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

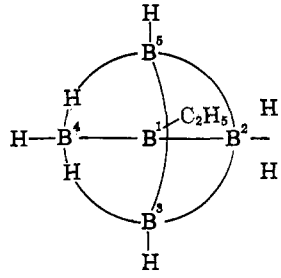
$$(CH_3)_3NHB_5H_7C_2H_5 \rightleftharpoons (CH_3)_3N + 2\text{-}C_2H_5B_5H_8$$

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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(2) T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, **1**, 742 (1962).
(3) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).
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(6) R. E. Williams, *Chem. Abstr.*, **54**, 24401a (1960).
(7) J. F. Ditter and J. Shapiro, *J. Am. Chem. Soc.*, **81**, 1022 (1959).
(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., Ltd., London, 1954.
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(12) W. N. Lipscomb, *J. Inorg. Nucl. Chem.*, **11**, 1 (1959).

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

Sir:

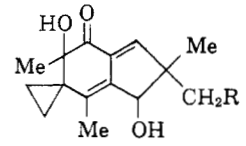
Isolation of illudin S and illudin M, antibiotic compounds from culture liquids of *Clitocybe illudens*, was reported earlier.[2] We now wish to propose the structure Ia for illudin S ($C_{15}H_{20}O_4$)[3] and (Ib) for illudin M ($C_{15}H_{20}O_3$) based on the following evidence: Illudin S has λ_{max}^{EtOH} 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);

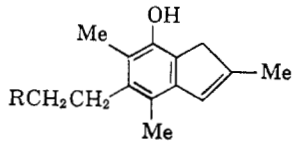
(1) This work was supported by a grant (E-226) from the National Institute of Allergy and Infectious Diseases, National Institutes of Health.
(2) M. Anchel, A. Hervey and W. J. Robbins, *Proc. Natl. Acad. Sci.*, **36**, 300 (1950); **38**, 927 (1952).
(3) M. Anchel, in "Essays in Biochemistry," Samuel Graff, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 3.

τ[4] 8.92 and 7.33 (triplet and quartet, ethyl); 7.79, 7.72 (aromatic methyls); 7.89 (broad singlet, olefinic methyl); 3.48 (quartet, olefinic proton); 6.83 (singlet, cyclic methylene); and 5.7 (very broad peak, hydroxyl); and a residue $C_{15}H_{20}O_2$ (IIb), m.p. 147–149°. This has very similar properties to IIa, but it contains a methoxyl group (singlet at τ 6.63) which results from solvent interaction during hydrogenation. With ethanol as solvent, the corresponding ethoxyl compound $C_{16}H_{22}O_2$ (IIc), m.p. 121–123°, is obtained.

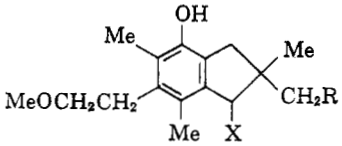
These idenes are smoothly hydrogenated to the corresponding indanes. They react readily with tetrachloro-1,2-benzoquinone to give adducts (1,4-dioxenes).[5] Ozonization of IIb (with phenolic hydroxyl methylated)



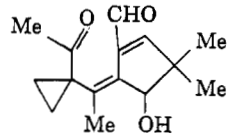
Ia, R = OH
b, R = H



IIa, R = H
b, R = OMe
c, R = OEt



IIIa, R = H, X = OH
b, R = X = H
c, R = X = OH



IV

gives a stable ozonide, $C_{16}H_{22}O_5$, m.p. 95–96°.[6]

Illudin M has λ_{max}^{EtOH} 228, 318 mμ (ϵ 13,900, 3,600); ν_{max} 1695, 1661, 1595 cm.$^{-1}$). It forms a monoacetate, m.p. 75–76°, which still shows hydroxyl absorption in the infrared. Hydrogenation (methanol, *ca.* 1.5-mole uptake) gives the phenol $C_{16}H_{24}O_3$ (IIIa), m.p. 163–165°; τ 8.98, 8.76 (*gem*-dimethyl); 7.77, 7.65 (aromatic methyls); 6.62 (methoxyl); 5.40 (proton α to hydroxyl); 8.5, 5.40 (hydroxyls); 7.5–6.4 (cyclic methylene and $-CH_2CH_2OMe$).

Hydrogenolysis of IIIa yields the compound IIIb, m.p. 123–125°; τ 8.82 (*gem*-dimethyl); 7.86, 7.78 (aromatic methyls); 7.37, 7.30 (two singlets, two cyclic methylenes); 7.25–6.34 ($-CH_2\cdot CH_2-O$ Me); 6.62 (methoxyl) and 5.60 (hydroxyl).

By analogy with IIIa, a primary hydrogenation product of illudin S may be represented by IIIc. Illudin S itself possesses a hydroxymethyl group as evidenced by a singlet at τ 6.53 (2 protons) which on acetylation moves to 5.94 (AB spectrum J_{AB} = 11 c.p.s., δ_{AB} = 0.16 p.p.m.).

