

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°.

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Phenylated Dihydrofurans. Photo- and Acid-Catalyzed Rearrangements and Intermediacy in Cyclopropyl Ketone Cleavage¹

Sir:

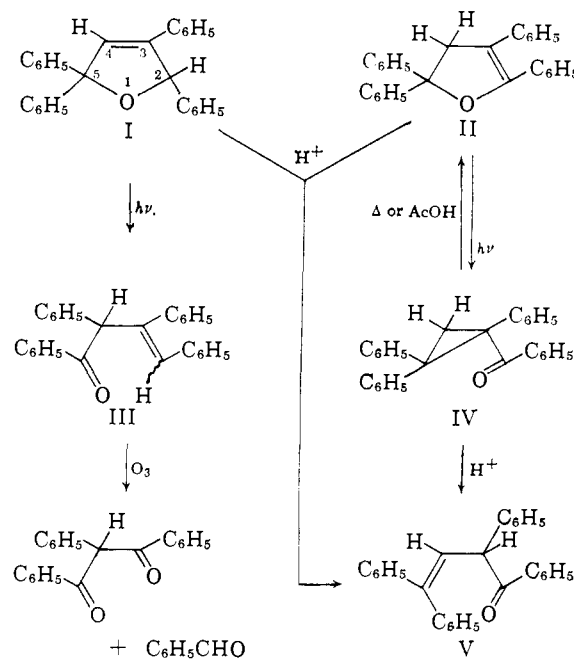
This concerns novel photochemistry in a new area stemming from our recent investigation of the 5→2 phenyl group migration during pyrolysis and photolysis of bis(2,3,5,5-tetraphenyl-2-dihydrofuranyl)hydrazine.² 2,3,5,5-Tetraphenyl-2,5-dihydrofuran (I^{2a}) was made and shown not to be involved in this rearrangement.^{2a} The dihydrofuran I and its 4,5-isomer II³ were selected for further study because the former (an allyl ether) could cleave at either C—O bond to

(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.

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→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 (II³) was synthesized by addition of phenylmagnesium bromide to the unhindered carbonyl group of desylacetophenone and cyclodehydration of the resulting keto alcohol VI³ (which in solution slowly equilibrates with the 2-hydroxytetrahydrofuran⁵). This 4,5-dihydrofuran under irradiation^{2b} in benzene reacted differently from the

(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.