A MECHANISM FOR THE ISOMERIZATION OF ALKYL PENTABORANES

Sir:

Onak recently reported the isomerization of 1-alkylpentaborane-9 to 2-alkylpentaborane-9 in the presence of 2,6-dimethylpyridine.[1,2] He suggests that the mechanism of the reaction may involve "symmetrical" cleavage[3] of the alkylpentaborane-9 or an internal rearrangement facilitated by hydrogen tautomerism.[4]

We have observed the isomerization of ethylpentaboranes in the presence of trimethylamine.[5] A detailed investigation of the reaction of trimethylamine with 1-ethylpentaborane-9[6] led to the isolation of a product evidenced to be a trimethylammonium salt, $(CH_3)_3NHB_5H_7C_2H_5$. The ethylhydropentaborate ion, $B_5H_7C_2H_5^-$, is thought to be the key intermediate for the isomerization. 2-Ethylpentaborane-9 was recovered when the salt was heated above its dissociation temperature (28°). The isomerization of excess 1-ethylpentaborane-9 was not observed below the dissociation temperature of the salt.

In a typical experiment to prepare the trimethylammonium salt $(CH_3)_3NHB_5H_7C_2H_5$, 5.15 mmoles of $(CH_3)_3N$ was recovered from a charge of 10.10 mmoles of $(CH_3)_3N$ and 4.72 mmoles of 1-$C_2H_5B_5H_8$ after 1 hr. at room temperature giving the reaction ratio $(CH_3)_3N$: 1-$C_2H_5B_5H_8$ of 1.00:0.96. Product analyses were: B, 34.7%; N, 9.5%; C, 38.7%; H, 14.5%; calculated for $C_5B_5H_{22}N$: B, 36.0%; N, 9.3%; C, 39.9%: H, 14.7%.

Evidence for the trimethylammonium ion was obtained from the identification of a strong infrared band at 2700 cm.$^{-1}$. It is unlikely that the band be related to BH bonding because the decrease in the frequency of BH stretching which is normal for coördination compounds was observed. An increase in BH stretching to near 2700 cm.$^{-1}$ has only been observed under extremely unusual circumstances.[7] On the other hand, the fundamental singlet band observed was in the normal region for tetrahedral NH.[8] Furthermore, the hydrodecaborate salt $(CH_3)_3NHB_{10}H_{13}$[9,10] and 2-ethylpentaborane[11] were formed quantitatively *via* the reaction

$$(CH_3)_3NHB_5H_7C_2H_5 + H^+B_{10}H_{13}^- \xrightarrow{(C_2H_5)_2O} (CH_3)_3NHB_{10}H_{13} + 2\text{-}C_2H_5B_5H_8$$

Trimethylammonium monoethylhydropentaborate melts at 27–28° with dissociation

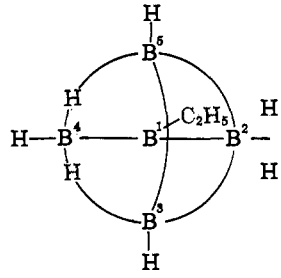
$$(CH_3)_3NHB_5H_7C_2H_5 \rightleftharpoons (CH_3)_3N + 2\text{-}C_2H_5B_5H_8$$

Although vacuum fractionation of the dissociation products could not be accomplished without partially reforming the salt, due to the greater volatility of $(CH_3)_3N$, a sufficient quantity of product was isolated for identification as 2-ethylpentaborane-9 by comparison of infrared, mass spectrometric, and vapor tension data to those obtained on authentic samples.

At elevated temperatures a symmetrical cleavage of ethylpentaborane-9 occurred. For example, a sample of 5.65 mmoles of the salt $(CH_3)_3NB_5H_8C_2H_5$ heated in a sealed ampoule for 0.5 hr. at 75° gave 4.73 mmoles of trimethylamine–borane and only 0.12 mmole of 2-ethylpentaborane-9 was recovered after repeated fractionation of the volatile materials present.

Storage of a large excess of 1-ethylpentaborane-9 with its trimethylamine adduct at 25° yielded no isomerized product after two days. On the other hand, when 13.0 mmoles of 1-ethylpentaborane was warmed to 39° for 80 min. with 4.35 mmoles of trimethylamine, we recovered the excess ethylpentaborane-9 as a mixture containing 45 mmole % of the 2-ethyl derivative. In other experiments up to 80% of the excess ethylpentaborane-9 was isomerized after 2 hr. at temperatures in the range 30–40°.

As a result of these data we propose that the isomerization of alkylpentaborane-9 involves the intermediate formation of a pseudo-hydropentaborate ion the topology of which is similar to that of the $B_{10}H_{13}^-$ ion[12]



The attraction of the two bridge protons toward the negative BH_2 group facilitates the re-arrangement to the 2-ethyl derivative involving little more than relocation of the bridges between the 5-1 and 3-1 borons.

Although our observations show that hydrogen tautomerism is not entirely responsible for the base catalyzed isomerization, the formation of the intermediate salt and re-arrangement of the $C_2H_5B_5H_7^-$ ion is, no doubt, related to such tautomerism. On the other hand, it is unlikely that "symmetrical" cleavage is involved since the non-reversible formation of trimethylamineborane occurs only at elevated temperatures.

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THE STRUCTURES OF THE BASIDIOMYCETE METABOLITES ILLUDIN S AND ILLUDIN M[1]

Sir:

Isolation of illudin S and illudin M, antibiotic compounds from culture liquids of *Clitocybe illudens*, was reported earlier.[2] We now wish to propose the structure Ia for illudin S ($C_{15}H_{20}O_4$)[3] and (Ib) for illudin M ($C_{15}H_{20}O_3$) based on the following evidence: Illudin S has λ_{max}^{EtOH} 233, 319 mμ (ε 13,200 3,600) (cross-conjugated dienone); ν_{max} 1706, 1653, 1610 cm.$^{-1}$. It forms a diacetate, m.p. 99–100°, which still shows hydroxyl absorption in the infrared, and a 2,4-dinitrophenylhydrazone, m.p. 227–230°.

Hydrogenation (palladized charcoal) in methanol (*ca.* 1.5-mole uptake) gives an amorphous phenolic product. This on steam distillation, after addition of acid, gives the volatile compound $C_{14}H_{18}O$ (IIa), m.p. 130–132°; λ_{max}^{EtOH} 266, 300, 311 mμ (ε 9,700, 2,800, 2,600);

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