be exceptions to Bell and Roblin's theory such as sulfanilylurea, sulfanilylguanidine and sulfanilamido-1,2,4-triazole, or compounds which do not fall within the scope of their theory such as the sulfones and the ring N-methyl and N^1-methylsulfapyridine and sulfathiazole compounds can be adequately accounted for on the basis of this resonance theory.

4. These ideas appear to apply to other bacteriostatic compounds including the monoaminoacridines.

5. Whether the active species is an anion, cation or neutral molecule appears to be an incidental property as far as bacteriostatic activity of these compounds is concerned. The important factor is the contribution of the resonating form.

6. It is proposed that the reason for the maximum in the activity *vs.* *pKa* curve for the N^1 mono-substituted sulfanilamides is that in these compounds neutral molecules are more effective in getting the agent to the site of action and once it gets there, the ion then interferes with essential metabolic processes resulting in bacteriostasis. It is suggested that this is also the reason the activities of various other types of bacteriostatic agents and local anesthetics are correlated with their acidic or basic dissociation constants.

SAN FRANCISCO, CALIFORNIA RECEIVED JUNE 29, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Role of Neighboring Groups in Replacement Reactions. VII. The Methoxyl Group

BY S. WINSTEIN AND R. B. HENDERSON

Participation of a neighboring group in replacement reactions of the so-called S_N1 type has been demonstrated in a number of cases.[1] On the qualitative side, we have been studying the generality[2] of this participation with respect to variations in the nature of both the group and the rest of the reacting molecule. Any findings are not only of immediate interest but may prove equally useful in connection with other processes, for example, certain addition reactions. In the course of this work, most of which has been interrupted for the present, we studied the steric result of some reactions in the presence of a neighboring methoxyl group. These reactions involved the action of silver acetate in acetic acid on the *threo-* and *erythro*-2-bromo-3-methoxybutanes II and VII and *trans*-1-bromo-2-methoxycyclohexane XII.

The diastereomeric 2-bromo-3-methoxybutanes were prepared by the addition of the elements of methyl hypobromite to the known *cis-* and *trans*-2-butenes[3] I and VI. Acetbromamide in methyl alcohol[4] was used. It seems safe to assume *trans*-addition[5] to the double bond in assigning configurations to the 2-bromo-3-methoxybutanes.

Diastereomeric 2-acetoxy-3-methoxybutanes III and VIII were prepared by acetylation of the corresponding 3-methoxy-2-butanols IV and IX. The latter were prepared by the reaction of the known[6] *cis-* and *trans*-2,3-epoxybutanes V and X with methyl alcohol. Analogy with the reactions of oxides with water,[6a,7a] acetic acid[7b] and malonic ester[7c] warrants the assumption of *trans*-opening of the oxide ring by methyl alcohol.

The cyclohexene derivatives, *trans*-1-bromo-2-methoxycyclohexane XII and *trans*-2-methoxycyclohexanol XIV (acetate XIII) were prepared from cyclohexene XI and cyclohexene oxide XV, respectively. Configurations were assigned as in the case of the butene derivatives.

Comparison of the reaction products from the methoxybromides with the known compounds is shown in Table I. Except for the preliminary

TABLE I

COMPARISON OF REACTION PRODUCTS WITH KNOWN COMPOUNDS

Compound	B. p. °C.	B. p. Mm.	$n^{25}D$	M. p. of derivative, °C.
3-Methoxy-2-butanol from *erythro*-bromide	131.4–131.5	746	1.4105	108–110[a]
Known *erythro*-3-methoxy-2-butanol	132.3–132.5	748	1.4107	111–112[a]
3-Methoxy-2-butanol from *threo*-bromide	126.5–126.6	746	1.4076	82– 84[a]
Known *threo*-3-methoxy-2-butanol	126.4–126.5	752	1.4074	84– 85[a]
2-Methoxycyclohexyl acetate from bromide	87 – 89	10	1.4437	
Known *trans*-2-methoxycyclohexyl acetate	87.5– 88.0	10	1.4440	
2-Methoxycyclohexanol from bromide	72.8– 73.3	10	1.4586	101–102[b]
Known *trans*-2-methoxycyclohexanol	72.5– 73.2	10	1.4586	101–102[b]

[a] α-Naphthylurethan. [b] 3,5-Dinitrobenzoate.

