

of many other classes of naturally occurring and synthetic compounds and they are particularly valuable in investigations of complex mixtures of natural origin.

E. C. Horning, *ibid.*, **3**, 356 (1960) (adrenal cortical steroid hormones); W. J. A. VandenHeuvel, C. C. Sweeley and E. C. Horning, "Separation of Steroids by Gas Chromatography," Symposium on Drugs Affecting Lipid Metabolism, Milan, Italy, June 2-4, 1960 (sterols and sterol esters); C. C. Sweeley and E. C. Horning, *Nature*, **187**, 144 (1960) (steroids); H. Ziffer, W. J. A. VandenHeuvel, E. O. A. Haahti and E. C. Horning, *J. Am. Chem. Soc.*, **82**, 6411 (1960) (Vitamins D<sub>2</sub> and D<sub>3</sub>); W. J. A. VandenHeuvel, E. C. Horning, Y. Sato and N. Ikekawa, *J. Org. Chem.*, in press (steroidal amines); E. O. A. Haahti, W. J. A. VandenHeuvel and E. C. Horning, *ibid.*, in press (polyester phases for steroids); W. J. A. VandenHeuvel and E. C. Horning, *ibid.*, in press (sapogenins); W. J. A. VandenHeuvel, J. Sjövall and E. C. Horning, *Biochim. Biophys. Acta*, in press (trifluoroacetyl derivatives of steroids); E. O. A. Haahti, W. J. A. VandenHeuvel and E. C. Horning, *Anal. Biochem.*, in press (urinary 17-ketosteroids).

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#### OBSERVATIONS ON THE COMPOUND REPORTED AS "DI-TRIMETHYL STANNYL ETHYLENE"

Sir:

Because of current interest in vinylmetallics<sup>1</sup> it was desired to obtain the compound reported<sup>2</sup> as  $(\text{CH}_3)_3\text{SnCH}=\text{CHSn}(\text{CH}_3)_3$  in order further to study its chemical and spectroscopic properties.

Trimethyltin chloride (28.3 g., 0.142 mole) suspended in 250 ml. of anhydrous ammonia at  $-70^\circ$  was treated with sodium (6.53 g., 0.284 g. atom) in small portions, giving a yellow solution of trimethylstannylsodium. To this, chloroform (5.66 g., 0.0474 mole) was added with stirring over one hour, discharging the yellow color. After evaporation of ammonia, the reaction flask was washed with *n*-pentane, the solution filtered and solvent removed. The liquid remaining yielded 19.0 g. of distillate, boiling range  $53-60^\circ$  (6 mm.). The infrared spectrum for this gross reaction product in the region  $4000-650\text{ cm}^{-1}$  showed absorptions from methyl groups on tin, similar to those given for tetramethyltin,<sup>3</sup> with the addition of a sharp strong peak at  $955\text{ cm}^{-1}$ .

The proton n.m.r. spectrum<sup>4</sup> for the gross product consisted of a complex series of peaks. Among other resonances discussed below, an intense peak at 9.81 indicated presence of hexamethylditin, a product reported in the earlier work.<sup>2</sup> Gross product was titrated with ethereal iodine and the trimethyltin iodide formed precipitated as the

ammoniate. The solution was filtered and solvent removed. In this manner, 19.0 g. of reaction product yielded 20.0 g. (0.065 mole) of  $(\text{CH}_3)_3\text{SnNH}_3^+\text{I}^-$ , accounting for 10.6 g. (55%) of the gross product as hexamethylditin. There remained purified product, I, of which 8.0 g. distilled at  $58-60^\circ$  (6 mm.).

The infrared spectrum for I was similar to that described for the gross product. Removal of hexamethylditin was not accompanied by loss of any bands in the region  $4000-650\text{ cm}^{-1}$ .

