

on C₂, C₃, C₄, C₅ and C₆, being at low field primarily because these carbons bear most of the positive charge. The two hydrogens on C₁ and C₇ give rise to the multiplet at 3.4 τ , an abnormally low value for cyclopropyl hydrogens, and which probably indicates the extent to which C₁ and C₇ participate in the cyclic conjugation. Perhaps the most significant aspect of the spectra is the large chemical shift (5.8 τ) between hydrogens H_a and H_b on C₈. 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 D₂SO₄ the spectrum shows the same gross structure as in H₂SO₄ 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.

(6) Union Carbide Fellow, University of Texas, 1961-1962.

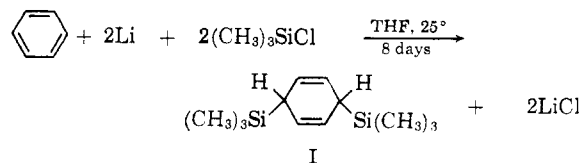
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THE SYNTHESIS OF 3,6-DISILYL-1,4-CYCLOHEXADIENES BY THE TRAPPING OF BENZENE ANION-RADICALS

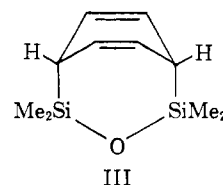
Sir:

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.



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 C₁₂H₂₄Si₂: 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*_D²⁵ 1.4736-46). *Anal.* Calcd for C₁₂H₂₄O₂Si₂: 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 C₁₀H₁₈O₂Si₂: 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).



The structure of I was confirmed by its n.m.r. spectrum¹ and by dehydrogenation to II on treatment with quinone at 25° in CCl₄² (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 ₂ K 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 phenide⁶ with a chlorosilane^{7,8} and are consistent with this reaction scheme

(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).

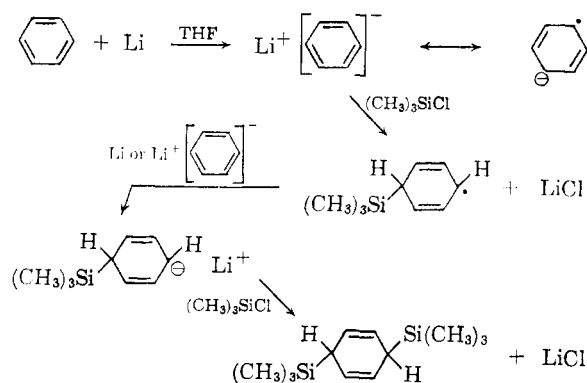
(3) T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954).

(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.



This reaction represents the first example of the use of benzene-alkali metal addition products in aprotic organic solvents⁹ as well as a unique synthesis for 1,4-disilylcyclohexadienes and 1,4-disilylbenzenes.

Toluene and anisole give 30 to 50% yields of 1-methyl- and 1-methoxy-3,6-bis-(trimethylsilyl)-1,4-cyclohexadiene, respectively, under the above conditions. Work is in progress on the scope of this new synthetic procedure and the stereochemistry of the disilylcyclohexadienes.

(8) The use of chlorosilanes to trap short-lived anion-radicals has been demonstrated by the synthesis of disilylalkanes and disilylalkenes from aryl olefins or 1,3-dienes, alkali metals and chlorosilanes: D. R. Weyenberg, L. H. Toporcer and M. J. Napoli, Abstracts of the 140th ACS Meeting, Chicago, Ill., September, 1961, p. 31-Q.

(9) The reduction of benzene by alkali metals in ammonia or low molecular weight amines involves the solvolysis of alkali metal-benzene addition products: A. J. Birch, *Quart. Revs.* (London), **4**, 69 (1950).

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RECEIVED JUNE 6, 1962

UNSATURATED MACROCYCLIC COMPOUNDS.