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(1) Winstein, Hess and Buckles, THIS JOURNAL, **64**, 2796 (1942).

(2) Winstein and Buckles, *ibid.*, **64**, 2780 (1942).

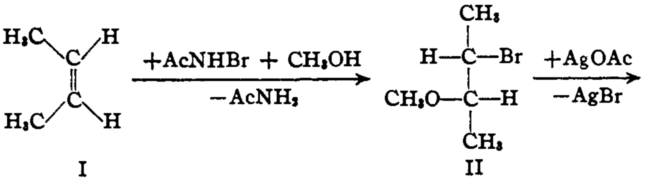
(3) Young, Dillon and Lucas, *ibid.*, **51**, 2528 (1929); (b) Brockway and Cross, *ibid.*, **58**, 2407 (1936); (c) Kistiakowsky, *et al.*, *ibid.*, **57**, 876 (1935).

(4) Schmidt, Knilling and Ascherl, *Ber.*, **59B**, 1280 (1926).

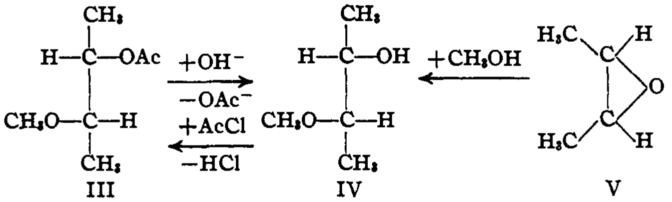
(5) (a) Michael, *J. prakt. Chem.* **52**, 344 (1895); (b) Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925); (c) Bartlett and Tarbell, *ibid.*, **58**, 466 (1936); (d) Roberts and Kimball, *ibid.*, **59**, 947 (1937); (e) Winstein and Lucas, *ibid.*, **61**, 1576 (1939); (f) Lucas and Gould, *ibid.*, **64**, 601 (1942).

(6) (a) Wilson and Lucas, *ibid.*, **58**, 2396 (1936); (b) Brockway and Cross, *ibid.*, **59**, 1147 (1937).

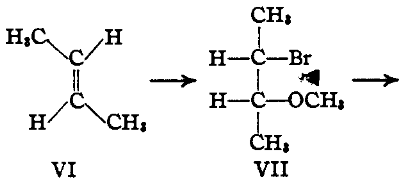
(7) (a) Böeseken, *Rec. trav. chim.*, **47**, 683 (1928); (b) Winstein and Lucas, THIS JOURNAL, **61**, 1581 (1939); (c) Grigsby, Hind, Chanley and Westheimer, *ibid.*, **64**, 2606 (1942).



