record average bond distances with their average deviations on the assumptions that the molecular symmetry is C_{2v} and that the two B'–H and the four B''–H distances are all equal. Molecular parameters[1] are four B'–B'' = 1.845 ± 0.002Å., B'–B' = 1.750Å., B''–B'' = 2.786Å., six B–H = 1.11 ± 0.04, four B'–H$_b$ (bridge) = 1.21 ± 0.03Å. and four B''–H$_b$ = 1.37 ± 0.10Å. Assuming a boron radius of 0.75Å., and therefore single bond distances of 1.50Å. for B–B and 1.10Å. for B–H, bond orders are 0.27 for B'–B'', 0.38 for B'–B', 0.01 for B''–B'', 0.96 for B–H, 0.65 for B'–H$_b$ and 0.35 for B''–H$_b$. The total bond order for the molecule is thus 11.2, close to the expected value of 11. The assumed boron radius is smaller than that calculated for B_2H_6 (0.79Å.), B_5H_9 (0.78Å.) and $B_{10}H_{14}$ (0.81), and as in B_5H_9 the over-all size of the molecule is smaller than that reported in the preceding electron diffraction study by Jones, Hedberg and Schomaker. A similar effect has been observed in B_5H_9 and in hexamethylenetetramine.

It is of interest that the B''B'B'' bond angle is 98° which is a value about midway between the corresponding angle of 90° in the octahedron and 108° in the icosahedron. Thus the boron arrangement may be regarded as a fragment from either the octahedron or the icosahedron. The relatively open structure of this, the first member of the B_nH_{n+6} series compared with the relatively compact higher B_nH_{n+4} structures, probably is a factor relating to the comparatively greater reactivity.

Support of this research by the Office of Naval Research is gratefully acknowledged. All of the three-dimensional Fourier syntheses were carried out on the X-Ray Analogue Computer at Pennsylvania State College through the courtesy of Professor R. Pepinsky. We are also indebted to Dr. L. V. McCarty of the General Electric Company for supplying us with a sample of pure B_4H_{10}.

Details of this investigation will be submitted elsewhere.

(1) Where the distance is observed more than once we record average deviations, which are comparable with estimated probable errors, except for B'–B'' for which a probable error of ±0.01 Å. is estimated.

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STEROIDS.   XLIX.[1]   19-NOR-DESOXYCORTICOS-TERONE, A POTENT MINERALOCORTICOID HORMONE

Sir:

19-Nor-progesterone,[1,2] 19-nor-17-methyltestosterone,[3] and 19-nor-17-ethinyltestosterone (I)[3] have all been shown to possess biological activity of a higher order than the parent hormones. It was therefore of considerable interest to make available for biological testing the 19-nor analogs of

(1) Steroids. XLVIII. C. Djerassi. L. Miramontes and G. Rosenkranz, THIS JOURNAL. 75, November (1953).

(2) L. Miramontes, G. Rosenkranz and C. Djerassi. *ibid.*, 73, 3540 (1951).

(3) C. Djerassi. L. Miramontes and G. Rosenkranz, Abstracts. 121st Meeting of the Am. Chem. Soc., Milwaukee. 1952.

