method is unsatisfactory. However, ozonolysis of 0.240 g. of VI in ethyl acetate at −78°, treatment of the ozonide with hot aqueous 30% hydrogen peroxide and isolation of the acidic products yielded, after crystallization from benzene–cyclohexane, 0.134 g. (59%) of III, m.p. 132–133°. Two recrystallizations of this material from the same solvent and then sublimation (100°, 0.1 mm.) gave an analytical sample, m.p. 133–134°, $[\alpha]^{21}D$ +16° (*c* 2.9, ethanol).[9] *Anal.* Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10; neut. equiv., 87. Found: C, 54.97, 55.00; H, 8.14, 8.21; neut. equiv., 86. The infrared absorption spectrum (KBr pellet) of this material was found to be identical in all respects with that of an authentic sample of (+)-α-methyl-α-isopropylsuccinic acid, m.p. 128–130°, but definitely different in small details from that of an authentic sample of the racemic form, m.p. 154–155°.

We are grateful to the National Science Foundation for a grant (G14524) in support of this work, to Dr. Richard H. Eastman for a generous gift of umbellulone and to Dr. Arne Fredga for authentic samples of both the optically active and racemic forms of α-methyl-α-isopropylsuccinic acid.

(9) Reported (ref. 6a), m.p. 126.5–127°, $[\alpha]^{25}D$ +19° (*c* 1.57, ethanol).

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RECEIVED MAY 31, 1962

THE PHOTOSENSITITED DIMERIZATION OF CYCLOPENTADIENE[1]

Sir:

As was reported recently,[2] butadiene can be dimerized through the agency of a variety of photosensitizers. The sensitizers used are compounds believed to decay by way of triplet states after photoexcitation. The detailed mechanism of the dimerization may be written as (1) to (3) (where A is the sensitizer):

$$A_{S_0} \xrightarrow{h\nu} A_{S_1} \longrightarrow A_{T_1} \qquad (1)$$

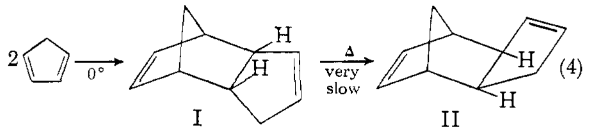
$$A_{T_1} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow A_{S_0} + \cdot\overset{\downarrow}{C}H_2{-}CH{=}CH{-}\overset{\downarrow}{C}H_2\cdot \qquad (2)$$

$$\overset{\downarrow}{\cdot C}H_2CH{=}CH\overset{\downarrow}{C}H_2\cdot + CH_2{=}CHCH{=}CH_2 \longrightarrow \begin{array}{l} CH_2{-}CH{\cdots}CH{\cdots}CH_2\downarrow \\ | \\ CH_2{-}CH{\cdots}CH{\cdots}CH_2\downarrow \end{array} \qquad (3)$$

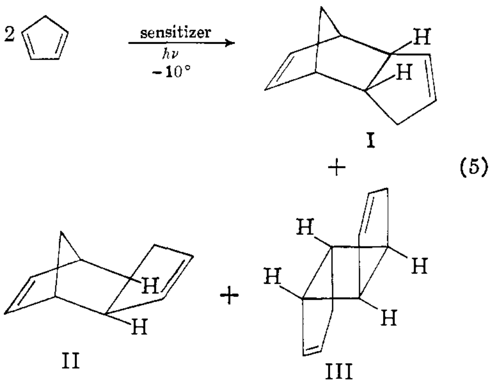
$$\downarrow$$
$$\text{dimers}$$

The composition of the mixture of dimers is rather different from that obtained by thermal dimerization of butadiene.[3] However, these results are difficult to compare since the two experiments were carried out at widely different temperatures. It seemed of interest to carry out a photosensitized dimerization under conditions which would also permit thermal dimerization. This experiment would be of particular interest because of the recent suggestions[4,5,6] that Diels–Alder reactions may involve transient intermediates in which one bond has been formed. One possible formulation of such an intermediate would be a triplet biradical of the type produced in reaction (3).

