

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE ILLINOIS INSTITUTE OF TECHNOLOGY AND THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Role of Neighboring Groups in Replacement Reactions. III. Retention of Configuration in the Reaction of the 3-Bromo-2-butanols with Phosphorus Tribromide

By S. WINSTEIN

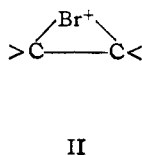
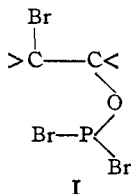
When the *erythro*- and *threo*-3-bromo-2-butanols react with phosphorus tribromide, the steric result is predominant retention of configuration. This is clear from Table I which lists the properties and compositions of the dibromobutanes derived from the bromohydrins.¹ It is seen that *erythro*-3-bromo-2-butanol gives a dibromide which is 95% *meso* and *threo*-3-bromo-2-butanol yields one which is approximately 90% *dl*. Thus, the retention of configuration in the reaction is rather high. Perhaps it would be higher if one learned if there should be made a correction for stereo-mutation of the dibromides under the reaction conditions.

TABLE I

PROPERTIES AND COMPOSITIONS OF 2,3-DIBROMOBUTANES PREPARED FROM 3-BROMO-2-BUTANOLS AND PHOSPHORUS

Bromohydrin	TRIBROMIDE	
	<i>erythro</i>	<i>threo</i>
Dibromide, b. p., °C.	74.0-74.2 (51 mm.)	76.0-76.7 (50 mm.)
Dibromide, n_D^{25}	1.5087	1.5115
Dibromide, K_D^2	0.0531	0.0324
Dibromide, % <i>meso</i>	95	11
Dibromide, % <i>dl</i>	5	89

The steric result of predominant retention of configuration may be accounted for by the operation, for the most of the reaction, of one or the other of two mechanisms. One mechanism is the cyclic rearrangement³ of an intermediate compound such as I.



The other mechanism involves the formation of the bromonium ion^{1,4} II. Then II reacts with bromide ion with another inversion.

(1) For a discussion of configuration see (a) Winstein and Lucas, *THIS JOURNAL*, **61**, 1576 (1939); (b) Winstein and Buckles, *ibid.*, **64**, 2780 (1942).

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

(3) (a) Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1252 (1937); (b) Hughes, Ingold and Whitfield, *Nature*, **147**, 206 (1941).

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

A definite choice between these two mechanisms would be possible from the results with active *threo*-3-bromo-2-butanol.^{1,4} However, it seems very probable that the retention of configuration observed is another result of the participation of a neighboring group (Br) in the replacement process. Lucas and Gould⁵ have shown that the 3-chloro-2-butanols react with thionyl chloride by way of a chloronium ion, in spite of the small tendency for a chlorine atom to participate in this manner.^{1,5} Thionyl chloride is the type reagent most addicted to the cyclic mechanism; thus there seems to be no great tendency for the cyclic rearrangement mechanism to operate in systems such as those under consideration.

It is interesting to compare the present results with the findings of Lucas and Gould⁵ for the reaction of phosphorus trichloride with the 3-chloro-2-butanols. Phosphorus trichloride reacted with the 3-chloro-2-butanols with predominant inversion of configuration, whereas phosphorus tribromide reacted with the bromohydrins with predominant retention of configuration. This would seem to be at least partly due to the greater tendency to participate in a replacement process that a neighboring bromine atom displays relative to a chlorine atom.

Experimental

erythro- and *threo*-3-Bromo-2-butanols.—The *erythro*-bromohydrin was an old sample prepared from pure low-boiling 2,3-epoxybutane.¹ It was quite dark by the time it was used in this work. The *threo*-bromohydrin was prepared as previously described¹ by way of 2-butene starting with *meso*-diacetate.

Conversion of Bromohydrins to Dibromides with Phosphorus Tribromide.—The bromohydrin (0.1-0.15 mole) was added dropwise with cooling and stirring to a 50% excess of phosphorus tribromide in a 3-necked flask equipped with a mercury-sealed stirrer, a reflux condenser and a dropping funnel and protected against moisture. With the *threo*-bromohydrin the addition was too rapid at first and the reaction mixture erupted once, causing some loss. There appears to be considerable heat evolution in some reaction step before the one producing the final products. After the bromohydrin was added, the reaction mixture was surrounded by a bath which was brought to 100° and kept at this temp. for one and one-half hours. Then the

(5) Lucas and Gould, *ibid.*, **63**, 2541 (1941).

reaction mixture was cooled and poured onto ice. The dibromide was separated with the aid of some carbon tetrachloride and the extract was washed with potassium carbonate. Distillation at reduced pressure through a Weston-type⁶ column yielded 39 and 42% yields of dibromides, from *threo*- and *erythro*-bromohydrins, respectively.

