

mechanism involving the intermediacy of triplet 1,2-dimethylcyclopropane in the triplet methylene reaction.

Further work now in progress on this system and more detailed interpretation will be presented at a later date.

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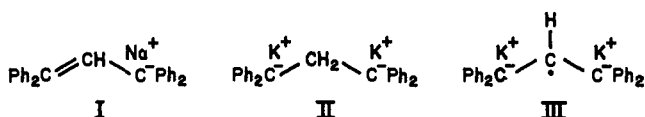
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The Tetraphenylallyl Dianion Radical

Sir:

Sodium-potassium alloy reduction of the allylic anion I yields the dianion II. This unexpected reaction has been shown to proceed through the dianion radical III.¹

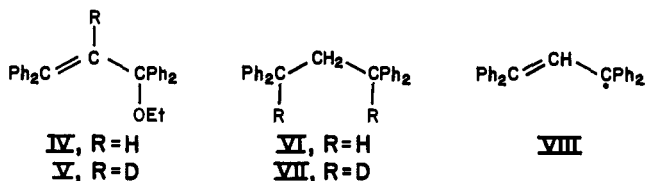


Reaction of the allylic anion I or the ethyl ether IV² with sodium-potassium alloy in ether or dimethoxyethane yielded after 8 hr. 1,1,3,3-tetraphenylpropane (VI)³ (78%). Quenching with D₂O resulted in the



Figure 1. First derivative e.s.r. spectrum of the dianion radical III in dimethoxyethane.

incorporation of two atoms of deuterium, giving VII, as shown by n.m.r. and mass spectrometry. In contrast, treatment of the allylic ether IV with sodium for 3 days followed by quenching with D₂O resulted in the production of 1,1,3,3-tetraphenylpropene-d₃ (80%); none of the propane VII could be detected in the total crude reaction product.⁴



When a dimethoxyethane solution of the anion I or

(1) Related investigations have been reported by P. Brassem, R. E. Jesse, and G. J. Hoihtink, *Mol. Phys.*, **7**, 587 (1964); P. H. Rieger, I. Bernal, W. H. Rheinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963); P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962); and N. L. Bauld, *J. Am. Chem. Soc.*, **86**, 2305, 3894 (1964).

(2) W. Schlenk and E. Bergmann, *Ann.*, **463**, 228 (1928).

(3) D. Vorlander and C. Siebert, *Ber.*, **39**, 1024 (1906).

the ether IV was shaken with sodium-potassium alloy and the electron spin resonance (e.s.r.) spectrum measured immediately thereafter, a strong doublet ($a = 7.6 \pm 0.3$ gauss, $g = 2.0025 \pm 0.0001$) was observed. This spectrum is shown in Figure 1. The radical thus produced has an apparent half-life of ca. 30 min. at 25°. It is quite stable at -50°. At room temperature the signal can be regenerated several times simply by vigorously shaking the e.s.r. tube. That the doublet is due to the hydrogen atom on the central carbon atom of the propene chain was shown by preparing the deuterium-substituted ether V. This compound when treated with sodium-potassium alloy showed a singlet in its e.s.r. spectrum. Further, the doublet was not observed when tetraphenylpropane, tetraphenylpropene, or tetraphenylcyclopropane were treated with the alloy under the reaction conditions.⁵ Thus, in order that the dianion radical may be observed, it is necessary that each of the carbon atoms of the propene chain be in the sp² configuration. As expected, no free radical could be detected by e.s.r. when sodium was allowed to react with the tetraphenylpropenyl ether IV.

For purposes of approximate comparison, Ziegler's radical VIII⁷ was prepared. It shows a doublet ($a = 8.0 \pm 0.3$ gauss, $g = 2.0025 \pm 0.0001$) very similar in appearance to that of the dianion radical III. In particular, as in the case of III, hyperfine splitting from the hydrogens on the benzene rings was not detected.⁸ The larger than normal splitting value for the vinyl hydrogen⁹ is presumably due to out-of-plane twisting of the molecule.¹⁰

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(4) Reduction with potassium metal in ether gives, after 1 week, a mixture (80% yield) composed of three parts of tetraphenylpropane one part of tetraphenylpropene.

(5) All of the tetraphenylpropane derivatives discussed above gave the e.s.r. spectrum of the biphenyl anion radical⁶ on prolonged contact with the sodium-potassium alloy.

(6) A. Carrington and J. Santos Veiga, *Mol. Phys.*, **5**, 21 (1962).

(7) K. Ziegler, *Ann.*, **434**, 34 (1932). In the present work this radical was prepared by oxidation of the anion I using tetramethylethylene dibromide. The resulting radical is stable in the solid state under nitrogen. The e.s.r. signal of this radical has decreased in intensity by roughly half after standing for 4 months at room temperature while sealed in an e.s.r. tube in dimethoxyethane solution.

(8) Cf. J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2441 (1955); and A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 157, 164. The latter makes reference to the work of D. C. Reitz, *J. Chem. Phys.*, **34**, 701 (1961), who has succeeded in resolving the spectrum of pentaphenylcyclopentadienyl which was previously reported as a single line: J. E. Wertz, C. F. Koelsch, and J. L. Vivo, *ibid.*, **23**, 2194 (1955).

(9) Cf. R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963), and references cited therein.

(10) The author is indebted to Dr. A. L. Kwiram for this suggestion and for his assistance in the measurement of the g values. The g values were measured by means of a proton gaussmeter and a transfer oscillator in conjunction with a Hewlett-Packard counter.

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The Structure of Ophiobolin, a C₂₅ Terpenoid Having a Novel Skeleton

Sir:

A metabolic product, ophiobolin, of the plant pathogenic fungus *Ophiobolus miyabeanus*¹ was first isolated