yield of about 50% of the theoretical; however, the material contained iodine as well as chlorine. Repeated refractionation indicated that approximately one-third of the product was the anticipated methyl 1-(2-chloroethoxy)-ethyl ketone, while the remainder was the iodo analog; however, the latter was not isolated in a state of analytical purity. This replacement of chlorine (or of bromine) in a reaction with methylmagnesium iodide has been recognized previously in this Laboratory.[5]

In general, the keto ethers prepared and studied in this Laboratory are characterized by the presence of a reactive carbonyl group, as evidenced by the ease with which they yield semicarbazones. In the majority of the attempts to prepare semicarbazones of the ketones included in this report, no evidence of reaction was observed and the unchanged ketone was recovered. Likewise, we have never before failed to convert an alkoxy ketone with unbranched alkyls by means of the procedure of Bucherer[8] into the correspondingly substituted hydantoins. It was not possible to produce hydantoins from the majority of the keto ethers prepared in this investigation. Data for the semicarbazones and hydantoins obtained are listed in Tables IV and V.

TABLE IV

SEMICARBAZONES OF CHLORO KETO ETHERS DERIVED FROM ETHYLENE CHLOROHYDRIN

$$ClCH_2CH_2—O—CHRC=NNHCONH_2$$
$$\underset{R'}{|}$$

—R	—R'	M. p., °C. (corr.)	Chlorine, % Calcd.	Found
H	CH₃	103	18.31	18.28
H	C₂H₅	92.5	17.08	16.95
H	C₆H₅	119.5–120.0	13.92	13.94
CH₃	C₂H₅	104	15.99	15.96
CH₃	n-C₃H₇	127	15.04	14.93

TABLE V

HYDANTOINS DERIVED FROM β-CHLOROETHOXYALKYL KETONES

$$\begin{array}{c} HN——CO \\ |\qquad| \\ OC\qquad| \\ |\qquad|\,CHR—O—CH_2CH_2Cl \\ NH——C< \\ \qquad\qquad R' \end{array}$$

—R	—R'	Yield, %	M. p., °C. (corr.)	Chlorine, % Calcd.	Found
H	i-C₅H₁₁	87	152.5	13.20	13.33
H	C₆H₅	91	159.8	12.81	12.71
CH₃	C₂H₅	85	168.8	15.11	14.99
CH₃	n-C₃H₇	81	140.5	14.26	14.13

Summary

1. The utilization of ethylene chlorohydrin in the synthesis of α-chloro ethers has been studied.

2. Four examples of the new type of chloro-alkoxy nitriles have been obtained from the dichloro ethers. No evidence of the formation of any dinitrile was observed.

3. From two of the β-chloroethoxy nitriles there have been obtained, by means of the Grignard reaction, ten examples of a new type of monochloro keto ether.

In an attempted preparation of α-(β-chloroethoxy)-ethyl methyl ketone from methylmagnesium iodide, partial replacement of the chlorine by iodine was observed.

4. In these ketones the carbonyl group appears to be less reactive, as judged by the ability of these compounds to yield semicarbazones and hydantoins, than in the analogous keto ethers previously reported.

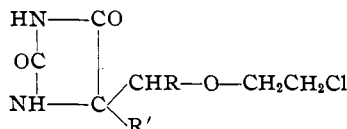(8) Bucherer and Lieb, J. prakt. Chem., [2] **141**, 5 (1934).

AUSTIN, TEXAS

Retention of Configuration in the Reaction of the 3-Bromo-2-butanols with Hydrogen Bromide

BY S. WINSTEIN AND H. J. LUCAS

When 2,3-diacetoxybutane is converted into 2,3-dibromobutane by the action of fuming hydrobromic acid, the transformation appears to be accompanied by an odd number of inversions, for the dl-diacetate gives rise to the meso-dibromide, and the meso-diacetate to the dl-dibromide.[1] Moreover, the purity of the products shows that the various reaction steps proceed with either 100% inversion, or 100% retention of configuration. One would have expected, on the assumption that the reaction proceeds similarly at each asymmetric carbon atom, an even number of inversions. In order to ascertain the number of inversions and the steps at which they take place, it has been necessary to follow the reaction step by step, through the isolation of intermediate products and to study the behavior of each intermediate with hydrobromic acid.

