The Reaction of Alkyl Isocyanides with Decaborane-14

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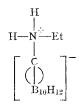
THERE have been several recent reports concerning the novel reactions of alkyl and aryl isocyanides with diborane-6¹ and trialkylboranes.²⁻⁵ We have found that ethyl isocyanide reacts with one equivalent of decaborane-14 in benzene at room temperature to produce an initial deep purple solution which fades within one hour leaving a white precipitate(I). Only a very small amount of hydrogen gas is evolved during the reaction. The crude product can be purified by recrystallization from hot water or sublimation at 190° (10^{-5} mm.), m.p. 234-235°. The molecular formula is substantiated by a cut-off in the mass spectrum at m/e179 which corresponds to the ${}^{12}C_{3}{}^{1}H_{19}{}^{11}B_{10}{}^{14}N^{+}$ ion.

The infrared spectrum of (I) (hexachlorobutadiene and nujol mulls) exhibits v_{max} 3228, 3203, 3180, 3125, and 1575 cm.⁻¹ Deuterium exchange of (I) in D₂O causes a shift of the infrared peaks given above to ν_{max} 2415, 2405, 2360, 2320, and 1080 cm⁻¹. These frequencies are similar to those assigned to N-H stretching and deformation modes in a large number of secondary amine salts studied by Heacock and Marion.⁶

The p.m.r. of (I) (in perdeuteroacetone) exhibits signals at $\tau 2.49$ (broad singlet, 2H); 6.59 (quartet, J = 7.5 c./sec., 2H) and 8.66 (triplet, J = 7 c./sec., 3H).

When (I) is treated with excess of sodium hydride two equivalents of hydrogen are evolved based on the quantity of (I) used. Subsequent treatment with dimethyl sulphate produces a dimethyl derivative of (I). The p.m.r. of the dimethyl derivative indicates that the two methyl groups are equivalent and have a chemical shift (τ 6.83) expected for methyls attached to a quaternary nitrogen.

This information prompts us to make the tentative suggestion that (I) has the gross structure shown in the accompanying figure.



Thus (I) would be a derivative of the unknown $B_{10}CH_{13}$ ion which is isoelectronic with the known $B_9C_2H_{13}$ and $B_{11}H_{13}^{2-}$ molecules.^{7,8} If this structure proves correct, this represents the second example of a one-carbon carborane-like molecule.⁹

The n-propyl and t-butyl analogues of (I) have also been prepared and their properties serve to confirm the findings described above.

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