

1-Methyl-1-boracyclohepta-2,4,6-triene, the First C-Unsubstituted Borepin¹⁾Yasuhiro NAKADAIRA,[†] Ryuji SATO, and Hideki SAKURAI

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The first C-unsubstituted boracycloheptatriene, 1-methylborepin, is prepared and characterized spectroscopically. Some extent of conjugation through boron atom is suggested.

A borepin is a 6π -electron system and isoelectronic with the tropylium cation, and from consideration of the covalent radius and electronegativity of boron a borepin is expected to form a cyclic conjugated "aromatic" system. However, the borepins prepared so far have been limited to benzo- or highly substituted derivatives in which the intrinsic electronic character becomes obscure.^{2,3)} We now report herein the first C-unsubstituted borepin prepared by the metal-metal exchange reaction from the corresponding stannepin. Very recently, Ashe and Drone have reported the preparation of 1-methyl-4,5-cyclopentenoborepin.⁴⁾

To a solution of 1,1-di-n-butylstannepin (**1**)⁵⁾ in chloroform-d was added a slightly excess amount of dibromomethylborane at $-20\text{ }^{\circ}\text{C}$ under argon. The exchange reaction took place quite readily and rather vigorously by the addition of the haloborane.

The reaction mixture was distilled directly into an NMR tube, which was sealed under vacuum. Its ^1H NMR spectrum shows a little broad singlet assignable to that of the BMe at δ 0.99 and three kinds of olefinic proton signals, one multiplets and two broad doublets centered at δ 7.19, 7.69, and 7.76, respectively, as shown in Fig. 1. The relative intensity of the BMe signal to those of olefinic proton signals is 1:2. In addition to these NMR signals, the presence of the molecular ion peak at m/z 104 on GC-MS spectrum shows that 1-methylborepin **2** is formed under these conditions.⁶⁾

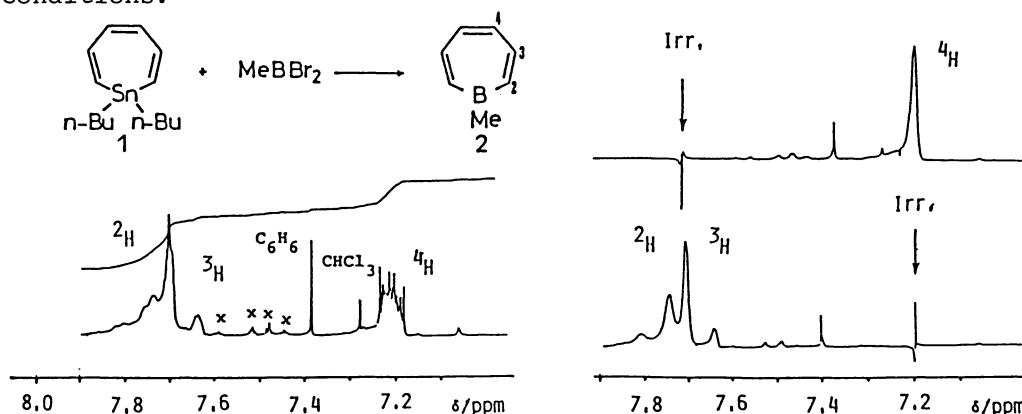


Fig. 1. Non-decoupled and decoupled ^1H NMR spectra (olefinic protons) of **2**

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In ^1H NMR, irradiation of the signal at δ 7.19 demonstrates that the signals at δ 7.69 and 7.76, assignable to boron-substituted cis-olefin protons, should be coupled each other with $J = 13.5$ Hz. On the other hand, 4,5-dihydro-methylborepin (3), a reference compound, shows a singlet due to the BME at δ 1.03, a doublet ($J = 13$ Hz) due to H-2 and 7 at δ 6.39, and a broad doublet due to H-3 and 6 at δ 7.02 in the ^1H NMR spectrum.^{7a)} On the basis of these data, two NMR signals of 2 are assigned reasonably to those of H-2 and 7 and H-3 and 6, respectively. The ^{13}C NMR signals of the ring carbons of 2 are observed at δ 134.7 (d, C-4, 5), 146.3 (d, C-3, 6), and 150.5 (m, C-2, 7).

A large down field shift of the olefinic proton signals of 2, especially of H-2 and 7, relative to the corresponding signals of 3 and 1-methyl-1-boracyclohexa-2,5-diene (4)⁸⁾ is explained reasonably by the decrease of electron densities at the olefinic protons due to the overlap between the boron vacant p orbital and the π system, and/or by a diamagnetic ring current induced by the cyclic conjugation through the boron atom. Indeed, the magnitude of down field shift, observed in these cyclic boranes, is far larger than those for cyclic germane and stannane systems; 1,1-dimethylgermepin (5)⁵⁾ ($\delta_{\text{H-2}}$ 5.83, $\delta_{\text{H-3}}$ 6.82), stannepin (1) ($\delta_{\text{H-2}}$ 6.08, $\delta_{\text{H-3}}$ 7.07), 1,1-dimethylgermacyclohexadiene (6) ($\delta_{\text{H-2}}$ 6.02, $\delta_{\text{H-3}}$ 6.55), and 4,5-dihydro-1,1-di-n-butylstannepin (7)^{7b)} ($\delta_{\text{H-2}}$ 5.94, $\delta_{\text{H-3}}$ 6.70).

1-Methylborepin (2) was heated at 160 °C for 1.5 h in degassed carbon tetrachloride without decomposition in contrast to group 4B heteropins which are thermochemically decomposed to give benzene.¹⁾ These results may be connected with predictions made by ab initio molecular orbital calculations that show the optimized geometry of borepin planar. However, 2 in degassed chloroform-d decomposed gradually to benzene even at -20 °C presumably due to a trace amount of acid.

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