

left **7b** unchanged. However, irradiation of a solution of **7b** in hexafluoroacetone hydrate using a medium-pressure Hanovia lamp led, on concentration of the solution, to the separation of **4** in 30% yield as white crystals: mp 320 °C dec; NMR τ 7.65 (s, 8 H), 6.44 and 7.07 (d, 16 H, $J = 11$ Hz); m/e 312, 284, 156.

Cyclophane **4** is of interest both as a first example of a cyclophane having a fused cyclobuteno moiety and as an example of a completely substituted [2.2]paracyclophane.¹⁶ Longone and Simanyi have previously synthesized 4,5,7,8,12,13,15,16-octamethyl[2.2]paracyclophane and reported that the molecule was not very stable, significant losses occurring owing to polymerization during isolation and even on storage at 0 °C in the solid state.¹⁷ Cyclophane **6** is appreciably more stable and can be sublimed unchanged at 190 °C and 10^{-5} mm. The pyrolysis of **4** is discussed in the accompanying communication.¹⁸

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

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- Supplied by Aldrich Chemical Co.
- Prepared by chloromethylation of 2,6-dibromo-*p*-xylene using chloromethyl methyl ether in 30% fuming sulfuric acid. Obtained, after recrystallization from carbon tetrachloride, in 62% yield as colorless crystals: mp 183–185 °C; ¹H NMR (CDCl₃), a singlet at τ 5.12 (4 H, -CH₂Cl) and a singlet at 7.30 (6 H, -CH₃). The structure of this, as well as all other new compounds reported in this communication, is supported by satisfactory elemental analyses and/or high resolution mass spectra. Unless otherwise specified, NMR spectra were taken using deuteriochloroform as solvent.
- Benzo[1,2:4,5]dicyclobutene (**3a**) was first prepared by M. P. Cava, A. A. Deana, and K. Muth (*J. Am. Chem. Soc.*, **82**, 2524 (1960)), who report its melting point at 101 °C.
- The parent molecular ions of **3a**, **3b**, and **3c** each show an envelope of peaks corresponding to loss of one, two, and three hydrogens. The peaks for **3c** at 288 and 244 show the typical isotope pattern for the presence of two bromine atoms.
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- During the course of this investigation Blickle and Hopf have been able to prepare a [2.2]paracyclophane having two fused cyclobuteno rings (private communication from Professor Henning Hopf).
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- See L. G. Harruff, M. Brown, and V. Boekelheide, *J. Am. Chem. Soc.* following paper in this issue.

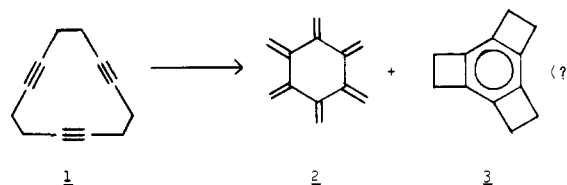
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Hexaradialene: Precursors and Structure

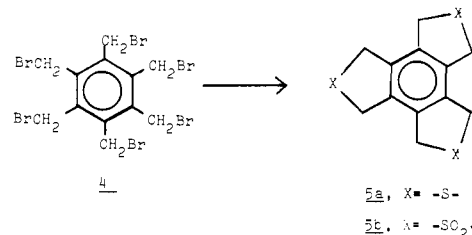
Sir:

Barkovich, Strauss, and Vollhardt have discussed the theoretical interest in hexaradialene and have assigned the hexaradialene structure **2** to the C₁₂H₁₂ hydrocarbon obtained on pyrolysis of 1,5,9-cyclododecatriyne **1**.¹ Whether or not benzo[1,2:3,4:5,6]tricyclobutene **3** should be proposed as an intermediate in the conversion of **1** to **2** is not clear, although in an earlier communication,² in which the same authors described the synthesis of **1**, it was stated that the thermal reorganization of **1** most likely proceeds via intermediate **3**.

