The Reaction of cis-1,4-Epoxycyclohexane with Hydrochloric Acid and with Hydrobromic Acid

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Crystalline trans-4-chlorocyclohexanol has been prepared from cis-1,4-epoxycyclohexane by reaction of the latter compound with aqueous hydrochloric acid at 25°. At higher temperatures both the cis-epoxide and the trans-chlorohydrin gave a mixture of dichlorocyclohexanes from which two crystalline compounds were obtained. One of these compounds is the known trans-1,4-dichlorocyclohexane and the other is probably the corresponding cis isomer. Reaction of the epoxide with boiling aqueous hydrobromic acid gave a complex reaction product from which the known cis- and trans-1,4-dibromocyclohexanes were isolated.

Crystalline trans-4-chlorocyclohexanol, m.p. 82–83°, phenylurethan, m.p. 134–135°,[3] has been prepared in good yield by the reaction of cis-1,4-epoxycyclohexane[3,4] with concentrated hydrochloric acid at room temperature. At the time this investigation was completed trans-4-chlorocyclohexanol had been obtained previously only as a liquid contaminated with the cis isomer by the reaction of lithium chloride with the monotosylate of cis-1,4-cyclohexanediol[3] or by the reaction of a mixture of cis- and trans-1,4-cyclohexanediol with hydrochloric acid.[5] However, it has been shown recently that crystalline trans-4-chlorocyclohexanol, m.p. 82–83°, may be prepared by the reaction of the 1,4-epoxide, at its boiling point, with anhydrous hydrogen chloride.[6]

When either cis-1,4-epoxycyclohexane or trans-4-chlorocyclohexanol is heated with concentrated hydrochloric acid at 105°, a mixture of dichlorocyclohexanes is obtained. Fractionation of this mixture gave two crystalline dichlorocyclohexanes, m.p. 100–102° and 15–16°, and a liquid fraction of the same elementary composition. The higher melting dichlorocyclohexane is the known trans-1,4-dichlorocyclohexane[7] and it is likely that the other solid product, m.p. 15–16°, is the previously undescribed cis-1,4-dichlorocyclohexane. An examination of the infrared spectra of the various fractions suggested that the liquid dichlorocyclohexane fraction was not a simple mixture of the above two compounds, although both were undoubtedly present. It is possible that a substantial portion of the liquid fraction is a mixture of cis- and trans-1,3-dichlorocyclohexane.[3]

It is noteworthy that an increase in the reaction time, from three to five hours, resulted in an increase, from 15 to 25%, in the amount of crystalline trans-1,4-dichlorocyclohexane that could be isolated from the reaction mixture. Furthermore, when a mixture of cis-1,4-dichlorocyclohexane and the dichlorocyclohexanes of unknown structure was heated with aqueous hydrochloric acid at 105° a small amount of trans-1,4-dichlorocyclohexane was

obtained. Conversely, when the trans-compound was similarly treated a limited amount of the starting material was transformed into the cis-isomer and the dichlorocyclohexanes of unknown structure.

When cis-1,4-epoxycyclohexane was heated with aqueous hydrobromic acid trans-1,4-dibromocyclohexane, m.p. 110–112°,[4,8] was isolated as the main crystalline product with a small amount of cis-1,4-dibromocyclohexane, m.p. 45–47.5°,[7] also being obtained. However, the major product of the above reaction was a liquid which was not definitely identified. Its physical properties were such that its separation from the two isomeric 1,4-dibromocyclohexanes by fractional distillation was only partially successful and elementary analyses clearly indicated that it could not be regarded as a mixture of isomeric dibromocyclohexanes. Rothstein[8] states that three dibromides are obtained by the reaction of 1,4-dihydroxycyclohexane with hydrobromic acid, i.e., cis- and trans-1,4-dibromocyclohexane and a third product which is apparently a mixture of the isomeric 1,3-dibromocyclohexanes.

