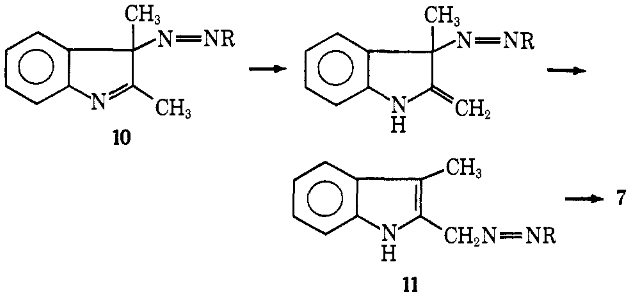

shift with alkali, confirming speculation in the literature that such shifts observed with 3-azo products from indole[16] or 2-methylindole[14] arise from removal of the indole N–H proton.

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A New Boron Hydride, Pentadecaborane(23)

Sir:

A new crystalline boron hydride has been prepared in high yield by reaction of i-B_9H_{15} with B_6H_{10}. The air sensitive compound has moderate thermal stability.

In a typical reaction KB_9H_{14} (2.06 mmol) was treated with excess HCl at −78° for 30 min. The unreacted HCl was then distilled from the reactor by pumping for 3 hr at −78° yielding a mixture of solid i-B_9H_{15} and KCl as described elsewhere.[1] Hexaborane(10) (10.20 mmol) was condensed into the reactor and melted onto the frozen i-B_9H_{15} mixture, being certain to cover each portion of the solid with liquid B_6H_{10}. The mixture was warmed to 0° for 20 min. Hydrogen (2.00 mmol) and B_6H_{10} (8.12 mmol) were removed at −196 and 0°, respectively. The solid remaining in the reactor was extracted with CH_2Cl_2 and separated from KCl by filtration. Evaporation of the clear colorless solution gave crystalline $B_{15}H_{23}$ (2.01 mmol). The KCl was dissolved in water and precipitated with $AgNO_3$ yielding AgCl (1.86 mmol). Therefore, the reaction proceeded according to the following stoichiometry assuming quantitative yields of i-B_9H_{15}.

$$(1.00)\ i\text{-}B_9H_{15} + (1.01)\ B_6H_{10} = (0.97)\ H_2 + (0.98)\ B_{15}H_{23}$$

Hydrolysis of the borane with dilute HCl and titration of the boric acid as the D-mannitol complex resulted in hydrolytic H_2 to $B(OH)_3$ ratios of 2.265 and 2.265, calcd for $B_{15}H_{23}$, 2.267. Six determinations of the molecular weight by vapor pressure depression in CH_2Cl_2 solvent at 0 and +5° gave an average molecular weight of 204, calcd for $B_{15}H_{23}$, 185. The value is probably high due to slow evolution of hydrogen from the sample during the determinations.

The 70.6-MHz ^{11}B nmr spectrum measured in $CDCl_3$ is shown in Figure 1. The sets of peaks have integrated intensities of 1 (a):3 (b + c):3 (d + e):2 (f):2 (g + 2h):2 (i + j) in agreement with a borane molecule containing 15 boron atoms. Resolution of peaks d and e was accomplished by "artificial line narrowing" as described elsewhere.[2]

In view of the established basicity of B_6H_{10}[3,4] and the preparation of B_9H_{13}·ligand compounds from i-B_9H_{15},[1,5] we picture the hydride as an acid–base adduct, possibly one in which the two boron frameworks are held together by a three-center bond.

An X-ray crystallographic study, isotopic labeling, and other nmr studies, as well as a study of the chemistry of this hydride, are in progress. Furthermore, attempts to extend the reaction of B_6H_{10} to other boron hydride Lewis acids have already given encouraging results.

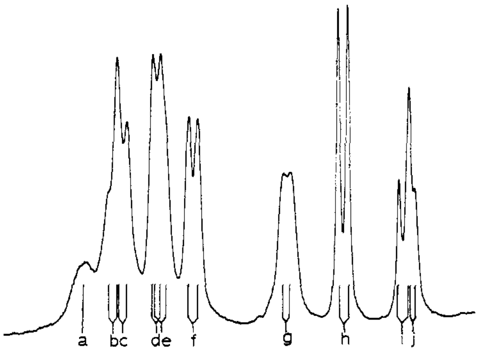

Figure 1. The 70.6-MHz ^{11}B nmr spectrum of $B_{16}H_{23}$ measured in $CDCl_3$. Chemical shifts (ppm referenced to $BF_3 \cdot Et_2O$) and coupling constants (+10 Hz) are as follows: a (−20.9), b (−14.3, 140), c (−12.0, 146), d (−4.5, 128), e (−3.1, 160), f (+3.6, 139), g (+24.4, 113), h (+36.9, 153), i (+50.5, 155), j (+52.4, 101).

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Resonance Raman Spectra of Vitamin B_{12} Derivatives[1]

Sir:

Resonance Raman spectroscopy offers promise as a sensitive structural probe for biological chromophores.[2] Excitation within an electronic absorption band can produce large enhancements of certain of the Raman bands of the absorbing molecule.[3] We have obtained Raman spectra of several vitamin B_{12} derivatives (Figure 1), in dilute solution (10^{-3}–10^{-4} *M*) using laser excitation (4880 Å) within the visible absorption bands of the molecules (Figure 2). The technique may be useful

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