Analysis of Dibromides.—Comparison of the boiling points and refractive indices of the dibromides with the known^{2,7} properties of the 2,3-dibromobutanes indicates that the dibromide samples are largely either *meso*- or *dl*-2,3-dibromobutane. Also, the samples are contaminated with a trace of some low-refractive index impurity, possibly bromohydrin. For samples not absolutely free of foreign materials, the best method of analyzing a mixture of *meso*- and *dl*-2,3-dibromobutanes is by way of the rate constant K_2 for the reaction of the sample with potassium iodide in methanol.² Mr. Harold Pokras kindly determined these rates and they are included in Table I along

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

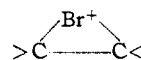
(7) Wilson and Lucas, *THIS JOURNAL*, **58**, 2396 (1936).

with the calculated compositions for the dibromide samples. The values of K_2 are slightly in doubt because of an uncertainty about the solvent correction of the solvent used in the rate measurements. The uncertainty in the compositions is about 4%.

Summary

The *erythro*- and *threo*-3-bromo-2-butanol are converted to dibromides by the action of phosphorus tribromide with a steric result of predominant retention of configuration.

It is considered probable that the steric result is due to the participation of the neighboring bromine atom in the replacement process with the formation of the bromonium ion



as an intermediate.

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The Role of Neighboring Groups in Replacement Reactions. IV. The Identity of Various Preparations of 1,2-Dibromocyclohexane

BY S. WINSTEIN

A number of reactions leading to 1,2-dibromocyclohexane have been investigated as to the steric result because of the interest in effects^{1,2} of neighboring groups on replacement processes.

All of the preparations of 1,2-dibromocyclohexane, summarized in Table I, have been compared with the dibromide from cyclohexene. The latter dibromide has been assigned the *trans*-configuration for the following reasons. First, the predominance of *trans*-addition of halogen to olefins³ leads one to this configuration. Further, the second-order rate constant at 74.90° for the reaction of cyclohexene dibromide with potassium iodide in methanol is 0.0204.⁴ This value compares favorably with 0.0301 for *dl*-2,3-dibromobutane⁵ and 0.0562 for *meso*-2,3-dibromobutane.⁵ Since the favored mechanism⁶ of the reaction is a *trans*-elimination of bromine by potassium iodide, the *trans*-configuration for cyclohexene dibromide is strongly indicated.

(1) (a) Winstein and Lucas, *THIS JOURNAL*, **61**, 1576 (1939); (b) Winstein and Lucas, *ibid.*, **61**, 2845 (1939).

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

(3) (a) Michael, *J. prakt. Chem.*, **62**, 344 (1893); (b) Terry and Eichelberger, *THIS JOURNAL*, **47**, 1067 (1925).

(4) Kindly determined by Dr. D. Pressman.

(5) Dillon, *THIS JOURNAL*, **54**, 952 (1932).

(6) Winstein, Pressman and Young, *ibid.*, **61**, 1645 (1939).

TABLE I
PROPERTIES OF DIFFERENT PREPARATIONS OF
1,2-DIBROMOCYCLOHEXANE

Prepn. no.	Source	n_D^{25}	M. P., °C.
1 ^a	Cyclohexene + Br ₂	1.5507	-4.5
2 ^b	<i>trans</i> -Diacetate + HBr - AcOH	1.5498	-6
3	<i>cis</i> -Diacetate + HBr - H ₂ O	1.5506	-4
4	<i>cis</i> -Diacetate + HBr - AcOH	1.5504	-4
5 ^c	Oxide + HBr - H ₂ O	1.5504	-5
6	Bromohydrin from olefin + HBr - H ₂ O	1.5506	-4
7	Bromohydrin from ketone + HBr - H ₂ O	1.5490	-6
8	Bromohydrin from oxide + PBr ₃	1.5497	-8
9	Bromohydrin <i>p</i> -toluenesulfonate + HBr - H ₂ O	1.5504	-4

^a d_{25}^{25} 1.7826, $M_R D$ 43.28. ^b K_2 at 74.90° for reaction with KI is 0.0203. ^c K_2 at 74.90°, 0.0205.

One group of dibromocyclohexane samples was prepared from 2-bromocyclohexanol. The 2-bromocyclohexanol, which is prepared from cyclohexene and which is presumably^{2,7} of the *trans*-configuration, reacts smoothly with fuming hydrobromic acid to yield dibromide. In preparing

(7) Bartlett, *ibid.*, **57**, 224 (1935).