The 1,3-glycol system of IIIc would cleave under acidic conditions ("reverse Prins reaction")[7] to give IIb and formaldehyde (which also has been isolated).

The illudins exhibit a multiplet in the region τ 9.7–8.95 (cyclopropyl protons). The cyclopropane ring opens on hydrogenation to give the fragment $-CH_2-CH_2OMe$ in III.[8] The ready formation of these phenols indicates a hydrindane-type skeleton for the illudins. Since the aromatic ring in the phenols is fully substituted, the olefinic proton (singlet at τ 3.5) in their precursors is placed on the double bond exocyclic to the six-membered ring and its position defines that of the carbonyl group.

Sodium borohydride reduction of Ib gives a triol $C_{15}H_{22}O_3$, m.p. 142–144°, λ_{max}^{EtOH} 256 mμ (ϵ 22,400) (conjugated diene),[9] which is oxidized by sodium periodate to the aldehyde IV, m.p. 102–103°. This has τ 0.3 (aldehyde); 9.2, 8.65 (two quintets, two pairs of equivalent cyclopropyl protons); 8.98, 8.80, 7.92, 7.80 (four methyls); 7.58 (hydroxyl); 5.70 (proton α to hydroxyl); 3.22 (olefinic proton).

The α-ketol in I can also be demonstrated by cleavage with sodium periodate.

The methyl groups in Ia give singlets at τ 8.82 (tertiary methyl), 8.65 (methyl α to hydroxyl) and 8.32 (olefinic methyl) and in Ib at 8.92, 8.81 (*gem*-dimethyl), 8.67 (methyl α to hydroxyl) and 8.33 (olefinic methyl). There is clearly only one position for attachment of the cyclopropane ring. The orientation of substituents in the aromatic ring of II and III follows from the structure of I.

(4) N.m.r. spectra were determined by Dr. D. P. Hollis of Varian Associates, California, whom we thank for helpful discussion regarding their interpretation.

(5) L. M. Jackman, in "Advances in Organic Chemistry; Methods and Results," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 335.

(6) P. S. Bailey, *Chem. Rev.*, **58**, 928 (1958).

(7) T. E. Maggio and J. English, Jr., *J. Am. Chem. Soc.*, **83**, 968 (1961).

(8) *Cf.* spiro[2,5]octa-1,4-diene-3-one; R. Baird and S. Winstein, *ibid.*, **79**, 4238 (1957).

(9) The cyclopropane ring is expected to contribute a bathochromic shift. See L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, pp. 318–320.

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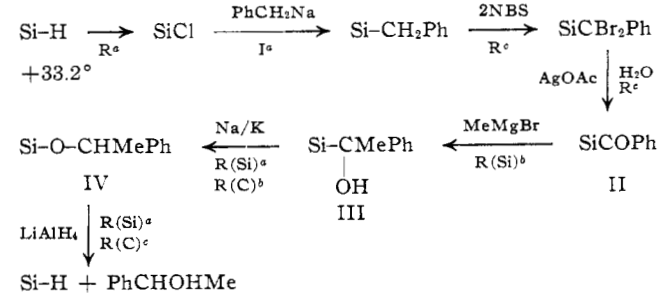
STEREOCHEMISTRY OF α-SILYLCARBINOL REARRANGEMENTS. II. THE ABSOLUTE CONFIGURATION OF ASYMMETRIC SILANES

Sir:

Recently we reported the stereochemistry at the asymmetric silicon atom involved in the synthesis and rearrangement to its isomeric silyl ether of methyl-α-naphthylphenylsilyldiphenylcarbinol.[1] We now wish to report a related Walden cycle which permits the assignment of the stereochemistry at both asymmetric centers (silicon and carbon) in methyl-α-naphthylphenylsilylmethylphenylcarbinol (III) and as well permits the assignment of the absolute configuration of (+)-methyl-α-naphthylphenylsilane (I) and all of its derivatives which are formed by reactions of known stereochemistry.

The Walden cycle, summarized below, results in overall inversion with respect to the silicon atom and logically follows the same stereochemical course at silicon as was reported earlier,[1] *viz.*, inversion of configuration during coupling of the chlorosilane with organometallic and retention during rearrangement from the carbinol to the ether. Treatment of the intermediate optically active benzoylsilane (II) with methyl Grignard reagent introduces an asymmetric carbon atom. This reaction and the subsequent steps proceed with considerable se-



Attached to Si in each case are methyl, α-naphthyl, and phenyl. R = retention; I = inversion. [a] Previous assignment.[1,10] [b] Assignment this work. [c] Reaction does not involve asymmetric center.

(1) A. G. Warner and C. M. Warner, *Tetrahedron Letters*, **18**, 815 (1962).