cally pure D-*erythro*-4-phenyl-3-hexyl tosylate, and the resulting solution was allowed to stand for fourteen hours. The mixture was then cautiously treated with ice-cold dilute sulfuric acid, the layers were separated, and the ether layer was washed with dilute acid, dilute base and again with water. The solution was dried, and the solvent was evaporated through a short column. The residual oil was mixed with 5 g. of 2,4-dinitrobenzenesulfenyl chloride and 30 ml. of glacial acetic acid and heated at 100° for one hour. The solution was then cooled, and shaken with pure pentane and water. The pentane solution was washed with water, with sodium carbonate solution, again with water and dried. The solvent was evaporated through a short column, and the residual oil was allowed to pass through a short column of alumina (2.5 cm. by 15 cm.) with pure pentane as eluant. The column filtrate was evaporated through a short column, and the residue was flash distilled to give 1.15 g. of 3-phenylhexane (52% yield), n^{25}D 1.4850, α^{29}D −7.78° (*l* 1 dm., homog.). This material is regarded as optically pure.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 88.54; H, 11.24.

Similar treatment of D-*threo*-4-phenyl-3-hexyl tosylate (5.7 g. of starting material plus 390 ml. of the same ether solution of lithium aluminum hydride) gave a 49% yield (1.33 g.) of 3-phenylhexane, n^{25}D 1.4849, α^{29}D −4.30° (*l* 1 dm.. homog.).

LOS ANGELES, CALIFORNIA

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

The Role of Neighboring Groups in Replacement Reactions. XX. Some Conversions of Cyclopentane and Indan Derivatives[1]

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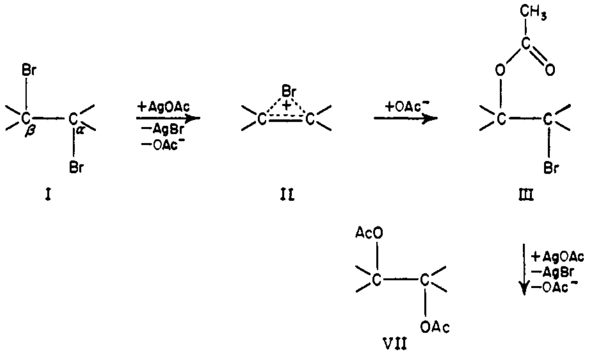
The control of the steric result and the nature of the product of replacement reactions by participation of neighboring bromine and acetoxy groups is further illustrated by reactions of several cyclopentane and indan derivatives. Cyclopentene dibromide, indene dibromide and *trans*-1-acetoxy-2-bromoindan all react with silver acetate in acetic acid to give the ester of *trans*-glycol in anhydrous solvent and the ester of *cis*-glycol in moist solvent. Participation by both neighboring bromine and acetoxy is indicated in the present cases. When acetoxy participates, the presence of water in the acetic acid gives rise to monoacetate, introduction of hydroxyl competing quite successfully with introduction of acetoxy. This furnishes a criterion for acetoxy participation and cases in the literature may be diagnosed in this way. Acetoxy participation may compete very successfully with bimolecular (S_N2) displacement by acetate ion even at substantial concentrations of the latter. This is the case also with acetolysis of 1-acetoxy-2-bromoindan.

Previous work has demonstrated the participation of the neighboring bromine atom and acetoxy group in replacement reactions of materials such as 2,3-substituted butanes[3] and 1,2-substituted cyclohexanes.[4] For example, treatment of 2,3-dibromobutane[4a,b] with silver acetate in acetic acid gives first acetoxy bromide III with an even number of Walden inversions by way of the ethylenebromonium ion II. The acetoxy bromide III reacts with acetoxy group participation to give the cyclic intermediate IV. The final fate of this intermediate depends on the medium in which it is produced. When the acetic acid solvent is dry, diacetate VII with over-all retention of configuration is the product. In glacial acetic acid containing more than an equivalent amount of water, orthomonoacetate V is derived from the cyclic intermediate IV and thus monoacetate VI with over-all inversion of configuration is the final product. In studying this type of neighboring group participation we investigated two five-membered ring systems, cyclopentane and indan, and the results are reported in the present paper. Also included are comments on still some other cases in the literature which add further evidence on the generality of the effect of the acyloxy group.