With the acyclic 1,2-halohydrins or the corresponding glycol monoacetates Lucas and Winstein and their collaborators[9] have found that cyclic bromonium, iodonium or acetonium intermediates appear to be formed with considerably greater ease than are the analogous chloronium intermediates. The evidence for the existence of cyclic intermediates derived from certain of the trans-1,4-disubstituted cyclohexanes rests upon the formation of principally trans-1,4-diiodocyclohexane from the bistosylates of both cis- and trans-1,4-cyclohexanediol by reaction of the latter compounds with sodium iodide in acetone[3] and upon the isolation of trans-1,4-diacetoxycyclohexane as the only crystalline product of the reaction of cis-1,4-epoxycyclohexane with acetic anhydride.[10] In the former experiments the reaction products are those expected on the basis of an odd number of inversions with the formation of a cyclic iodonium intermediate in the case of the cis-bistosylate and an even number of inversions with the trans-bistosylate where the formation of a cyclic iodonium compound from the intermediate cis-monotosylate of 4-iodocyclohexanol is not likely.[9] In the latter experiment the

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(3) L. N. Owen and P. A. Robins, J. Chem. Soc., 320 (1949).

(4) R. Olberg, H. Pines and V. Ipatieff, This Journal, 66, 1096 (1944).

(5) S. Sabetay and L. Palfray, Bull. soc. chim., 43, 906 (1928).

(6) E. A. Fehnel, S. Goodyear and J. Berkowitz, This Journal, 73, 4978 (1951).

(7) L. Palfray and B. Rothstein, Compt. rend., 189, 701 (1929).

(8) B. Rothstein, Ann. chim., 14, 461 (1930).

(9) (a) H. J. Lucas and C. W. Gould, This Journal, 63, 2541 (1941); (b) S. Winstein and R. E. Buckles, ibid., 64, 2780 (1942); (c) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, ibid., 70, 816 (1948); (d) S. Winstein, E. Grunwald and L. L. Ingraham, ibid., 70, 821 (1948).

(10) W. Nudenberg and L. W. Butz, ibid., 66, 307 (1944).

trans-diacetate is the expected product if the reaction involves a cyclic acetonium intermediate and proceeds with an odd number of inversions.

The fact that Olberg, Pines and Ipatieff[4] obtained only the *trans*-1,4-dibromocyclohexane from the reaction of *cis*-1,4-epoxycyclohexane with aqueous hydrobromic acid might lead one to believe that the reaction proceeded *via* an odd number of inversions and the formation of a cyclic bromonium intermediate. While it is true that the amount of *trans*-1,4-dibromocyclohexane obtained in the present investigation greatly exceeded the amount of isolable *cis*-isomer, the low yield of the former compound, *viz.*, 11%, certainly affords one the opportunity to question the validity of postulating the existence of a cyclic bromonium intermediate in this particular instance. It is not apparent what considerations prompted Owen and Robins[3] to postulate two basically different mechanisms for the reaction of *cis*-1,4-epoxycyclohexane with hydrobromic acid and with acetic anhydride.

The observation that the amount of crystalline *trans*-1,4-dichlorocyclohexane that can be obtained from the reaction of *cis*-1,4-epoxycyclohexane with aqueous hydrochloric acid at 105° increases with increasing reaction time suggests that the the the former compound is not a primary reaction product. While it is probable that the above reaction proceeds through the intermediate *trans*-1,4-chlorohydrin the designation of the *cis*-1,4-dichloride as the primary reaction product rests in large part on an assumed inability of the *trans*-chlorohydrin to form a cyclic chloronium intermediate rather than upon the results obtained in the present investigation where secondary reactions appear to have played a major role.

