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[1:2,9:10]Bismethano[2.2]paracyclophane

Sir:

Strained hydrocarbons of the cyclophane class have been studied both theoretically and experimentally as a function of the length of the polymethylene chains which connect the π systems.[1] Changes in the electronic and magnetic resonance spectra, as well as in the chemical and thermal behavior of these compounds, have been observed with increasing deformation of the aromatic rings and bond angles, and as a function of the proximity of transannularly located benzene rings.[2] In recent years the possibility of a hyperconjugative effect between the C-C σ bond of the bridge and the aromatic π system has been proposed as an explanation for the anomalous electronic behavior of [2.2]paracyclophane.[3] Further enhancement of the changes might be expected if the benzene rings were bridged not by ethylene, but by cyclopropane rings. Previous attempts to prepare such a system by cyclopropanation of [2.2]paracyclophane-1,4-diene with diazomethane were unsuccessful.[4] This reaction leads to preferential attack on the aromatic double bonds and yields products similar to those observed from the reaction of diazomethane with other [2.2]paracyclophane derivatives.[4,5]

In the preparation of [2.2.2](1,2,4)cyclophane, it was demonstrated that carbon-carbon bond formation via transannular reductive dehalogenation was an effective and efficient means of introducing additional bridges (and additional ring strain) into cycles which already contained benzene rings in a face-to-face configuration.[6] A simple extension of this procedure was used in an attempt to synthesize [1:2,9:10]bismethano[2.2]paracyclophane (1) through a double ring contraction of [3.3]paracyclophane.

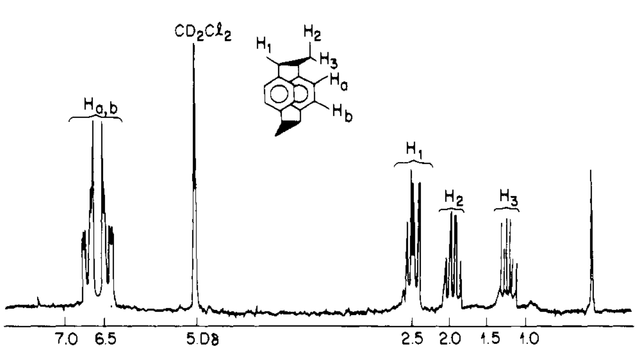
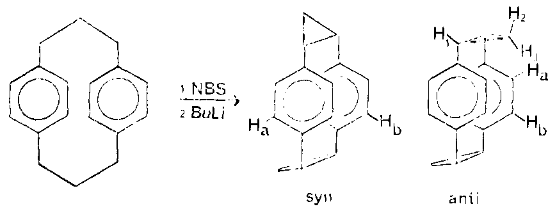


Figure 1.



II

I

The starting material was prepared by the method of Longone, Küsefoglu, and Gladysz.[7] Treatment of [3.3]paracyclophane (0.4 g) with 5 equiv (1.5 g) of recrystallized *N*-bromosuccinimide in refluxing carbon tetrachloride with a trace of benzoyl peroxide yielded 0.9 g (95%) of a material with approximate composition $C_9H_9Br_2$, mp >300 °C.[8] No attempt was made to separate the numerous isomers, but an NMR spectrum of this (barely soluble) material in tetrahydrofuran-d_8 gave a multiplet at δ ~5 (Me$_4$Si), indicative of the presence of a secondary benzylic bromide. A dilute solution of the brominated material in tetrahydrofuran was treated with excess butyllithium, added dropwise over a period of 30 min at −70 °C under argon. After the usual workup in water-dichloromethane, the organic residue was subjected to thin layer chromatography (first on silica gel-chloroform, then several times on alumina-hexane) which resulted in the isolation of ~5% (based on [3.3]paracyclophane) of a crystalline, sparingly soluble colorless solid which sublimes readily and melts on rapid heating at 246-250 °C.

