[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Role of Neighboring Groups in Replacement Reactions. XXI. Front-side Participation of the Acetoxy Group. Catalytic Effect of Acetic Acid on the Reaction of Glycols with Hydrogen Chloride[1,2]

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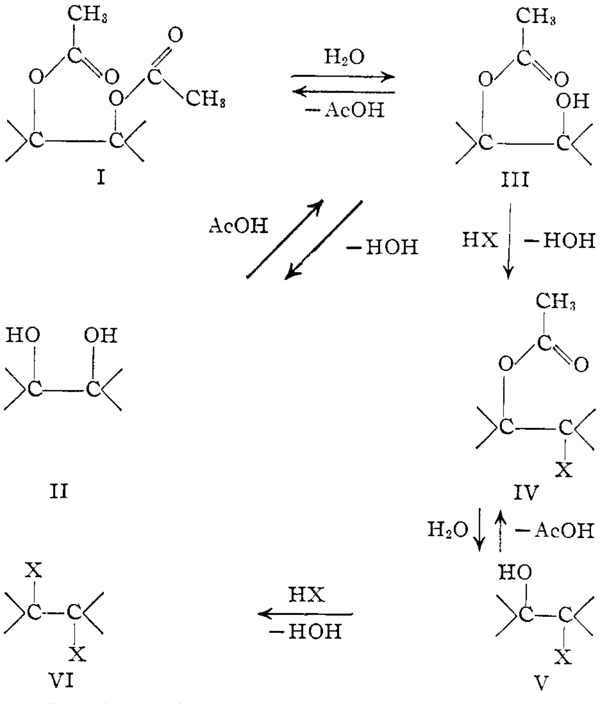
The present work was directed toward elucidation of the mechanism of the substitution reaction which introduces the first of the two halogen atoms in the stereospecific conversion of diacetates to dibromides with fuming hydrobromic acid. To isolate the first replacement reaction for inspection, fuming hydrochloric instead of hydrobromic acid was employed. The *cis*- and *trans*-1,2-cyclohexanediols and their acetates, as well as ethylene glycol, were treated with the hydrochloric acid reagent. Chlorocyclohexanol or its acetate was not formed from *trans*-1,2-cyclohexanediol or its diacetate. On the other hand, chlorocyclohexanol or its acetate, exclusively *trans*, was obtained from either *cis*-1,2-diacetoxycyclohexane or the *cis*-glycol to which some acetic acid was added. No chlorohydrin was obtained from *cis*-glycol in the absence of the acetic acid catalyst. Analogously, ethylene chlorohydrin was obtained from ethylene glycol in the presence of, but not in the absence of added acetic acid. The suggested mechanism for the introduction of the halogen atom involves the reaction of the glycol monoacetate in the tautomeric ortho-monoacetate form. The latter ionizes to the olefin acetoxonium ion, which occasionally reacts with chloride ion to yield acetoxy-chloride. This mechanism, involving "front-side participation" of an acetoxy group, explains: (i) the catalytic effect of acetic acid; (ii) the successful reaction of the *cis*-glycol derivative contrasted with the failure of the *trans*; (iii) the stereochemical result of clean-cut inversion of configuration in the conversion of diacetate or glycol to chlorohydrin.

Introduction

There are a number of known cases of stereospecific reaction between vicinal diacetates and hydrobromic or hydrochloric acids. With fuming hydrobromic acid, diacetate I is converted to dibromide VI by a series of hydrolysis and replacement reactions.[3] With hydrochloric acid,[4] the diacetate I is converted only to the chlorohydrin V because the subsequent reaction of the chlorohydrin with hydrochloric acid is so slow.[4,5] The usual stereochemical results[3] involve inversion in the first replacement reaction, producing the halohydrin acetate IV, and over-all retention of configuration in the second replacement reaction which converts halohydrin V to dihalide VI; the latter reaction proceeds by way of the olefin halonium ion. Consequently, dibromides VI are customarily formed with an over-all odd number of Walden inversions. For example, *dl*-2,3-diacetoxybutane is converted to *meso*-dibromobutane, whereas *meso*-diacetoxybutane is converted to *dl*-dibromobutane.[6] Also, *cis*-1,2-diacetoxycyclohexane is converted smoothly to *trans*-1,2-dibromocyclohexane.[7] Chlorohydrins V are formed from diacetates with one inversion of configuration. Thus, *meso*-2,3-diacetoxybutane yields *dl*-*threo*-3-chloro-2-butanol.[4] The high degree of stereochemical specificity of this latter conversion is further demonstrated by the conversion of D(+)-2,3-diacetoxybutane to a chlorohydrin which was converted through a series of reactions to a 2-butanol which was 99% optically pure.[8]

