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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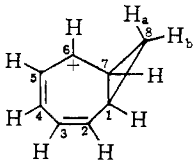
RECEIVED JANUARY 16, 1962

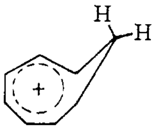
THE BICYCLO[5,1,0]OCTADIENYL CATION,[1] A NEW STABLE CARBONIUM ION

Sir:

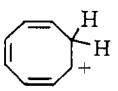
We wish to report the isolation of salts of the bicyclo[5,1,0]octadienyl carbonium ion[2] (I) and to present evidence for the structure of this new, stable cation.



I



II



III

Addition of antimony pentachloride to equimolar amounts of HCl and cycloöctatetraene 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.

on C_2, C_3, C_4, C_5 and C_6, being at low field primarily because these carbons bear most of the positive charge. The two hydrogens on C_1 and C_7 give rise to the multiplet at 3.4 τ, an abnormally low value for cyclopropyl hydrogens, and which probably indicates the extent to which C_1 and C_7 participate in the cyclic conjugation. Perhaps the most significant aspect of the spectra is the large chemical shift (5.8τ) between hydrogens H_a and H_b on C_8. This separation can be explained readily on the basis of the cation having the configuration shown in I. H_a (10.6 τ) being held over the seven membered ring will experience shielding due to ring currents while H_b (4.8 τ) which lies almost coplanar with the ring is deshielded by the same effect. This assignment is supported by the fact that in D_2SO_4 the spectrum shows the same gross structure as in H_2SO_4 except that the areas are now 5, 2, $^1/_2$, $^1/_2$ with the fine structure being changed considerably in the latter three bands. Furthermore this also implies that deprotonation is not taking place at any rapid rate.

The data clearly eliminate the cyclooctatrienyl structure (III) for the cation and strongly support the configuration (I).

We thank the Robert A. Welch Foundation and the Alfred P. Sloan Foundation for financial assistance. We also thank Humble Oil and Refining Co., Baytown, Texas, for providing the n.m.r. spectrum.

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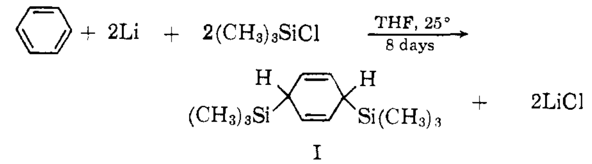
RECEIVED JUNE 11, 1962

THE SYNTHESIS OF 3,6-DISILYL-1,4-CYCLOHEXADIENES BY THE TRAPPING OF BENZENE ANION-RADICALS

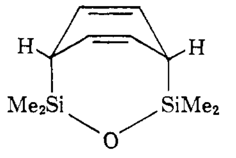
Sir:

We wish to report a synthesis of 3,6-bis-(trimethylsilyl)-1,4-cyclohexadiene (I) which involves the trapping, *via* reaction with a chlorosilane, of an anion-radical formed by the reaction of lithium or sodium with benzene in tetrahydrofuran.



I

Stirring benzene (3.0 moles), lithium sand (9.0 moles) and trimethylchlorosilane (6.0 moles) in 750 ml. of tetrahydrofuran resulted in a gradual loss of chlorosilane and formation of lithium chloride over an eight-day period. Filtration and fractional distillation yielded 217 g. (0.97 mole) of I (b.p. 90° (4.5 mm.), m.p. 50–51°. *Anal.* Calcd. for $C_{12}H_{24}Si_2$: Si, 25.01; C, 64.2; H, 10.78. Found: Si, 24.78; C, 64.4; H, 10.80) and 30 g. (0.14 mole) of 1,4-bis-(trimethylsilyl)-benzene (II) (m.p. 95–96°). Table I shows the yield of I and II obtained upon variation of reaction conditions. Benzene, lithium, and dimethylmethoxychlorosilane under the above conditions gave a 52% yield of 3,6-bis-(dimethylmethoxysilyl)-1,4-cyclohexadiene (b.p. 121–124° (10 mm.), n^{25}_D 1.4736–46. *Anal.* Calcd for $C_{12}H_{24}O_2Si_2$: Si, 21.9; C, 56.2; H, 9.40. Found: Si, 22.1; C, 55.9; H, 9.58) which upon hydrolysis and condensation of the resulting silanol gave a 20% yield of 2,2,4,4-tetramethyl-3-oxa-2,4-disilabicyclo[3.2.2]-nona-6,8-diene (III) (m.p. 71–72. *Anal.* Calcd for $C_{10}H_{18}OSi_2$: Si, 26.7; C, 57.1; H, 8.6; mol. wt., 210.4. Found: Si, 26.5; C, 57.4; H, 8.7; mol. wt., 216).



III

The structure of I was confirmed by its n.m.r. spectrum[1] and by dehydrogenation to II on treatment with quinone at 25° in CCl_4[2] (70% yield), refluxing for 2 hours in ethanol with platinum on carbon (73% yield), or on standing for 6 days in ethanol containing 15% by volume of 30% hydrogen peroxide (50% yield). The facile dehydrogenation of I and the absence of phenyltrimethylsilane among the reaction products indicate that II arises *via* dehydrogenation of I either during the reaction or isolation of products.

TABLE I

REACTION OF ALKALI METALS, TRIMETHYLCHLOROSILANE, AND BENZENE IN TETRAHYDROFURAN

Reaction conditions		Yield of I[a]	
Metal	Days at 25°	%	Contained
Li (wire)	2	40%	15% II[b]
Na + catalytic amount of Li	6	32%	10% II
Na_2K alloy	5	41%	9% II

[a] Isolated by distillation as a mixture of I and II. [b] By infrared and n.m.r. analyses.

Although biphenyl and naphthalene react with alkali metals in tetrahydrofuran to give high concentrations of ion-radicals,[3,4] benzene gives no reaction under these conditions.[5] The products of this reaction, however, are those expected from the reaction of lithium phenide[6] with a chlorosilane[7,8] and are consistent with this reaction scheme

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[1] We are grateful to Mr. P. C. Lauterbur of Mellon Institute of Industrial Research, Dr. E. B. Baker of The Dow Chemical Company and Mr. N. C. Angelotti of Dow Corning Corporation for the n.m.r. spectra.

[2] Rapid reaction with quinone to give quinhydrone and the corresponding aromatic structure is characteristic of 1,4-cyclohexadienes: A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).

[3] T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954).

[4] D. E. Paul, D. Lipkin and S. I. Weissman, *ibid.*, **78**, 116 (1956).

[5] Soluble ion-radicals have been formed at −80° from benzene and an alkali metal in 1,2-dimethoxyethane: T. R. Tuttle and S. I. Weissman, *ibid.*, **80**, 5342 (1958).

[6] It has been suggested that the names of these anion-radicals be derived from the names of the corresponding hydrocarbons by substituting the suffix -ide for the terminal -e in the name of the parent hydrocarbon.[4]

[7] Sodium naphthalenide and trimethylchlorosilane in tetrahydrofuran yield 1,2- and 1,4-bis-(trimethylsilyl)-dihydronaphthalene.