adrenal cortical hormones, especially in view of the report by Ehrenstein[4] that an amorphous product, believed to be a 19-nor-desoxycorticosterone isomer and obtained by a lengthy degradation from strophanthidin, was devoid of biological activity. In this communication we record the synthesis and physiological activity of 19-nor-desoxycorticosterone (IIIb), which possesses the same configuration at all asymmetric centers as does desoxycorticosterone.
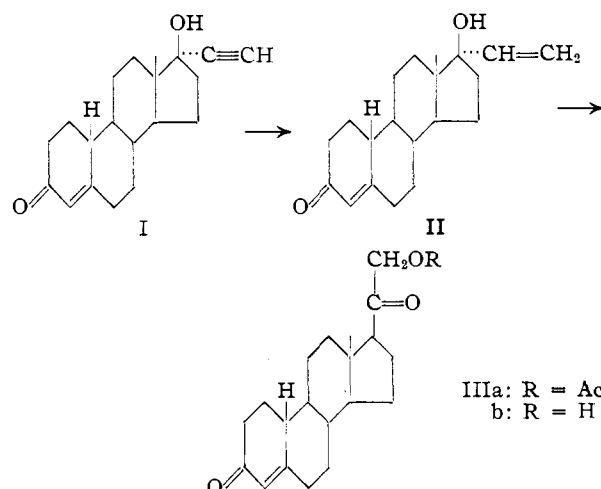
Chromic acid oxidation of 19-nor-testosterone[5] yielded 19-nor-Δ^4-androstene-3,17-dione [m.p. 171–172°, $[\alpha]^{20}$D +139° (CHCl$_3$), $\lambda_{max.}^{EtOH}$ 240 mμ, log ϵ 4.24. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.39; H, 8.99] which upon conversion to 19-nor-3-ethoxy-$\Delta^{3,5}$-androstadien-17-one [m.p. 141–143°, $[\alpha]^{20}$D −87° (pyridine), $\lambda_{max.}^{EtOH}$ 242 mμ, log ϵ 4.26. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.80; H, 9.15], ethinylation with potassium in t-amyl alcohol and acid hydrolysis furnished 19-nor-17-ethinyltestosterone (I) [m.-p. 203–204°, $[\alpha]^{20}$D −25° (CHCl$_3$), $\lambda_{max.}^{EtOH}$ 240 mμ, log ϵ 4.24. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.83; H, 8.80]. Partial hydrogenation in pyridine solution over a 5% palladium-calcium carbonate catalyst[6] led to the corresponding vinyl carbinol II [m.p. 169–170°, $[\alpha]^{20}$D +25° (CHCl$_3$), $\lambda_{max.}^{EtOH}$ 240 mμ, log ϵ 4.25. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.64; H, 9.27]. This latter compound was hydroxylated with osmium tetroxide,[7] and the product without purification was acetylated and subjected to a Serini reaction in toluene solution.[8] The resulting 19-nor-desoxycorticosterone acetate (IIIa) [m.p. 169–171°, $[\alpha]^{20}$D +153° (CHCl$_3$), $\lambda_{max.}^{EtOH}$ 240 mμ, log ϵ 4.26, infrared bands (chloroform) at 1744 and 1718 cm.$^{-1}$ (21-acetoxy-20-ketone) and 1668 cm.$^{-1}$ (Δ^4-3-ketone). Calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.88; H, 8.23] was saponified with sodium bicarbonate in aqueous methanol

(4) M. Ehrenstein, *J. Org. Chem.*, 9, 435 (1944).

(5) A. J. Birch. *J. Chem. Soc.*, 367 (1950); A. L. Wilds and N. A. Nelson. THIS JOURNAL, in press.

(6) Cf. L. Ruzicka and P. Müller. *Helv. Chim. Acta.*, 22, 755 (1939).

(7) Cf. A. Serini and W. Logemann, *Ber.*, 71, 1362 (1938).

(8) Inter al. A. Serini. W. Logemann and W. Hildebrand. *ibid.*, 72, 391 (1939); C. Djerassi and C. R. Scholz, THIS JOURNAL. 71, 8962 (1949).

at room temperature,[9] and yielded 19-nor-desoxy-corticosterone (IIIb) (m.p. 131–132°, λ_{max}^{EtOH} 240 mμ, log ϵ 4.24).

19-Nor-desoxycorticosterone was tested for its mineralocorticoid activity by the assay method of Simpson and Tait[10] and found to be *ca.* twice as active as desoxycorticosterone.

JOINT CONTRIBUTION FROM THE   A. SANDOVAL
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(9) We are indebted to Dr. A. Zaffaroni and Mr. J. Iriarte for carrying out this step.

(10) S. A. Simpson and J. F. Tait, *Endocrinology.* **50.** 150 (1952). We would like to thank Drs. Simpson and Tait for carrying out this assay.

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A CHEMICAL SYNTHESIS OF SUCROSE

Sir:

Tri-*O*-acetyl-D-glucosan<1,5>α<1,2>,[1] 4 mM., and sirupy 1,3,4,6-tetra-*O*-acetyl-D-fructofuranose,[2] 4 mM., dried by azeotropic distillation with benzene, were heated together in a sealed tube at 100° for 104 hours. The product was deacetylated and the sugars were fractionated by preparative paper chromatography[3] using butanol–ethanol–water (5:1:4)[4] on Whatman 3 MM paper. The fraction expected to contain sucrose was acetylated and the product was chromatographed on Magnesol–Celite (5:1) according to the general procedure developed by McNeely, Binkley and Wolfrom.[5] A zone was detected at the position on the column expected for sucrose octaacetate. Elution with acetone and crystallization from ethanol gave 147 mg., 5.5% yield, of a substance with melting point 81–86°. After three crystallizations from ethanol, the substance possessed the physical constants expected for sucrose octaacetate,[6] m.p. 89–90°, $[\alpha]^{25}D$ +60° (*c*, 1 in chloroform). The melting point was unchanged on admixture with authentic sucrose octaacetate. The substance pressed with potassium bromide into a window[7] possessed an infrared absorption spectrum identical to that measured for sucrose octaacetate under the same conditions. Deacetylation yielded a substance, m.p. 187°, $[\alpha]D$ +66.7° (water), which gave a positive Raybin test.[8] The mixed melting point with sucrose, m.p. 187°, $[\alpha]D$ +66.5° (water), was 187°.

