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NMR STUDIES OF RIGID BICYCLIC SYSTEMS. V.[1] REACTIONS OF HEXABROMOCYCLOPENTADIENE; NMR SPECTRA OF SOME BROMONORBORNANES AND ENDO-5-SUBSTITUTED 1,2,3,4,7,7-HEXABROMONORBORN-2-ENES.

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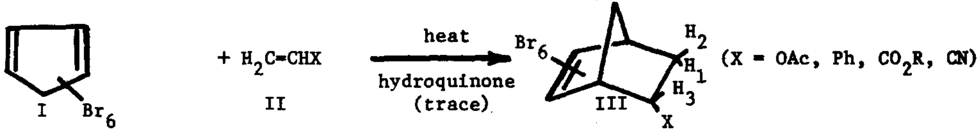
Recent reports regarding the chemistry of hexabromocyclopentadiene[2] prompt us to communicate the results of our current work with this compound. Hexabromocyclopentadiene (I) has been reported to enter reluctantly into Diels-Alder reactions with various dienophiles;[2] in this communication, we report on its reactions with monosubstituted ethylenes:



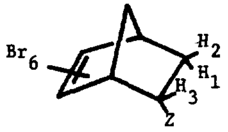
Compounds of the type III could be conveniently prepared by reacting diene I with an excess of the dienophile (II) in a glass bomb heated at 100-125°. Yields were generally poor, and accompanied by considerable tar formation. The lone exception to this statement was the reaction of I with methyl acrylate (15 hrs. at 120°), which afforded the adduct in essentially quantitative yield.

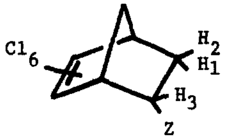
The ABC spectra of the adducts (III) were obtained at 60 MHz, and the spectral parameters (chemical shifts, coupling constants) were extracted using Bothner-By's[3] LAOCOON III computer program. The calculated spectra are shown in Table I, where the results are compared with those obtained for the corresponding endo-5-substituted hexachloronorborn-2-enes (IV).[4] In agreement with Williamson's observations[4] in his study of the nmr spectra of system IV, we also find that the ABC "internal chemical shifts"[4] and the coupling constants J_{12}, J_{13} and J_{23} of system III, all correlate linearly with the electronegativities[5] of the 5-endo substituents, X, in III.

Inspection of Table I reveals that the difference between the cumulative effects of the six bromines in system III vs. those of the six chlorine atoms in system IV is negligible with regard to the coupling constants. However, the chemical shifts in system III are uniformly greater than are the corresponding shifts in system IV; the cumulative inductive-field-anisotropy effects of the bromine atoms in III appear to be net deshielding relative to the chlorine atoms in IV.

TABLE 1

CALCULATED CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (J) FOR THE ABC NMR SPECTRA OF ENDO-5-SUBSTITUTED 1,2,3,4,7,7-HEXABROMONORBORN-2-ENES (III) AND ENDO-5-SUBSTITUTED 1,2,3,4,7,7-HEXACHLORONORBORN-2-ENES (IV).[a]





[b]

Z =	OAc	Ph	CO_2Me	CN	OAc	Ph	CO_2H	CN
$\delta(1)$	116.55	147.02	153.21	139.88	114.	143.	146.	129.
$\delta(2)$	185.05	179.24	163.78	179.38	177.	172.	163.	162.
$\delta(3)$	343.05	245.14	219.53	226.58	330.	232.	217.	204.
J_{12}	-13.31	-12.95	-12.43	-12.54	-13.3	-12.7	-12.6	-12.6
J_{13}	2.45	4.19	4.03	4.09	2.5	4.2	4.4	4.6
J_{23}	7.56	9.06	8.78	9.10	7.6	8.9	8.5	9.3

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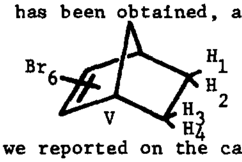
[a] Calculated from spectra measured at 60 MHz. Spectra were measured on 10% w/w solutions of III and IV in CS_2.

[b] Values reported by K. L. Williamson, reference 4.