A Raman spectrum<sup>5</sup> for I recorded these shifts in  $\text{cm}^{-1}$  from the mercury exciting line of  $4358\text{ \AA}$ . (relative intensities in parentheses): 106 (4.4), 128 (6.7), 150 (7.6),  $\delta\text{Sn-C}$ ; 469 (3.7), 518 (10), 610 (0.4),  $\nu\text{Sn-C}$ ; 956 (0.7),  $\delta\text{C-H}$ ; 1196 (2.7), 1352 (0.3),  $\delta\text{CH}_3$ ; 2897 (2.3), 2913 (3.1), 2981 (1.7),  $\nu\text{C-H}$ . These lines correspond approximately to those of tetramethyltin<sup>3</sup> or hexamethylditin,<sup>6</sup> with the addition of the line at  $956\text{ cm}^{-1}$ . Absence of any lines in the region  $1500-1800\text{ cm}^{-1}$  of the Raman spectrum, however, is a compelling argument against postulating any  $\text{C}=\text{C}$  bonds<sup>7</sup> in I.

Cleavage<sup>8</sup> of 1.05 g. of I by 137 cc. (6.1 mmole) of dry hydrogen chloride yielded a solid and a non-condensable gas identified as methane (infrared spectrum), and no other volatile products, in particular, *no ethylene*. The solid, identified as trimethyltin chloride by its infrared spectrum and melting point ( $38-39^\circ$ ), weighed 1.2 g. (6.05 mmole). A second cleavage, carried out on 2.31 g. of I with 150 cc. (6.7 mmole) of dry hydrogen chloride, yielded a liquid, a solid, and no volatile gases. The liquid was separated, and identified as tetramethyltin by infrared spectrum and vapor pressure at  $0^\circ$ ; found, 33 mm., reported<sup>9</sup> 34 mm. The solid was identified as trimethyltin chloride; yield of each of these products was  $6.5 \pm 0.2$  mmole.

The accumulated data give no support to the earlier formulation of I as  $(\text{CH}_3)_3\text{SnCH}=\text{CHSn}(\text{CH}_3)_3$ . Instead, all evidence leads to  $(\text{CH}_3)_3\text{SnCH}_2\text{Sn}(\text{CH}_3)_3$  as the composition and structure of I. Analysis yielded: C, 24.5; H, 5.70; required for  $\text{C}_7\text{H}_{20}\text{Sn}_2$ : C, 24.6; H, 5.9; for  $\text{C}_8\text{H}_{20}\text{Sn}_2$ : C, 27.2; H, 5.70. Bis-trimethyl stannylmethane, independently synthesized from dichloromethane and trimethylstannylsodium according to Kraus and Neal,<sup>10</sup> gave infrared and proton n.m.r. spectra identical with those of I.

It is evident that trimethylstannylsodium and chloroform in liquid ammonia yield the products  $(\text{CH}_3)_3\text{SnCH}_2\text{Sn}(\text{CH}_3)_3$  and hexamethylditin in equimolar quantities (over-all yields 70-80%) by the reactions

(1) H. D. Kaesz and F. G. A. Stone, Chapter 3, A.C.S. Monograph 147, "Organometallic Chemistry" (Editor, H. Zeiss), Reinhold Publishing Corp., New York, N. Y., 1960.

(2) C. A. Kraus and A. M. Neal, *J. Am. Chem. Soc.*, **52**, 4426 (1930).

(3) W. F. Edgell and C. H. Ward, *ibid.*, **77**, 6486 (1955).

(4) Proton resonances were obtained using a Varian V-4310A spectrometer, 40 Mcs. Resonances were observed for neat liquids and then measured for 10-20% solutions in carbon tetrachloride relative to the methyl-group protons of 1-2% internal toluene standard. Tetramethylsilane under these conditions appeared at  $91.7 \pm 0.5$  c.p.s. All resonances are reported here as  $\tau$  values,  $\pm 0.01\tau$ ; cf. L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 47, and G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(5) Cary Raman Spectrophotometer, Model 81, Applied Physics Corporation—instrument settings: region  $100-200\text{ cm}^{-1}$ , single slit/2  $\text{cm}^{-1}$ , sensitivity  $1 \times 200$ ; region  $200-3000\text{ cm}^{-1}$ , single slit/10  $\text{cm}^{-1}$ , sensitivity  $1.35 \times 10$ ; sample volume, 0.25 ml.