In the chain of reactions from diacetate I to dihalide VI, the substitution reaction which introduces the first halogen atom with inversion of configuration is of considerable interest.[3] This reaction must benefit in some special way from the presence of an acetoxy group in the molecule undergoing reaction. Thus, butylene glycol, in contrast with its diacetate, produces mainly 2-butanone.[6] On the other hand, the addition of some acetic acid to the glycol–hydrobromic acid solution does[3] cause formation of dibromide VI, presumably because the acetic acid esterifies the glycol II to monoacetate III. There are many known instances[9] where diacetate is superior to glycol for formation of dibromides with fuming hydrobromic acid. Obviously, replacement with inversion is



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[1] Most of the material of this paper was reported in summary before the Organic Division of the American Chemical Society, St. Louis, September, 1948. This paper was presented at the Regional Meeting of the Southern California Section of the American Chemical Society, Los Angeles, May 8, 1954.

[2] Abstracted from part of the Ph.D. thesis of Robert Boschan, UCLA, 1950.

[3] S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1576, 1581, 2845 (1939).

[4] H. J. Lucas and C. Gould, *ibid.*, **63**, 2541 (1941).

[5] (a) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780 (1942); (b) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948).

[6] C. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

[7] S. Winstein, *ibid.*, **64**, 2792 (1942).

[8] P. J. Leroux and H. J. Lucas, *ibid.*, **73**, 41 (1951).

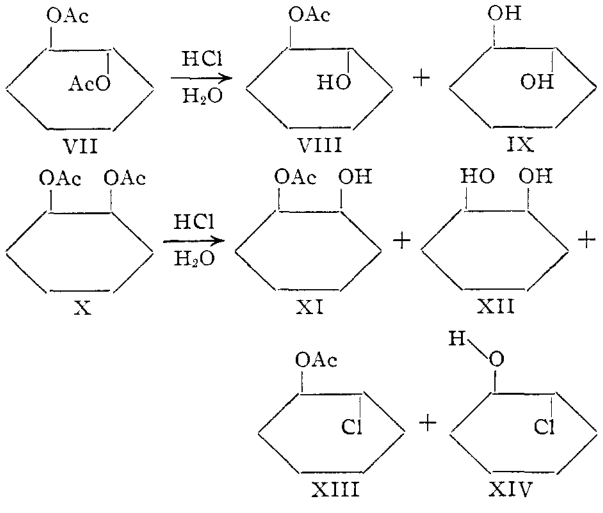
[9] *E.g.*, W. G. Young, Z. Jasaitis and L. Levanas, *ibid.*, **59**, 403 (1937).

made to dominate over pinacol rearrangement by the presence of the acetoxy group in the molecule undergoing substitution.

In the present paper, we report and discuss the implications of a few further experiments which have a bearing on the mechanism of this first replacement reaction. These experiments follow up the observation that *trans*-1,2-diacetoxycyclohexane, in contrast with the *cis* isomer, does not yield dibromide on treatment with fuming hydrobromic acid.[7] In the present work, we employed fuming hydrochloric acid in order to isolate the first replacement reaction for inspection. Not only were cyclohexanediols and their derivatives employed, but also ethylene glycol was studied. Further, trichloroacetates instead of acetates were examined briefly.

Results

Treatment of *trans*-1,2-diacetoxycyclohexane VII with fuming hydrochloric acid in a glass bomb at room temperature for 7 days gave rise only to the normal hydrolysis products, the monoacetate VIII and the glycol IX. The analogous reaction with *cis*-1,2-diacetoxycyclohexane X yielded, however, in addition to hydrolysis products, XI and XII, appreciable amounts of *trans*-2-chlorocyclohexanol XIV and its acetate XIII. The chlorohydrin XIV was characterized by conversion to its α-naphthylurethan. The exclusively *trans*-configuration of the chlorohydrin XIV was shown by its behavior toward alkali. As Bartlett[10] has shown, the *trans*-chlorohydrin yields oxide, but the *cis*-chlorohydrin yields cyclohexanone. Thus, the presence of *cis*-chlorohydrin could be detected by a test for cyclohexanone in the product of reaction with alkali. However, no cyclohexanone could be detected in the reaction product, indicating the absence of *cis*-chlorohydrin in the chlorohydrin product XIV from the diacetate X. Thus, the over-all stereochemical result from diacetate X to chlorohydrin XIV was clean inversion.



As was observed[3] in the case of the reaction of 2,3-butylene glycol with hydrobromic acid, the reaction between *cis*-1,2-cyclohexanediol XII and fuming hydrogen chloride in the presence of acetic acid was found to proceed smoothly to give the same products as were obtained from diacetate X. To reduce the number of products, the ether-extractable components were acetylated, so that only diacetate X and chloroacetate XIII were obtained. The yield of chloroacetate XIII was 74%. When the *cis*- and *trans*-cyclohexanediols were treated with fuming hydrochloric acid in the absence of acetic acid, no chlorohydrins were formed; only unreacted glycol and non-volatile tarry material were found.

