

at room temperature,⁹ and yielded 19-nor-desoxycorticosterone (IIIb) (m.p. 131–132°, $\lambda_{\text{max}}^{\text{EtOH}}$ 240 m μ , log ϵ 4.24).

19-Nor-desoxycorticosterone was tested for its mineralocorticoid activity by the assay method of Simpson and Tait¹⁰ and found to be *ca.* twice as active as desoxycorticosterone.

JOINT CONTRIBUTION FROM THE
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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 chromatography³ 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°, $[\alpha]_{\text{D}}^{25} +60^\circ$ (*c*, 1 in chloroform). The melting point was unchanged on admixture with authentic sucrose octaacetate. The substance pressed with potassium bromide into a window⁷ possessed an infrared absorption spectrum identical to that measured for sucrose octaacetate under the same conditions. Deacetylation yielded a substance, m.p. 187°, $[\alpha]_{\text{D}} +66.7^\circ$ (water), which gave a positive Raybin test.⁸ The mixed melting point with sucrose, m.p. 187°, $[\alpha]_{\text{D}} +66.5^\circ$ (water), was 187°.

This appears to be the first purely chemical synthesis of sucrose. Levi and Purves⁹ have reviewed

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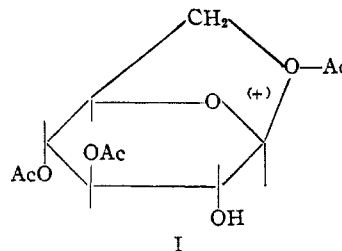
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(7) M. M. Stimson and M. J. O'Donnell, *ibid.*, **74**, 1805 (1952).

(8) H. W. Raybin, *ibid.*, **56**, 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 prepared¹³ through reaction of the anhydride with 1,2,3,6-tetra-*O*-acetyl- β -D-glucopyranose.



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OBSERVATIONS ON THE MECHANISM OF ELECTRON TRANSFER IN SOLUTION¹

Sir:

An important problem in the field of mechanisms of "electron transfer" reactions is concerned with the changes taking place in the coordination spheres of the oxidant and the reductant on electron transfer. This problem has been but little elucidated for reaction of cations, as for example $\text{Ti}^{+++} + \text{Fe}^{+++} = \text{Ti(IV)} + \text{Fe}^{++}$ (net change) or $\text{Fe}^{*+++} + \text{Fe}^{+++} = \text{Fe}^{++++} + \text{Fe}^{++}$ (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 coordination 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 $\text{Cr}^{++} \rightarrow \text{Cr(III)}$. 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.*

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