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THE SYNTHESIS OF HEXACYCLOPROPYLBENZENE *via* CYCLOTRIMERIZATION OF DICYCLOPROPYLACETYLENE BY $Fe_3(CO)_{12}$

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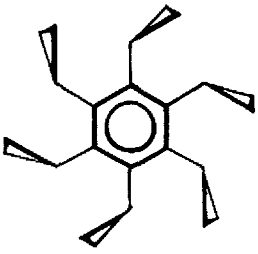
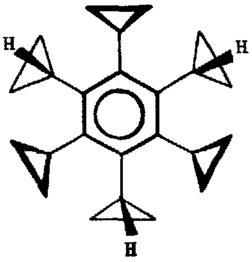
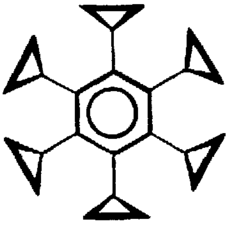
We report here a facile preparation of hexacyclopropylbenzene by exposure of dicyclopropylacetylene[1] to the action of $Fe_3(CO)_{12}$. Reactions were carried out by heating a neat 1:10 (w/w) mixture of $Fe_3(CO)_{12}$ and dicyclopropylacetylene at 180° for 2 hrs. in a sealed-tube.[2] Two main products, hexacyclopropylbenzene (1) and the tricarbonyliron complex of tetracyclopropylcyclopentadienone (2), were isolated by chromatography from the reaction mixture. In addition to 1 and 2 and to unreacted dicyclopropylacetylene minute quantities of two organometallic compounds were obtained which agree, by mass spectral and ir analyses, with $C_{16}H_{20}Fe(CO)_3$ and $C_{16}H_{20}Fe_2(CO)_6$ formulae.



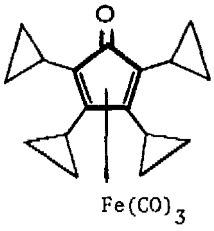
1a



1b



1c



2

Hexacyclopropylbenzene was obtained in ∿ 20% yield, based on original dicyclopropylacetylene, after recrystallization from hexane (colorless plates, m.p. 266-270°).[3]

The infrared spectrum[3] of hexacyclopropylbenzene is simple, and shows the characteristic bands of cyclopropyl at 3080 and 1030 cm^{-1}. The aromatic band in the 1500 cm^{-1} region is absent, similar to hexaisopropylbenzene and hexamethylbenzene.[4] The ultraviolet spectrum[3] resembles those of other hexaalkylbenzenes.[4,5,6] In the proton nmr spectrum[3] small downfield shifts are observed for all three hydrogen resonances relative to the respective ones for cyclopropylbenzene.[7] By contrast, the methine signal of hexaisopropylbenzene is shifted over 0.7 ppm downfield compared to the methine signal in cumene.[8] The H-decoupled ^{13}C nmr spectrum[3] shows only three peaks: a very weak signal for the aromatic carbons and one signal for each of the two types of cyclopropyl carbons. The low solubility of hexacyclopropylbenzene in appropriate organic solvents has so far precluded low temperature nmr studies.

An attempt to form a charge-transfer complex between hexacyclopropylbenzene and tetracyanoethylene proved to be unfruitful.

The yield of 2, based on original quantity of dicyclopropylacetylene, after recrystallization from pentane (yellow crystals, m.p. 89-91°) was ∿ 30%. The structural assignment was based on the mass spectrum (M^+, m/e 380 followed by successive loss of three CO groups and iron to yield the base peak, m/e 240), the ir spectra (hexane): 2050, 1990 and 1970 cm^{-1} (metal carbonyl) and (KBr): 3080, 3000, 1030 (cyclopropane) and 1640 cm^{-1} (ketonic carbonyl), the proton nmr spectrum, in which only resonances typical for cyclopropyl hydrogens are observed, and elemental analysis.

Examination of the Dreiding model of hexacyclopropylbenzene (1) shows that unlike hexaisopropylbenzene the rotation of the substituents in this molecule is almost unrestricted. In the case of hexacyclopropylbenzene conformation 1a which represents a stereochemical situation similar to that of hexaisopropylbenzene should be preferred on electronic grounds over the strain-free limiting conformations 1b and 1c. In this conformation (1a) all cyclopropyl units point in the same direction with the plane of each cyclopropane ring bisecting the benzene ring. This should provide maximum interaction between the cyclopropane banana-like ring-orbitals and the aromatic π-electron cloud.[9]

The data presented here, however, strongly suggest that conformation 1a is not favored in solution, and the observed properties are characteristic of an aromatic molecule with mobile, unobstructed substituents. Nevertheless, the high melting point and the low solubility of hexacyclopropylbenzene in organic solvents indicate a highly ordered structure in the crystalline state.

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3. Elemental and mass spectral analyses are in agreement with the $C_{24}H_{30}$ formulation. Characteristic spectral absorptions: cm^{-1} (KBr): ∿ 3080, 3000, 1450, 1415, 1320, 1245, 1090, 1050, 1030, 950, 900, 830; λmax (hexane) nm: 276 (ε 275), 225 (ε 1.36×10^4); ^1H δ (ppm; $CDCl_3$): 1.96 (m, CH), 1.05 (m, CH_2), 0.76 (m, CH_2) in the ratio 1:2:2, respectively; ^{13}C δ (ppm rel. to TMS; $CDCl_3$) : 143.25 (very weak signal), 15.80, 9.54.
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