Additionally, we have successfully reacted I with ethylene; however, this reaction proceeds in good yield only at 3000 atm. and 125-150°.[6] The 60 MHz nmr spectrum of the adduct, 1,2,3,4,7,7-hexabromonorborn-2-ene (V) has been obtained, and the spectral parameters have been calculated:[3]

$$\text{I} + H_2C{=}CH_2 \xrightarrow[\text{3000 atm.}]{\text{125-150°}}$$



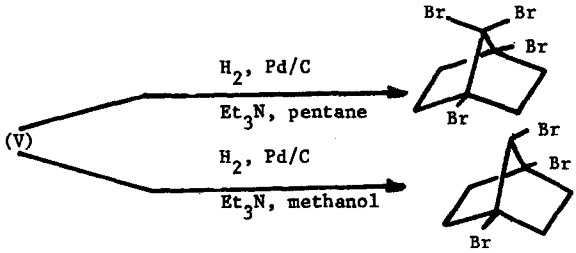
V

$\delta(1) = \delta(3) = 156.53$ $J_{12} = J_{34} = -12.3$

$\delta(2) = \delta(4) = 120.89$ $J_{14} = J_{23} = 3.7$

$J_{13} = 9.6$; $J_{24} = 8.9$

In a previous paper, we reported on the catalytic hydrogenation-hydrogenolysis of 1,2,3,4,7,7-tetrachloronorbornene.[7] To extend this study, the corresponding reaction of V has been investigated. Interestingly, the reaction of V with H_2-Pd/C (Parr hydrogenation apparatus: 40 lb/in^2 H_2, room temperature) has been found to be strongly solvent dependent. The reaction in pentane affords 1,4,7,7-tetrabromonorbornane (VI), but in methanol, further reduction of VI occurs with the formation of 1,4,7-tribromonorbornane (VII):



(VI)

(VII)

To extend previous studies of aromatic solvent effects on the nmr spectrum of 1,4,7,7-tetrachloronorbornane (VIII)[1,7], we have examined the nmr spectrum of the corresponding tetrabromonorbornane (VI) in the solvents benzene, pyridine, and chloroform, (Figure 1). Two observations are apparent upon examination of Figure 1: first, that the spectra of VIII are more compressed than are the corresponding spectra of VI, and second, we see again that the cumulative effect of the bromines on the proton nmr spectrum of VI is net deshielding relative to that of the chlorines on the spectrum of VIII.[8] It appears that system VI is less demanding of solvation than is VIII, (and, hence, the smaller degree of variation in the appearance of the spectrum of VI in the three solvents studied).

The decreased demand for solvation by the bulkier solute VI (relative to VIII) is consistent with predictions based upon Engler and Laszlo's "general solvation" approach[9] which has been successfully utilized recently to account for observed solvent effects upon the nmr spectrum of VIII.[1] More extensive studies of solvent effects on the nmr spectrum of VI are in progress. Additionally, work at present is aimed toward preparing specifically-deuterated bromonorbornanes and analyzing completely their nmr spectra. We hope to communicate the results of these efforts shortly.

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1. (a) Presented in part at the 27th Southwest Regional Meeting of the American Chemical Society, San Antonio, Texas, December 1-3, 1971. (b) Part IV: A. P. Marchand, W. R. Weimar, Jr., A. L. Segre, and A. M. Ihrig, J. Magnetic Resonance, 6, 316 (1972).
2. See R. G. Pews, C. W. Roberts, and C. R. Hand, Tetrahedron, 26, 1711 (1970), and references cited therein.
3. S. Castellano and A. A. Bothner-By, J. Chem. Phys., 41, 3863 (1964).
4. K. L. Williamson, J. Amer. Chem. Soc., 85, 516 (1963).
5. J. R. Cavanaugh and B. P. Dailey, J. Chem. Phys., 34, 1099 (1961).
6. We thank Dr. James C. Kauer, Central Research Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware, for kindly performing the high pressure reaction of I with ethylene.
7. A. P. Marchand and W. R. Weimar, Jr., J. Org. Chem., 34, 1109 (1969).
8. As might be expected, the deshielding effect of bromine (relative to chlorine) is slightly greater for the exo ring protons (lowfield half of the spectrum) than for the endo protons (upfield half); see A. P. Marchand, N. W. Marchand, and A. L. Segre, Tetrahedron Letters, 5207 (1969).
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10. Physical data for new compounds reported herein: III (X = OAc), m.p. 112.5-113.5° (corr.); III (X = Ph), m.p. 116.5-117.2° (corr.); III (X = CO_2Me), m.p. 108.0-108.5° (corr.); III (X = CN) m.p. 239-242° (uncorr.); V, m.p. 74.5-75.2° (uncorr.); VI, m.p. 270.5-271° (corr.); VII, m.p. 77.7-78.3° (corr.). All new compounds gave satisfactory microanalyses and/or mass spectra.

