

Figure 2. View of the crystal structure: $\text{Ca}^{2+}\text{-O} = 2.3 \text{ \AA}$.; $\text{Br}^{-}\text{-Ca}^{2+} = 5.2 \text{ \AA}$.; N-H-O (broken line) = 2.8 \AA .; $(\text{C-N})_{\text{av}} = 1.47 \text{ \AA}$.; $\angle(\text{C-N-C})_{\text{av}} = 108^{\circ}$; $\angle(\text{N-C-N})_{\text{av}} = 112^{\circ}$.

dimensional network in the (001) plane. These layers are linked together only by chains of hydrogen bonds between water and HMT nitrogen atoms and van der Waals interactions. The Br^{-} ions are at 5.2 \AA . from the Ca^{2+} ion, which appears to be the distance of closest approach, taking into account the screening effect of the water molecules surrounding the central cation and the van der Waals interactions between the Br^{-} and HMT molecules. It is gratifying that all bond angles and bond lengths in the HMT are in good agreement with the values found in the structure of HMT recently refined by Cruickshank.⁷

Acknowledgment. We wish to thank Dr. E. Benedetti and Dr. G. Elefante for their collaboration and Professor V. Caglioti for initially suggesting this problem.

(7) L. N. Becka and D. W. J. Cruickshank, *Proc. Roy. Soc. (London)*, **273**, 435 (1963).

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Benzene- and Toluene-Photosensitized Isomerization of 1,2-Dimethylcyclopropane. The Triplet State of Cyclopropane

Sir:

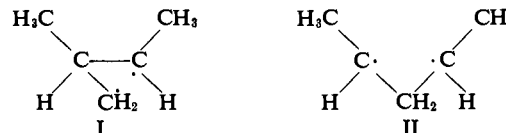
We wish to report the initial results of a study undertaken to shed more light on the mechanism of triplet methylene addition to olefins. Previous work has shown that *cis*- or *trans*-1,2-dimethylcyclopropane activated thermally¹ or "chemically"²⁻⁶ yields *trans*-

(1) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc. (London)*, **A257**, 122 (1960); **A260**, 424 (1961).

(2) H. M. Frey, *ibid.*, **A251**, 575 (1959).

or *cis*-1,2-dimethylcyclopropane, *cis*- and *trans*-pentene-2, 2-methylbutene-1, and 2-methylbutene-2 as products. The reaction of triplet methylene with butene-2⁴⁻⁹ yields the foregoing products and, in addition, 3-methylbutene-1.

A mechanism suggested for the triplet methylene reaction⁹ involves the initial formation of a triplet addition complex (biradical I). Since the relative



yields of products in this reaction do not, however, appear to be consistent with this mechanism, another mechanism has been proposed¹⁰ which involves the initial formation of triplet 1,2-dimethylcyclopropane. This species may be visualized as a resonance hybrid of valence bond structures like I and II and readily explains the observed product yields.

This latter mechanism requires that the exothermicity of the triplet methylene-butene-2 reaction be greater than or equal to the unknown triplet state energy of 1,2-dimethylcyclopropane. Since the heats of formation of butene-2 and 1,2-dimethylcyclopropane are probably nearly the same (by analogy with other olefins and

(3) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

(4) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964).

(5) S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965).

(6) R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965).

(7) F. A. L. Anet, R. F. W. Bader, and A. M. Van der Auwera, *J. Am. Chem. Soc.*, **82**, 3217 (1960).

(8) H. M. Frey, *ibid.*, **82**, 5947 (1960).

(9) F. J. Duncan and R. J. Cvetanović, *ibid.*, **84**, 3593 (1962).