It has been found that 3-bromo-2-butanol is

(1) Wilson and Lucas, THIS JOURNAL, **58**, 2396 (1936).

TABLE I

PROPERTIES OF 2,3-DIBROMOBUTANES

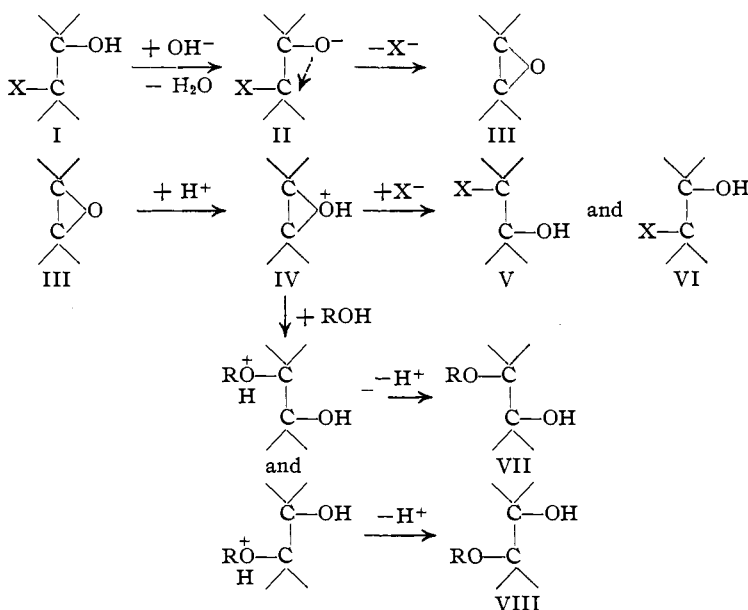| Source	B. p., °C. (50 mm.)	$n^{25}D$	K_1	ϵ
erythro - 3 - Bromo - 2 - butanol from *trans* oxide	73.2	1.5090	0.0558	
threo - 3 - Bromo - 2 - butanol from *cis* oxide	76.5	1.5125	.0299	
threo - 3 - Bromo - 2 - butanol from *cis* - 2 - butene	76.3	1.5125		5.771
Previously described				
Pure *meso* - 2,3 - dibromobutane	73.3[1]	1.5092[3]	.0544[3]	6.245[4]
Pure *dl* - 2,3 - dibromobutane	76.4[1]	1.5125[3]	.0297[3]	5.758[4]

the last of three intermediates.[2] In this paper is reported the preparation of the pure inactive erythro- and threo-3-bromo-2-butanols and a detailed study of their behavior with hydrobromic acid. These compounds were prepared by the action of hydrobromic acid upon the pure *trans*- and *cis*-2,3-epoxybutanes, respectively. The *threo* isomer was prepared also by the addition of hypobromous acid to *cis*-2-butene. With fuming, aqueous hydrobromic acid these bromobutanols were found to give *meso*- and *dl*-2,3-dibromobutanes, respectively, with complete retention of configuration. The identification of the resulting dibromobutanes is indicated in Table I, where their properties are compared with the already known properties of pure *meso*- and *dl*-2,3-dibromobutanes.[1,3,4]

Configurations of the *dl*-3-Bromo-2-butanols.—Of these two, one must have the *erythro* (or *cis*) configuration, the other the *threo* (or *trans*) configuration. The determination of the configuration of these bromobutanols is not absolute, but is reasonably certain. It is based upon the assumption that one stereomutation (inversion) accompanies the addition of hydrogen bromide to 2,3-epoxybutane (*trans* opening of the ring), in line with the effect of acetic acid[2] on 2,3-epoxybutane and with the known effect of water on oxide rings[5] in general; and also

that one stereomutation accompanies the reaction of hypobromous acid with 2-butene (*trans* addition to the olefin bond) in line with the known behavior[6] of other reagents, especially bromine, toward the double bond. The configurations are known for the 2,3-epoxybutanes[1,7] and for the 2-butenes.[8] These conclusions are in agreement with those regarding configurations of other halohydrins,[9] in connection with cyclic compounds. The fact that the same product is predicted and obtained from both *cis*-2,3-epoxybutane and *cis*-2-butene shows that the assumed configurations are reasonably certain.

