has the virtue that any group found in the coördination 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 rapid[6].)

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 $[ClCr^{+}\cdot water\cdot Fe^{+++}]$ (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 $Co(NH_3)_5Cl^{++}$ is reduced by Cr^{++} in 1 *M* $HClO_4$, 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 reëntry of Cl^-, and leads to the formulation of the activated complex as $[(NH_3)_5Co{-}\underset{\curvearrowright}{Cl{-}Cr}]^{+4}$ (apart from the participation by solvent and its ions). Transfer from $Co(NH_3)_5Br^{++}$ to Cr(III) is also found to be complete. In both cases the net changes are to form $Cr(H_2O)_6^{+++}$ 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: $Co(NH_3)_6^{+++}$, $Co(NH_3)_5H_2O^{+++}$, $Co(NH_3)_5Cl^{++}$, $Co(NH_3)_5Br^{++}$. The groups H_2O, Cl^- and Br^- have available pairs of unshared electrons as points of attack. the polarizability of the groups increasing in the order named. With $Co(NH_3)_6^{+++}$, 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 coördination shell.

We propose an activated complex of the type $[(NH_3)Co{-}X{-}Cr]^{+4}$ 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 $Co(NH_3)_5H_2O^{+++}$. These have significance in their relation to processes involving activated complexes such as $[Ti^{+++}\cdot Fe^{+++}]$aq., $[Fe^{++}\cdot Fe^{+++}]$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.

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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*-toluenesulfinates[2] 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 piperidine[3] could be effected by heating, without solvent or in xylene solution, at 130° for twen-

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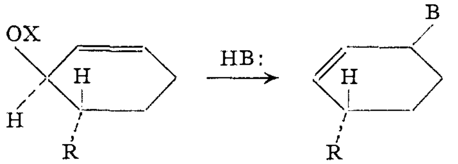
[6] H. Taube, *Chem. Reviews*, **50**, 99–101 (1952).

[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. Winstein 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. Pfluger, THIS JOURNAL, **55**, 4079 (1933); J. F. Bunnett, M. M. Robison and F. C. Pennington, *ibid.*, **72**, 2378 (1950).

ty-four to seventy-two hours. The unsaturated amines which were formed in good yield were reduced catalytically to the corresponding cyclohexyl compounds. Conversion in high yields to pure picrates, picrolonates and methiodides demonstrated that in each instance a *single isomer had been formed in the displacement reaction.* This single isomer was shown in each of the three cases studied to be a *trans*-4-(1-piperidyl)-alkylcyclohexane by infrared evidence as well as by direct comparison with the proper derivatives of the authentic reference compound (methyl: picrate, m.p. 153.3–154.3°; picrolonate, m.p. 188.5–188.9°; methiodide, m.p. 239.4–239.7°; isopropyl: picrate, m.p. 123.5–124.2°; picrolonate, m.p. 174.7–175.1°; methiodide, m.p. 250.2–250.4°; *t*-butyl: picrate, m.p. 166.5–167.5°; picrolonate, m.p. 199.4–199.9°; methiodide, m.p. 253.0–253.2°). *The reaction followed bimolecular kinetics in each case* as demonstrated by the use of the van't Hoff differential method.[4] *The cis relationship of the entering and departing groups is thus demonstrated in the* S_N2' *reaction.*[5,6]



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(4) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 14–15.

(5) The possibility that the ester might rearrange before displacement was ruled out by isolation of the original ester in a state of purity from incomplete reactions.

(6) The steric results are in agreement with the ideas of Winstein and of Young: see W. G. Young, I. D. Webb and H. L. Goering, reference 1.

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RECEIVED JULY 15, 1953

BOOK REVIEWS

Polysaccharide Chemistry. By ROY LESTER WHISTLER, Professor of Biochemistry and Assistant Head, Department of Agricultural Chemistry, Purdue University, Lafayette, Indiana, and CHARLES LOUIS SMART, Purdue University, Lafayette, Indiana. Academic Press, Inc., 125 East 23rd Street, New York 10, N. Y. 1953. xv + 493 pp. 16 × 23.5 cm. Price $10.80.

Polysaccharide chemistry stands as an interesting record of man's inquisitiveness. It reveals that in this area his unquenchable and inexhaustible curiosity runs the gamut from the albumin glands of the vineyard snail (*Helix pomatia*) to the antigens which enable human beings to be separated into blood groups. Along the way, to select but a few examples, he has asked searching questions about red and brown algae, timothy pollen, gastric mucosa, slippery elm mucilage, lobster shells, wing remains of *Coleoptera* from the middle Eocene Period, chondromalacia, and type-specificity and virulence of pneumococci. Huge industries, based on starch and cellulose, prove once again that academic thirst for knowledge can lead to the market place.

There has long been a need to have the entire field of polysaccharides presented as a unified division of carbohydrate chemistry, and the authors merit praise and thanks for their achievement. This compilation of information will enable workers in apparently unrelated spheres of work to see their common ground and techniques, and it will save much time and effort for those who desire a compact presentation of subject matter as well as a guide to significant publications. The authors have made judicious selections from the extensive literature of cellulose, starch and pectic substances.

The first chapter, consisting of twenty-six pages, deals with the occurrence, nomenclature and classification of polysaccharides. Detailed tables summarize the classes of substances which are to be treated in later chapters. The second chapter condenses a vast amount of information regarding methods of analysis and proofs of structure. In the next thirty-three chapters each family of polysaccharides is systematically developed under the subdivisions of Occurrence, Preparation, Composition and Structure, Properties, Derivatives and Uses.

Abridgment and terseness are functional necessities in a book of this size, but condensation is carried to such an extent in the description of laboratory methods that the uninitiated reader may be beguiled into thinking that a procedure which in reality is difficult or which has pitfalls, is easy to carry out. The authors obviously and for good reason decided mainly to give the reader reassurance that methods are available, and where to find them. For useful information and critical evaluations, however, the original literature will have to be consulted. An example of this is the statement: "Xylose may be quantitatively and selectively fermented in the presence of other sugars." At times the authors are disarmingly uninformative, and the reader will, to use a theatrical term, do a "double-take." This is illustrated by the following: "Analysis of agar containing plants are sometimes in error because the raw material may not be uniform." The reviewer's favorite is found on page 334. "The acid pulp from the (Tamarind) seeds has been used for many years in the making of preserves and in the preparation of a cooling laxative drink."

There are evidences in the book that a balanced picture of the average reader was a matter of editorial concern because tritylation is explained parenthetically "with triphenylchloromethane." On the other hand, on page 105 the chemical formula of *bis*-chloromethylsulfone is uniquely presented in place of the name of the compound. However, on page 425 it is assumed that the word *bleb* is part of the vocabulary of that average reader. The most mysterious editorial decision is to list Anonymous in the author index.

These are minor criticisms of an excellent book. The important thing to bear in mind is that the authors have eminently succeeded in their objectives, and that there is now a book on polysaccharides which should be widely read and used.

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LOUIS SATTLER

Structure of Metals—Crystallographic Methods, Principles, and Data. Second Edition. By CHARLES S. BARRETT, Ph.D., Professor, Institute for the Study of Metals, University of Chicago. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1952. xvi + 661 pp. 16.5 × 23.5 cm. Price, $10.00.

The laudable plan of Dr. Barrett's book consists of background chapters on crystallography, X-ray diffraction, re-