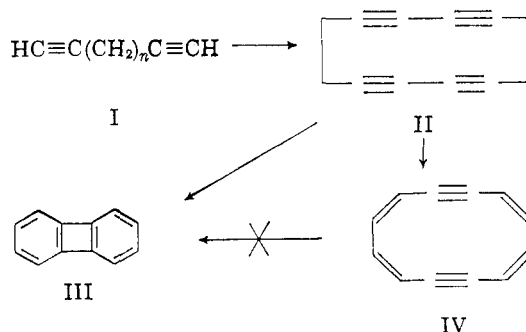
XXVI.¹ SYNTHESIS OF BISDEHYDRO- [12]ANNULENE (CYCLODODECATETRAENE- DIYNE) AND BIPHENYLENE FROM 1,5-HEXADIYNE

Sir:

We have shown previously that the oxidation of 1,6-heptadiyne (I, $n = 3$), 1,7-octadiyne (I, $n = 4$) and 1,8-nonadiyne (I, $n = 5$) with oxygen in the presence of cuprous chloride and ammonium chloride in aqueous ethanol gave rise to the corresponding cyclic "dimers" in addition to linear substances.² In contrast, the oxidation of 1,5-hexadiyne (I, $n = 2$) under these conditions did not furnish the cyclic dimer II, but gave a brown polymer which might have arisen from this highly strained compound.^{2b}

It has now been found that when the reaction with 1,5-hexadiyne (I, $n = 2$) is carried out as before,^{2b} but in the presence additionally of benzene (to keep the products in solution),³ the cyclic dimer II is indeed formed. Chromatographic purification on alumina gave fractions containing II as well as linear dimeric material, since full

hydrogenation (platinum, ethyl acetate) yielded a mixture of cyclododecane and *n*-dodecane (gas-liquid chromatographic analysis).⁴ It was not possible to isolate II, in view of its extreme instability; e.g., the substance was converted to an insoluble brown-black polymer as soon as its solution was taken to dryness at 0° under nitrogen, and it even decomposed gradually in solution. The estimated yield of II was 5–6%.



Isomerization of the chromatography fractions containing II in pentane-ether with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol for 20 minutes at room temperature, then chromatography on alumina, led to two cyclic compounds. The first (ca. 25% yield; straw-colored crystals, m.p. 111–112°) proved to be biphenylene (III), as evidenced by the identity (infrared and ultraviolet spectra, mixture m.p.) with an authentic sample kindly provided by Dr. J. F. W. McOmie. This represents the first synthesis of biphenylene from non-benzenoid precursors.

The second cyclic isomerization product (ca. 2% yield) was bisdehydro[12]annulene (cyclo-dodecatetraene-diyne; e.g., IV). It formed brown needles (pink-violet in solution), m.p. 54–55°; $C_{12}H_8$ (found C, 93.74; H, 5.56); $\lambda_{\text{max}}^{\text{isooctane}}$ 244, 249 and 468 μ (ϵ 51,400, 54,800 and 170, respectively; with absorption above 600 μ); acetylene band at 4.60 μ in the infrared (KBr); homogeneous by thin-layer chromatographic analysis. Full hydrogenation (platinum, ethyl acetate) yielded cyclododecane as sole product (gas-liquid chromatographic analysis).⁴

The rearrangement of II to bisdehydro[12]annulene is analogous to our previously described rearrangements of higher cyclic polymers of 1,5-hexadiyne to dehydro-annulenes.⁵ For symmetry reasons, we believe the bisdehydro[12]annulene most likely to possess the structure IV, containing the acetylene bonds in a 1,7-relationship, as in the other dehydro-annulenes.⁴

Treatment of IV with potassium *t*-butoxide under the conditions of its formation gave no detectable amount of III, and IV is therefore not an intermediate in the transformation of II to III.

Bisdehydro[12]annulene is theoretically non-aromatic, since it does not comply with Hückel's rule. The substance proved to be quite unstable;

(1) Part XXV, F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, in press.

(2) (a) F. Sondheimer and Y. Amiel, *ibid.*, **79**, 5817 (1957); (b) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 6263 (1957).

(3) Five hundred cc. of benzene were used for the oxidation of .5 g. of 1,5-hexadiyne.

(4) The saturated hydrocarbons were identified with authentic samples by the identical retention times. Samples of cyclododecane were kindly donated by Prof. V. Prelog and by Dr. A. J. Hubert.

(5) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **84**, 280 (1962).