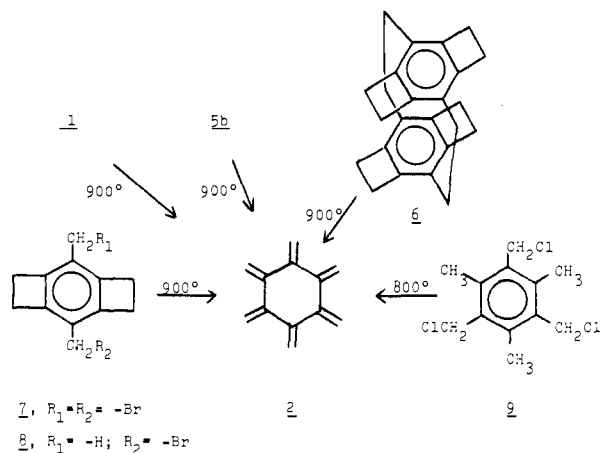


In a study of the thermal behavior of [2.2](3,6)benzo[1,2:4,5]dicyclobutene (**6**),³ in which we had hoped to observe the formation of [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane, we obtained instead a C₁₂H₁₂ hydrocarbon having identical spectral properties with that obtained by the Berkeley group from the pyrolysis of **1**. In particular, the mass spectral fragmentation pattern of this hydrocarbon is very characteristic, showing only a low intensity parent molecular ion at m/e 156 in an envelope of signals varying by one mass unit each from 157 to 151 and with additional peak envelopes at 141 and 128.⁴ Although the chemical properties observed for the C₁₂H₁₂ hydrocarbon fit the hexaradialene structure **2**,¹ this behavior could likewise be rationalized in terms of structure **3**, and the mass spectral fragmentation pattern seems easier to interpret for structure **3** than for **2**. The single piece of evidence strongly favoring **2** over **3** was the proton spectrum which has a singlet at τ 4.69 (toluene-*d*₈). This chemical shift corresponds closely to the value (τ 4.7) reported for the vinyl protons of hexamethylhexaradialene,⁵ and, although such a chemical shift would not be impossible for **3**, it would be quite unusual.

In an attempt to obtain an authentic sample of **3** for comparison, we have prepared the trissulfone **5b** and examined its pyrolysis. Treatment of hexa(bromomethyl)benzene⁶ (**4**) with sodium sulfide using a phase transfer technique readily gave the trissulfide **5a** in 40% yield, after recrystallization from chloroform, as colorless crystals: mp 241–246 °C dec; NMR (CDCl₃), a singlet at τ 5.82; mass spectrum m/e 252.⁷ Oxidation of the trissulfide **5a** with *m*-chloroperbenzoic acid in chloroform gave the trissulfone **5b** as colorless crystals: mp >350 °C dec; NMR ((CF₃)₂C(OD)₂), a singlet at τ 5.56.



Pyrolysis of **5b** at 900 °C, using the technique described previously,^{1,8} gave the same C₁₂H₁₂ hydrocarbon as had been obtained from pyrolyses of **1** and of **6**. The mass spectral fragmentation pattern was reproduced in complete detail. With this result, we began examining other compounds on hand that might yield a C₁₂H₁₂ hydrocarbon on pyrolysis. Quickly, we found that the benzo[1,2:4,5]dicyclobutene derivatives **7** and **8**⁷ both gave the same hydrocarbon and the same mass spectral fragmentation pattern. Ironically, the compound which gives



the desired pyrolysis most cleanly, at the lowest temperature, and in the best yield is the commercially available 2,4,6-tris(chloromethyl)mesitylene (**9**).⁹ The ¹H NMR spectra of the C₁₂H₁₂ hydrocarbon from each of these precursors were identical, showing only a singlet at τ 4.69.