The materials studied in the present investigation were cyclopentene dibromide VIII, indene dibromide IX and 1-acetoxy-2-bromoindan X. The cyclopentene dibromide was obtained by addition of bromine to cyclopentene. The indene dibromide was the crystalline product from addition of bromine to indene and the 1-acetoxy-2-bromoindan was the acetate derived from acetylation of crystalline *trans* indene bromohydrin. On the basis of the usual considerations[4] the *trans* configuration is assigned to all three starting materials.

The treatment of cyclopentene dibromide VIII with silver acetate in dry glacial acetic acid gave rise to a diacetate which on saponification yielded a glycol XI, very nearly pure *trans* as demonstrated

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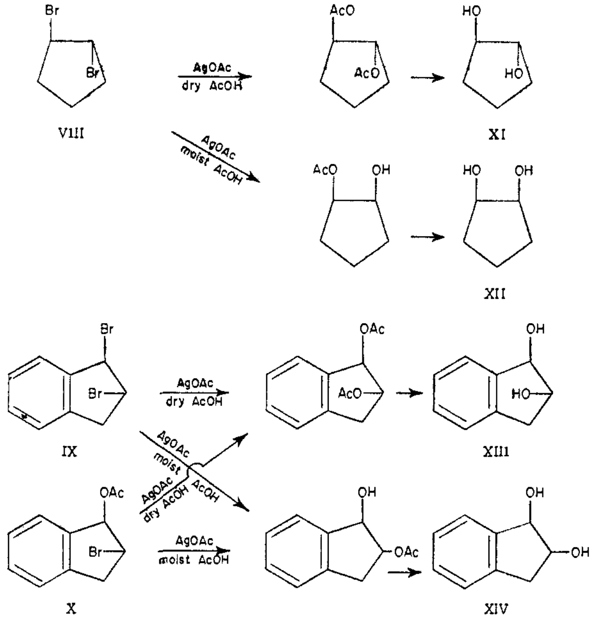
[1] The material of this paper was presented in summary: (a) before the Organic Division of the American Chemical Society, St. Louis, Mo., Sept., 1948; (b) at the Eleventh National Organic Symposium, Madison, Wisconsin, June 21, 1949, page 65 of Abstracts; (c) at Montpellier, France, April 26, 1950 [*Bull. soc. chim.*, [5] **18**, 55C (1951)].

[2] Research Fellow, 1946–1947. Research supported by Research Corporation.

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

[4] S. Winstein, *et al.*, *ibid.*, **64**, (a) 2780, (b) 2787, (c) 2792, (d) 2796 (1942).

by the preparation of the phenylurethan[5] and 3,5-dinitrobenzoate. The treatment of the dibromide with silver acetate in acetic acid containing 1.5 equivalents of water yielded an ester, partly monoacetate, partly diacetate, which on saponification gave a glycol XII, very predominantly *cis* as demonstrated again by conversion to solid derivatives. The treatment of indene dibromide IX with silver acetate in dry acetic acid gave the *trans*-diacetate. In this case the glycol itself is suitable for identification; a good yield of essentially pure *trans*-1,2-indandiol[6] (XIII) was obtained by saponifying the ester. The inclusion of 1.5 equivalents of water in the reaction mixture gave a glycol XIV, at least 84–88% *cis*, but definitely contaminated with some *trans* isomer. The 1-acetoxy-2-bromoindan (X) gave results very similar to those obtained with the dibromide. The treatment with silver acetate in dry acetic acid yielded essentially pure *trans*-glycol, while inclusion of 1.5 equivalents of water reversed the steric result so that the glycol product was at least 93% *cis*.