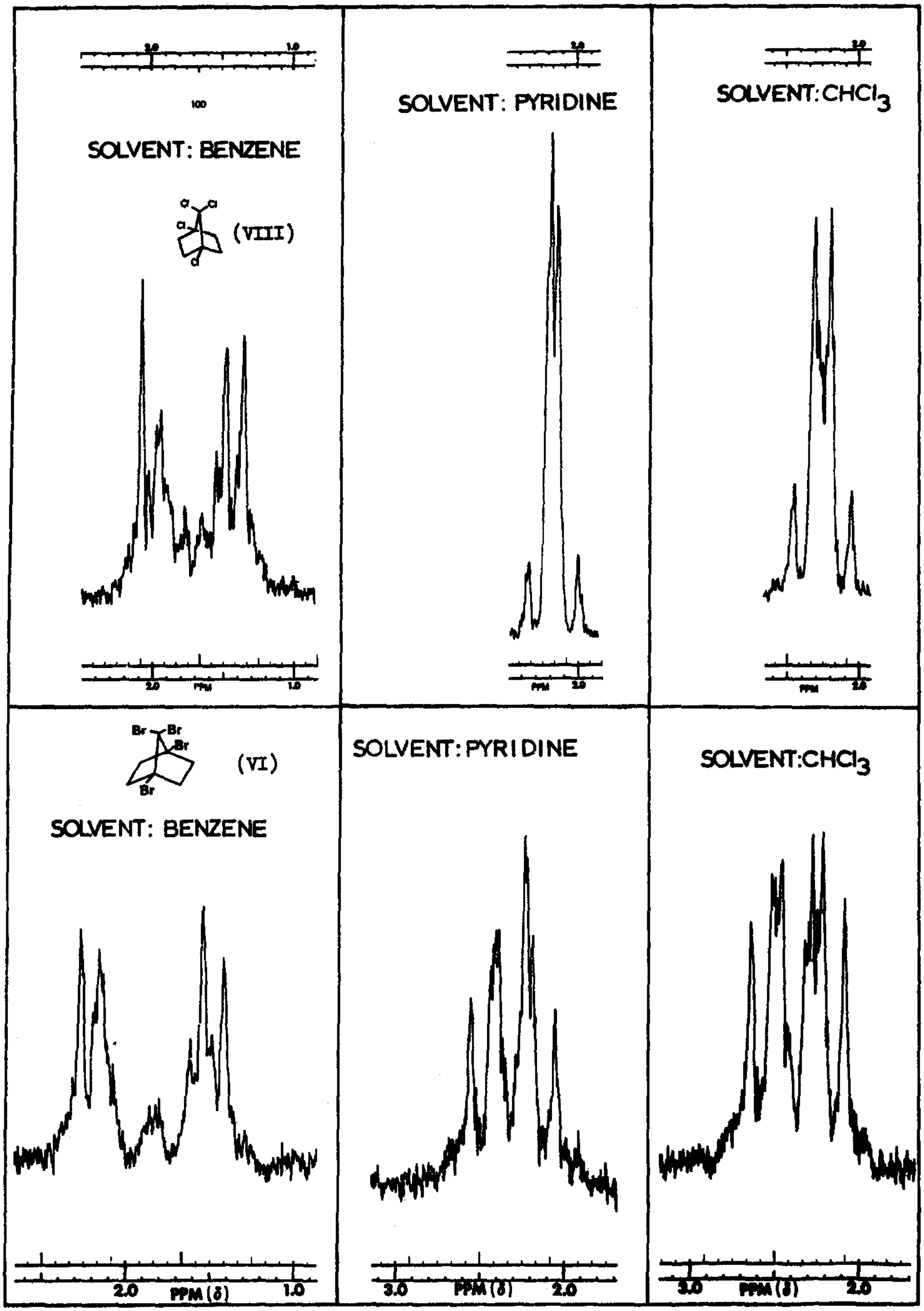

Figure 1. 60 MHz NMR Spectra of 1,4,7,7-Tetrabromonorbornane (VI, Bottom) and 1,4,7,7-Tetrachloronorbornane (VIII, Top) in Benzene, Pyridine, and Chloroform Solutions.