When a sample of the C₁₂H₁₂ hydrocarbon from the pyrolysis of 2,4,6-tris(chloromethyl)mesitylene was washed from the cold finger with tetrahydrofuran on to a palladium/charcoal catalyst and hydrogen was introduced, the only product observed on workup was hexamethylbenzene, formed in 60% yield.¹⁰

That the C₁₂H₁₂ hydrocarbon is in fact hexaradialene (**2**) was then established by measuring its ¹³C NMR spectra.¹¹ Its proton decoupled spectrum shows two singlets: one at -145.0 ppm (ring carbon) and the other at -110.0 ppm (methylene carbon). Its undecoupled (gated) spectrum shows the methylene carbon as a triplet with a coupling constant ($J_{C,H}$) of 159 Hz. These values correspond quite closely with those (-106.9 ppm ($J_{C,H} = 153.5$ Hz) and -149.2 ppm) found for methylenecyclohexane.¹² Thus, the ¹³C NMR spectra of hexaradialene are surprisingly normal and provide no support whatsoever for a diamagnetic ring current in the six-membered ring.

The availability of hexaradialene in high yield in a single step from commercially available 2,4,6-tris(chloromethyl)mesitylene makes it attractive as a potential synthetic intermediate. We are exploring some of the obvious possibilities.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

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- (8) For all of the pyrolyses described in this communication, the products leaving the hot zone of the quartz pyrolysis tube were collected at -78 °C. The cold condensate was then subsequently allowed to warm to a temperature providing an appropriate rate of introduction into the mass spectrometer (Hewlett-Packard Model 5930A). This permitted a separation of the C₁₂H₁₂ hydrocarbon from the other pyrolysis products such as sulfur dioxide, hydrogen bromide, bromine, and hydrogen chloride.
- (9) Aldrich Chemical Co., Milwaukee, Wis.

- (10) Apparently, the only loss in the generation of the C₁₂H₁₂ hydrocarbon from **9** is due to some polymerization of the substance in the neat state on the cold finger. The identity of the hexamethylbenzene was shown by a mixture melting point determination as well as spectral comparison with an authentic sample.
- (11) Samples of hexaradialene (**2**) collected in carefully dried and degassed tetrahydrofuran are stable at -90 °C and no changes in spectra are observed for times as long as 48 h. The ¹³C NMR spectra were taken in perdeuteriotetrahydrofuran and the chemical shift values are relative to Me₄Si.
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Carbon Alkylation of Aliphatic *N*-Sulfinylamines

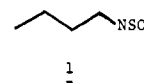
Sir:

In recent years there has been a tremendous amount of activity directed toward the inversion of normal reactivity of organic functional groups.¹ Although reversal of carbonyl reactivity has been investigated most thoroughly,^{5,6} the conversion of amino carbons to nucleophiles has received considerable attention.⁷⁻⁹ In the area of primary amine activation, Schöllkopf's work with isocyanides appears to be the broadest solution to the problem. We have recently discovered another method for activation of primary amines which allows reversible inversion of their reactivity.

Aliphatic *N*-sulfinylamines have been known for many years;¹⁰ however, their synthesis and chemistry have received little attention. Although their known chemistry is dominated by nucleophilic attack at sulfur,¹¹ the potentially strong electron-withdrawing properties of the *N*-sulfinylamine group suggested to us that strong base treatment of such compounds might provide access to stabilized carbanions. We now wish to report the facile generation of such ions and their applications to carbon-carbon bond formation.

The synthesis of aliphatic *N*-sulfinylamines is readily accomplished by treatment of the appropriate primary amine with thionyl chloride.^{10,11} When preservation of the amine is required, the reaction is best carried out in the presence of excess tertiary amine to absorb the liberated hydrogen chloride. Although moderate to good yields of products have been reported using pyridine,¹² we have found that quinoline is far superior. Yields of pure distilled¹³ aliphatic *N*-sulfinylamines are routinely 70% or better using this base at -20 °C.

The known propensity of *N*-sulfinylamines to undergo attack at sulfur by a variety of nucleophiles¹¹ dictated initially the use of bulky, nonnucleophilic bases for carbanion formation. Lithium triphenylmethide generated in tetrahydrofuran from triphenylmethane and *n*-butyllithium serves well. Slow addition of 1 equiv of *N*-sulfinyl-*n*-butylamine (**1**) to such a solution at -78 °C results in immediate conversion of the intense blood red color of the triphenylmethide solution to a light yellow.



Addition of methyl iodide or other simple alkylating agents to a solution containing **2**, at a variety of temperatures, provides

