

These results (1) establish the configurations of photolytically generated II and its previously unknown epimer and (2) uncover a novel rearrangement of IIA and B to give VII and an isomeric acid of unknown structure.

(9) Fellow of the Alfred P. Sloan Foundation.

(10) National Science Foundation Cooperative Fellow, 1959-1960.

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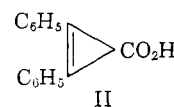
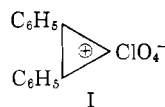
RECEIVED MARCH 24, 1960

THE DIPHENYLCYCLOPROPENIUM ION: PYROLYSIS OF 3,3-BIS-(1,2-DIPHENYLCYCLOPROPENYL) ETHER

Sir:

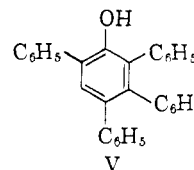
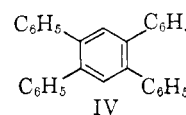
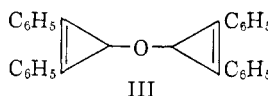
We wish to report a convenient synthesis of diphenylcyclopropenium perchlorate (I).¹ Reaction of 1,2-diphenylcyclopropene-3-carboxylic acid (II)² with 10% perchloric acid in acetic anhydride³ at 0-10° resulted in the evolution of carbon monoxide⁴ with concomitant formation of colorless needles of the explosive I, isolated in 70% yield, m.p. 149.5-150.5° (dec.) (from acetonitrile-benzene). Found: C, 61.81; H, 4.25; Cl, 12.23. The presence of perchlorate ion in the product was indicated by a positive test with methylene blue⁵ and the presence of strong absorption at 9.1μ characteristic of perchlorate ion in its infrared spectrum. The substance is insoluble in benzene and dichloromethane, but soluble in acetonitrile, dimethylformamide and aqueous sulfuric acid. The spectral properties of I provide interesting confirmation of its ionic nature in that the infrared spectrum exhibits a sharp band at 3.18μ absent from the spectra of the covalent diphenylcyclopropenes encountered in this work, while the ultraviolet spectrum in acetonitrile-10% ethanol exhibits a transition from that characteristic of the covalent diphenylcyclopropenes⁶ (λ_m 318, 303, 288, 231, 223 mμ; log ϵ 4.38, 4.50, 4.37, 4.22, 4.31) below ca. 0.05 N perchloric acid to one very similar (λ_m 305, 292, 246; log ϵ 4.52, 4.50, 4.03) to that of the triphenylcyclopropenium ion⁶ in 0.05 to 0.1 N perchloric acid. Chemical evidence for the assigned structure was provided by hydrolysis of I in aqueous potassium hydroxide to give α -phenylcinnamaldehyde identical with an authentic sample.⁷ The general utility of the preparative method for I is

suggested by the similar preparation of dipropylcyclopropenium perchlorate by Breslow and Höver.⁸



Hydrolysis of I in aqueous sodium bicarbonate resulted in the formation of 3,3-bis-(1,2-diphenylcyclopropenyl) ether (III), m.p. 163-165° (dec.). Found: C, 90.37; H, 5.58. The structural assignment follows from the spectroscopic properties of the product; λ_m (CH₃CN) 319, 303, 290, 231, 224; log ϵ 4.63, 4.74, 4.63, 4.54, 4.61; λ_m (0.1 N HClO₄, CH₃CN) 305, 292, 246; log ϵ 4.82, 4.80, 4.28. Pyrolysis of III at 180° for a short time yielded a mixture of products containing, as the major component, 1,2,4,5-tetraphenylbenzene (IV), m.p. 264.5-267°, identical with an authentic sample.⁹ In addition, 2,3,4,6-tetraphenylphenol (V) m.p. 247-248°, identical with an authentic specimen,¹⁰ was isolated as the only phenolic component detectable by infrared spectroscopy.

The photolysis of III, and the mechanistic implications of its pyrolysis are currently under investigation.



(8) R. Breslow and H. Höver, *THIS JOURNAL*, **82**, 2644 (1960).

(9) W. Dilthey, I. Thewalt and O. Trosken, *Ber.*, **67B**, 2004 (1934).

(10) P. Yates and J. Hyre, unpublished work. The authors affirm their indebtedness to Professor Yates for supplying spectroscopic data and comparison samples of the three isomeric tetraphenylphenols.

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RECEIVED APRIL 7, 1960

A CARBON-SKELETON REARRANGEMENT DURING THE OXIDATIVE DEPHOSPHORYLATION OF A NEW TYPE OF PHOSPHORUS COMPOUND. REACTION OF MOLECULAR OXYGEN WITH THE CRYSTALLINE 1:1 ADDUCTS DERIVED FROM TERTIARY PHOSPHITE ESTERS AND α -DIKETONES¹

Sir:

During our investigations² of the reactions of phosphite esters with quinones and with other carbonyl compounds, we have encountered a carbon-skeleton rearrangement which we believe to be new and significant. This rearrangement

(1) Acknowledgment is made to the Donors of the Petroleum Research Fund Administered by the American Chemical Society for partial support of this Research (Grant 286-A), and to the National Cancer Institute of the National Institutes of Health (Grant CY-4769).

(2) (a) F. Ramirez and N. B. Desai, *THIS JOURNAL*, **82**, 2652 (1960); (b) F. Ramirez, E. H. Chen and S. Dershowitz, *ibid.*, **81**, 4338 (1959), and reference therein.

(1) Salts of this cation have been prepared independently by R. Breslow and J. Lockhart, unpublished work, by reaction of phenylchlorocarbene with phenylacetylene. We wish to thank Professor Breslow for a pre-publication account of his results.

(2) R. Breslow, R. Winter and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

(3) Cf. M. J. S. Dewar and C. Ganellin, *J. Chem. Soc.*, 2438 (1959).

(4) F. Feigl, "Spot Tests in Organic Analysis," Elsevier, New York, N. Y., 1956, p. 327.

(5) G. Charlot, "Quantitative Inorganic Analysis," John Wiley and Sons, New York, N. Y., (1954) p. 271 (Translation).

(6) R. Breslow and C. Yuan, *THIS JOURNAL*, **80**, 5991 (1958).

(7) K. Alder, J. Hayden, K. Heimbach, K. Neufang, G. Hansen and W. Gerhard, *Ann.*, **586**, 110 (1954).