The composition of this material is $C_{18}H_{16}$ according to the mass spectrum (precise mass 232.1237, calcd 232.1223) which also indicated major fragments at m/e^+ 115, 117 (probably C_9H_9, a characteristic fragment of [3.3]paracyclophane[9]), and 128. The ultraviolet spectrum (ethanol, 2×10^{-5} M) indicates substantial perturbation of the π system: λ_{max} (ϵ) 230 (15 000), 260 (5000, sh), 304 (900).[10] The carbon magnetic resonance spectrum (22.62 MHz, CD$_2$Cl$_2$, Me$_4$Si) confirmed the presence of the cyclopropane rings (137.45 (quaternary carbon),[11] 134.10 (C$_B$), 128.11 (C$_A$), 23.90 (C$_1$), and 4.10 (C$_{23}$)) in the ratio 0.3:2:2:2:1, respectively. A proton magnetic resonance spectrum of the material (CD$_2$Cl$_2$, 90 MHz, Me$_4$Si) is shown in Figure 1. Aromatic protons H$_b$ and H$_a$ appear at δ 6.74 and 6.51 (J_{ab} = 8.0, $J_{ab'}$ = 1.8 Hz). Cyclopropane protons appear at δ 2.49 (H$_1$), 1.96 (H$_2$), and 1.20 (H$_3$) (J_{12} = 5.7, J_{13} = 7.9, J_{23} = 6.6 Hz). A computer simulation based on these data generated a spectrum essentially identical with the one shown in Figure 1. Aromatic coupling constants in the range of 7-9 Hz are characteristic of ortho splittings in previously isolated cyclophanes, while meta coupling constants are on the order of 1-2 Hz.[5] For the syn isomer of 1, protons H$_a$ and H$_b$ are meta (or para) to one another, and therefore a large aromatic coupling would not be expected. For the anti isomer of 1, however, H$_a$ and H$_b$ should give rise to an AB quartet further complicated by meta coupling as was observed in the proton spectrum of 1. On the basis of these data we have assigned to compound 1 the structure *anti*-[1:2,9:10]bismethano[2.2]paracyclophane.

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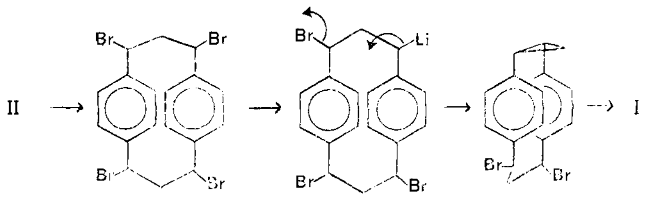
It has been assumed that the mechanism of this reaction is a metal-halogen exchange followed by nucleophilic displacement of the transannular benzylic bromide:



III IV

An examination of molecular models (Dreiding) reveals that, once the first cyclopropane ring is formed, steric interference exists between H_a and H_3. This interaction is lessened somewhat if the remaining trimethylene chain adopts a conformation anti to the cyclopropane ring. However, the 1,3,10,12-tetrabromo[3.3]paracyclophane (III) which is presumed to be the precursor of *anti*-I has five possible isomers (not including racemates) and may contain tri- or pentabrominated compounds as well.[8] The low yield of the cyclization step may well be an indication that the reaction is dependent on the relative stereochemistry of the benzylic bromides, and that not all of the tetrabromides will undergo cyclization under these reaction conditions. The intermediate lithio derivative (IV) can also decompose via 1,6-elimination to form a *p*-xylylene derivative, and, indeed, a large amount of polymeric material is formed during the cyclization step which does not yield to chromatographic separation or sublimation conditions. Clearly further experimental evidence is necessary to clarify these mechanistic points.

The shift of the aromatic protons from δ 6.45 for [2.2]paracyclophane to 6.51 and 6.74 for H_a and H_b, respectively, in *anti*-I, may be the result of the proximity of H_3 and/or the cyclopropane rings, or it may be the result of additional deformation of the aromatic rings. Conclusions on this point must be delayed until an X-ray crystallographic examination is completed.

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