Ethylene glycol was similar to *cis*-1,2-cyclohexanediol in its behavior toward fuming hydrochloric acid. Ethylene glycol is quite inert to fuming hydrochloric acid, yielding practically no ether-extractable product on treatment with fuming hydrochloric acid in a glass bomb for 6 days. In the presence of some acetic acid, however, a similar treatment produced ethylene chlorohydrin in approximately 64% yield. The chlorohydrin was characterized by conversion to its α-naphthylurethan.

Mechanism.—It is quite obvious that any mechanism for the conversion of glycol to halohydrin must explain: (i) why the acetoxy group is necessary for facile reaction; (ii) why the *trans*-cyclohexanediol fails to react and (iii) why clean inversion of configuration attends the replacement process. One could consider[3] a mechanism involving SN2 displacement of water from the conjugate acid of the monoacetate by halide ion in the sense of formula XV or XVI. Such a mechanism is improbable for several reasons. First, it is not clear why such an SN2 displacement should take place with the molecules containing the neighboring acetoxy group but be absent in the case of molecules such as the glycol with the neighboring hydroxyl group or the chlorohydrin with the neighboring chlorine atom. There is little to suggest why such a displacement should be so much more rapid with the neighboring acetoxy group than with the neighboring hydroxyl or chlorine atoms. In the case of displacement of chloride by iodide ion, available reactivity measurements show 2-acetoxyethyl chloride to be actually somewhat less reactive than 2-hydroxyethyl chloride.[11] Further, such a mechanism does not explain why the cyclohexanediol derivatives are so reactive relative to the ethylene glycol derivatives, for it is well known that the cyclohexane structure is very inert[11a,12] to bimolecular nucleophilic displacement reactions.

A further difficulty with an SN2 mechanism is that it does not explain why the *cis*-cyclohexanediol derivative reacts with hydrochloric acid but the *trans*-isomer does not. Conformational considerations suggest no reason for such a difference on the basis of a bimolecular displacement reaction. The preferred conformations would be predicted[13] to be XVIIA for the *trans*-isomer and XVIIIA for the *cis*-isomer. In both of these, the hydrogen bond in the sense of XVI is possible. Since the preference for the preferred conformation on the part of the *trans*- and *cis*-isomers is not terribly large,[13] and the rates of bimolecular nucleophilic displace-

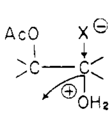
(10) P. D. Bartlett, This Journal, **57**, 224 (1935).

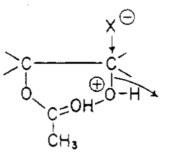
(11) (a) J. B. Conant, W. Kirner and R. E. Hussey, *ibid.*, **47**, 488 (1925); (b) W. Kirner, *ibid.*, **48**, 2745 (1926).

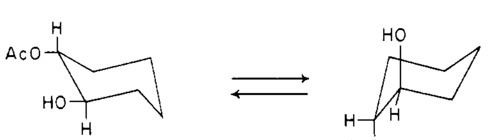
(12) P. D. Bartlett and L. Rosen, *ibid.*, **64**, 543 (1942).

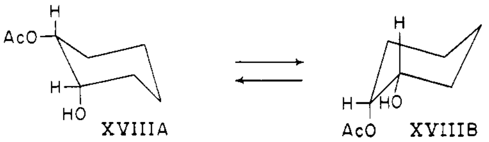
(13) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

ment do not differ enormously between *equatorial* and *axial* positions of leaving groups on the cyclohexane ring,[14,15] no large difference in behavior between the *cis*- and *trans*-cyclohexanediol derivatives would be predicted.