Mechanism of Formation and Opening of Oxide Rings.—Since *dl*-threo-3-bromo-2-butanol is converted by alkali to *cis*-2,3-epoxybutane, the same oxide which yields this bromobutanol with hydrogen bromide, it is reasonable to assume that a clean-cut inversion accompanies the formation of the oxide ring. The mechanisms shown below are proposed for the closing and opening of oxide rings

When the halohydrin, I, is converted into the oxide, III, by the action of alkali, the first step is the formation of an alcoholate ion II, for the presence of the halogen atom enhances the acidic

(2) Winstein and Lucas, THIS JOURNAL, **61**, 1581 (1939).

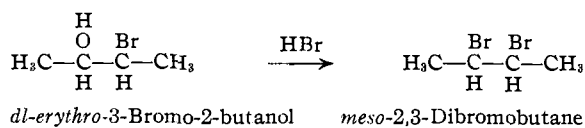(3) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).

(4) Winstein and Wood, unpublished work.

(5) (a) Kuhn and Ebel, *Ber.*, **58B**, 919 (1925); (b) Böeseken, *Rec. trav. chim.*, **47**, 683 (1928).

(6) (a) Michael, *J. prakt. Chem.*, **52**, 344 (1893); (b) Chavanne, *Rev. gen. sci.*, **35**, 229 (1924); (c) Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925).

(7) Brockway and Cross, *ibid.*, **59**, 1147 (1937).

(8) (a) Young, Dillon and Lucas, *ibid.*, **51**, 2528 (1929); (b) Brockway and Cross, *ibid.*, **58**, 2407 (1936).

(9) (a) Suter and Lutz, *ibid.*, **60**, 1361 (1938); (b) Bartlett and White, *ibid.*, **56**, 2785 (1934); (c) Bartlett and Rosenwald, *ibid.*, **56**, 1892 (1934); (d) Bartlett, *ibid.*, **57**, 224 (1935).
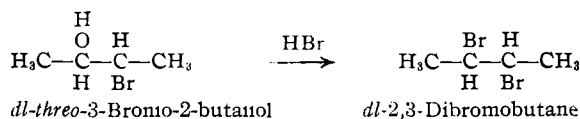
character of the alcoholic hydroxyl group. The negatively charged oxygen atom of II attacks the adjacent carbon atom on the face opposite the bromine atom, thus leading to a Walden inversion of the usual bimolecular exchange type[10] except that in this case the reaction is intramolecular. Here the carbon atom to which the halogen atom originally was attached has been inverted. In the case of the *erythro* bromohydrin, one would expect the active forms to give rise to active forms of the *trans* oxide.

When the oxide, III, reacts with a hydrogen halide or with a compound having the hydroxyl group, the reactions are acid catalyzed. In this case the first step is believed to be the formation of the oxonium complex, IV, by the attachment of a proton. This cation may then be attacked by a negative ion (chloride, bromide, etc.) at the opposite face of either carbon atom, producing both halohydrins V and VI. Or it may be attacked by a solvent molecule (water, alcohol, organic acid, etc.) producing first the oxonium complexes which then lose the proton to form the hydroxy compounds VII and VIII. These may be glycols, glycol monoesters or glycol monoethers, depending upon the nature of ROH. In case the original oxide were *cis*-2,3-epoxybutane, the final product, in any case, would be a *dl*-mixture, for V and VI, also VII and VIII, are pairs of antipodes. In case it were a *d*- or *l-trans*-2,3-epoxybutane, the final product would be expected to be active, unless it were a glycol.

