

at room temperature,⁹ and yielded 19-nor-desoxycorticosterone (IIIb) (m.p. 131–132°, $\lambda_{\text{max}}^{\text{EtOH}}$ 240 μ , $\log \epsilon$ 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 A. SANDOVAL
INSTITUTO DE QUÍMICA L. MIRAMONTES
UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO
TACUBA, MÉXICO D. F., AND G. ROSENKRANZ
RESEARCH LABORATORIES OF SYNTAX, S.A.
LAGUNA MAYRAN 413 CARL DJERASSI¹¹
MEXICO CITY 17, D. F. FRANZ SONDSHEIMER

RECEIVED JUNE 25, 1953

(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.

(11) Department of Chemistry, Wayne University, Detroit, Mich.

A CHEMICAL SYNTHESIS OF SUCROSE

Sir:

Tri-*O*-acetyl-D-glucosyl- α -1,5- α -1,2- β -D-fructofuranose,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

(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).

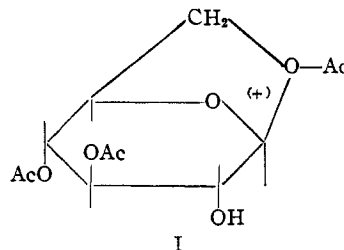
(6) R. P. Linstead, A. Rutenberg, W. G. Dauben and W. L. Evans, *THIS JOURNAL*, **62**, 3260 (1940).

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

(8) H. W. Raybin, *ibid.*, **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.



(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.

PRAIRIE REGIONAL LABORATORY
NATIONAL RESEARCH COUNCIL
SASKATOON, SASKATCHEWAN, CANADA

R. U. LEMIEUX
G. HUBER

RECEIVED JULY 13, 1953

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.*

(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).

has the virtue that any group found in the coordination sphere of Cr(III) when it is formed from Cr⁺⁺ must have been present in the activated complex. Substitution reactions on Cr(III) are sufficiently slow so that entry of groups after completion of the oxidation can be ruled out at least for some systems. (For Cr(II), however, substitutions are rapid⁶.)

A significant result is that when Cr⁺⁺ is oxidized by Fe⁺⁺⁺ in perchloric acid medium (1 *M*) in a solution containing Cl⁻ (0.05 *M*), chloride ion is found attached to the product Cr(III) (0.5 mole/mole Cr(III) for these conditions). Hence, we can conclude that Cl-Cr bonds must have been established in the activated complex. The experiments, however, do not distinguish the activated complexes [Cr-Cl-Fe]⁺⁴ (implying Cl atom transfer as the act producing electron transfer) or [ClCr⁺·water-Fe⁺⁺⁺] (implying electron transfer through the solvent facilitated by Cl⁻ attached to Cr⁺⁺). A decision in favor of the former type of explanation is reached on the basis of experiments we have done using as oxidizing agents complex ions which are slow with respect to substitution. We find that when Co(NH₃)₅Cl⁺⁺ is reduced by Cr⁺⁺ in 1 *M* HClO₄, one Cl⁻ appears attached to chromium for each Cr(III) which is formed or Co(III) reduced. Furthermore, when the reaction is carried out in a medium containing radioactive chloride, the mixing of the Cl⁻ attached to Cr(III) with that in solution is found to be less than 0.5%. The experiment with radioactive chloride shows that transfer of chlorine from the oxidizing agent to the reducing agent is direct, rather than by release and reentry of Cl⁻, and leads to the formulation of the activated complex as [(NH₃)₅Co-Cl-Cr]⁺⁴ (apart from the participation

by solvent and its ions). Transfer from Co(NH₃)₅Br⁺⁺ to Cr(III) is also found to be complete. In both cases the net changes are to form Cr(H₂O)₆⁺⁺⁺ and X⁻ as final products, with, however, CrX⁺⁺ as a recognizable intermediate stage.

The observations on relative rates are also significant. Rates of reduction increase in the order: Co(NH₃)₆⁺⁺⁺, Co(NH₃)₅H₂O⁺⁺⁺, Co(NH₃)₅Cl⁺⁺, Co(NH₃)₅Br⁺⁺. The groups H₂O, Cl⁻ and Br⁻ have available pairs of unshared electrons as points of attack, the polarizability of the groups increasing in the order named. With Co(NH₃)₆⁺⁺⁺, a proton must be removed to provide a pair of electrons as point of attack for Cr⁺⁺, or the electron must be transferred through the proton coordination shell.