(10) J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 45 (1964); in ref. 6 this same idea is advanced.

cyclopropanes), the exothermicity of the reaction will be determined by the heat of formation of triplet methylene, which is probably in the range 75–90 kcal./mole.^{11,12}

Observation of geometric and structural photoisomerization of phenyl- and benzoyl-disubstituted cyclopropane,¹³ perhaps through a triplet-state intermediate,¹⁴ and the triplet photosensitized geometric isomerization of 1,2-diphenylcyclopropane¹⁵ probably do not represent the energetics of "free" cyclopropane since the cyclopropyl group appears to interact with conjugated systems.^{16,17} Study of the mercury-photosensitized isomerization of 1,2-dimethylcyclopropane¹⁸ does not yield any information pertinent to the present discussion because the mercury triplet can transfer 112 kcal./mole of energy to the cyclopropane, and this is some 22 kcal. in excess of the probable maximum available in triplet methylene reactions.

To circumvent the above objections we have begun an investigation of the benzene- and toluene-photosensitized isomerization of 1,2-dimethylcyclopropane. *cis*-1,2-Dimethylcyclopropane was synthesized as described by Flowers and Frey¹ and was partially purified by preparative gas chromatography. The reactant used contained small amounts of 1,1-dimethylcyclopropane, *trans*-1,2-dimethylcyclopropane, and *cis*- and *trans*-pentene-2. All analyses were made gas chromatographically (5-ft. column of 30% SF-96 on Chromosorb W) with flame ionization detection. Matheson Coleman and Bell Spectroquality benzene and reagent grade toluene were degassed by repeated freezing and pumping before use. The appropriate amounts of benzene or toluene and cyclopropane were measured in a conventional vacuum system; the mixtures were then passed repeatedly through a gold-foil trap to free the gases of mercury. All the results presented were obtained from photolyses of mixtures containing about 1×10^{-3} and 2×10^{-3} mole/l. (20 and 40 mm. pressure at 25°), respectively, of the cyclopropane and photosensitizer, irradiated in a cylindrical Vycor cell 20 cm. long with the unfiltered radiation from a 200-w. high-pressure mercury arc.¹⁹ For temperature studies the reaction cell was heated with a heating tape that maintained the temperature to $\pm 3^\circ$ with about a 10° variation along the length of the cell. The results of a number of other studies of benzene photosensitizations^{20–22} indicate that under the conditions used in this work, energy transfer occurs by a

triplet-triplet mechanism that excites the 1,2-dimethylcyclopropane to a triplet state from which the observed isomerizations occur. It is assumed that the same mechanism is operative in the toluene sensitizations. The products of the benzene-photosensitized isomerization of the *cis*-1,2-dimethylcyclopropane are *trans*-1,2-dimethylcyclopropane, *cis*- and *trans*-pentene-2, and 3-methylbutene-1.²³

Table I gives the results of temperature studies (in the range 300–500°K.) which yield apparent activation energies and relative values of Arrhenius frequency

Table I. Rate Parameters for the Photosensitized Isomerization of *cis*-1,2-Dimethylcyclopropane (DMCP)

Product	Benzene		Toluene	
	E_{act}^a	Rel. A^b	E_{act}^a	Rel. A^b
<i>cis</i> -1,2-DMCP ^c	1.8	2.4	4.3	1.7
<i>trans</i> -1,2-DMCP	1.5	1	4.2	1
3-Methylbutene-1	4.4	11	7.1	8.9
Pentene-2	4.7 ^d	29	... ^e	... ^e

^a Units in kcal./mole; uncertainty is about 20–30%. ^b Uncertainty is about 50%. ^c Rate of disappearance. ^d Uncertainty is about 40%. ^e Not reported because analytical difficulties and small amounts of product made it impossible to obtain a reliable result.

factors for the appearance of products and the disappearance of the reactant *cis*-1,2-dimethylcyclopropane. The difference in activation energies between benzene and toluene as photosensitizers for a given mode of reaction is 2.5–2.7 kcal./mole. This difference in energy is just that between the lowest triplet state energies of benzene and toluene, 85²⁴ and 82²⁵ kcal./mole, respectively. The correspondence of energy differences lends credence to the assumption that energy transfer is occurring *via* the triplet state of the sensitizer.