The results with cyclopentene dibromide VIII clearly indicate[4] that replacement of the first bromine atom yields *trans*-1-bromo-2-acetoxycyclopentane (III) by way of a cyclopentenebromonium ion (II). The acetoxybromocyclopentane then reacts with participation of the acetoxy group, the products from IV being different in dry or moist acetic acid solvent. Geometric considerations make it likely that the situation is less favorable[7] for neighboring group participation in a *trans*-1,2-disubstituted cyclopentane than in either a *trans*-1,2-disubstituted cyclohexane in a polar–polar (pp) conformation,[8] or in an open-chain case with the favored arrangement with respect to rotation about the $C\alpha$–$C\beta$ bond. Nevertheless, neighboring bromine and acetoxy control the course of substitution in this five-ring case. In the case of neighboring bromine in the cyclopentyl system, kinetic work[9] has also shown that the driving force due to participation is very substantial.

The results with the indan derivatives IX and X show that even in substitution at the resonance-affected C_1-position,[10] *trans*-bromoacetate (very probably X) is the product from dibromide IX (over-all retention of configuration). Participation by acetoxy in the reactions of X is clearly very dominant. The over-all steric results of reactions of the indan derivatives in moist acetic acid are not as clean as in other cases,[4] but it is not clear whether this is due to intrinsic factors such as a change in the competition between the various modes of reaction of intermediate IV or to some configurational instability of some of the materials involved.

The reversal of the steric result of substitution by stoichiometric amounts of water in glacial acetic acid observed in the present work with VIII, IX and X parallels the previous reversals in cases involving neighboring acetoxy participation. These involve treatment of 2,3-dibromobutanes,[4b] 3-acetoxy-2-bromobutanes,[4b] *trans*-1,2-dibromocyclohexane,[4b] *trans*-1-acetoxy-2-bromocyclohexane[4b] or stilbene dichlorides[10a] with silver acetate in acetic acid, or treatment of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate,[4d] the 3-acetoxy-2-butyl *p*-toluenesulfonates[11] or the 2,3-di-*p*-toluenesulfoxybutanes[11] with potassium acetate in acetic acid. The accidental presence of moisture in the acetic acid solvent has given a random nature to the earlier literature reports of results of treatment of dihalides with silver acetate. Thus Godchot and Taboury[5b] reported *trans*-glycol, although clearly not pure, from treatment of cyclopentene dibromide, their solvent being fairly free of water. On the other hand, earlier results[12] on cyclohexene dibromide and stilbene dichloride were those which are now[4,10a] known to correspond to the presence of stoichiometric amounts of water in the solvent.

When, with a neighboring acetoxy group participating in a replacement process, the presence of water reverses the steric result, it also largely replaces the diacetate product by monoacetate.[4,10a,11] In the present work, the reaction product from treatment of *trans*-1-acetoxy-2-bromoindan (X) with silver acetate in moist acetic acid yielded a major share of crystalline monoacetate of *cis*-glycol. We do not yet have sufficient information on the competition between introduction of hydroxyl and acetoxyl in replacement reactions in slightly moist acetic acid, but the indications are that water does not compete so well in cases without a participating acetoxy group. In addition to the behavior of dibromides,[4b] where water does not enter in the re-

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(5) (a) W. Meiser, *Ber.*, **32**, 2050 (1899); (b) M. Godchot and F. Taboury, *Bull. soc. chim.*, [4] **13**, 536 (1913).

(6) P. E. Verkade, J. Coops, Jr., C. J. Maan and A. Verkade-Sandbergen, *Ann.*, **467**, 217 (1928).

(7) For example, neighboring phenyl in *trans*-2-phenylcyclopentyl *p*-bromobenzenesulfonate fails to control the stereochemical result of acetolysis (R. Heck, unpublished work).

(8) (a) S. Winstein, *et al.*, THIS JOURNAL, **74**, 1127 (1952), footnote 21; (b) S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952).

(9) H. Marshall, unpublished work.

(10) (a) S. Winstein and D. Seymour, THIS JOURNAL, **68**, 119 (1946); (b) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

(11) H. J. Lucas, F. W. Mitchell, Jr., and H. K. Garner, *ibid.*, **72**, 2138 (1950).