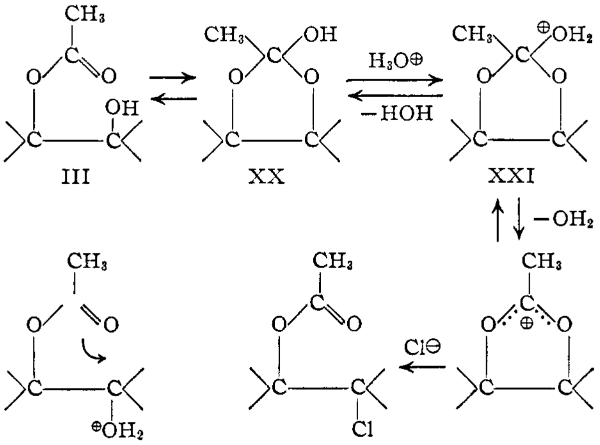

XV


XVI


XVIIA XVIIB


XVIIIA XVIIIB

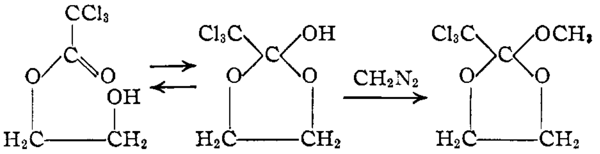
It seems obvious that some other mechanism is much preferred over one which involves the S_N2 displacement reaction. Whatever this mechanism is, the facts make it obvious that it is also preferred over one which begins with alkyl–oxygen ionization in the conjugate acid of the monoacetate, assisted by neighboring acetoxy group participation.[5,16] Such a process is depicted in XIX. In this case, *trans*-glycol derivative would be much more reactive[5b,17] than the *cis*-isomer, contrary to the facts. We suggest that the preferred mechanism of formation of chlorohydrin acetate XXIII from glycol monoacetate III involves what we term "front-side participation" of the acetoxy group. This gives rise to the ortho-monoacetate form XX, tautomeric[16] with the ordinary form of the monoacetate III. Acyl–oxygen ionization of the ortho-monoacetate XX by way of the conjugate acid XXI should be extremely facile.[16c] Thus, the rate of formation of the olefin acetoxonium ion[5] XXII can be very rapid from a monoacetate III in fuming hydrochloric or hydrobromic acid. Although the cation XXII is very often returned to XXI and on to XX and III, judging by the indications from other work,[16] apparently it reacts sufficiently often with halide ion[16c] with inversion of configuration to yield XXIII, so that it is the intermediate for the formation of chloroacetate XXIII. This mechanism explains the special role of the acetoxy group, and, also, it explains the comparable behavior of ethylene glycol and cyclohexanediol. Further, it explains the difference in behavior of the *cis*- and *trans*-cyclohexanediols, for it requires formation of a five-membered ring fused to a six-membered ring. With the *cis*-cyclohexanediol, the five-ring is fused *cis* to the six-ring, while with the *trans*-cyclohexanediol, the fusion must be *trans*. The latter is sufficiently more difficult to explain the lack of reaction of the *trans*-cyclohexanediol



III XX XXI

XIX XXIII XXII

The Trichloroacetoxy Group.—Since the special function of the acetoxy group involved formation of the ortho-monoacetate XX, we were prompted to explore the trichloroacetoxy group in place of the acetoxy group. With the trichloroacetoxy group, there is considerably greater tendency for a glycol monoester to exist as the ortho form. Thus, in the case of ethylene glycol monotrichloroacetate XXIV, methylation with diazomethane gives the orthoester[18] XXVI. While the trichloroacetoxy group might be anticipated to be favorable to the ortho-monoacetate form XX, it could also be expected to be unfavorable to the generation of the olefin acetoxonium ion XXII due to the presence of the three chlorine atoms. The latter point is illustrated by the very low rate of acetolysis observed for *trans*-2-trichloroacetoxycyclohexyl *p*-toluenesulfonate. At 99.7° the observed rate constant,[19] 3.5×10^{-7} sec.$^{-1}$, is almost 3 powers of ten slower than the value for *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate.[20] In practice, the trichloroacetoxy group failed to play the role of the acetoxy group in the hydrochloric acid reaction. When *cis*- and *trans*-2-trichloroacetoxycyclohexanol were subjected to the action of concentrated hydrochloric acid, nearly quantitative yields of the corresponding glycols were isolated, hydrolysis being the predominant reaction.



XXIV XXV XXVI

The reaction of *cis*-cyclohexanediol with trichloroacetyl chloride in dry ether was studied. In this system, the hydrogen chloride liberated in esterification with the acid chloride would be given an oppor-

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[14] S. Winstein, D. Darwish and N. J. Holness, THIS JOURNAL, **78**, 2915 (1956).

[15] E. L. Eliel and R. S. Ro, *Chemistry and Industry*, 251 (1956).

[16] (a) S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2787 (1942); (b) S. Winstein, H. V. Hess and R. E. Buckles, *ibid.*, **64**, 2796 (1942); (c) S. Winstein and R. E. Buckles, *ibid.*, **65**, 613 (1943).

[17] S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[18] H. Meerwein and H. Sönke, *J. prakt. Chem.*, **137**, 295 (1933).

[19] A. Scattergood and H. M. Hershenson [THIS JOURNAL, **72**, 2808 (1950)] have reported a value of 1.9×10^{-7} sec.$^{-1}$ at 91°.

[20] S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948).

tunity to react with the monotrichloroacetate to give *trans*-2-chlorocyclohexyl trichloroacetate. However, a product was obtained which was shown to be the monotrichloroacetate of *cis*-cyclohexanediol. As a matter of fact, this method was found to be the best way to prepare *cis*-2-trichloroacetoxycyclohexanol, one mole of trichloroacetyl chloride being used per mole of *cis*-cyclohexanediol. Attempted preparation of the *cis*-monotrichloroacetate from equimolar amounts of *cis*-1,2-cyclohexanediol and trichloroacetyl chloride in pyridine gave rise to a reaction product from which glycol and bis-trichloroacetate were isolated.