Retention of Configuration in the Conversion of *dl*-3-Bromo-2-butanol to 2,3-Dibromobutane. —*erythro-dl*-3-Bromo-2-butanol with hydrobromic acid under the same conditions as 2,3-diacetoxybutane,[1] is converted into pure *meso*-2,3-dibromobutane, while the *threo* isomer yields pure *dl*-2,3-dibromobutane (see Table I). In this reaction, in which, unlike the reaction of 2,3-diacetoxybutane, the final product is formed directly from the initial compound without the complication of intermediates, complete retention of configuration unaccompanied by racemization (*i. e.*, partial inversion at one carbon atom) holds.
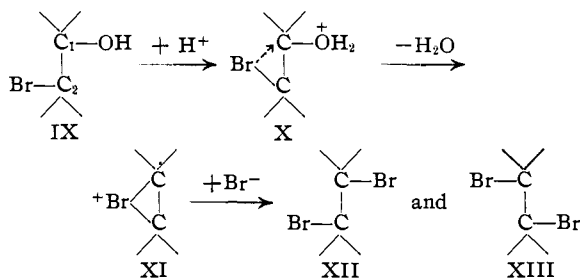
$$
\begin{array}{c}
\text{H} \\
\text{O} \quad \text{Br} \\
\text{H}_3\text{C—C—C—CH}_3 \\
\text{H} \quad \text{H}
\end{array}
\xrightarrow{\text{HBr}}
\begin{array}{c}
\text{Br} \quad \text{Br} \\
\text{H}_3\text{C—C—C—CH}_3 \\
\text{H} \quad \text{H}
\end{array}
$$

dl-erythro-3-Bromo-2-butanol   *meso*-2,3-Dibromobutane

$$
\begin{array}{c}
\text{H} \\
\text{O} \quad \text{H} \\
\text{H}_3\text{C—C—C—CH}_3 \\
\text{H} \quad \text{Br}
\end{array}
\xrightarrow{\text{HBr}}
\begin{array}{c}
\text{Br} \quad \text{H} \\
\text{H}_3\text{C—C—C—CH}_3 \\
\text{H} \quad \text{Br}
\end{array}
$$

dl-threo-3-Bromo-2-butanol   *dl*-2,3-Dibromobutane

This striking phenomenon warrants discussion and also additional investigation because of its bearing upon the mechanism of substitution reactions.

In developing a mechanism to account for the retention of configuration in these two cases, one should bear in mind the difference in behavior of the bromobutanols and ordinary monohydric alcohols. When the latter[11] react with hydrobromic acid, inversion predominates, and more or less extensive racemization accompanies the reaction. The unusual behavior of the bromobutanols must be ascribed to the presence of the bromine atom. The following is offered as a plausible mechanism to account for the retention of configuration.

The proton converts the bromohydrin, IX, to an oxonium compound, X. The bromine atom may attack the back face of the carbon atom holding the hydroxonium group in the same way that an independent bromine anion may, giving rise to a cyclic, intermediate, positively charged complex, XI, which resembles closely the other intermediate, IV. A negatively charged ion, such as bromide ion, may attack the opposite face of either carbon atom of XI, giving rise to both dibromides XII and XIII. In either event, two inversions have accompanied the change, two on carbon atom C_1 when XII is the product, one each on carbon atoms C_1 and C_2, when XIII is the product. If the initial compound is an active *threo*-3-bromo-2-butanol, the resulting 2,3-dibromobutane is predicted[12] to be inactive, since XII and XIII are antipodes.
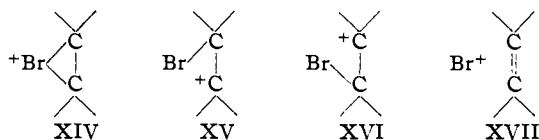
The extension of the idea of initial attack by one part of the molecule in substitution reactions at an asymmetric center in the neighborhood,

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(10) (a) Olson, *J. Chem. Phys.*, **1**, 418 (1933); (b) Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **20**, 161 (1933).

