is correct, and if the molecular configuration of the tetramethylplatinum tetramer is unaltered,[1] $y$-parameters of all platinum positions are determined. Intensities of $(0k0)$ reflections can then be calculated, and are in good agreement with observation (Table I). One could not achieve this agreement if the molecular structure of the tetramer were seriously altered by complexing with benzene.

TABLE I

INTENSITIES OF (0k0) REFLECTIONS

| | Intensity | | | Intensity | |
|---|---|---|---|---|---|
| *k* | Obsd. | Calcd. | *k* | Obsd. | Calcd. |
| 2 | S | 1475 | 16 | $M^-$ | 75 |
| 4 | $M^+$ | 641 | 18 | O | 0 |
| 6 | O | 0 | 20 | O | 12 |
| 8 | W | 173 | 22 | $M^-$ | 325 |
| 10 | S | 1178 | 24 | $M^+$ | 573 |
| 12 | VS | 1575 | 26 | $M^+$ | 630 |
| 14 | $S^+$ | 722 | | | |

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## HYDROLYSIS OF THE $\alpha$-1,6-GLUCOSIDIC LINKAGE IN ISOMALTOSE BY CULTURE FILTRATE OF *ASPERGILLUS NIGER* NRRL 330

*Sir:*

The $\alpha$-1,6-glucosidic linkage in the amylopectin fraction of starch is resistant to hydrolysis by the action of the more common amylolytic enzymes. Inasmuch as the linkage between the two glucose residues in isomaltose is of the $\alpha$-1,6 type, it was of interest to test the ability of a culture filtrate of *Aspergillus niger* NRRL 330 to hydrolyze this disaccharide. Isomaltose is now available in crystalline form. The sample of sugar used in these experiments was prepared from starch by the method of Montgomery, Weakley and Hilbert[1] and characterized as 6-($\alpha$-D-glucopyranosyl)-$\alpha$-D-glucose monohydrate, rotating +120° in water (anhydrous). This particular strain of *A. niger* was selected because it elaborates, when grown in submerged culture, an enzyme capable of hydrolyzing maltose in large amounts.

To 20 ml. of 0.06 *M* isomaltose monohydrate, buffered at *p*H 4.4 (acetate buffer, 0.3 *M*), was added 10 ml. of culture filtrate. The reaction mixture was held at 50°. The extent of hydrolysis was measured at two and five hours by the increase in reducing power as determined by the method of Somogyi.[2] The glucose formed in the reaction mixture after five hours was identified biologically by "fermentation" at *p*H 8.8 with an excess of yeast by the procedure of Somogyi.[3] A collection of some of our experimental data is given in Table I.

TABLE I

| Reaction mixture no. | | 1 | 2 | 3 |
|---|---|---|---|---|
| Culture filtrate diluted | | Un- | 1:1 50% | 1:3 25% |
| Two hr. | Isomaltose hydr./ml. culture filt., mg. | 27.4 | 19.4 | 14.3 |
| | Hydrolysis, % | 63.4 | 44.9 | 33.1 |
| Five hr. | Isomaltose hydr./ml. culture filt., mg. | 39.0 | 35.1 | 29.0 |
| | Hydrolysis, % | 90.2 | 81.2 | 67.1 |
| "Fermentable" glucose per ml. cult. filt., mg. | | 37.5 | 33.0 | 25.7 |

It will be noted that the undiluted culture filtrate hydrolyzed 90.2% or 39.0 mg. of the isomaltose per ml. of culture filtrate in five hours. The amount of fermentable glucose produced, 37.5 mg., per ml. of culture filtrate checks reasonably well with this figure. (The hydrolysis of isomaltose proceeds more slowly than the hydrolysis of maltose as indicated by the fact that 38.2 mg. of maltose is hydrolyzed per ml. of culture filtrate in one hour at 30°). In addition, the sugar formed in a reaction mixture identical to No. 1 in Table I, but incubated for six hours, was isolated as crystalline $\alpha$-D-glucose monohydrate; $[\alpha]^{25}\text{D}$ +47.8° (*c*, 4 in water); m. p., 82.8°[4]; yield, 83.4%.

Further work on characterization of the enzyme system responsible for the hydrolysis of isomaltose is in progress.

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[1] Edna M. Montgomery, F. B. Weakley and G. E. Hilbert, THIS JOURNAL, **71**, 1682 (1949).

[2] M. Somogyi, *J. Biol. Chem.*, **160**, 61 (1945).

[3] M. Somogyi, *ibid.*, **119**, 741 (1937).

[4] *Cf.* Nat. Bur. Stand. Circ. No. C440, p. 728.

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## DERIVATIVES OF DIBORINE

*Sir:*

Although tetrachlorodiborine, $B_2Cl_4$, first prepared by Stock, Brandt and Fischer (*Ber.*, **58**, 855 (1925)) by striking an arc across zinc electrodes immersed in liquid boron trichloride, is a compound of considerable potential interest, the original preparative method gave such poor yields (about 1%) of material of such low purity (less than 90%) that detailed study of the compound was not feasible.

Much better results have now been obtained by passing gaseous boron trichloride at 1 to 2 mm. through a glow discharge established between mercury electrodes. The mercurous chloride and other non-volatile products remain in the discharge tube; the volatile material is passed through a −78.5° trap, which retains the tetrachlorodiborine and allows the unchanged trichloride to pass. The latter is repeatedly subjected to the action of mercury in the discharge tube, since the amount converted per pass is small. The yield, however, is approximately 50%. There is evidence that other less volatile boron–chlorine compounds are obtained.

