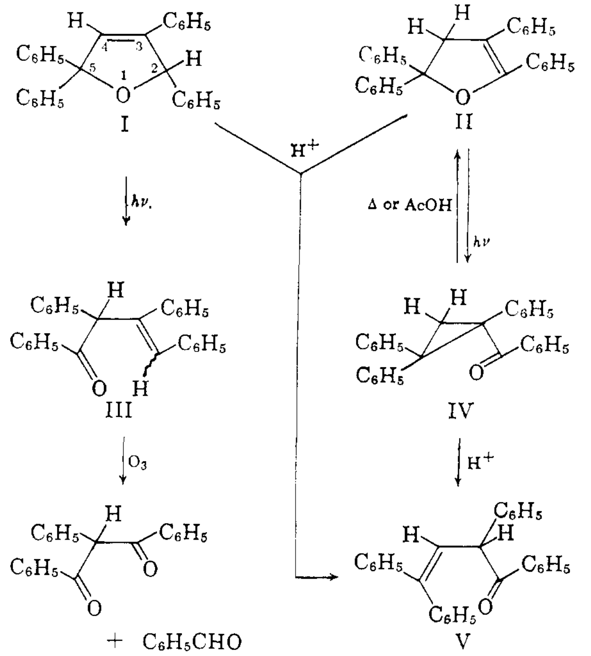
RECEIVED SEPTEMBER 14, 1964

Phenylated Dihydrofurans. Photo- and Acid-Catalyzed Rearrangements and Intermediacy in Cyclopropyl Ketone Cleavage[1]

Sir:

This concerns novel photochemistry in a new area stemming from our recent investigation of the $5\rightarrow 2$ phenyl group migration during pyrolysis and photolysis of bis(2,3,5,5-tetraphenyl-2-dihydrofuranyl)hydrazine.[2] 2,3,5,5-Tetraphenyl-2,5-dihydrofuran (I[2a]) was made and shown not to be involved in this rearrangement.[2a] The dihydrofuran I and its 4,5-isomer II[3] were selected for further study because the former (an allyl ether) could cleave at either C–O bond to give an acyclic unsaturated ketone (III or V), whereas the latter (an enol ether) would be expected to break at the 1,5 C–O bond with possible valence tautomerization to the cyclopropyl ketone IV.



The 2,5-dihydrofuran (I) upon irradiation[2b] ($10^{-3}\ M$ in benzene) underwent 1,2 ring cleavage at the presumably stronger C–O bond, with $5\rightarrow 4$ phenyl group migration, and gave the acyclic β,γ-unsaturated ketone, 1,2,3,4-tetraphenyl-3-buten-1-one (III,[3] 37%, structure shown by spectral data,[3] n.m.r. spectrum of its carbinol, 1,2,3,4-tetraphenyl-3-buten-1-ol, and by ozonolysis to dibenzoylphenylmethane and benzaldehyde). This apparently novel rearrangement may be classed as a vinylogous pinacol type in which the oxygen atom plays the dual role of the two hydroxyls of a pinacol.[2a,4]

In contrast to photolysis the 2,5-dihydrofuran (I) under acid catalysis underwent cleavage at the presumably weaker 1,5 C–O bond, without phenyl group migration, and it gave the isomeric β,γ-unsaturated ketone V[4a] (64%), presumably through the enol of V, possibly *via* the 4,5-dihydrofuran II.

2,3,5,5-Tetraphenyl-4,5-dihydrofuran (II[3]) was synthesized by addition of phenylmagnesium bromide to the unhindered carbonyl group of desylacetophenone and cyclodehydration of the resulting keto alcohol VI[3] (which in solution slowly equilibrates with the 2-hydroxytetrahydrofuran[5]). This 4,5-dihydrofuran under irradiation[2b] in benzene reacted differently from the

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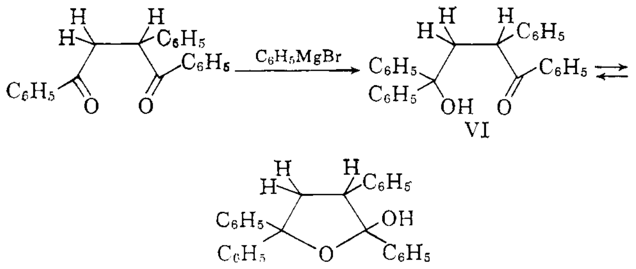
(1) This work was supported by (a) a National Science Foundation Research grant and (b) a Philip Francis du Pont Fellowship (1963–1964).