(11) (a) Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1252 (1937); (b) Winstein and Lucas, unpublished work.

(12) It is planned to investigate this reaction, for it constitutes a test of the hypothesis.

gives a satisfactory explanation of phenomena observed by others. Thus, the first order hydrolysis or alcoholysis of α-bromopropionate ion with complete retention of configuration observed by Cowdrey, Hughes and Ingold,[13] is due more likely to initial attack by the carboxylate ion group with formation of an α-lactone, than to the removal of bromine by ionization with the necessity of assuming stabilization of the resulting dipolar ion in a pyramidal form, as postulated by these authors.[11a] At the step of lactone formation, there is according to the point of view enunciated above complete inversion at the α-carbon atom. This is the slow, rate-determining step. Then the lactone reacts quickly with solvent molecules, again with complete inversion as in the case of oxides, and of β-lactones under some conditions.[14] Those two inversions would lead to the retention of the initial configuration, and the rate would be first order, as these workers observed.

The Positive Bromo-Olefin Complex.—Such a complex has been postulated by others as an intermediate in reactions of bromine with compounds having a double bond.[15] The formulation of this complex as a cyclic compound XI was first proposed by Roberts and Kimball.[15d] We believe that this intermediate is the same as the one assumed above in the reaction of the bromobutanol with hydrobromic acid, and we believe with Roberts and Kimball[15d] that the mechanism of the bromine addition to olefins, except for the initial attack by the bromine molecule, is shown satisfactorily by XI, XII and XIII. The existence of such a postulated intermediate seems more reasonable than formerly, now that a similarly constituted positive ion, the olefin-silver ion complex, has been shown to exist in aqueous solution.[16] The possibility of resonance among four forms, XIV, XV, XVI and XVII, contributes to the stability of the complex.

The first form, XIV, probably contributes most, and the last form, XVII, least, because of the stabilizing effect arising from bond formation be-

tween bromine and carbon. In the case of the silver–olefin complex,[16] it was held that the form similar to XIV is not as important as the other three.

This bromo-olefin complex can be formed not only in the reaction of hydrobromic acid with bromohydrins and of bromine with ethylenic compounds, but also by the reaction of a variety of bromine donating substances with ethylenic compounds, as pointed out by Bartlett and Tarbell.[15b] To their list of bromine donating compounds should be added N-bromoacetamide,[17] and other compounds of similar structure.

Even an ion group in the same molecule may attack one or the other of the carbon atoms of XI. Thus Bartlett and Tarbell[15c] found that in the action of bromine upon sodium dimethylmaleate, a bromo-β-lactone is formed; moreover, this lactone is different from the one obtained from sodium dimethylfumarate. In these cases the negative carboxylate group is the attacking group.

The authors desire to express their appreciation of the advice given by Professor Linus Pauling, in connection with structural considerations.

Synthesis of Both 2-Butenes from the Same Oxide.—A practical result of the observation that a bromohydrin can be converted into a dibromobutane with retention of configuration is the possibility of preparing both cis- and trans-2-butenes from the same 2,3-epoxybutane, for example

trans-2,3-Epoxybutane

↓HBr   H₃O⁺↓

erythro-3-Bromo-2-butanol   meso-2,3-Butanediol

↓HBr   ↓Ac₂O

meso-2,3-Dibromobutane   meso-2,3-Diacetoxybutane

↓Zn   ↓HBr

trans-2-Butene   dl-2,3-Dibromobutane

↓Zn

cis-2-Butene

Experimental

cis- and *trans-*2,3-Epoxybutanes.—These compounds were prepared as previously described,[1] and in a higher state of purity.[18] Some physical properties of these pure oxides are shown in Table II.

*meso-*2,3-Butanediol.—From 2 pounds of Lucidol butylene glycol, m. p. 27°, four crystallizations from a fourfold weight of isopropyl ether gave 300 g. of quite pure *meso* glycol, m. p. 34.0°.