Tetrachlorodiborine is completely hydrolyzed by aqueous sodium hydroxide at 70°.

$$B_2Cl_4 + 6NaOH \longrightarrow 2NaBO_2 + 4NaCl + 2H_2O + H_2$$

Determination of the amounts of hydrogen, boron and chlorine in the hydrolysate of an unweighed sample by the usual methods gave the following results: H, 74.64 cc.; B, 0.0727 g.;

Cl, 0.481 g., corresponding to the atomic ratio H:B:Cl = 1.98:2.00:4.03. A 0.0995-g. sample gave 0.0131 g. of boron and 0.0878 g. of chlorine, a total of 0.1009 g. The vapor density corresponds to a molecular weight of 163 (calcd., 163.5). The vapor tensions, measured between $-63.5$ and 22.5°, are satisfactorily reproduced by the equation: $\log P_{(\text{mm.})} = -1753/T + 8.057$.

Liquid tetrachlorodiborine at room temperature for seventy-two hours undergoes 21% decomposition, yielding boron trichloride, a very slightly volatile red substance and a white solid. The latter two must be hitherto unknown boron chlorides of as yet undetermined composition. At 0° the decomposition is much slower.

The following reactions of tetrachlorodiborine have been studied in preliminary fashion. (1) It yields the hitherto unknown *tetrabromodiborine* by treatment with boron tribromide, but does not react with boron trifluoride. (2) With dimethyl or diethyl ether it forms a liquid monoetherate and a solid dietherate. The latter has an appreciable dissociation pressure and is somewhat soluble in the ether. (3) It yields the corresponding tetramethoxy and tetraethoxy derivatives on treatment with the appropriate alcohols. (4) It reacts with lithium borohydride and aluminum borohydride to give boron hydrides among which diborane and dihydrotetraborane ($B_4H_{10}$) have been definitely identified; pentaboranes and decaboranes are probably present. It does not seem to react with lithium aluminum hydride at 0°. (5) It absorbs hydrogen at room temperature, by which reaction all of the chlorine is converted to boron trichloride, and the residue is a compound or mixture of the approximate composition $BH_{1.37}$ ($B_{10}H_{14}$?). (6) It reacts with ammonia in complex fashion. These and other reactions, as well as the preparative method, will receive further intensive study.

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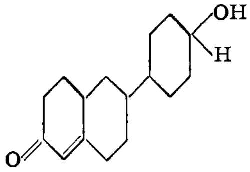
## SYNTHESIS OF PHYSIOLOGICALLY ACTIVE ANALOGS OF TESTOSTERONE

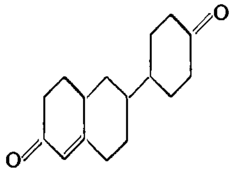
*Sir:*

The discovery of several hundred compounds possessing the physiological activity of the estrogenic hormones has prompted a number of investigators to search for synthetic analogs having activity similar to the other steroid hormones. While some claims of activity for such analogs have been made, particularly in patents, so far as we are aware no such claim has yet been substantiated [*cf.*, for example, the reported androgenic activity for certain reduction products related to diethylstilbestrol, apparently irrespective of configuration, Schoeller, Inhoffen, Steinruck and Höss, U. S. Patent 2,392,864 (Jan. 15, 1948)].

Since 1941 we have directed efforts toward the synthesis of analogs of the non-aromatic steroid hormones lacking ring C, and wish to report now the synthesis of two such analogs of the androgens: I, comparable to testosterone, and II, to androstenedione.



I



II

These $\alpha,\beta$-unsaturated ketones were synthesized using the Robinson–Mannich base method [du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 53 (1937)] with some modifications. Hydrogenation of 4,4′-dihydroxybiphenyl gave the three possible perhydro derivatives (m. p.'s 215–216°, 176.5–177° and 194–195°, all m. p.'s cor.). Half-oxidation of the first two stereoisomers with chromium trioxide afforded the same 4-(4′-hydroxycyclohexyl)-cyclohexanone (III, probably *trans*), m. p. 129–130°. *Anal.* Calcd. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 73.6; H, 10.1. When sufficient 195° diol becomes available, it will presumably lead to the other possible isomer. More complete oxidation gave 4-(4′-ketocyclohexyl)-cyclohexanone (IV), m. p. 115–116°. *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3. Found: C, 74.3; H, 9.2.

Formylation of the keto alcohol (III) with ethyl formate and sodium methoxide, reaction of the derivative with the methiodide of 1-diethylaminobutanone-3 and cyclization with *ca.* 4% methanolic potassium hydroxide at room temperature gave 6-(4′-hydroxycyclohexyl)-$\Delta^{1-9}$-octalone-2 (I), purified by chromatography on alumina and recrystallization from cyclohexane–ethyl acetate, m. p. 127–127.5°; max. 238.5 m$\mu$ ($E_{\text{molar}}$ = 16,870). *Anal.* Calcd. for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7. Found: C, 77.7; H, 9.8. The semicarbazone melted at 235–236° (dec.). *Anal.* Calcd. for $C_{17}H_{27}N_3O_2$: C, 66.9; H, 8.9. Found: C, 67.0; H, 8.7.

Similarly, monoformylation of the diketone (IV), reaction with the Mannich base methiodide and cyclization gave 6-(4′-ketocyclohexyl)-$\Delta^{1-9}$-octalone-2 (II), also obtained in small yield by oxidation of I (as the dibromide), m. p. 88.5–89.5°; max. 238 m$\mu$ ($E_{\text{molar}}$ = 16,400). *Anal.* Calcd. for $C_{16}H_{22}O_2$: C, 78.0; H, 9.0. Found: C, 77.9; H, 8.7. The disemicarbazone decomposed at 256–257°. *Anal.* Calcd. for $C_{18}H_{28}N_6O_2$: C, 60.0; H, 7.8. Found: C, 59.9; H, 7.5.

Preliminary assays in day-old chicks, under the direction of Drs. R. K. Meyer and Elva G. Ship-