(12) (a) B. Rothstein, *Ann. chim.*, **14**, 461 (1930); (b) Th. Zincke, *Ann.*, **198**, 115 (1879).

placement of the first bromine atom, can be quoted cases such as the treatment of 1-chlorindan with sodium acetate,[13] benzylamine with potassium nitrite[14] and α-phenylethyl chloride with silver acetate,[15] all in acetic acid, and all giving quite a predominance of acetate over alcohol in the product. Thus one can use the entrance of the hydroxyl group in a replacement reaction with a substance possessing a neighboring acetoxy group as evidence for participation of the acetoxy group. Therefore one can analyze cases in the literature with this criterion. For example, glycol monoacetate is formed from treatment of 1-aryl-1-acetoxy-2-bromopropanes[16] with sodium acetate in supposedly glacial acetic acid. Similarly, a glycol monoacetate is obtained from treatment of 3-acetoxy-4-chloro-Δ^5-cholestene with potassium acetate[17] in supposedly glacial acetic acid. On the present basis both of these cases involve participation of the acetoxy group.

In some of the transformations already mentioned, reaction with acetoxy group participation competes very successfully with bimolecular substitution by acetate ion even in the presence of substantial concentrations of sodium or potassium acetate. This same thing was evident in the present work when 1-acetoxy-2-bromoindan (X) was treated with potassium acetate in glacial acetic acid. In dry acetic acid nearly pure *trans*-diacetate was produced. In moist solvent the product was largely *cis* (at least 68% *cis*). However, a very large share of the *trans* material which was produced must have been due to isomerization of *cis* to *trans* ester under the reaction conditions prevailing. Thus *cis*-diacetate (*ca.* 93% *cis*) under the reaction conditions gave rise to a glycol mixture which contained *ca.* 21–30% *trans* isomer. Thus the reversal of the steric result by water must have been very considerably larger than 68%.

Experimental Part

trans-1,2-**Dibromocyclopentane.**—This material was prepared in 74% yield by the addition of bromine to cyclopentene[18]; b.p. 89.5–90° (26.5 mm.), $n^{25}\mathrm{D}$ 1.5466 [reported[19] b.p. 76.5–77.5° (18.5 mm.), $n^{19}\mathrm{D}$ 1.5510].

trans-1,2-**Dibromoindan.**—Pure indene (84.4 g.) was dissolved in 250 cc. of dry ether, cooled to −5°, and bromine was added at a rate such that the temperature stayed below 0° until the red color persisted. The ether was removed at room temperature on the water-pump, leaving 187 g. of light yellow liquid. This product was dissolved in 700 cc. of petroleum ether; 10 g. of anhydrous potassium carbonate was added and the mixture was shaken and then allowed to stand two hours. The potassium carbonate was removed by filtration, and the solution was cooled in a Dry Ice–ethanol-bath for three days. The crystals which formed were recrystallized repeatedly from petroleum ether to yield 85.7 g., 43%, of material, m.p. 30–33° (reported[20] m.p. 31.5–32.5°).

trans-1-**Hydroxy-2-bromoindan.**—This bromohydrin was prepared in 66% yield by the method of Suter and Milne[21]; m.p. on recrystallization from 95% ethanol, 129.5–130°.

Anal. Calcd. for C_9H_9OBr: C, 50.73; H, 4.26. Found: C, 50.76; H, 4.40.

trans-**1-Acetoxy-2-bromoindan.**—1-Hydroxy-2-bromoindan (32.0 g., 0.15 mole) was dissolved in 125 cc. of warm glacial acetic acid, the mixture was cooled to room temperature, and 19 cc. (0.20 mole) of acetic anhydride and two drops of concentrated sulfuric acid were added. The starting material dissolved and the temperature rose to 50°. Neutralization of the sulfuric acid with calcium carbonate, filtration and addition of 500 ml. of water gave the ester which was taken up in chloroform. The extract was dried over potassium carbonate and the solvent was removed. The residual oil was distilled[22] to yield 31.7 g. (83%) of water-white material, b.p. 124–126° (1.7 mm.), $n^{25}\mathrm{D}$ 1.5584.