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Experimental[11]

cis-1,4-Epoxycyclohexane (I).—I, b.p. 119–121° (746 mm.), $n^{25}D$ 1.4467 was obtained in 50% yield from the mixture of dihydroxycyclohexanes resulting from the catalytic reduction of hydroquinone with Raney nickel.[4]

trans-4-Chlorocyclohexanol (II).—A solution of 26.7 g. of I in 100 ml. of 12 N hydrochloric acid was allowed to stand at 25° for five days, 100 ml. of water added, the phases separated, the aqueous phase extracted with ether, the ethereal extracts added to the non-aqueous phase, the latter washed with water until free of acid, dried, and fractionally distilled to give 28.5 g. (78%) of crude II, b.p. 134–135° (38 mm.), m.p. 60–76°. Two recrystallizations of 14 g. of crude II from 60–70° ligroin gave 8.2 g. of II, m.p. 82–83°.

Anal. Calcd. for $C_6H_{11}OCl$ (134.6): C, 53.5; H, 8.2; Cl, 26.4. Found: C, 53.7; H, 8.2; Cl, 26.8.

II was converted into the phenylurethan, m.p. 134–135°, after one recrystallization from 60–70° ligroin; lit.[3] m.p. 133–134°.

Anal. Calcd. for $C_{13}H_{16}O_2NCl$ (253.7): C, 61.6; H, 6.4. Found: C, 61.6; H, 6.4.

cis-1,4-Dichlorocyclohexane (III), *trans*-1,4-Dichlorocyclohexane (IV) and Isomeric Dichlorocyclohexanes (V).— A solution of 26.0 g. of I in 300 ml. of 12 N hydrochloric acid contained in a sealed tube was heated at 105° for five
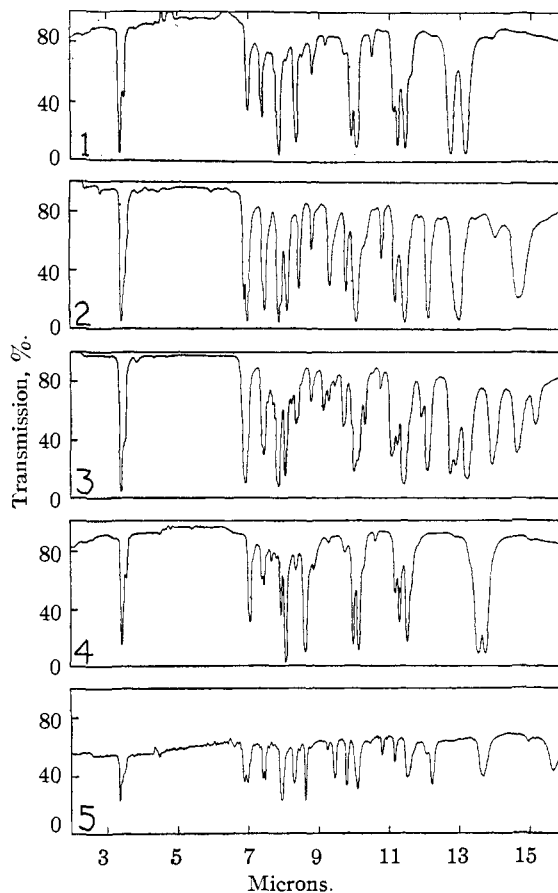
(11) All melting points are corrected.

Fig. 1.—Infrared spectra: 1, compd. IV in carbon disulfide; 2, compd. III; 3, mixture V; 4, compd. VII in carbon disulfide; 5, compd. VI.

hours with frequent shaking. To the cooled reaction mixture was added 300 ml. of water, the phases separated, the aqueous phase extracted with ether, the ethereal extracts added to the non-aqueous phase, the latter washed with water until free of acid, dried, and fractionally distilled to give 28.5 g. (70%) of a mixture of dichlorocyclohexanes, b.p. 92–96° (25 mm.), collected in several fractions. The fractions were stored at 5° and the crystalline solid which had formed, principally in the lower boiling fractions, was separated to give 7.0 g. (17%) of IV, m.p. 70–80°, and 21.5 g. (53%) of a mixture of dichlorocyclohexanes, $n^{25}D$ 1.491. Analysis of the mixture gave the following results.

