Hexavinylbenzene

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Although the title compound is a material of potential interest for a number of theoretical and practical uses, it has not so far been described in the literature. In response to a number of inquiries about our recent preparation of it,[2] we wish to present details of its synthesis and properties here.

Hexavinylbenzene was prepared by dehydrobromination with alcoholic potassium hydroxide of what we presume to be hexa[α-bromoethyl]benzene. We made the hexabromo compound in nearly the same way as Hopff[3] has reported, but our material decomposed at about 230°, whereas Hopff reported a decomposition point of 180° after recrystallization. Our material gives an infrared spectrum identical with Hopff's, and the decomposition point is reproducible from batch to batch and does not depend upon the rate of heating during the melting point determination. We are unable to give a satisfactory explanation of the different decomposition points.

Dehydrohalogenation of our crude material in refluxing ethanol gave an 8% yield of white crystalline hexavinylbenzene of mp 77–78.5°. Its structure was confirmed by its spectral properties, analysis, and conversion to hexaethylbenzene upon catalytic hydrogenation.

Experimental Section

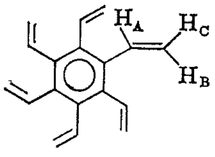
Preparation.—In a 100-ml round-bottom flask were placed 2.0 g (0.008 mole) of hexaethylbenzene (mp 126–127°) and 100 ml of carbon tetrachloride. To this solution was added 7.9 g (0.049 mole) of bromine. The flask was fitted with a reflux condenser and was stirred magnetically during illumination with a 60-w tungsten-filament lamp. In about 15 min the solution had heated to reflux and hydrogen bromide was evolved. After another 15 min of illumination, a white precipitate began to form. After a total illumination time of 2 hr, the solution was cooled to room temperature and the precipitate was separated by filtration. This material decomposed at 230°, whereas the reported decomposition point for hexa[α-bromoethyl]benzene is 180°.[3] It was too insoluble in carbon tetrachloride or carbon disulfide to give a meaningful nmr spectrum but was convertible to hexavinylbenzene. The yield was 5.7 g (95% based on hexaethylbenzene).

The bromination product from hexaethylbenzene (7.8 g or 0.01 mole, assuming the formula $C_{18}H_{24}Br_6$) was added to a solution of 20.0 g of potassium hydroxide (0.36 mole) in 70 ml of absolute ethanol in a 100-ml round-bottom flask. The solution was refluxed with magnetic stirring for 2.5 hr, then cooled and filtered to give 2.2 g of red-brown material as residue. It appeared to be crystalline and may have been mostly unreacted starting material.

The filtrate was poured into 200 ml of cold water and then extracted with three 75-ml portions of Skellysolve F. The combined extracts were washed with 50 ml of cold water. Removal of the solvent left a partially crystalline residue which on filtration gave 0.2 g of crude crystalline hexavinylbenzene (8% based on the amount of brominated compound added) which after recrystallization from methanol was still orange and had mp 76–78°. One sublimation at 75° and 100 μ pressure gave a white compound, mp 77–78.5°. The analytical sample was recrystallized once more from methanol and sublimed with no change in melting point.

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74; mol wt, 234. Found (Schwarzkopf): C, 92.07; H, 7.65; mol wt, 234 (mass spectrometer), 246 (ebullioscopic in benzene).

Spectra.—An nmr spectrum of hexavinylbenzene in carbon tetrachloride showed the characteristic multiplet for an ABC spectrum.[4] Twelve distinct lines were observed. The chemical shifts and the coupling constants are shown in Chart I.[6] These coupling constants are in good agreement with expected values.[7]



$\tau_A = 3.372 \pm 0.002$ ppm
$\tau_B = 4.771 \pm 0.002$ ppm
$\tau_C = 4.593 \pm 0.002$ ppm
$J_{AB} = +18.0 \pm 0.1$ cps
$J_{AC} = +11.5 \pm 0.1$ cps
$J_{BC} = +2.1 \pm 0.1$ cps

The infrared spectrum of hexavinylbenzene in carbon tetrachloride was relatively simple showing sharp bands at 3106, 3030, 1629, 987, and 918 cm^{-1} (strongest in the spectrum) all consistent with the vinyl group.[8]

The ultraviolet spectrum of hexavinylbenzene in *n*-hexane showed a maximum at 258 mμ (ϵ 4 × 10^4) and a smaller peak at 224 mμ (ϵ 2 × 10^4). There was no discernible structure before the maximum at 258 mμ.

The mass spectrum of this compound showed the parent peak at *m/e* 234 as the strongest peak in the spectrum, with other large peaks appearing *m/e* 219, 217, 215, 205, 204, 203, and 202.

Reactions of Hexavinylbenzene.—The following reactions were done as test-tube experiments with α-methylstyrene controls and stand in sharp contrast to results from hexaisopropenylbenzene.[2]

A solution of hexavinylbenzene in acetone decolorized 2% aqueous potassium permanganate instantly. Bromine in carbon tetrachloride gave the same result.

Addition of 2 drops of tetranitromethane to approximately 5 mg of hexavinylbenzene in 0.25 ml of carbon tetrachloride produced a deep yellow-orange color. Addition of several small crystals of tetracyanoethylene to the same concentration of hexavinylbenzene in carbon tetrachloride produced a faint violet color which became more intense on warming the solution and faded to about its original intensity on cooling. The same two compounds when added to hexavinylbenzene in acetone gave different results; tetranitromethane produced a yellow color of moderate intensity, whereas tetracyanoethylene produced a pale yellow-orange color. Neither compound gave significant coloration with acetone alone.

Crystals of hexavinylbenzene which lay exposed on the desk top turned yellow. This reaction did not take place in the dark.

Samples of hexavinylbenzene which had been sublimed and stored in the dark developed insoluble matter, probably polymer, after about a week.

Hydrogenation of Hexavinylbenzene.—Hydrogenation of 0.105 g of hexavinylbenzene in cyclohexane with 100 mg of Pd-Al catalyst gave a quantitative yield of hexaethylbenzene after recrystallization from ethanol. Authenticity was established by mixture melting point and infrared spectrum.

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(1) Supported by National Science Foundation Grant, GP-2014, for which we are most grateful.

(2) E. M. Arnett, J. M. Bollinger, and J. C. Sanda, *J. Am. Chem. Soc.*, **87**, 2050 (1965).

(3) H. Hopff and A. K. Wick, *Helv. Chim. Acta*, **44**, 19 (1961).

(4) The calculation of chemical shifts and coupling constants was performed on a 7090 computer (NSF G-11309) using the LAOCOON II program of Castellano and Bothner-By.[5] We thank Dr. S. Castellano of Mellon Institute for his assistance in performing these calculations.

(5) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(6) A trial calculation was made using a negative value of J_{BC} and the correlation of the experimental and calculated intensities was extremely poor.

(7) E. I. Snyder, *J. Phys. Chem.*, **67**, 2873 (1963).

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 3.