Anal. Calcd. for $C_{11}H_{11}O_2Br$: C, 51.78; H, 4.35. Found: C, 51.61; H, 4.49.

The Reaction of *trans*-**1,2-Dibromocyclopentane with Silver Acetate. A. In Dry Acetic Acid.**—The dibromide was treated with silver acetate as described previously,[4a] using acetic acid to which was added acetic anhydride in excess of the amount required to remove the water present. The heterogeneous reaction mixture was stirred and heated at 100–110° for 11 hours. 1,2-Diacetoxycyclopentane was obtained in 59% yield; b.p. 102–103° (9.7 mm.), $n^{25}\mathrm{D}$ 1.4400 [reported[23] b.p. 85.5–86.5° (3.5 mm.)].

A 2.00-g. sample of the ester, 4 cc. of absolute ethanol and 4 cc. of 35% sodium hydroxide were boiled under reflux for one hour. The reaction mixture was transferred to a continuous extraction apparatus with the aid of 4 cc. of water and extracted with ether for 46 hours. The ether extracts were distilled and three 75-cc. portions of benzene were added and distilled to remove alcohol and water, leaving about 10 cc. of benzene undistilled the last time. To this benzene solution of the product was added 2.4 cc. of freshly distilled phenyl isocyanate and the mixture was warmed in an oil-bath 100° for half an hour. The crude product, collected on a filter and washed with cold dry ether, weighed 3.31 g. and had m.p. 197–202°. After recrystallization from 125 cc. of absolute ethanol, 2.21 g. (61%, calculated from the ester) of *trans*-1,2-cyclopentanediol *bis*-(phenylurethan) was obtained as fine white needles, m.p. 218–219° (analytical sample, m.p. 221–222°) (reported[6] m.p. 211–212°; reported for isomeric urethan, m.p. 195°).

Anal. Calcd. for $C_{19}H_{20}O_4N_2$: C, 67.04; H, 5.92. Found: C, 67.05; H, 6.04.

A second 2.0-g. sample of the ester was saponified and the glycol was extracted as above. The ether solution was dried over potassium carbonate and distilled, at the end lowering the pressure to 20 mm. and heating at 120° to remove the ethanol. The residual glycol was treated with 10 ml. of dry pyridine and 4.3 g. of 3,5-dinitrobenzoyl chloride. Working up and crystallization from chloroform–ethanol yielded 2.33 g., 44%, of *trans*-1,2-cyclopentanediol *bis*-(3,5-dinitrobenzoate), m.p. 180–184°; m.p. after one recrystallization from ethyl acetate, 184–185.5° (analytical sample, m.p. 185.2–185.8°).

Anal. Calcd. for $C_{19}H_{14}O_{12}N_4$: C, 46.54: H, 2.88. Found: C, 46.61; H, 2.94.

B. In Wet Acetic Acid.—*trans*-1,2-Dibromocyclopentane (0.10 mole) was treated with silver acetate in acetic acid containing 1.5 equivalents of water, there being obtained 7.22 g. of material, b.p. 109–112.5° (10.6 mm.), $n^{25}\mathrm{D}$ 1.4517 and 5.10 g. of material, b.p. 112.5–118.5° (10.6 mm.), $n^{25}\mathrm{D}$ 1.4500, total yield, 86% calculated as cyclopentanediol monoacetate or 66% as diacetate.

A 2.00-g. sample of the combined distillate was saponified and the glycol was extracted and treated with 3.3 cc. of freshly distilled phenyl isocyanate in benzene solution. There was obtained 3.20 g. of white solid, m.p. 170–>200°. When this material was fractionated from 95% ethanol, a 1.02 g. total of two fractions, m.p. 195.0–195.7° and 195.5–196.5°, was obtained. On the basis of mixed melting point tests the contaminating material was *sym*-diphenylurea, not the isomeric urethan.