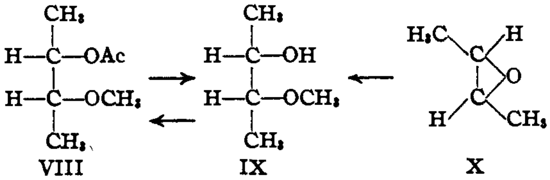
I II



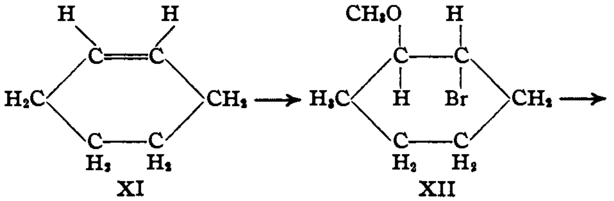
III IV V



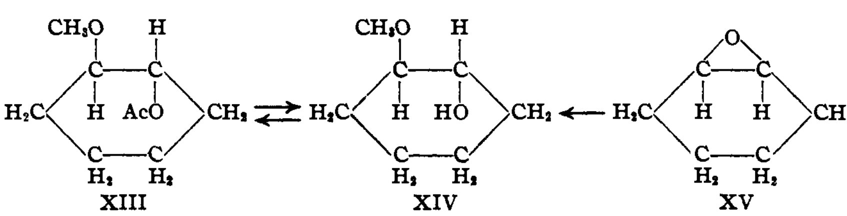
VI VII



VIII IX X



XI XII

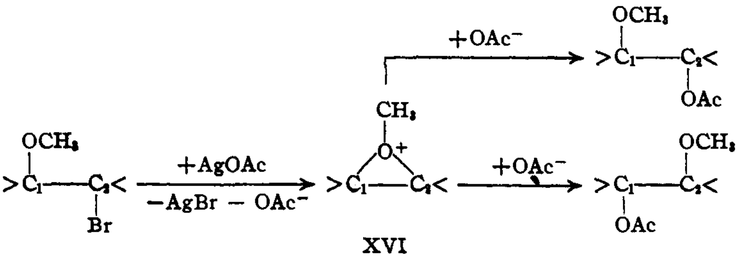


XIII XIV XV

study of the reaction using the methoxybutyl bromide, it was most convenient to hydrolyze the ester product directly to methoxybutanol. This was the case because of the similarity in physical properties of the diastereomeric esters. From Table I it is clear that the product from *erythro*-methoxybutyl bromide is nearly pure *erythro*-methoxybutanol and that from *threo*-bromide is nearly pure *threo*-alcohol. Similarly the acetate and alcohol from *trans*-2-methoxycyclohexyl bromide agree closely in properties with the known *trans*-compounds.

In this work, as in previous cases, a reaction, which in the absence of a neighboring group gives rise to predominant inversion of configuration, proceeds with quite complete retention of configuration. Preliminary attempts to obtain XII in an optically active modification were without success and the work was interrupted before we could extend this phase of it. However, even without the supporting evidence[1,2,5e,8] which could come from the use of optically active methoxybromides, it seems logical to ascribe the steric result of retention of configuration to the participation of the methoxyl group in the replacement process. There is formed, with the extraction of a bromide ion, intermediate XVI, carbon atom C-2 being inverted. The ring of intermediate XVI is opened, either acetate ion or acetic acid becoming attached to carbon atom C-1 or C-2. Two inversions of configuration occur in the whole process. It is interesting that we found no evidence of an attack by acetate ion on the methyl group of XVI to give rise to methyl acetate and an oxide (the latter being converted to glycol monoacetate). This can be reconciled either with an S_N1 type opening of the ring in XVI or an S_N2 type reaction in which unusual relative reactivities are ascribed to the primary and secondary carbon atoms because the latter are part of a strained ring.

It appears that the alkoxyl group should be classed with those groups which may participate in replacement reactions of the type used in this work. There is also some earlier evidence, in the cyclohexene series, that retention of configuration may turn out to be the steric result of a replacement reaction in the presence of a neighboring alkoxyl group. Brunel[9] treated with silver



XVI

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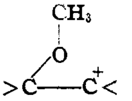
(8) Winstein and Lucas, THIS JOURNAL, 61, 2845 (1939).

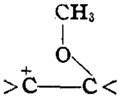
(9) Brunel, *Ann. chim.*, [8] 6, 200 (1905).

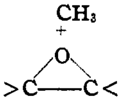
oxide the 2-methoxy- and 2-ethoxycyclohexyl iodide which he prepared from cyclohexene, iodine, mercuric oxide and the proper alcohol. He obtained, if his method of identification was reliable, the monalkyl ether of what is now known to be the *trans*-1,2-cyclohexanediol. Since Brunel's procedure presumably gives iodo compounds possessing the *trans*-configuration, the replacement reactions must have proceeded with retention of configuration.