Experimental

***cis*- and *trans*-1,2-Cyclohexanediols and their Diacetates.**—These compounds were prepared by the methods previously described.[5,7,16]

Reaction of *trans*-1,2-Diacetoxycyclohexane with Fuming Hydrochloric Acid.—To 30.0 g. (0.15 mole) of *trans*-1,2-diacetoxycyclohexane in a flask bomb was added 43.0 ml. of concd. hydrochloric acid. The mixture was cooled to *ca.* −15°, and gaseous hydrogen chloride was passed in until the weight of the mixture was constant, 19.9 g. of gaseous hydrogen chloride being absorbed. The closed flask bomb was set aside for seven days. Then it was opened carefully, and the reaction mixture was poured very slowly into a liter of saturated aqueous sodium bicarbonate solution containing excess solid bicarbonate. The resulting mixture was extracted with three portions of ether (400 ml. total). The ether extract was dried over anhydrous potassium carbonate and subjected to fractional distillation. The following fractions were collected at 12 mm.: (1) 0.3 g., b.p. 116–118°, $n^{25}\mathrm{D}$ 1.4617; (2) 0.7 g., b.p. 118–119°, $n^{25}\mathrm{D}$ 1.4600; (3) 4.1 g., b.p. 119°, $n^{25}\mathrm{D}$ 1.4599. These fractions are too high boiling for either cyclohexene chlorohydrin, b.p. 93° (27 mm.)[10] or its acetate, b.p. 98.0–98.5° (12 mm.).[5b] Their refractive indices exceeded substantially that of *trans*-1,2-diacetoxycyclohexane. Accordingly, the distillate appears to be mainly *trans*-2-acetoxycyclohexanol, the yield being 5.1 g. (21%).

The aqueous bicarbonate solution remaining from the ether extraction was subjected to continuous extraction with chloroform for 30 hr. The chloroform was evaporated under reduced pressure on a steam-bath. The non-volatile residue consisted of 8.1 g. (46.5%) of an almost colorless solid, m.p. 98–101° after one recrystallization from carbon tetrachloride. After recrystallization, the material was dissolved in boiling acetone, cooled to room temperature and filtered. Evaporation of the acetone gave rise to material, m.p. 100–103°, mixed m.p. with *trans*-1,2-cyclohexanediol 102–104°.

Reaction of *cis*-1,2-Diacetoxycyclohexane with Hydrochloric Acid.—A 34.0-g. (0.17 mole) quantity of *cis*-1,2-diacetoxycyclohexane was treated in the manner described above for the *trans*-diacetate. The ether extract from the work-up of the reaction mixture yielded the following fractions: (1) 3.36 g., b.p. 90–92° (27 mm.), $n^{25}\mathrm{D}$ 1.4860; (2) 3.42 g., b.p. 92–94° (27 mm.), $n^{25}\mathrm{D}$ 1.4845; (3) 0.88 g., b.p. 94–96° (27 mm.), $n^{25}\mathrm{D}$ 1.4830; (4) 1.88 g., b.p. 78–90° (12 mm.), $n^{25}\mathrm{D}$ 1.4782; (5) 2.45 g., b.p. 94–103° (12 mm.), $n^{25}\mathrm{D}$ 1.4655; (6) 0.87 g., b.p. 93–110° (12 mm.), $n^{25}\mathrm{D}$ 1.4618; (7) 3.17 g., b.p. 110–113° (12 mm.), $n^{25}\mathrm{D}$ 1.4590. Fractions (1), (2), (3) and (4), 9.54 g. (41%), consisted mainly of *trans*-2-chlorocyclohexanol (reported[10] $n^{25}\mathrm{D}$ 1.4832). Fractions (5) and (6), 3.32 g. (10.1%), consisted mainly of *trans*-2-chlorocyclohexyl acetate (reported[5b] $n^{25}\mathrm{D}$ 1.4630). Fraction (7), 3.17 g. (11.7%), consisted mainly of *cis*-2-acetoxycyclohexanol [reported[16a] b.p. 114–115° (12 mm.), $n^{25}\mathrm{D}$ 1.4615 (for a sample containing 92 mole % monoacetate and 8 mole % diacetate)], probably contaminated with *cis*-1,2-diacetoxycyclohexane [reported[5a] b.p. 120° (12 mm.), $n^{25}\mathrm{D}$ 1.4475].

To 0.25 g. of fraction (1) dissolved in 20 ml. of methanol was added excess 0.1 *N* sodium hydroxide, then 10 ml. of 1 *N* sodium hydroxide was added, and the solution was refluxed 6 minutes. The sodium hydroxide was neutralized with 6 *N* sulfuric acid and ten drops of a solution of 2,4-dinitrophenylhydrazine in sulfuric acid were added. No precipitate or turbidity was observed. To test whether cyclohexanone would have caused a precipitate in the final solution, two drops of a solution of one part cyclohexanone in four parts of methanol were added. This produced an almost immediate turbidity, and a precipitate settled in *ca.* 0.5 hr.