We propose an activated complex of the type [(NH₃)₅Co-X-Cr]⁺⁴ as a model for processes in which negative ions catalyze electron exchange between cations. Experiments are in progress to determine whether oxygen atom transfer occurs in the reaction of Cr⁺⁺ with Co(NH₃)₅H₂O⁺⁺⁺. These have significance in their relation to processes involving activated complexes such as [Ti⁺⁺⁺·Fe⁺⁺⁺]aq., [Fe⁺⁺·Fe⁺⁺⁺]aq., etc. We recognize that an activated complex of the type we have formulated is not always readily accessible, as for example, when both partners are inert to

substitution changes. When at least one partner is labile, the direct bridge complex seems a likely path.

GEORGE HERBERT JONES LABORATORIES HENRY TAUBE
UNIVERSITY OF CHICAGO HOWARD MYERS
CHICAGO 37, ILLINOIS RONALD L. RICH

RECEIVED JULY 6, 1953

THE STEREOCHEMISTRY OF THE SN₂' REACTION Sir:

During the last few years considerable evidence has accumulated that bimolecular displacement with rearrangement (SN₂' displacement) is possible with certain allylic halides.¹

We are now presenting evidence which demonstrates that in SN₂' reactions the entering group comes in *cis* to the departing group: 6-alkyl-2-cyclohexenones (alkyl group = methyl, isopropyl and *t*-butyl) prepared by modified Birch reduction of suitable derivatives of anisole and aniline, were purified by conversion to 6-alkyl-3-(1-piperidyl)-cyclohexanones and regeneration *via* the crystalline methiodides. The cyclohexenones were reduced with lithium aluminum hydride to the corresponding 6-alkyl-2-cyclohexenols which were obtained pure by hydrolysis of their crystalline 3,5-dinitrobenzoates (methyl, m.p. 117.9–118.6°; isopropyl, m.p. 79.7–80.7°; *t*-butyl, m.p. 105.7–106.4°). The stereochemistry of these cyclic allylic alcohols was proved to be *trans* by catalytic hydrogenation and comparison of the 3,5-dinitrobenzoates of the saturated compounds with the corresponding authentic *trans* 2-alkylcyclohexanol 3,5-dinitrobenzoates (methyl, m.p. 113.8–114.7°; isopropyl, m.p. 132.2–133.2°; *t*-butyl, m.p. 122.2–123.0°). Attempts to convert the cyclohexenols to *p*-toluenesulfonates were totally unsuccessful, even *via* oxidation of the easily accessible *p*-toluenesulfonates² which were themselves unreactive toward piperidine. A solution to the problem was eventually found in the use of the 2,6-dichlorobenzoates of the 6-alkyl-2-cyclohexenols (methyl, m.p. 56.8–57.6°; isopropyl, m.p. 66.5–67.2°; *t*-butyl, m.p. 71.2–71.9°). Displacement with piperidine³ could be effected by heating, without solvent or in xylene solution, at 130° for twen-

(1) Credit for the postulation and demonstration of this reaction is difficult to assign. The Ingold school has laid claim to the reaction as its appanage (see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 584–594), a claim all the more striking as it had been most active in adducing theoretical arguments against the possibility of SN₂' displacements. In any event, the first clear-cut demonstration of the reaction, Ingold's captious comments notwithstanding, is due to R. E. Kepner, S. Weinstein and W. G. Young, *THIS JOURNAL*, **71**, 115 (1949), and particularly clear examples were later published by W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951), see also W. G. Young and R. Clement, *Science*, **115**, 488 (1952). It may not be out of place to point out that the reactions of the halocodides offer much earlier instances of the phenomenon, although the reactions were only recently recognized as SN₂' displacements (G. Stork in R. H. F. Manske and H. Holmes, "The Alkaloids," Vol. II, Academic Press, New York, 1952, p. 185, and G. Stork and F. H. Clarke, *THIS JOURNAL*, **75**, in preparation).

(2) H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925); R. M. Hann, *THIS JOURNAL*, **57**, 2166 (1935).

(3) Displacement reactions have been carried out on esters previously; see L. P. Hammett and H. L. Pfüger, *THIS JOURNAL*, **55**, 4079 (1933); J. F. Bunnett, M. M. Robison and F. C. Pennington, *ibid.*, **72**, 2378 (1950).

(6) H. Taube, *Chem. Reviews*, **50**, 99–101 (1952).