Intermediate XVI is a ring analog of the tertiary oxonium salts such as XVII which Meerwein and co-workers[10] have been able to prepare.

$(C_2H_5)_3O^+ BF_4^-$
XVII

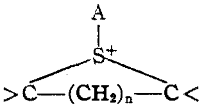

XVIII


XIX

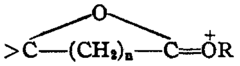

XX

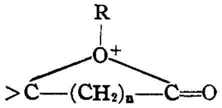
There is very considerable ionic character[11] to the carbon–oxygen bonds in the ring, forms XVIII and XIX contributing significantly to the structure of the hybrid intermediate indicated by XVI. We expect the contribution of form XX to be smaller but nevertheless important.

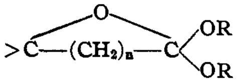
In almost all cases of participation of neighboring groups discussed in this series of papers a three-membered ring intermediate is formed. Whether the same participating groups may be situated more remotely from the seat of substitution remains to be seen. Of course, other kinds of ring closure have been extensively investigated.[12] In our expectations with regard to participation of groups we can be guided somewhat by this general experience. However, a few experiments are desirable with the type replacement reaction we are stressing. These would show which members of the class of general intermediate XXI are important in determining actual products and steric results.


XXI

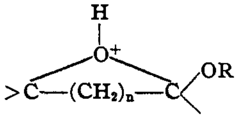
In addition to functional groups whose participation has been either investigated or discussed by us previously, the various forms of the carboxyl group and the carbonyl group deserve consideration. A good deal of information is available on the replacement reactions of acids and their derivatives.[13] In contrast to the α-halogen-substituted carboxylate ions, the α-halogen-substituted esters react with silver oxide in alcohol with inversion of configuration.[13] The most likely but not the unique explanation of this is that the reaction is S_N1 in type but that the carboalkoxy group does not participate. Perhaps, in special situations, the carboalkoxy group will be found to give rise to such intermediates as XXII or XXIII and will allow isolation of a product such as XXIV from the reaction of XXII.

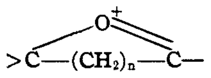

XXII

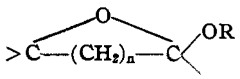

XXIII


XXIV

With regard to reactions of substituted carbonyl compounds, we might expect in certain favorable situations such intermediates as XXV and XXVI. Thus a product of the type XXVII might arise.


XXV


XXVI


XXVII

Experimental

***cis*- and *trans*-2-Butenes.**—These were prepared from the diacetoxybutanes by way of the dibromobutanes.[6a] The *meso*-diacetate was prepared from *meso*-glycol, m. p. 34.2°, which was obtained by recrystallizing Lucidol Corp. glycol from ether.[5e] Impure *meso*-diacetate from Lucidol glycol was converted to impure *dl*-diacetate by conversion to impure *dl*-dibromide with fuming hydrobromic acid and then to impure *dl*-diacetate with silver acetate in acetic acid.[2] Recrystallization from petroleum ether yielded *dl*-diacetate, m. p. 42.7°, which was used in subsequent syntheses.

***cis*- and *trans*-2,3-Epoxybutanes.**—These substances[5e,6a] were prepared from the 3-chloro-2-butanols.[6a,14] The latter substances were obtained from the treatment of the pure diacetoxybutanes with fuming hydrochloric acid by the general procedure used by Lucas and Gould[14] with *meso*-2,3-diacetoxybutane.

Acetbromamide.—This substance was prepared in the usual way.[15] Yields in excess of 60% were obtained when the potassium hydroxide was added slowly from a dropping funnel to the well-stirred reaction mixture kept below 5°. Four moles of acetamide were converted at one time.