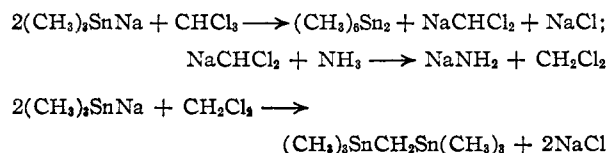
(6) M. P. Brown, E. Cartmell and G. W. A. Fowles, *J. Chem. Soc.*, 506 (1960).

(7) R. N. Jones and C. Sandorfy, Chapter IV, "Chemical Applications of Spectroscopy" (Editor, W. West), Interscience Publishers, New York, N. Y., 1956, p. 368.

(8) Carried out in a high vacuum system; all cc. given at S.T.P.

(9) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 148.

(10) C. A. Kraus and A. M. Neal, *J. Am. Chem. Soc.*, **52**, 695 (1930).



The proton n.m.r. spectrum of  $(\text{CH}_3)_3\text{SnCH}_2\text{Sn}(\text{CH}_3)_3$ , identical with that of I, is interpretable in terms of its structure. Two main peaks were observed<sup>4</sup> at 9.94 and 10.28 in ratios approximating 9:1. Naturally occurring isotopes  $\text{Sn}^{117}$  and  $\text{Sn}^{119}$  (abundance 7.7 and 8.7% respectively) split<sup>11</sup> these main peaks each into a pair of satellite-doublets, observed best in the neat liquid. The 9.94 line ( $\text{CH}_3\text{-Sn}$ ) was split by 50.7 and 52.9 cps., while the splitting of the 10.28 line ( $\text{Sn-CH}_2\text{-Sn}$ ) 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  $J_{(\text{CH}_3\text{-Sn}^{117})}=46.2$  c.p.s.,  $J_{(\text{CH}_3\text{-Sn}^{119})}=48.3$  c.p.s., and in addition showed weak spin-coupling of 16.3 c.p.s., from interactions  $\text{Sn}^{117}\text{-Sn-CH}_3$  and  $\text{Sn}^{119}\text{-Sn-CH}_3$  (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.

**Acknowledgment.**—The author is grateful for generous assistance: a Frederick Gardner Cottrell grant from the Research Corp., use of a Cary Model 81 Raman spectrophotometer at the Applied Physics Corp., and a sample of trimethyltin chloride from the Metal & Thermit Corp.

(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- $\text{Sn}^{119}$  spin-coupling constant in tetramethyltin is given as 54 c.p.s., with no mention of effects due to  $\text{Sn}^{117}$ . In our hands, the main peak of tetramethyltin at 9.93 showed splitting  $J_{(\text{CH}_3\text{-Sn}^{117})}=51.1$  c.p.s. and  $J_{(\text{CH}_3\text{-Sn}^{119})}=53.4$  c.p.s.

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#### REDUCTIVE RING-CLEAVAGE OF TETRAHYDROFURANS BY DIBORANE

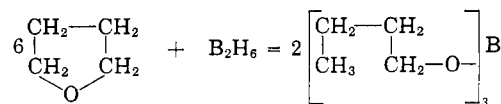
Sir:

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

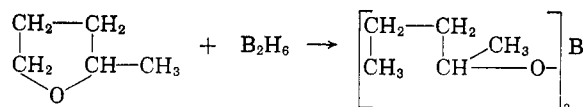
(1) Elliott, *et al.*, *J. Am. Chem. Soc.*, **74**, 5211 (1952); Coyle, *et al.*, *ibid.*, **81**, 2989 (1959); B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955); H. E. Wirth, *et al.*, *ibid.*, **62**, 870 (1958).

(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*.



Diborane generated by the addition of lithium aluminum hydride solution to boron trifluoride etherate in ether<sup>3</sup> 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



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.

**Acknowledgment.**—The author's thanks are due to Mr. V. Verdi for assistance in some of these experiments.

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

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#### THE STEREOCHEMISTRY OF RING A OF GIBBERELIC ACID

Sir:

Stork and Newman<sup>1</sup> assigned an  $\alpha$ -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.*,<sup>2</sup> 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).