

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.

(1) 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

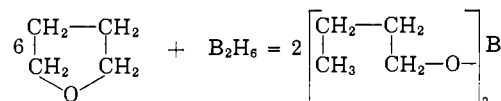
Sir:

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>

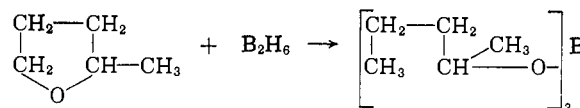
(1) Elliott, *et al.*, *J. Am. Chem. Soc.*, **74**, 5211 (1952); Coyle, *et al.*, *ibid.*, **81**, 2989 (1959); B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955); H. E. Wirth, *et al.*, *ibid.*, **62**, 870 (1958).

(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

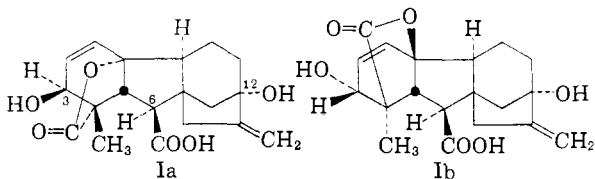
Sir:

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).

violates the Hudson-Klyne rule and they questioned the applicability of the rule to gibberellic acid. Since two stereochemical formulas (Ia and Ib) were predicted from optical rotatory dispersion curves of degradation products of I,<sup>3</sup> Edward and co-workers preferred the alternate expression Ib.



Because of the empirical nature of the Hudson-Klyne rule, the assignment of stereochemistry to the lactone ring awaited other experimental results. We now wish to present new evidence in favor of stereochemical formula Ia for gibberellic acid.

Catalytic hydrogenation of I with 2% Pd on CaCO<sub>3</sub> in tetrahydrofuran afforded tetrahydrogibberellic acid (II)<sup>1,4</sup> in high yield, the hydrogenolysed products amounting to less than 10%. The methyl ester (III), m.p. 245–246° (reported<sup>4</sup> m.p. 233–236°) (found: C, 65.95, H, 7.80), of II was treated with one mole of phenylglyoxalyl chloride<sup>5</sup> and then with isopropenyl acetate containing a trace of *p*-toluenesulfonic acid to afford methyl tetrahydrogibberellate 3-phenylglyoxalate 12-acetate (IV), m.p. 153–154°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +68.1° (chloroform), [ $\alpha$ ]<sub>D</sub><sup>24</sup> +75.5° (ethanol), infrared, 1775 cm.<sup>-1</sup>, 1730 (broad), 1685, 1600 (chloroform) (found: C, 66.87, H, 6.19). Slow addition of methylmagnesium iodide (1.3–1.4 moles) to a dilute (0.01 M) solution of IV in tetrahydrofuran resulted in selective reaction of the ketonic group of IV with the Grignard reagent. Alkaline hydrolysis of the Grignard product gives optically active atrolactic acid in 71% yield,<sup>6</sup> [ $\alpha$ ]<sub>D</sub><sup>25</sup> +3.63° (*c* 3.5 ethanol). This result establishes that the 3-hydroxyl group of III is  $\beta$ -oriented.

Methyl 3-epitetrahydrogibberellate (V), prepared in a manner similar to that described previously,<sup>1,7</sup> was converted to its 3-phenylglyoxalate 12-acetate (VI)<sup>5,8</sup> [ $\alpha$ ]<sub>D</sub><sup>25</sup> +39.4° (chloroform)

(3) B. E. Cross, J. F. Grove, P. McClosky, T. P. C. Mulholland and W. Klyne, *ibid.*, 1345 (1959). These authors favored Ia because of (i) the better agreement of the optical rotatory dispersion curves with formula Ia than Ib and (ii) the facile closure and stability of the lactone ring of methyl  $\alpha$ -dihydrogibberellate. However, Ib was not positively excluded.

(4) Compare with the yields under the hydrogenation conditions reported by B. E. Cross, *J. Chem. Soc.*, 3022 (1960). II is identical with Cross' 8-epitetrahydrogibberellic acid, as judged by comparison of m.p. and optical rotation of the methyl ester. The numbering system used in reference (1) is adopted in this Communication.