The acetbromamide, 70 mole % monohydrate by analysis, was kept for nine months in an icebox, after which time

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[10] Meerwein, *et al.*, *J. prakt. Chem.*, **147**, 257 (1937); **154**, 83 (1939); *C. A.*, **34**, 2325 (1940).

[11] In the case of the intermediate which is formed when an α-carboxylate ion group participates in a replacement reaction, and which has been termed a betaine[13] or an α-lactone,[5e] Professor Lucas and one of us have been incorrectly credited [Chadwick and Pacsu, THIS JOURNAL, **65**, 392 (1943)] with postulating a completely covalent α-lactone. We hope sometime to deal further[2] with the intimate mechanism of formation of such intermediates. However, in regard to the nature of the intermediate in question, Winstein and Lucas had no idea of a completely covalent lactone. The latter authors have always reasoned that, considering the ionic character of a usual carbon–oxygen bond and allowing for the effects of resonance within the carboxylate ion group and of ring strain, one arrives at the conclusion that there is a very large ionic character to the new carbon–oxygen bond in the intermediate.

[12] See, for example, Bennett, *Trans. Faraday Soc.*, **37**, 794 (1941).

[13] Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, **1252** (1937).

[14] Lucas and Gould, THIS JOURNAL, **63**, 2541 (1941).

[15] Mauguin, *Ann. chim.*, [8] **22**, 302 (1911).

analysis showed a loss of 0.6% of oxidizing power. The partially hydrated material was used in the syntheses.

erythro- and *threo*-**2-Bromo-3-methoxybutanes.**—For the preparation of these substances the apparatus and method were similar to those used[2,5e] to prepare the 2-butene bromohydrins from 2-butene and aqueous acetbromamide. To a ten-fold excess of cold anhydrous methanol containing an equivalent amount of acetbromamide and 2 drops of concd. sulfuric acid was added *ca.* 0.4 mole of 2-butene. An ice–salt bath was used to control the vigor of the reaction for the first fifteen minutes. Stirring was continued one-half hour longer and then the reaction mixture was left overnight. It was then poured into aqueous sodium chloride and the organic layer was separated. The aqueous layer was extracted with ether.

The ether extract was partially dried over potassium carbonate and the ether was distilled. The residue separated into two layers, whereupon it was diluted with water and the organic layer separated with the aid of ether. This ether solution was added to the original organic layer and the combination was dried over potassium carbonate. Distillation through a Weston-type column[16] at reduced pressure yielded the bromomethoxybutanes in approximately 50% yield. These were difficult to purify and after another fractionation had the properties:[17] *threo*, b. p. 55.6–55.7° (40 mm.), n^{25}_{D} 1.4478, d^{25}_{4} 1.2892, MR_D 34.68 (calcd. 34.70); *erythro*, b. p. 55.7–56.2° (40 mm.), n^{25}_{D} 1.4483, d^{25}_{4} 1.2970, MR_D 34.50.

Anal. Calcd. for $C_5H_{11}BrO$: C, 35.95; H, 6.64; Br, 47.84. Found, *threo:* C,[18] 36.06; H, 6.67; Br,[19] 49.25. Found, *erythro:* C, 35.69; H, 6.72; Br, 47.28.

trans-**1-Bromo-2-methoxycyclohexane.**—This substance was prepared[4] from cyclohexene very much as were the butene derivatives. For a large preparation, the cyclohexene was added from a dropping funnel. In isolating the product it was necessary to wash it well with water, otherwise acetamide remained in sufficient amount to crystallize in the condenser on distillation. Yields of 70% were obtained and could probably be improved. The product displayed the properties: b. p. 75.0–75.5° (10 mm.), n^{25}_{D} 1.4900.

erythro- and *threo*-**3-Methoxy-2-butanols.**—To a cold ten-fold excess of anhydrous methanol which contained several drops of concd. sulfuric acid was added the butene oxide. After the vigor of the reaction had subsided, the reaction mixture was refluxed gently for one-half hour and left over-night. The acid was neutralized with potassium carbonate and the reaction mixture was distilled through the Weston-type column to yield approximately 85% of methoxybutanol:[20] *threo*, b. p. 126.4–126.5° (752 mm.) n^{25}_{D} 1.4074, d^{25}_{4} 0.9032, MR_D 28.41 (calcd. 28.46); *erythro*, b. p. 132.3–132.5° (748 mm.), n^{25}_{D} 1.4107, d^{25}_{4} 0.9122, MR_D, 28.33.