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[13] W. F. Whitmore and A. I. Gebhart, THIS JOURNAL, **64**, 912 (1942).

[14] J. Meisenheimer and J. Link, *Ann.*, **479**, 211 (1930).

[15] H. Stimmel, unpublished work.

[16] P. Hoering, *Ber.*, **38**, 3464, 3477 (1905).

[17] V. A. Petrow, O. Rosenheim and W. W. Starling, *J. Chem. Soc.*, 135 (1943).

[18] C. Gärtner, *Ann.*, **275**, 331 (1893).

[19] N. D. Zelinskii and R. Ya. Levina, *Ber.*, **66B**, 477 (1933).

[20] A. Spilker and A. Dombrowsky, *ibid.*, **42**, 572 (1909).

[21] C. M. Suter and H. B. Milne, THIS JOURNAL, **62**, 3473 (1940).

[22] W. F. Whitmore and A. I. Gebhart[13] attempted to prepare 1-acetoxy-2-bromoindan from the bromohydrin and acetyl chloride. They reported an oil, stable at room temperature, but decomposing on attempted distillation at 4.5 mm.

[23] P. E. Verkade, *Ann.*, **477**, 279 (1930).

A 4.0-g. sample of the distilled reaction product was saponified and the glycol extracted as before. The ether solution was dried over potassium carbonate, the ether distilled and the residue was treated with pyridine (30 cc.) and recrystallized 3,5-dinitrobenzoyl chloride (12.8 g.) at reflux for one hour. Working up in the usual way gave 7.9 g. (58–75%) of crystalline ester, m.p. 160–170°. One recrystallization from ethyl acetate gave 4.7 g. of colorless needles, m.p. 173–174.5°. Recrystallized twice more for analysis, the pure *cis*-1,2-cyclopentanediol *bis*-(3,5-dinitrobenzoate) melted at 175.0–175.5°. A mixture of it and the *trans* derivative melted at 155–160°.

Anal. Calcd. for $C_{19}H_{14}O_{12}N_4$: C, 46.54; H, 2.88. Found: C, 46.67; H, 2.99.

The *cis* derivative is much more soluble in ethyl acetate than the *trans*.

The Reaction of *trans*-1,2-Dibromoindan with Silver Acetate. A. In Dry Acetic Acid.—The reaction was carried out as before, except that the heating and stirring were continued for 13.5 hours. 1,2-Diacetoxyindan was obtained in 70% yield, b.p. 134–136° (1.9 mm.), $n^{25}\mathrm{D}$ 1.5140 [reported[23] b.p. 160–160.2° (8 mm.)].

To 3.00 g. of the ester was added 10 cc. of absolute ethanol and 10 cc. of 6 *N* sodium hydroxide. The homogeneous mixture was heated to reflux for 2.5 hours. The reaction mixture, which had turned dark brown, was extracted with four 40-cc. portions of ether, the extracts were dried over potassium carbonate, 1 g. of Norit-A was added, and the mixture was boiled under reflux for 1.25 hours. Filtration and evaporation of the ether yielded 1.41 g., 74%, of crystalline material, m.p. 147–153°, m.p. 156.5–157.5° after one recrystallization from water (reported[6] m.p. 158.6–159.6°).

B. In Wet Acetic Acid.—The procedure used with dibromocyclopentane, applied to 0.10 mole of the indan derivative (15-hour reaction period), yielded 2.2 g. of product, b.p. 142–150° (*ca.* 3–5 mm.), $n^{25}\mathrm{D}$ 1.5391, and 13.0 g., b.p. 150–152° (*ca.* 3–5 mm.), $n^{25}\mathrm{D}$ 1.5293; combined yield 78% calculated as monoacetate or 65% as diacetate.