The dimerization of cyclopentadiene seemed appropriate for study since the diene undergoes the Diels–Alder reaction at 0° to give exclusively *endo*-dicyclopentadiene although on heating above 100° some *exo* isomer is formed.[7,8]



Cyclopentadiene containing acetophenone, benzophenone, fluorenone, mesityl oxide, acetone, benzil, or 2,3-pentadione when irradiated with a Hanovia 450-watt, quartz immersion lamp produces (after correction for the thermal reaction) *endo*-dicyclopentadiene (I), *exo*-dicyclopentadiene (II), and *trans*-(3,0,3,0)-tricyclo-2,8-decadiene (III) in approximately a 1:1:1 ratio, respectively. It is noteworthy that 9-anthraldehyde, which was incapable of sensitizing the isomerization of *cis*-piperylene,[9] is also inert as a photosensitizer for the dimerization of cyclopentadiene.



The reaction products were analyzed by vapor chromatography on a 7.3 m. length 6-mm. diameter column packed with 25% β,β′-oxydipropionitrile on 40/60 mesh firebrick. The products were separated by preparative vapor chromatography using first Apiezon J to separate *exo*- and *endo*-dicyclopentadiene from III and then using β,β′-oxydipropionitrile to separate *endo*- and *exo*-isomers.

The *exo*-dicyclopentadiene was identical in all respects with a sample of authentic material pre-

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(1) Mechanisms of Photoreactions in Solution XI. Part X is G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

(2) G. S. Hammond, A. Fischer and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(3) W. H. B. Reed, *J. Chem. Soc.*, 685 (1951).

(4) C. Walling and J. Peisch, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

(5) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(6) R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2198 (1961).

(7) K. Alder and G. Stein, *Ann*, **504**, 219 (1933).

(8) P. D. Bartlett and I. S. Goldstein, *J. Am. Chem. Soc.*, **69**, 2553 (1947).

(9) G. S. Hammond, P. A. Leermakers and N. J. Turro, *ibid.*, **83**, 2396 (1961).

pared by the method of Bartlett and Goldstein.[8] The gross structure of III was indicated by its n.m.r. spectrum which shows vinyl protons (−385 cps. from tetramethylsilane in carbon tetrachloride solution at 60 mc.), allylic cyclobutane protons (broad group centered about −180 cps.), and methylene and non-allylic cyclobutane protons as a pair of overlapping doublets (−147, −142 and −137 cps., respectively).

The identity of III was established by reference to compounds prepared by Eaton[10] in a study of the photodimers of cyclopentenone. Both the *syn*- and *anti-trans*-photodimers were converted to dienes by reduction and elimination from the ditosylates. The diene derived from *trans*-[3,0,3,0]-tricyclo-2,9-decanedione was identical with III. That derived from the 2,7-dione had significantly different spectra and a longer retention time in vapor chromatograms. Catalytic hydrogenation of III gave a hydrocarbon identical with that obtained by Wolf–Kishner reduction[10] of the *trans-anti*-dione. The *trans*-configuration of III is also indicated by the fact that the compound has no measurable dipole moment.

These results clearly disassociate the mechanisms of the photodimerization and the Diels–Alder reaction. In so far as the presumption that photosensitized reactions involve triplet intermediate is accepted, the results provide evidence against the intermediacy of open chain biradicals[4] in the Diels–Alder reaction but have no bearing on the possible involvement of spin-paired intermediates in the latter reaction.

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(10) P. E. Eaton, *J. Am. Chem. Soc.*, in press. We are indebted to Dr. Eaton for prepublication communication of his results.

(11) National Science Foundation Predoctoral Fellow.

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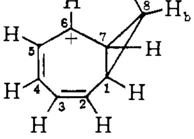
RECEIVED JANUARY 16, 1962

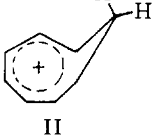
THE BICYCLO[5,1,0]OCTADIENYL CATION,[1] A NEW STABLE CARBONIUM ION

Sir:

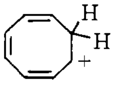
We wish to report the isolation of salts of the bicyclo[5,1,0]octadienyl carbonium ion[2] (I) and to present evidence for the structure of this new, stable cation.