Anal. Calcd. for $C_6H_{10}Cl_2$ (153.0): C, 47.1; H, 6.6. Found: C, 47.1; H, 6.6.

IV, m.p. 70–80°, was recrystallized from 60–70° ligroin to give IV, m.p. 100–102°; lit.[7] m.p. 102°.

Anal. Calcd. for $C_6H_{10}Cl_2$ (153.0): C, 47.1; H, 6.6. Found: C, 47.1; H, 6.5.

The infrared spectrum of IV is given in Fig. 1.

Since examination of the infrared spectra of several of the liquid dichlorocyclohexane fractions revealed differences in the relative intensities of the absorption bands exhibited by these fractions (*cf.* Fig. 1) 40 g. of the mixture of dichlorocyclohexanes, remaining after the isolation of IV, was distilled through a 20-plate column to give 15 fractions, b.p. range 90–95° (22 mm.). The fractions were then stored at 0° for several days.

From fractions 11–15, *i.e.*, the higher boiling fractions, there was obtained 10 g. of III, m.p. 15–16°, b.p. 94–95° (22 mm.), $n^{23.5}D$ 1.492.

Anal. Calcd. for $C_6H_{10}Cl_2$ (153.0); C, 47.1; H, 6.6. Found: C, 47.4; H, 6.8.

The infrared spectrum of III is given in Fig. 1.

From fractions 1–10, *i.e.*, the lower boiling fractions, there was obtained 5 g. of IV and 20 g. of V, $n^{23.5}D$ 1.492. The infrared spectrum of V (*cf.* Fig. 1) suggested that V is not

simply a mixture of III and IV but is possibly a mixture of 1,3-dichlorocyclohexanes contaminated with small amounts of III and IV. Analysis of V gave the following results.

Anal. Calcd. for $C_6H_{10}Cl_2$ (153.0): C, 47.1; H, 6.6. Found: C, 46.9; H, 6.5.

Treatment of II with 12 N hydrochloric acid, as described above, gave a mixture of dichlorocyclohexanes in 88% yield. Of this product 25% was subsequently isolated as IV and the remainder as a mixture of III and V.

When I was heated with 12 N hydrochloric acid at 105° for three hours only 15% of the total dichlorocyclohexane fraction was recovered as crystalline IV in contrast to the 25% yield obtained when the time of heating was five hours.

cis-1,4-Dibromocyclohexane (VI) and *trans*-1,4-Dibromo-cyclohexane (VII).—I, 18.1 g., was heated under refluxing conditions with 60 ml. of 48% hydrobromic acid for two hours. In the absence of any separation of a solid phase,[4] the products were isolated as described above for the di-chlorocyclohexanes. Distillation gave 16.3 g. of a fraction b.p. 100–104° (13 mm.) and 6 g. of a high boiling residue. Storage of the distillate at 0° gave 4.7 g. (11%) of VII, m.p. 110–112°, after one recrystallization from 60–70° ligroin, lit.[4,8] m.p. 112°, and 11.6 g. of a liquid. Analysis of VII gave the following results.

Anal. Calcd. for $C_6H_{10}Br_2$ (242.0): C, 29.8; H, 4.2. Found: C, 29.8; H, 4.3.

Further fractionation of the liquid through a 20-plate column gave a major portion consisting of a number of fractions, b.p. 104–105° (13 mm.), and a final fraction, b.p. 105–107° (13 mm.). From the latter fraction, after storage at 0°, there was obtained 0.5 g. of VI, m.p. 45–47.5°, lit.[8] m.p. 48°. Elementary analysis[12] and an examination of the infrared spectrum of VI indicated that the product isolated was contaminated with a small amount of material of lesser halogen content.

