$$2(CH_3)_3SnNa + CHCl_3 \longrightarrow (CH_3)_6Sn_2 + NaCHCl_2 + NaCl;$$

$$NaCHCl_2 + NH_3 \longrightarrow NaNH_2 + CH_2Cl_2$$

$$2(CH_3)_3SnNa + CH_2Cl_2 \longrightarrow$$

$$(CH_3)_3SnCH_2Sn(CH_3)_3 + 2NaCl$$

The proton n.m.r. spectrum of $(CH_3)_3SnCH_2$-$Sn(CH_3)_3$, identical with that of I, is interpretable in terms of its structure. Two main peaks were observed[4] at 9.94 and 10.28 in ratios approximating 9:1. Naturally occurring isotopes Sn^{117} and Sn^{119} (abundance 7.7 and 8.7% respectively) split[11] these main peaks each into a pair of satellite-doublets, observed best in the neat liquid. The 9.94 line (**CH₃-Sn**) was split by 50.7 and 52.9 cps., while the splitting of the 10.28 line (**Sn-CH₂-Sn**) was 57.7 and 60.3 cps. A more involved tin-proton spin-coupling was observed for a pure sample of hexamethylditin. The single intense peak at 9.81 was strongly split into satellite-doublets $J_{(CH_3-Sn^{117})} = 46.2$ c.p.s., $J_{(CH_3-Sn^{119})} = 48.3$ c.p.s., and in addition showed weak spin-coupling of 16.3 c.p.s., from interactions Sn^{117}-Sn-**CH₃** and Sn^{119}-Sn-**CH₃** (the difference in coupling of these two interactions too small to be resolved under the conditions used).

The complex n.m.r. spectrum of the gross reaction product mentioned above can be fully interpreted as a superposition of the proton resonance lines of hexamethylditin and bis-trimethylstannylmethane.

(11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 357. In this reference, the proton-Sn¹¹⁹ spin-coupling constant in tetramethyltin is given as 54 c.p.s., with no mention of effects due to Sn¹¹⁷. In our hands, the main peak of tetramethyltin at 9.93 showed splitting J(CH₃–Sn¹¹⁷) =51.1 c.p.s. and J(CH₃–Sn¹¹⁹) =53.4 c.p.s.

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REDUCTIVE RING-CLEAVAGE OF TETRAHYDROFURANS BY DIBORANE

Sir:

The diborane–tetrahydrofuran system has been the subject of detailed physico-chemical studies.[1] Furthermore, tetrahydrofuran was used as solvent in a large proportion of the extended chemical investigations dealing with diborane.[2] On the basis of these studies, tetrahydrofuran has been considered chemically inert toward diborane, even at 50–55°.[2b]

(1) Elliott, et al., J. Am. Chem. Soc., **74**, 5211 (1952); Coyle, et al, ibid., **81**, 2989 (1959); B. Rice and H. S. Uchida, J. Phys. Chem., **59**, 650 (1955); H. E. Wirth, et al., ibid., **62**, 870 (1958).
(2) For example see: (a) H. C. Brown, et al., J. Am. Chem. Soc., **82**, 4233 (1960); (b) H. C. Brown, A. Tsukamoto and D. B. Bigley, ibid., **82**, 4703 (1960).

In contrast to all these views, we find that *diborane does react with tetrahydrofuran* to give *n*-butylborate.

$$6 \begin{matrix} CH_2\!-\!CH_2 \\ | \quad\quad | \\ CH_2 \quad CH_2 \\ \diagdown O \diagup \end{matrix} + B_2H_6 = 2 \begin{bmatrix} CH_2\!-\!CH_2 \\ | \quad\quad | \\ CH_3 \quad CH_2\!-\!O\!- \end{bmatrix}_3 B$$
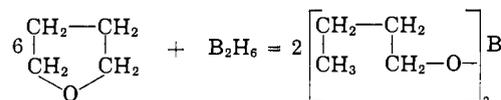
Diborane generated by the addition of lithium aluminum hydride solution to boron trifluoride etherate in ether[3] was swept by a slow stream of nitrogen into dry tetrahydrofuran kept at 0°. Thirty ml. of such a solution containing 0.63 g. of diborane (assayed by the decomposition of an aliquot with diluted hydrochloric acid and measuring the volume of hydrogen generated) was sealed in a Carius tube and kept at 60° for 64 hours. A second assay indicated only a trace of unreacted diborane. The excess tetrahydrofuran was distilled off *in vacuo* and the residue fractionated at 2 mm. Tri-*n*-butyl borate (6.4 g.) distilled at 70° (61% yield on the basis of the above equation). Its infrared spectrum was identical with that of an authentic sample. In a similar fashion, a solution of 0.345 g. of diborane in 50 ml. of 1-methyltetrahydrofuran kept at 60° for 40 hours gave a 30% yield of 2-pentyl borate

$$\begin{matrix} CH_2\!-\!CH_2 \\ | \quad\quad | \\ CH_2 \quad CH\!-\!CH_3 \\ \diagdown O \diagup \end{matrix} + B_2H_6 \rightarrow \begin{bmatrix} CH_2\!-\!CH_2 \\ | \quad\quad |\diagdown CH_3 \\ CH_3 \quad CH\!-\!\!-\!O\!- \end{bmatrix}_3 B$$
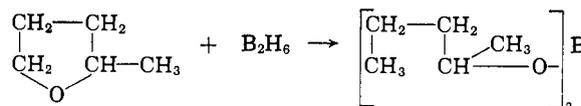
Hydrolysis of this product gave pure 2-pentanol (identified by infrared spectrum).

Other experiments, done at room temperature, gave completely analogous results; of course, the reaction rate is much lower. About sixteen weeks are necessary for a nearly complete reaction.

The extension of this novel reaction for reductive cleavage of other (cyclic and non-cyclic) ethers is being studied.

(3) I. Shapiro, et al., ibid., **74**, 901 (1952).

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THE STEREOCHEMISTRY OF RING A OF GIBBERELLIC ACID

Sir:

Stork and Newman[1] assigned an α-orientation to the lactone ring of gibberellic acid (I) as indicated in Ia, basing the assignment on the Hudson–Klyne lactone rule. Later Edward, et al.,[2] cited examples of four 1,5-bridged lactonic diterpenes in which the rotational change on ring opening

(1) G. Stork and H. Newman, J. Am. Chem. Soc., **81**, 5518 (1959).
(2) O. E. Edward, A. Nicolson, J. W. Apsimon and W. B. Whalley, Chem. and Ind., 624 (1960).