To one drop of a sample of *cis*-2-chlorocyclohexyl acetate was added 4 ml. of methanol. One ml. of this solution was transferred to a flask, 10 ml. of 1 *N* sodium hydroxide was added, and the mixture was refluxed 25 minutes. After this time, the base was neutralized with 6 *N* sulfuric acid, and ten drops of a solution of 2,4-dinitrophenylhydrazine in sulfuric acid were added. The solution became cloudy after a few minutes and, when the solution was cooled to 0° and warmed to room temperature, a precipitate settled.

In the latter experiment, one fourth of a drop (*ca.* 7 mg.) of *cis*-2-chlorocyclohexyl acetate caused a readily discernible precipitate of cyclohexanone 2,4-dinitrophenylhydrazone. This would correspond to *ca.* 5.3 mg. of chlorohydrin. Assuming that one fourth of this amount would have caused a noticeable precipitate, the chlorohydrin fraction contained less than 0.5% *cis*-chlorohydrin, since 0.25 g. of fraction (1) showed a completely negative test for cyclohexanone after refluxing with base.

The α-naphthylurethan of fraction (1) was prepared by heating 0.37 g. of the sample with 0.49 g. (4% excess) of α-naphthyl isocyanate on a steam-bath for 3 hr. The urethan was taken up in hot benzene, filtered and allowed to crystallize after the benzene solution was concentrated; m.p. 167°. The reported[10] melting points for the α-naphthylurethans of the cyclohexene chlorohydrins are: *trans*, 165°; *cis*, 94°.

Reaction of *cis*-1,2-Cyclohexanediol with Fuming Hydrochloric Acid Containing Acetic Acid.—*cis*-1,2-Cyclohexanediol (17.9 g., 0.154 mole) was placed in a small flask bomb, and 9.3 g. (0.155 mole) of glacial acetic acid and 5.79 g. of concd. hydrochloric acid were added. The mixture was cooled to 0°, and gaseous hydrogen chloride was passed in until the solution was saturated. A total of 8.3 g. of hydrogen chloride was absorbed. The closed flask bomb was placed in a thermostat maintained at 50° for 5 days. The reaction mixture was worked up in the usual way and the products were extracted into ether.

The ether was distilled from the dried ether extract through a short Vigreux column. To the residue was added 10.83 g. of acetic anhydride and two drops of concd. sulfuric acid. The reaction mixture became quite warm, and it was cooled under a stream of running water and then allowed to stand for 3 hr. The mixture was poured into saturated sodium bicarbonate solution and extracted with ether as before.

After removal of the ether, the residue was fractionated through a 24-inch center rod column. The following fractions were collected: (1) 1.10 g., b.p. 93–100° (12 mm.), $n^{25}\mathrm{D}$ 1.4640; (2) 7.42 g., b.p. 97.2° (12 mm.), $n^{25}\mathrm{D}$ 1.4620; (3) 4.28 g., b.p. 97.2–97.5° (12 mm.), $n^{25}\mathrm{D}$ 1.4613; (4) 3.13 g., b.p. 97.5–98.0° (12 mm.), $n^{25}\mathrm{D}$ 1.4617; (5) 1.79 g., b.p. 98.0–100.0° (12 mm.), $n^{25}\mathrm{D}$ 1.4611; (6) 1.91 g., b.p. 100.0–100.5°, $n^{25}\mathrm{D}$ 1.4603; (7) 0.57 g. collected at 3 mm., $n^{25}\mathrm{D}$ 1.4568; (8) 0.58 g. in Dry Ice trap, $n^{25}\mathrm{D}$ 1.4042. On the basis of fractions (1) through (6), the yield of *trans*-2-chlorocyclohexyl acetate was estimated at 74%.

Treatment of *cis*-1,2-Cyclohexanediol with Hydrochloric Acid.—To 18.1 g. of *cis*-1,2-cyclohexanediol in a flask bomb was added 29.7 g. of concd. hydrochloric acid. Hydrogen chloride gas was passed in after the mixture was cooled to −10°. A total of 12.5 g. of hydrogen chloride was absorbed. The flask was closed and inserted in a 50° thermostat for 5 days. Then the mixture was worked up in the usual way by neutralizing the acid with bicarbonate and extracting with ether.

The ether was distilled from the dried ether extract through a short Vigreux column. When the residue was cooled, a yellow solid precipitated, which was filtered and washed with pet. ether to yield 0.81 g. of material, m.p. 86.5–88.5°, m.p. 93–95° after two recrystallizations from carbon tetrachloride, mixed m.p. with *cis*-cyclohexanediol 96–97°. A liquid residue remained after isolation of the *cis*-glycol from the reaction mixture. When an attempt was made to distil this material, no definite fractions and only a few drops of distillate (0.19 g.) were obtained. Most of the material was not volatile even at 205° (2 mm.).