This appears to be the first purely chemical synthesis of sucrose. Levi and Purves[9] have reviewed

(1) P. Brigl. *Z. physiol. Chem.*. **122.** 245 (1922).

(2) W. W. Binkley and M. L. Wolfrom. THIS JOURNAL. **68.** 2171 (1946).

(3) C. Yanofsky. E. Wasserman and D. M. Bonner. *Science.* **111,** 61 (1950).

(4) E. L. Hirst and J. K. N. Jones. *Discuss. Faraday Soc..* **7.** 271 (1949).

(5) W. H. McNeely. W. W. Binkley and M. L. Wolfrom. THIS JOURNAL. **67.** 527 (1945).

(6) R. P. Linstead. A. Rutenberg. W. G. Dauben and W. L. Evans. THIS JOURNAL. **62.** 3260 (1940).

(7) M. M. Stimson and M. J. O'Donnell. *ibid..* **74,** 1805 (1952).

(8) H. W. Raybin. *ibid..* **55,** 2603 (1933).

(9) I. Levi and C. B. Purves. *Advances in Carbohydrate Chemistry,* **4,** 27 (1949).

the numerous unsuccessful attempts. Our present success is believed due to the formation of the ion I as an intermediate in reactions of the Brigl anhydride with alcohols at elevated temperature.[10,11,12] β-Maltose octaacetate was prepared[13] through reaction of the anhydride with 1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose.

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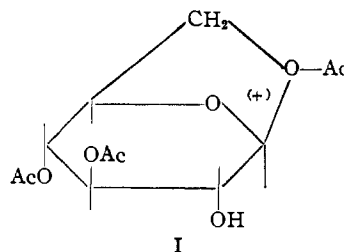
(10) W. J. Hickinbottom. *J. Chem. Soc..* 3140 (1928).

(11) W. N. Haworth and W. J. Hickinbottom. *ibid..* 2847 (1931).

(12) E. Hardegger and J. de Pascual. *Helv. Chim. Acta.* **31.** 281 (1948).

(13) R. U. Lemieux. *Can. J. Chem..* in press.

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OBSERVATIONS ON THE MECHANISM OF ELECTRON TRANSFER IN SOLUTION[1]

Sir:

An important problem in the field of mechanisms of "electron transfer" reactions is concerned with the changes taking place in the coördination spheres of the oxidant and the reductant on electron transfer. This problem has been but little elucidated for reaction of cations, as for example Ti^{+++} + Fe^{+++} = Ti(IV) + Fe^{++} (net change) or Fe*$^{++}$ + Fe^{+++} = Fe*$^{+++}$ + Fe^{++} (virtual change). Thus it is not known whether electron transfer takes place by an electron jump through several layers of solvent, or whether it accompanies the transfer of a group such as OH from oxidant to reductant; or H from reductant to oxidant.[2] Similarly the particular role played by negative ions such as Cl$^-$ or F$^-$ in catalyzing[3,4,5] the reaction of cations is not understood. The principal reason for the lack of a detailed understanding is that the systems are generally very labile with respect to changes in the coördination sphere so that intermediate stages which would supply evidence about the nature of the activated complexes change to final products too rapidly for convenient observation. One method of attack on these problems is to alter conditions so as to slow up the changes; another is to exploit the ions which are less labile with respect to substitution under ordinary conditions.

We have followed the latter line of attack, choosing the reductant Cr^{++} → Cr(III). This system

(1) This work was supported by the Office of Naval Research under Contract N6-Ori-02026.

(2) See W. F. Libby. "Symposium on Electron Transfer and Isotopic Reactions." *J. Phys. Chem..* **56.** 863 (1952); discussion by R. W. Dodson. N. Davidson. O. L. Forchheimer, pp. 866, *et seq.*

(3) J. Silverman and R. W. Dodson, *J. Phys. Chem.,* **56.** 846 (1952).

(4) D. J. Meier and C. S. Garner, *ibid.,* **56,** 853 (1952).

(5) H. C. Hornig and W. F. Libby, *ibid..* **56,** 869 (1952).