(2) (a) R. E. Lutz, J. I. Dale, and D. W. Boykin, Jr., *J. Am. Chem. Soc.*, **85**, 2340 (1963). The isomeric ketone V expected also as a product from this reaction has now been isolated (*ca.* 25%). (b) Hanovia high-pressure mercury arc lamp (450-w.), Pyrex filter.

(3) See Analytical Data section.

(4) (a) R. E. Lutz, R. G. Bass, and D. W. Boykin, Jr., *J. Org. Chem.*, in press. The ketone V was shown not to be intermediate in the photochemical conversion I → III; it reacted but behaved quite differently under the conditions involved, and the products are currently under investigation. (b) *Cf.* H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

(5) (a) This new and unique example of ring-chain tautomerism with a well-balanced equilibrium is important because it is a favorable one for the further detailed and quantitative study now in progress on the effects of temperature, solvent, and substituents; *cf.* (b) R. E. Lutz, C. L. Dickerson, and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 3062 (1962); (c) J. I. Dale, Ph.D. Dissertation, University of Virginia, 1962; (d) P. Bladon and W. McKeekin, *J. Chem. Soc.*, 3504 (1961); (e) G. Eglinton in "Physical Methods in Organic Chemistry," J. C. P. Schwartz, Ed., Oliver and Boyd Ltd., Edinburgh, 1964.



VI

2,5-isomer and underwent valence tautomerization[6] to 1-benzoyl-1,2,2-triphenylcyclopropane [IV (35%); structure shown by spectral data,[3] debenzoylation to 1,1,2-triphenylcyclopropane (VIII),[3,7,8a] and synthesis[8b]].

The 4,5-dihydrofuran (like the 2,5-isomer), and also the cyclopropyl ketone IV, underwent acid-catalyzed rearrangement without phenyl group migration to the acyclic β,γ-unsaturated ketone V. The cyclopropyl ketone, when fused or subjected to boiling acetic acid without added acid catalyst, underwent rapid rearrangement back to the 4,5-dihydrofuran. In proof of the sequence of reactions IV → II → V under strong acid catalysis, n.m.r. tracking in $CDCl_3$–CF_3COOH solution showed the rapid buildup of the dihydrofuran and relatively slow rearrangement of this to the unsaturated ketone.

The conversion of the cyclopropane through the 4,5-dihydrofuran to the β,γ-unsaturated ketone IV → II → V is of significance to small-ring chemistry and substituent effects on ring stabilities, and it is of particular importance to the mechanism of acid-catalyzed cleavages of cyclopropyl ketones where formation and intermediacy of the 4,5-dihydrofuran must now be considered as possibilities.[9]

Investigations of scope, by-products, mechanism, and detail of these and related reactions will be discussed in the forthcoming paper.

Analytical Data.[10] **II:** m.p. 106–108°; λ_{max} 245 and 303 mμ (ϵ 10,300 and 9800); infrared 1640 cm.$^{-1}$ (enol ether)[5d]; n.m.r. (Varian A-60) multiplet τ 2.6, singlet 6.05, intensities 10:1.

III: m.p. 181.5–183°; λ_{max} 248 mμ (ϵ 21,000), shoulder at 255 mμ, (ϵ 16,000); infrared 1680 cm.$^{-1}$; n.m.r. (140°, dimethyl sulfoxide-d_6)[11] multiplet τ 2.9, two singlets 3.63 and 4.23.

IV: m.p. 161–162°; λ_{max} 227 mμ (ϵ 20,900), shoulder at 240–245 mμ (ϵ 18,800–13,000); infrared 3050–3000, 1660, 1018 cm.$^{-1}$; n.m.r. ($CDCl_3$) multiplet τ 2.4, singlet 7.25, intensities 10:1 (in benzene the singlet appears as two doublets of equal intensity, τ 7.95, 8.15).