(13) Cowdrey, Hughes and Ingold, *J. Chem. Soc.*, 1208 (1937).

(14) Olson and Miller, THIS JOURNAL, **60**, 2687 (1938).

(15) (a) Ingold, *Chem. Rev.*, **15**, 225 (1934); (b) Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936); (c) Bartlett and Tarbell, *ibid.*, **59**, 407 (1937); (d) Roberts and Kimball, *ibid.*, **59**, 947 (1937).

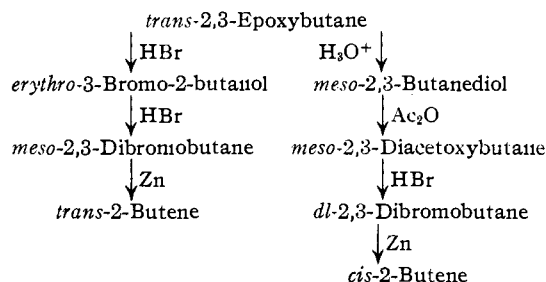(16) Winstein and Lucas, *ibid.*, **60**, 836 (1938).

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

(18) We are indebted to Messrs. K. D. Johnson and W. T. Stewart for the preparation of a large amount of the mixed oxides and to Mr. H. S. Sargent, Jr., for the careful fractionation.

TABLE II

PROPERTIES OF THE ISOMERIC 2,3-EPOXYBUTANES

Property	Configuration	
	trans	cis
B. p., °C. (742 mm.)	53.5 ± 0.05	59.7 ± 0.05
n^{20}D	1.3736	1.3828
n^{25}D	1.3705	1.3802
d^{25}_4	0.8010	0.8226

cis-2-Butene.—This substance was obtained from the *meso* glycol by the series of reactions described previously.[1]

Preparation of the *dl*-3-Bromo-2-butanols **from Oxides.**[19]—190 ml. of 48% hydrobromic acid in a 3-necked 500-ml. flask is cooled with an ice-bath. Then 72 g. (1 mole) of pure oxide is dropped in with stirring over a period of about one hour, the reaction temperature being maintained below 5°. After all the oxide is added, the reaction mixture is left for one hour longer; then it is partially neutralized with solid sodium carbonate, the bottom phase is separated, and the aqueous phase is extracted with two 70-ml. portions of isopropyl ether. The bromohydrin layer and ether extracts are combined, neutralized with sodium carbonate and dried with sodium sulfate. Distillation through a 15-cm. column of glass helices yields 126–130 g. (82–85%) of bromohydrin, boiling range *ca.* 1°. On distillation of a portion of the bromohydrin through a 40-cm. Weston column,[20] constant-boiling material is obtained. The properties of the *erythro*-3-bromo-2-butanol (from *trans* oxide) and the *threo*-3-bromo-2-butanol (from *cis* oxide) and the melting points of their 3,5-dinitrobenzoates and α-naphthylurethans are given in Table III.

TABLE III

PROPERTIES OF THE *dl*-3-BROMO-2-BUTANOLS

Property	Configuration	
	erythro	threo
B. p., °C. (13 mm.)	53.1	50.5
n^{25}D	1.4767	1.4756
d^{25}_4	1.4474	1.4437
MD	29.85	29.87
MD, calcd.	29.96	29.96
M. p. of 3,5-dinitrobenzoate, °C.	85	109
M. p. of α-naphthylurethan, °C.	133	103

threo-3-Bromo-2-butanol **from** *cis*-2-Butene.—17.3 g. (0.31 mole) of *cis*-2-butene, an equivalent of N-bromoacetamide,[21] 250 ml. of water and 6 ml. of glacial acetic acid were kept under reflux for two hours in a 3-necked 500-ml. flask equipped with a carbon dioxide–alcohol reflux condenser and a mechanical stirrer and surrounded by an ice-bath. After this time butene still refluxed vigorously when the ice-bath was removed. This was contrary to expectations.[22] Then 2 ml. of 6 N sulfuric acid was added and this catalyzed the reaction so that the butene disappeared in less than an hour. The reaction mixture was extracted with two 100-ml. and one 50-ml. portions of ether, the extracts were neutralized with sodium bicarbonate and dried over sodium sulfate. Distillation at reduced pressure

(19) See Cottle and Powell, THIS JOURNAL, **58**, 2267 (1936).