The aqueous sodium bicarbonate solution remaining after the ether extraction was extracted with chloroform for 24 hr. on a continuous extractor to yield 5.02 g. of white plates, m.p. 92–95°, bringing the total recovery of *cis*-1,2-cyclohexanediol to 5.83 g. (32%).

Treatment of *trans*-Cyclohexanediol with Hydrochloric Acid.—A 20.0-g. quantity of *trans*-1,2-cyclohexanediol was treated with hydrochloric acid at 50° as described above for the *cis*-glycol. After 5 days, the mixture was poured into bicarbonate solution and extracted with ether; 4.73 g. of a viscous liquid, which was not further characterized, was obtained.

The aqueous bicarbonate solution was extracted with chloroform as before. There was obtained 11.00 g. of white crystalline material, m.p. 88–92°, m.p. 101.5–102° after one recrystallization from carbon tetrachloride, corresponding to a 55% recovery of *trans*-cyclohexanediol.

Action of Hydrochloric Acid on Ethylene Glycol.—To 39.3 g. of redistilled ethylene glycol, b.p. 95.7° (12 mm.), was added 120 ml. of concd. hydrochloric acid, and the solution was saturated with hydrogen chloride at −15°, 41.9 g. of the gas being absorbed. The flask was closed, inserted in a 35° thermostat for 6 days and then opened. The contents were poured into bicarbonate solution and extracted with ether as in the cyclohexanediol runs. When the ether extract was evaporated, there was less than 0.5 g. of residue.

Distillation of the water from the water layer at reduced pressure left a mixture of salts, which was extracted several times with a total of 150 cc. of hot acetone. After the acetone and water had been distilled off, the glycol was distilled to yield 13.61 g. (35% recovery) of ethylene glycol, b.p. 90° (11 mm.).

To 15.1 g. of redistilled ethylene glycol in a flask bomb was added 15.0 g. of glacial acetic acid and 90 ml. of concd. hydrochloric acid. After 48 g. of gaseous hydrogen chloride was passed in at −15°, the flask was closed and inserted in a 35° thermostat for 10 days. The mixture was worked up as before. The residue from the ether extract yielded the following fractions: (1) 0.42 g., b.p. 35°; (2) 0.86 g., b.p. 105–128°, n^{20}_{D} 1.4258; (3) 8.15 g., b.p. 128.0–128.2°, n^{20}_{D} 1.4375; (4) 3.99 g., b.p. 129°, n^{20}_{D} 1.4370; (5) 0.16 g., b.p. 129°; (6) 1.07 g. column holdup. Fractions (2), (3) and (4) represent a 67% yield of ethylene chlorohydrin (reported[21] b.p. 128.8°, n^{20}_{D} 1.4419).

Fractions (2) and (3) were redistilled, the following fractions being collected: (1) 1.09 g., b.p. 126.3–127.0°, n^{20}_{D} 1.4400; (2) 1.78 g., b.p. 127.0–127.5, n^{20}_{D} 1.4399; (3) 5.27 g., b.p. 128.0–128.2°, n^{20}_{D} 1.4388; (4) 1.34 g., b.p. 129.0°, n^{20}_{D} 1.4373. The chlorohydrin was probably contaminated with 2-chloroethyl acetate (reported[21] b.p. 145°, n^{20}_{D} 1.4247). The α-naphthylurethan of fraction (3) of the redistilled material was prepared by heating 1.35 g. of fraction (3) and 3.14 g. of α-naphthyl isocyanate for 4 hr. on a steam-bath. The urethan was taken up in hot benzene and the benzene solution filtered and cooled to yield 1.59 g. of crystalline material, m.p. 99–100° (48%) (reported[22] m.p. for the α-naphthylurethan of ethylene chlorohydrin 101°).

***cis*-1,2-Ditrichloroacetoxycyclohexane.**—To a solution of 2.00 g. (0.017 mole) of *cis*-1,2-cyclohexanediol dissolved in 65 ml. of anhydrous pyridine was added dropwise with stirring 7.67 g. (0.042 mole) of trichloroacetyl chloride. After 15 minutes of stirring, a granular precipitate (probably pyridine hydrochloride) appeared. After 0.5 hr. the acid chloride had all been added and 15 ml. more pyridine was added to wash down the dropping funnel. The mixture was stirred for an additional hour and allowed to stand overnight. Then it was poured into *ca.* 200 cc. of distilled water. Sulfuric acid (6 *N*) was added until the solution was acid to methyl orange. The precipitate (5.92 g.) was filtered off. A second crop of 0.26 g. brought the yield to 88% of crude product, m.p. 61.0–61.3° after reprecipitation from methanol solution by water, m.p. 61.7° after two recrystallizations from water–methanol.