Anal. Calcd. for $C_5H_{12}O_2$: C, 57.66; H, 11.61. Found, *threo:* C, 57.50; H, 11.46. Found, *erythro:* C, 57.40; H, 11.53.

The methoxybutanols were converted to α-naphthylurethans with the aid of triethylamine as a catalyst.[21]

Anal. Calcd. for $C_{16}H_{19}NO_3$: C, 70.32; H, 7.01. Found, *erythro:* C, 70.38; H, 7.08. Found, *threo:* C, 70.26; H, 6.84.

trans-**2-Methoxycyclohexanol.**—A mixture of 49.1 g. (0.5 mole) cyclohexene oxide, 202 ml. of anhydrous methanol and 4 drops of concd. sulfuric acid was held under reflux for four hours. The catalyst was neutralized with barium carbonate and the mixture filtered. The filtrate was subjected to distillation, first at atmospheric pressure, then at 10 mm. through a 40-cm. column of glass helices: 53.1 g., 82%, of methoxycyclohexanol,[22] b. p. 72.5–73.2° (10 mm.), n^{25}_{D} 1.4586, was obtained. The 2-methoxycyclohexanol was characterized as the 3,5-dinitrobenzoate.

Anal. Calcd. for $C_{14}H_{16}N_2O_7$: C, 51.85; H, 4.97. Found: C, 52.10; H, 5.00.

erythro- and *threo*-**2-Acetoxy-3-methoxybutanes.**—To 0.2 mole of methoxybutanol was added with cooling a 20% excess of acetyl chloride. The mixture was left overnight and then poured into sodium bicarbonate solution. The product was separated with the aid of some ether. The ether solution was dried over potassium carbonate and then fractionated through the Weston-type column to yield 80–82% of the 2-acetoxy-3-methoxybutane:[23] *threo*, b. p. 154.8–155.4° (750 mm.), n^{25}_{D} 1.4047, d^{25}_{4} 0.9460, MR_D 37.85 (calcd. 37.82); *erythro*, b. p. 153.4–154.0° (749 mm.), n^{25}_{D} 1.4045, d^{25}_{4} 0.9452, MR_D 37.87.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found, *threo:* C, 57.39; H, 9.71. Found, *erythro:* C, 57.49; H. 9.68.

trans-**2-Methoxycyclohexyl Acetate.**—From the acetylation of 26.0 g. methoxycyclohexanol by the procedure used with the methoxybutanols was obtained 27.9 g., 81%, of product, b. p. 87.5–88.0° (10 mm.), n^{25}_{D} 1.4440, d^{25}_{4} 1.0157, MR_D 45.04 (calcd. 44.86).

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H. 9.37. Found: C, 62.53; H, 9.17.

Conversion of Halides to Alcohols.—The treatment of the halides (0.2 or 0.3 mole) with silver acetate was carried out as in the case of other butene and cyclohexene derivatives previously investigated.[2] No precautions were taken to use completely anhydrous acetic acid except with the cyclohexyl halide. A reaction time of eleven hours at 110° was allowed, a preliminary experiment with a mixture of *erythro*- and *threo*-2-bromo-3-methoxybutanes having shown that virtually complete formation of silver bromide occurred in this time.