A 3.0-g. sample of the 13-g. fraction was saponified by boiling with 10 cc. of 6 *N* sodium hydroxide and 10 cc. of absolute ethanol for half an hour. The reaction mixture was extracted with six 50-cc. portions of ether. The ether extracts were washed with a 50-cc. portion of water, and then dried over potassium carbonate. The dry ether solution was treated with Norit and evaporated to yield 1.48 g. of white crystals, m.p. 83–97°.[24] This material was fractionated by repeatedly shaking with ether at room temperature and filtering to collect the undissolved solid. The results showed the product to be predominantly *cis*-1,2-indandiol (at least 84 to 88%), the remainder being the *trans*-glycol.

The Reaction of *trans*-1-Acetoxy-2-bromoindan with Silver Acetate. A. In Dry Acetic Acid.—The acetoxy bromide was treated in the same manner as the dibromides (11 hours), 1,2-diacetoxyindan, b.p. 163° (10.0 mm.), $n^{25}\mathrm{D}$ 1.5139, being obtained in 74% yield.

Saponification of a 3.0-g. sample of the ester gave 1.6 g., 84%, of glycol, m.p. 150–156°. One recrystallization from 25 ml. of water gave 1.1 g. (57%) of fine slender needles, m.p. 157–158°.

B. In Wet Acetic Acid.—From 0.10 mole of acetoxy bromide was obtained 14.9 g. of product, b.p. 132–135° (2 mm.), $n^{25}\mathrm{D}$ 1.5308 and 2.7 g., b.p. 135–139° (2 mm.), $n^{25}\mathrm{D}$ 1.5271. Both fractions crystallized on standing.

A 3.0-g. sample of the larger fraction was saponified to yield 2.0 g. of crude glycol, m.p. 95–100°. By a procedure similar to that described above, this product was found to be predominantly *cis*-1,2-indandiol containing a small amount (not over 7%) of the *trans* isomer.

Recrystallization of a sample of the distillate several times from ether gave material, m.p. 103–104°, sintering at 97°. A mixture of this with *cis*-1,2-indandiol (m.p. 105.5–107°) melted at 76–86°.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.60; H, 6.32.

The Reaction of *trans*-1-Acetoxy-2-bromoindan with Potassium Acetate. A. In Dry Acetic Acid.—To a solution of 3.0 g. of dry potassium acetate in 30 cc. of dry glacial acetic acid (containing excess acetic anhydride) was added 5.1 g. (0.02 mole) of *trans*-1-acetoxy-2-bromindan, and the reaction mixture was heated under reflux for two hours. Dilution with 200 cc. of water and neutralization with 6 *N* sodium hydroxide gave an oil which was extracted with three 100-cc. portions of ether. The ether extract was dried and distilled, the residual 4.3 g. of crude ester being saponified directly. Continuous extraction of the glycol yielded 2.3 g., 77%, of material, m.p. 144–156°. Recrystallization from water gave 1.71 g., m.p. 157–158°, and 0.21 g., m.p. 155–158°; combined yield, 64%.

B. In Wet Acetic Acid.—To a mixture of 30 cc. of gl. acetic acid, m.p. 16.2°, 3.0 g. of dry potassium acetate and 0.55 cc. (0.03 mole) of water was added 5.0 g. (0.02 mole) of *trans*-1-acetoxy-2-bromoindan. The reaction mixture was heated to reflux for two hours and allowed to stand at room temperature overnight. The isolated 4.0 g. of crude ester was saponified and the glycol was extracted to yield 2.4 g. of material, m.p. 85–105°. This was recrystallized from water, yielding 1.66 g. of white needles, m.p. 98–125°. Fractionation with ether showed these crystals to be more than 68% *cis*-1,2-indandiol, but there was appreciably more of the *trans*-glycol produced than in the runs with silver acetate in moist acetic acid.

A control run on *cis*-1,2-diacetoxyindan (*ca.* 93% *cis*) under the reaction conditions was carried out. The glycol mixture obtained melted at 87–122°, and fractionation with ether showed it contained 21 to 30% of the *trans* isomer.

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(24) The melting point of pure *cis*-1,2-indandiol has been variously reported as 107.0–107.8°, 107–108.2°, 105.5–108° (ref. 6). When it is contaminated with *trans*-glycol it is difficult to raise the melting point above 102–104° without a large loss of material in recrystallization.