The activation energies for disappearance of *cis*-1,2-dimethylcyclopropane and formation of *trans*-1,2-dimethylcyclopropane indicate that the energy state being populated by triplet energy transfer from benzene is about 2 kcal./mole higher in energy than the benzene triplet. If transfer occurs from the lowest vibrational state of the benzene triplet, the cyclopropane triplet state is probably at about 87 kcal./mole.

This value for the cyclopropane triplet energy is within the range suggested above for the exothermicity of the triplet methylene-butene-2 reaction and thus lends support to a mechanism in which the products arise from the triplet 1,2-dimethylcyclopropane.¹⁰ This mechanism is also corroborated by the appearance of 3-methylbutene-1 as a product of both the triplet photosensitization reactions and the triplet methylene-butene-2 reaction. Moreover, since the activation energies for formation of 3-methylbutene-1 and pentene-2 are very close, one would anticipate that the production of these two products from the activated molecule formed in the triplet methylene reaction would be largely determined by the ratio of frequency factors for these reactions; that the ratio of frequency factors in Table I and the product yield ratio in the methylene reaction⁹ are both about 1:3 further supports a

(23) Other, as yet unidentified, C₅ products account for about 1–3% of the *cis*-1,2-dimethylcyclopropane that isomerizes.

(24) D. F. Evans, *J. Chem. Soc.*, 3885 (1957).

(25) Y. Kanda and H. Sponer, *J. Chem. Phys.*, 28, 798 (1958).

- (11) J. A. Bell, *J. Chem. Phys.*, 41, 2556 (1964).
 (12) G. S. Paulett and R. Ettinger, *ibid.*, 39, 825, 3534 (1963); 41, 2557 (1964).
 (13) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, 87, 1410 (1965).
 (14) This conclusion is based on an interpretation of unpublished results that were communicated to the author by J. K. Foote.
 (15) G. S. Hammond and R. S. Cole, *J. Am. Chem. Soc.*, 87, 3256 (1965).
 (16) J. F. Music and F. A. Matsen, *ibid.*, 72, 5256 (1950).
 (17) V. T. Aleksanyan, Kh. E. Sterin, M. Yu. Lukina, I. L. Safonova, and B. E. Kazanskii, *Opt. i Spektroskopiya*, 7, 178 (1959); *Opt. Spectry.*, 7, 114 (1959).
 (18) D. W. Setser, B. S. Rabinovitch, and E. G. Spittler, *J. Chem. Phys.*, 35, 1840 (1961).
 (19) Identical results were obtained with and without a mercury vapor filter between the cell and the lamp. The 1,2-dimethylcyclopropane irradiated in the absence of photosensitizer did not isomerize.
 (20) W. A. Noyes, Jr., and H. Ishikawa, *J. Chem. Phys.*, 37, 583 (1962); *J. Am. Chem. Soc.*, 84, 1502 (1962).
 (21) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, 60, 1146 (1964).
 (22) P. Sigal, *J. Chem. Phys.*, 42, 1953 (1965).

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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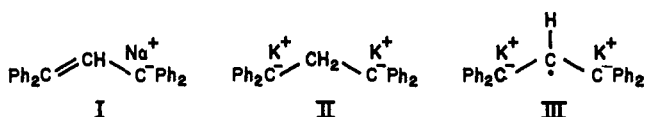
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The Tetraphenylallyl Dianion Radical

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

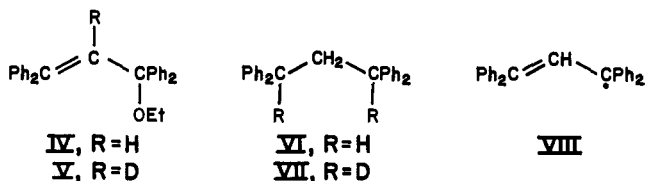


Reaction of the allylic anion I or the ethyl ether IV² with sodium-potassium alloy in ether or dimethoxyethane yielded after 8 hr. 1,1,3,3-tetraphenylpropane (VI)³ (78%). Quenching with D₂O resulted in the



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

Acknowledgment. This work was generously supported by the William F. Milton Fund of Harvard University and the Petroleum Research Fund of the American Chemical Society.

(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