Anal. Calcd. for $C_{10}H_{10}O_4Cl_6$: C, 29.52; H, 2.48. Found: C, 29.60; H, 2.86.

***trans*-1,2-Ditrichloroacetoxycyclohexane.**—Acylation of 2.00 g. of *trans*-1,2-cyclohexanediol with trichloroacetyl chloride gave rise to 5.99 g. (86%) of product, m.p. 60.8–61.0° after four recrystallizations from methanol-water (reported[19] m.p. 60–61°).

***trans*-2-Trichloroacetoxycyclohexanol.**—This compound was prepared from cyclohexene oxide and trichloroacetic acid, as previously described by Criegee and Stanger.[23]

***cis*-2-Trichloroacetoxycyclohexanol.**—To 10.00 g. (0.086 mole) of *cis*-1,2-cyclohexanediol suspended in 180 ml. of anhydrous diethyl ether was added dropwise with mechanical stirring 15.66 g. (0.086 mole) of trichloroacetyl chloride. After about 1 hr., the mixture was homogeneous. Stirring was continued for an additional 1.5 hr., and the mixture was allowed to stand overnight. Evaporation of the ether left a yellow crystalline solid. Recrystallization from pet. ether, b.p. 30–60°, yielded 11 g. (49%) of white fluffy crystals, m.p. 52–54.5°, m.p. 56.0° after three additional recrystallizations.

Anal. Calcd. for $C_8H_{11}O_3Cl_3$: C, 36.73; H, 4.24. Found: C, 36.74; H, 4.45.

An oily residue of 9.4 g. remained after evaporation of the mother liquors. This material was not further characterized.

The treatment of *cis*-1,2-cyclohexanediol with an equivalent amount of trichloroacetyl chloride was attempted in pyridine. From 10.0 g. (0.086 mole) of glycol, after the reaction mixture was allowed to stand overnight, 17 g. of crude material was obtained. Attempts at purification led only to oils which crystallized with difficulty. Sublimation yielded disproportionation products. Materials melting at 42–46°, 61–61.5° and 82–88° were isolated from the sublimate. The high melting material was shown to be *cis*-1,2-cyclohexanediol, mixed m.p. with *cis*-glycol 89°. The middle fraction, m.p. 61–61.5°, proved to be *cis*-1,2-ditrichloroacetoxycyclohexane, mixed m.p. with authentic material 60–61°.

***trans*-2-Trichloroacetoxycyclohexyl *p*-Toluenesulfonate.**—To a solution of 4.27 g. (0.0163 mole) of *trans*-2-trichloroacetoxycyclohexanol in 10 ml. of dry pyridine was added a solution of 3.30 g. (0.0173 mole) of purified *p*-toluenesulfonyl chloride in 15 ml. of dry pyridine. The mixture was allowed to stand for a day and worked up in the usual manner to yield 3.47 g. (51%) of crystals, m.p. 102–103.5°, m.p. 105.0–105.5° after three recrystallizations from pet. ether–chloroform (reported[19] m.p. 104.0–104.5°).

Anal. Calcd. for $C_{15}H_{17}O_5Cl_3S$: C, 43.33; H, 4.12. Found: C, 43.04; H, 4.20.

Reaction of *cis*-2-Trichloroacetoxycyclohexanol with Hydrochloric Acid.—To a sample of 0.73 g. (0.0028 mole) of *cis*-2-trichloroacetoxycyclohexanol was added 40 cc. of concd. hydrochloric acid. This mixture, sealed in a glass-stoppered erlenmeyer flask, was inserted in a 35° thermostat for 5 days. The reaction mixture was worked up in the usual way. The ether extract was dried and evaporated to yield 0.03 g. of yellow crystals. Extraction of the water layer with chloroform on a continuous extractor yielded 0.24 g. of yellow crystals, m.p. 96–97° after one recrystallization from 3 ml. of carbon tetrachloride, mixed m.p. with *cis*-1,2-cyclohexanediol 97–98°, to bring the total yield of *cis*-glycol to 0.27 g. (83%).

Reaction of *trans*-2-Trichloroacetoxycyclohexanol with Hydrochloric Acid.—*trans*-2-Trichloroacetoxycyclohexanol (0.69 g., 0.0026 mole) was treated with hydrochloric acid in the same manner as with the *cis*-derivative. There was obtained 0.29 g. (95%) of unpurified *trans*-glycol, m.p. 101–102°, mixed m.p. with *trans*-1,2-cyclohexanediol 102–103.5°.

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[21] N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 6th Ed., 1946.

[22] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, New York, N. Y., 1940, p. 185.

[23] R. Criegee and H. Stanger, *Ber.*, **69B**, 2753 (1936).