I



II



III

Addition of antimony pentachloride to equimolar amounts of HCl and cyclooctatetraene in nitromethane, then dilution with benzene affords almost quantitative yields of the hexachloroantimonate salt of I. The salt is extremely soluble in nitromethane and liquid sulfur dioxide yielding rather dark colored solutions from which pale yellow prisms crystallize, m.p. 100°, dec. (*Anal.* Calcd. for $C_8H_9SbCl_6$: C, 21.86; H, 2.06. Found: C, 23.88; H, 2.32.) Some decomposition obviously accompanies dissolution of the salt rendering purification somewhat tedious. The material is insoluble in all non-polar solvents; it may be stored indefinitely under nitrogen in the refrigerator without apparent change, but it quickly decomposes when exposed to a humid atmosphere and immediately reacts with water and alcohol. The salt reacts with cycloheptatriene to produce tropylium hexachloroantimonate in yields of about 40%. Reaction with sodium acetate in acetic acid and catalytic hydrogenation gives cyclooctyl acetate and cyclooctane along with other products which have not yet been conclusively identified.

Addition of hydrogen bromide to a solution of cyclooctatetraene in anhydrous benzene at 0° yields cyclooctatrienyl bromide.[3] Reaction of this material with antimony pentachloride in cold anhydrous benzene produces an immediate pale yellow crystalline precipitate of the bromopentachloroantimonate salt of I, m.p. 84–85°, dec. This salt behaves in a manner identical with the hexachloroantimonate analog.

There can be little doubt as to the presence of a carbonium ion in these compounds, but the factors contributing to its stability are perhaps less palpable. It seems likely that part of the stability of the salt might arise from the fact that a cyclopropyl ring can, under certain conditions, emulate a carbon–carbon double bond. In other words a p orbital component on C_1 and C_7 may interact with the p orbitals on the adjacent C_2 and C_6 atoms to form a "pseudoaromatic" ring somewhat analogous to tropylium, as is implied in structure (II).

Evidence supporting this argument is seen in the n.m.r. spectrum of the salt in nitromethane or, better, of solutions of cyclooctatetraene in 98% H_2SO_4.[4] The n.m.r. spectrum of the latter solution consists of four distinct hydrogen multiplets exhibiting only partially resolved fine structure centered about τ values of 1.4, 3.4, 4.8, and 10.6, and having relative areas of 5, 2, 1, 1, respectively.[5] The spectrum can be interpreted satisfactorily on the basis of structure I as follows. The multiplet about 1.4 τ is assigned to the five hydrogens

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(1) This work was presented in part at the Carbonium Ion Symposium, 154th National Meeting of the American Chemical Society, St. Louis, March, 1961.

(2) This nomenclature is applicable regardless of the nature of the electronic interactions in effect in the molecule and in particular at the 1,7 bond. Another name which might be satisfactory is "homotropylium," *cf.* S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3248 (1961).

(3) The addition of HBr to cyclooctatetraene in acetic acid is reported to produce α-bromo-ethylbenzene, W. Reppe, A. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 47 (1948). The products obtained employing the conditions stated above gave cyclooctane plus a lesser amount of ethylbenzene upon catalytic hydrogenation; the bromide does thermally isomerize to α-bromo-ethylbenzene.

(4) The proton resonance spectrum in nitromethane appears to contain the identical bands that are obtained from cyclooctatetraene in H_2SO_4, but the methyl absorption in nitromethane obscures part of the spectrum. Furthermore, one extra band appears in the nitromethane solution spectrum which varies with the purity of the solvent and is apparently due to decomposition. The solution of cyclooctatetraene in H_2SO_4 yields cyclooctyl acetate, cyclooctane and another component present in the products obtained from reaction of the salts with sodium acetate in acetic acid.

(5) Chemical shifts were measured relative to external tetramethylsilane.