(20) Weston, *Ind. Eng. Chem., Anal. Ed.,* **5**, 179 (1933).

(21) The N-bromacetamide was prepared very satisfactorily by the method of Mauguin, *Ann. chim.,* [8] **22**, 302 (1911).

(22) Sikhosherstov and Alekseev, *J. Gen. Chem.* (U. S. S. R.), **3**, 927 (1933); see *C. A.,* **28**, 3054 (1934).

yielded 34.4 g. (72.5%) of *threo*-3-bromo-2-butanol, b. p. (13 mm.) 49.5–51.0°, n^{25}D 1.4748. The physical properties of the bromohydrin and its complete solubility in fuming aqueous hydrobromic acid show that dibromobutane was not a contaminant of the bromohydrin prepared as described.

cis-2,3-Epoxybutane **from** *threo*-3-Bromo-2-butanol.—15.3 g. (0.1 mole) of bromohydrin was converted to oxide as previously described in the case of the chlorohydrins. A 3-necked 100-ml. flask was used and a few minutes were sufficient for the experiment. To the oxide-water distillate was added potassium carbonate, and the oxide layer was separated and dried with potassium carbonate; yield 6.0 g. (83%). On distillation through the Weston column, 80% of the distillate was at 59.8–60.1° and 20% at 58.2–59.8°. Thus, the oxide was essentially pure *cis* oxide.

Preparation of the 2,3-Dibromobutanes from the Bromohydrins.—130 g. of 48% hydrobromic acid is saturated with hydrogen bromide gas (from tetralin and bromine) in a glass ampoule at 0°, then 23.0 g. (0.15 mole) of the bromohydrin is added, the ampoule is sealed and the mixture is left at room temperature with occasional shaking. After a day or more, the ampoule is opened, the dibromide layer at the bottom is separated, washed with water and potassium carbonate solution, and dried over calcium chloride. The average yield is 30.4 g. (94%). On distillation through the Weston column, more than 95% of the distillate is at constant temperature (Table I).

Analysis of the 2,3-Dibromobutanes.—The properties of the 2,3-dibromobutanes obtained from the bromohydrins are given in Table I. Reference to boiling point and refractive index indicates that the dibromobutanes are essentially pure. A better criterion of purity is K_2, the second-order reaction rate constant[3] for the reaction of the dibromobutane with potassium iodide in methanol at 74.93°, or ε, the dielectric constant,[4] a property by means of which the isomers are most accurately identified. From K_2 and ε, also, it can be concluded that these 2,3-dibromobutanes are pure.

Summary

It has been found that fuming hydrobromic acid converts *dl-erythro-* and *dl-threo*-3-bromo-2-butanol quantitatively into *meso-* and *dl*-2,3-dibromobutane, respectively, with complete retention of configuration.

It is proposed: (a) that the closing of an oxide ring brought about by the action of alkali, involves an intramolecular variety of the usual bimolecular exchange reaction in which the attacking group is the adjacent negatively charged oxygen atom; (b) that the acid catalyzed opening of the oxide ring involves attack by a negative ion or by a solvent molecule at one of the two ring carbon atoms of a cyclic intermediate positive oxonium complex; and (c) that the transformation of the bromobutanols to the dibromides involves attack by a bromide ion at one of two carbon atoms of a cyclic intermediate positive bro-

mine complex. This positive bromine complex is identical with the intermediate usually assumed in connection with halogen addition to olefins,

and chemically is analogous to the oxide–proton complex.