Although the various fractions comprising the major portion of the distillate exhibited very similar infrared spectra, elementary analysis clearly indicated that this material was not a pure compound but a mixture of components of varying halogen content. Attempts to resolve this mixture were unsuccessful.

Infrared Spectra.—The infrared spectra given in Fig. 1 were determined with a Baird infrared spectrophotometer using either liquid films (0.001″) or 25% solutions in carbon disulfide (0.1 mm. cell thickness).

(12) Found: C, 30.9; H, 4.3.

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The Preparation and Properties of Triphenylsulfonium Polyhalides[1]

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Triphenylsulfonium tribromide, triiodide and dichlorobromide have been prepared by the action of the appropriate halogen on triphenylsulfonium bromide in aqueous solution. Triphenylsulfonium chloride and iodide are also described for the first time. Triphenylsulfonium pentabromide and probably higher polybromides were obtained by action of bromine vapor on triphenylsulfonium bromide or tribromide. The ultraviolet and infrared absorption spectra of these substances have been examined in an attempt to deduce structural information about them. Electrolysis of triphenylsulfonium salts has been found to result in decomposition of the triphenylsulfonium cation to diphenyl sulfide and polymeric materials.

In contrast to the more widely known trisubstituted sulfonium halides, trisubstituted sulfonium polyhalides have received only limited investigation. Steinkopf and Müller[2] report the preparation of phenyldimethylsulfonium triiodide by action of methyl iodide on diphenyl disulfide, and Werner[3] has prepared trimethylsulfonium tetrachloroiodide by the action of chlorine on trimethylsulfonium iodide. Treatment of the latter compound with sodium hydroxide produced trimethylsulfonium dichloroiodide. We became interested in a more detailed study of such polyhalides by way of electrolysis experiments described briefly below. The present investigation is concerned with the preparation of triphenylsulfonium (TPS) polyhalides and an attempt to obtain structural information concerning them.

In general a TPS polyhalide resulted by action of an aqueous solution of a halogen on a TPS halide. Thus TPS tribromide was produced in good yield by treating an aqueous solution of TPS bromide[4] with bromine water. TPS triiodide resulted when TPS bromide reacted with an iodine–potassium iodide solution. An attempt was made to prepare TPS trichloride by action of chlorine water on TPS bromide in the presence of a large excess of

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(2) W. Steinkopf and S. Müller, *Ber.*, **56**, 1926 (1923).

(3) E. A. Werner, *J. Chem. Soc.*, **89**, 1625 (1906).

(4) B. S. Wildi, S. W. Taylor and H. A. Potratz, THIS JOURNAL, **73**, 1965 (1951).

chloride ion. The product, however, proved to be TPS dichlorobromide. Accordingly, TPS chloride was prepared by neutralization of TPS hydroxide solution[4] with hydrochloric acid. The action of chlorine water on aqueous TPS chloride, however, produced no insoluble trichloride. When TPS chloride was treated with bromine water, TPS dichlorobromide rather than TPS dibromochloride was formed.

The physical properties of the TPS polyhalides are in marked contrast to those of the simple TPS halides. The latter are white, high-melting solids which, with the exception of the iodide, are highly water soluble and insoluble in most organic solvents. The polyhalides are relatively low-melting solids, virtually insoluble in water, but soluble in dilute alkali and in many typical organic solvents. The colors of the TPS polyhalides vary with the halogen present; the dichlorobromide is cream-yellow, the tribromide bright orange, and the triiodide red-purple.

Both TPS bromide and tribromide show the interesting property of being deliquescent with respect to bromine. When either salt is exposed to bromine vapor the latter is absorbed until the salt dissolves into a red liquid. When this is exposed to air bromine is lost rapidly, crystallization occurs, and the material finally reverts to TPS tribromide. When the loss of bromine from the red liquid was followed quantitatively (Fig. 1) it was found that the weight loss reached a plateau