In the case of the butene derivatives, the esters were saponified directly to alcohols. This was carried out as follows. The reaction mixture was filtered and the filtrate was neutralized with potassium carbonate. The organic layer was separated and combined with the ether extract of the aqueous layer and the solid silver salts. The ether solution was dried over potassium carbonate and then the ether was distilled off. The residue was refluxed one-half hour with twice the theoretical amount of 6 *N* sodium hydroxide, enough alcohol being added to make a homogeneous mixture. After standing overnight the reaction mixture was extracted with ether and the ether extract dried over potassium carbonate. Distillation through a small bore 12-inch Podbielniak-type column served to isolate sharp-boiling methoxybutanols, whose properties are shown in Table I. The average yield for the two diastereomers was 30%, partly due to the small amounts of material being distilled but mostly due to a small yield in the reaction step involving the silver acetate.

The methoxycyclohexyl acetate (Table I) was isolated in 59% yield by distillation of the filtered reaction mixture through a 16 inch column of glass helices. This ester was saponified and the reaction mixture was diluted with water. The methoxycyclohexanol was separated with the aid of ether, dried and distilled (Table I). The series of reactions starting with methoxycyclohexyl bromide has been previously carried out by Meinel[22] but the configuration of the product was not investigated.

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[16] Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

[17] Likhosherstov, Arkhangel'skaya and Shalaeva [*J. Gen. Chem.* (U.S.S.R.), **9**, 2085 (1939); *C. A.*, **34**, 3673 (1940)] have prepared a mixture of the diastereomeric methoxybutyl bromides.

[18] All carbon and hydrogen analyses by Mr. Raymond Clinton.

[19] Bromine analyses by Arlington Laboratories.

[20] Preparations which were presumably mixtures of the diastereomeric methoxybutanols have been previously reported: [Petrov, *J. Gen. Chem.* (U. S. S. R.), **10**, 981 (1940); *C. A.*, **35**, 3603 (1941); Likhosherstov, Guryanova and Alekseev, *Acta Univ. Voronegiensis*, **8**, No. 2, 80 (1935); *C. A.*, **32**, 4523 (1938); Chappell, *Iowa St. Coll. J. Sci.*, **11**, 45 (1936); *C. A.* **31**, 1361 (1937)].

[21] Tarbell, Mallatt and Wilson, THIS JOURNAL, **64**, 2229 (1942).

[22] Previous preparations of this substance presumably with the same configuration have been reported[4] [Meinel, *Ann.*, **510**, 129 (1934); Mousseron and Granger, *Compt. rend.*, **205**, 327 (1937); Petrov[20]].

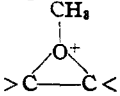
[23] Likhosherstov, Guryanova and Alekseev[20] have reported a mixture of the diasteromeric methoxybutyl acetates.

Identification of Alcohols.—This was carried out as indicated in Table I by a comparison of the physical properties of the alcohols and their derivatives with those of authentic specimens. Mixed melting points with the proper authentic derivatives gave no lowering. The physical properties of the alcohols and the melting points of the crude derivatives indicated small but appreciable stereoisomeric impurity.

Attempted Resolution[5f] of 2-Methoxycyclohexyl Bromide.—The halide, 0.3 mole, and 0.1 mole of brucine were mixed and left for twenty-four hours. The bromide, recovered in the usual way,[3] was inactive. The recovered bromide was similarly inactive when the brucine-bromide mixture was kept at 120° for 26 hours.

Summary

The diastereomeric 2-bromo-3-methoxybutanes, 3-methoxy-2-butanols and 2-acetoxy-3-methoxybutanes have been prepared.

The steric result of the reaction of silver acetate in acetic acid with the 2-bromo-3-methoxybutanes and *trans*-1-bromo-2-methoxycyclohexane is retention of configuration. This steric result is ascribed to the participation of the neighboring methoxyl group in the replacement process,  being an intermediate.

Possible participation of the carbomethoxy and carbonyl groups is briefly mentioned.