The Reaction Steps in the Conversion of 2,3-Diacetoxybutane to 2,3-Dibromobutane

By S. Winstein and H. J. Lucas

The result obtained by Wilson and Lucas[1] that the reaction of 2,3-diacetoxybutane with fuming aqueous hydrogen bromide to replace the acetoxy groups by bromide gave rise to an odd number of Walden inversions, has led us to examine more closely the mechanism of the transformation and to study the presence or absence of Walden inversion at each of the several steps involved in the transformation.

Ester Splitting.—Splitting of esters by hydrogen bromide is little used except with carbohydrate derivatives.[2] Acetic acid is generally used as a solvent for the splitting of esters by hydrogen bromide.[2,3] Sapper did not use a solvent but studied[4] the splitting reaction with hydrogen bromide dissolved in the ester. He obtained a slow reaction and claimed the reaction to be even slower with aqueous hydrogen bromide. However, Sapper probably mistook an equilibrium effect for a rate effect. It has been our experience in this Laboratory that when aqueous hydrogen bromide gives the halide on reaction with an ester it does so much more rapidly than in acetic acid as solvent, and much more rapidly than reported by Sapper for the reaction without a solvent. In the presence of very high concentrations of hydrogen bromide, acid–alcohol–ester–water equilibria are established[4] quite rapidly so that when the splitting of an ester by hydrogen bromide is carried out in the presence of water, it becomes possible that the mechanism is chiefly one of hydrolysis of the ester to the alcohol and acid, with consequent reaction of the alcohol with hydrogen bromide. This mechanism seems to operate in the case of the diacetoxybutanes.

The Intermediates.—On the above basis, the intermediates in the transformation of 2,3-diace-toxybutane to 2,3-dibromobutane would be 3-acetoxy-2-butanol, 2-acetoxy-3-bromobutane, and 3-bromo-2-butanol. 2,3-Butanediol is ruled out as a possible intermediate because it was shown to undergo rearrangement[1] under the conditions of the experiments.

Isolation experiments in which reaction mixtures were neutralized and organic material extracted disclosed the fact that these formulated intermediates are present. The preparation of the inactive *erythro*- and *threo*-3-bromo-2-butanols and their reaction with hydrogen bromide with retention of configuration are reported elsewhere.[5]

The inactive 2-acetoxy-3-bromobutanes have been prepared by acetylation of the corresponding bromohydrins. One of the 3-acetoxy-2-butanols was prepared from *meso*-2,3-butanediol by acetylation, and from *trans*-2,3-epoxybutane by acetic acid addition, both preparations proving identical.

In regard to configurations, that of the *meso*-2,3-butanediol is known[1] and those of the inactive 3-bromo-2-butanols are discussed elsewhere.[5] Since no inversion can occur in the acetylation of these compounds, the configurations of 3-acetoxy-2-butanol (monoacetate of the glycol) and of the inactive 2-acetoxy-3-bromobutanes (acetates of the bromohydrins), are also known. Since the monoacetate from the *meso* glycol and the monoacetate from the known[1,6] *trans*-2,3-epoxybutane give the same 2,3-dibromobutane (Table I), a Walden inversion is proved in the opening of an oxide ring by acetic acid.

The synthesized predicted intermediates, in contrast to the 2,3-butanediols, reacted smoothly with aqueous fuming hydrobromic acid to give essentially quantitative yields of 2,3-dibromobutanes. The qualitative rates of dibromide formation are in such order as to make reasonable the formulation of these substances as intermediates.

(1) Wilson and Lucas, This Journal, **58**, 2396 (1936).

(2) E. Fischer, *Ber.*, **44**, 1899 (1911).

(3) (a) Perkin and Simonsen, *J. Chem. Soc.*, 855 (1905); (b) Tronow and Ssibgatullin, *Ber.*, **62**, 2850 (1929).

(4) Sapper, *Ann.*, **211**, 178 (1882).

(5) Winstein and Lucas, This Journal, **61**, 1576 (1939).

(6) Brockway and Cross, *ibid.*, **59**, 1147 (1937).