(5) The 3-phenylglyoxalates of III and VI resisted crystallization and were purified by silicic acid chromatography using infrared spectra as criteria of purity.

(6) The degree of selectivity is surprising in view of the presence of the four ester carbonyls in the molecule. This modified procedure should widen the applicability of the Prelog-McKenzie method to polyfunctionalized compounds; see S. Masamune, *J. Am. Chem. Soc.*, **82**, 5253 (1960).

(7) Usually a mixture (15–25:65–40) of III and V resulted and was separated by silicic acid chromatography.

(8) VI is an amorphous solid. The homogeneity of VI was confirmed upon silicic acid chromatography by the identical infrared and ultraviolet spectra and optical rotation of every fraction.

infrared, 1775 cm.<sup>-1</sup>, 1720 (broad), 1680, 1600 (chloroform) (found: C, 66.96, H, 6.51). Atrolactic acid was obtained in 68% yield from VI using conditions identical with those used for IV. This acid exhibits negative rotation, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -2.20° (*c* 4.0 ethanol). Therefore, the 3-hydroxyl group of V must be  $\alpha$ -oriented.

The finding that atrolactic acid of opposite rotational signs arises from IV and VI is consistent with the known epimeric relation of the 3-hydroxyl groups of III and V. Further, the assignment of absolute configuration to the 3-hydroxyl group of I has now been confirmed independently.<sup>9</sup> Since a *trans* configuration of the lactone ring and the 3-hydroxyl group of I already has been established,<sup>1</sup> the lactone ring must be assigned an  $\alpha$ -orientation. Optical rotatory dispersion studies definitely rule out the possibility of a *cis* juncture with an  $\alpha$ -oriented lactone ring.<sup>3,10</sup> We must conclude, therefore, that the stereochemistry of gibberellic acid is represented by Ia.<sup>11</sup>

(9) All the compounds cited by Edward, *et al.*,<sup>2</sup> possess a phenanthrene skeleton, whereas the A, B and C rings of gibberellic acid constitute a fluorene system. Apparently the anomaly observed in Edward's examples does not apply to a ring system like gibberellic acid.

(10) III was treated with sodium methoxide in methanol-*d* and deuterium oxide under conditions which afforded a mixture of III and V (or the corresponding acids) in more than 50% yield, but no deuterium was incorporated at C<sub>8</sub>. The lack of deuterium uptake means that the C<sub>8</sub>-carbomethoxy group cannot epimerize under these conditions. Therefore, one can draw no conclusion about the stereochemistry of the A,B ring juncture from the observed failure of the C<sub>8</sub>-carbomethoxy group to epimerize during alkaline hydrolysis.<sup>1</sup>

(11) This work was supported by a research grant (RG-6646) from the National Institute of Health, Public Health Service.

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## BICYCLOHEPTADIENE DIBROMIDES

Sir:

Because of the widespread interest in the behavior of bicycloheptene derivatives and related structures, we report the isolation and properties of the three dibromides and append our urgent warning regarding the possible danger of working with these compounds.

From the addition of bromine to a slight excess of bicycloheptadiene I at 0 to -20°, in carbon tetrachloride, chloroform and methylene chloride, the resulting dibromide mixture is only 17–24% unsaturated.<sup>1,2</sup> The unsaturated component is clearly dibromide III, treatment of a 23% unsaturated dibromide fraction with potassium permanganate leading to a 65% yield of a dibromoglycol, m.p. 127–128°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>O<sub>2</sub>Br<sub>2</sub>: C, 29.40; H, 3.50. Found: C, 29.24; H, 3.72.

This dibromoglycol has been shown elsewhere<sup>3</sup> to have structure VI. The unsaturated dibromide III,

(1) S. Winstein and M. Shatavsky, *Chemistry and Industry*, 56 (1956).

(2) L. Schmerling, J. P. Luvisi and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).

(3) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).