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[Contribution from the Iowa Agricultural Experiment Station]

The Configuration of Starch in the Starch–Iodine Complex. IV. An X-Ray Diffraction Investigation of Butanol-Precipitated Amylose[1]

By R. E. Rundle and Frank C. Edwards

In the previous papers of this series[2] evidence has been presented that both in the starch–iodine complex and in alcohol-precipitated starch the starch chains assume a helical configuration. X-Ray diffraction diagrams of the starch–iodine complex have revealed the type of packing of the helices and the dimensions of a turn in the helix.[2c] Similar diffraction diagrams of alcohol-precipitated starch might be expected to confirm the information obtained from the starch–iodine complex and perhaps supplement it by providing details of the structure not obtained from the starch-iodine complex, since diffraction patterns from the latter are largely the result of the scattering of the iodine molecules.

Bear[3] has already discussed the possibility of a helical structure for Katz's "V" modification[4] of starch on the basis of three or four diffraction maxima obtained from a sample of ethanol-precipitated whole starch. It is now possible to get much better diffraction diagrams, and hence to obtain considerably more information than was possible at that time.

Preparation of Samples and Diffraction Diagrams.—There is evidence that many of the lower alcohols precipitate starch in the helical configuration. Thus starch precipitated by nearly any alcohol will absorb iodine vapor readily,[2c] and Bear[3] has shown that the dried precipitates yield identical or nearly identical X-ray diffraction patterns of the "V" type. In our experience, however, butanol precipitation produces very superior samples for diffraction purposes. Equally, or even more important in obtaining good diffraction diagrams is the use of amylose or the unbranched component of starch in place of whole starch.

The amylose used in this investigation was prepared by Schoch's fractionation.[5] Since in Schoch's procedure the amylose is precipitated by butanol in excellent crystalline form, samples were taken directly from the precipitated fraction. The precipitated material occurs as highly birefringent rosets, an optical study of which has already been made.[2b] This amylose contains about 10% amylopectin.[6] The purer[6] "crystalline amylose" of Kerr[7] was not superior for diffraction purposes.

Diffraction diagrams were prepared from both wet and dry samples. The wet samples dripping with the saturated butanol solution were sealed in thin glass capillaries. Other samples were dried to constant weight over phosphorus pentoxide in an Abderhalden drier. Diffraction diagrams from samples dried below 80° were best. The dried samples were very hygroscopic, and so were sealed in thin-walled glass capillaries.

Powder diagrams were prepared with Ni filtered Cu K radiation in a camera of 10-cm. radius. Exposure periods were varied from 360 to 1500 ma. hrs. at 40 Kv. peak.

The Unit Cells.—The pattern from the dried precipitate can be indexed on the basis of a hexagonal unit A_0 = 27.4 Å., C_0 = 8.05 Å., or of an orthorhombic unit a_0 = 13.7 Å., b_0 = 24.8 Å., c_0 = 8.05 Å. (Table I). The relation between the two unit cells is shown in Fig. 1. As will be seen later, the orthorhombic unit is probably the true unit. In either case the packing of the helices approximates the closest packing of cylinders, a packing very similar to that found for the starch–iodine complex.[2c] There are four helices running through the hexagonal unit, two through the orthorhombic unit.

Assuming 6 glucose residues per turn of the

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[2] (a) R. Rundle and R. Baldwin, This Journal, **65**, 554 (1943); (b) R. Rundle and D. French, *ibid.*, **65**, 558 (1943); (c) R. Rundle and D. French, *ibid.*, **65**, 1707 (1943).

[3] R. S. Bear, *ibid.*, **64**, 1388 (1942).

[4] J. Katz, *Z. physik Chem.*, **A150**, 60 (1930), applied this term to gelatinized starch precipitated by alcohol. Starch so treated produces a characteristic diffraction pattern, distinct from granular and retrograded starch.

[5] T. J. Schoch, This Journal, **64**, 2957 (1942).

[6] F. Bates, D. French and R. Rundle, *ibid.*, **65**, 142 (1943).

[7] R. Kerr and G. Severson, *ibid.*, **65**, 193 (1943).