V.[4a]

VI: m.p. 160–161°; λ_{max} (acetonitrile) 243 mμ (ϵ 13,600); infrared 3455 and 1675 cm.$^{-1}$; $CDCl_3$ solution in *ca.* 50:50 equilibrium with its cyclic tautomer (determined by n.m.r. analysis).[5a]

VII: m.p. 50–52°; λ_{max} 225 mμ (ϵ 17,800), shoulder at 232 mμ (ϵ 16,400); infrared 3025 and 1020 cm.$^{-1}$; n.m.r. multiplet τ 2.5, quartet 7.0, multiplet 8.0, intensities 18:1:2.

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RECEIVED JULY 22, 1964

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(6) (a) Apparently novel, although thermal, interconversions of this type are known, *e.g.*, cyclopropanecarboxaldehyde–2,3-dihydrofuran equilibration at 375°: C. L. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947); (b) N. I. Shuikin, I. F. Bel'skii, and R. A. Karakhanov, *Dokl. Akad. Nauk SSSR*, **126**, 1051 (1959); (c) *cf.* W. A. Gibbons, W. F. Allen, and H. E. Gunning, *Can. J. Chem.*, **40**, 568 (1962).

(7) By potassium *t*-butoxide; *cf.* P. G. Gassman and F. V. Zaler, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, Abstracts, p. 7N.

(8) Syntheses by photocondensation of diphenyldiazomethane and (a) styrene or (b) α-phenylacrylophenone; *cf.* (c) H. M. Walborsky and L. Plonsker, *J. Am. Chem. Soc.*, **83**, 2138 (1961); (d) J. E. Hodgkins and M. P. Hughes, *J. Org. Chem.*, **27**, 4187 (1962); (e) C. G. Overberger and J. P. Anselme, *ibid.*, **29**, 1188 (1964).

(9) *E.g.*, the acid-catalyzed cleavage of two highly substituted benzoylcyclopropanes, where optical activity at C-1 is lost at a measurably higher rate than production of the acyclic β,γ-unsaturated ketone, was explained in terms of rapid reversible formation of a homoallylic carbonium intermediate.[8c]

(10) All analyses for C and H were correct.

(11) By H. H. Freeman, Dow Chemical Company.

Photoreduction of Aminobenzophenones[1]

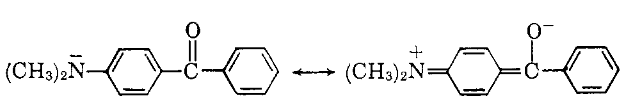
Sir:

Photoreduction of benzophenone and other ketones and aldehydes[2,3] occurs readily *via* abstraction of hydrogen from alcohols and other hydrogen atom donors by the excited carbonyl compounds (eq. 1). Amino

$$RR'C{=}O^* + AH \rightarrow RR'\dot{C}{-}OH + A\cdot \qquad (1)$$

and hydroxy substituents[4,5] suppress, or greatly decrease, rates of photoreduction of benzophenones. It has been suggested[4,5] that the lowest lying triplet in such compounds is π–π^* rather than n–π^* in nature, and is unreactive in abstraction of hydrogen. Recently[6] *p*-aminobenzophenone and *p*-hydroxybenzophenone have been reported to be unreactive in 2-propanol but to be photoreduced in cyclohexane. This unusual effect was attributed[6] to the lowest lying triplet in the former solvent being of a "charge-transfer" type which is unreactive in abstraction of hydrogen, while in the hydrocarbon solvent it is of the reactive n–π^* type. We report now that aminobenzophenones undergo rapid photoreduction by 2-propanol when converted to their "onium" derivatives, either by protonation or methylation.

p-Dimethylaminobenzophenone,[7] DMABP, has important contributions in the ground state from forms I and II. It shows intense absorption bands in 2-propanol at 249 (log ϵ 4.22) and 352 mμ (log ϵ 4.33), the former presumably arising from π–π^* excitation of the aromatic ring and the latter from excitation to



I II

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(1) We are pleased to acknowledge generous support of this work by the U. S. Atomic Energy Commission, AT(30-1)2499. This work was reported at the International Symposium on Organic Photochemistry, Strasbourg, France, July 21, 1964.

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(3) C. Weizmann, F. Bergmann, and Y. Hirshberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938); F. Bergmann and Y. Hirshberg, *ibid.*, **65**, 1429 (1943).

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(6) G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964).

(7) C. D. Hurd and C. N. Webb, in "Organic Syntheses," Coll. Vol. I, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 217.