recrystallized from benzene to give white crystals: mp 298–300°; ir (KBr disk) 1790, 1740, 1620, 770, 700 cm^{-1}; nmr ($CDCl_3$) τ 1.75 (s, 2 H), 2.00 (s, 2 H), 2.85–3.50 (m, 10 H), 5.85 (s, 6 H), 6.10 (s, 6 H), 6.75 (d, 2 H), 7.35 (d, 2 H); mass spectrum m/e 678 (M^+), 339 (M/2).

Anal. Calcd for $C_{38}H_{30}O_{12}$: C, 67.25; H, 4.46. Found: C, 67.43; H, 4.44.

Reaction of Tetramethyl Pyromellitate (Id) with Cumene.—A solution of Id (3.1 g, 1×10^{-2} mol) in cumene (600 g, 5 mol) was irradiated for 10 hr. After removal of cumene and methanol, benzene was added to the residual solid (5.8 g). The precipitate XVIIa was separated by filtration. XVIIa (0.92 g, 34.7%) was recrystallized from benzene to give white crystals: mp 258.5–260°; ir (KBr disk) 1795, 1730, 1620, 765, 695 cm^{-1}; nmr ($CDCl_3$) τ 1.52 (s, 1 H), 1.68 (s, 1 H), 2.46 (s, 1 H), 2.58 (s, 1 H), 5.93 (s, 12 H), 6.81 (s, 6 H); mass spectrum m/e 527 ($M - OCH_3$), 279 (M/2), 248 ($M/2 - OCH_3$).

Anal. Calcd for $C_{26}H_{22}O_{14}$: C, 55.92; H, 3.97. Found: C, 56.01; H, 3.77.

The filtrate was concentrated and the residual solid (4.8 g) was chromatographed on a silica gel column (120 g). Bicumyl (0.85 g) was eluted with petroleum ether as colorless needles, mp 117–118°. The benzo-γ-lactone derivative XVIII (20 mg) was eluted with benzene–petroleum ether (1:1). Recrystallization from benzene gave white crystals: mp 233–235°; ir (KBr disk) 1790, 1775, 1620, 1500, 785, 750, 700 cm^{-1}; nmr ($CDCl_3$) τ 2.11 (s, 1 H), 2.76 (m, 10 H), 3.46 (s, 1 H), 7.11 (s, 6 H), 8.48 (s, 6 H), 8.54 (s, 6 H); mass spectrum m/e 486 (M^+), 367 ($M - 119$), 119.

Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.05; H, 6.22. Found: C, 73.84; H, 6.31.

The benzo-γ-lactone derivative XVI (1.87 g, 49.5%) was eluted with benzene–petroleum ether (9:1). Recrystallization from ether gave colorless plates: mp 88–90°; ir (KBr disk) 1780, 1730, 1620, 1500, 770, 760, 700 cm^{-1}; nmr (CCl_4) τ 2.03 (s, 1 H), 2.81 (broad, 5 H), 3.29 (s, 1 H), 6.12 (s, 3 H), 6.18 (s, 3 H), 7.00 (s, 3 H), 8.33 (s, 3 H), 8.66 (s, 3 H); mass spectrum m/e 398 (M^+), 367 ($M - OCH_3$), 279 ($M - 119$), 119.

Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.31; H, 5.35.

XIX (23 mg) was eluted with benzene as white crystals, which were insoluble in organic solvents: mp 341–343°; ir (KBr disk) 1785, 1630, 700 cm^{-1}; mass spectrum m/e 615 ($M - 119$), 119.

Anal. Calcd for $C_{42}H_{38}O_{12}$: C, 68.65; H, 5.21. Found: C, 68.83; H, 5.16.

Unreacted Id (0.14 g) was eluted with benzene. XVIIb (0.17 g, 6.4%) was eluted with ether. Recrystallization from benzene gave white crystals: mp 278–280°; ir (KBr disk) 1780, 1745, 1730, 1630, 775, 695 cm^{-1}; nmr ($CDCl_3$) τ 1.47 (s, 1 H), 1.67 (s, 1 H), 2.49 (s, 1 H), 2.57 (s, 1 H), 5.94 (s, 6 H), 5.97 (s, 6 H), 7.00 (s, 6 H); mass spectrum m/e 527 ($M - OCH_3$), 279 (M/2), 248 ($M/2 - OCH_3$).

Anal. Calcd for $C_{26}H_{22}O_{14}$: C, 55.92; H, 3.97. Found: C, 55.96; H, 3.60.

Reaction of I with Cyclohexane.—The solution of Ia (1.94 g, 1×10^{-2} mol), Ib (0.81 g, 5×10^{-3} mol), or Ic (0.97 g, 5×10^{-3} mole) in cyclohexane was irradiated for 270 hr and the reaction mixtures were treated in the same way as described in the reaction of Ia with toluene. However, neither methanol, bicyclohexyl, nor photoreductants was isolated.

Registry No.—Ia, 120-61-6; Ib, 1129-35-7; Ic, 1459-93-4; Id, 635-10-9; IIIa, 34566-34-2; IIIb, 34566-35-3; IIIc, 34566-36-4; IVa, 34566-37-5; IVb, 34566-38-6; IVc, 34599-29-6; Va, 34566-39-7; VIa, 34599-30-9; VIb, 34566-40-0; X, 34566-41-1; XI, 34566-42-2; XII, 34599-31-0; XIII, 34566-43-3; XV (1,7-dioxobenzofuran), 34566-44-4; XV (1,5-dioxobenzofuran), 34566-45-5; XVI, 34566-46-6; *meso*-XVII; 34599-32-1; (±)-XVII, 34599-33-2; XVIII (1,7-dioxobenzodifuran), 34566-47-7; XVIII (1,5-dioxobenzodifuran), 34566-48-8; XIX, (1,7-dioxobenzodifuran), 34599-34-3; XIX (1,5-dioxobenzodifuran), 34566-49-9; toluene, 108-88-3; cumene, 98-82-8; *p*-cymene, 99-87-6; cyclohexane, 110-82-7.

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Notes

A Stereochemical Study of the Ring Opening of Indene Oxide by Benzoic Acid[1]

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The stereochemistry of epoxide ring opening reactions has been extensively studied in recent years with the accrual of considerable information concerning the mechanisms of such reactions. The generally accepted mechanism is a bimolecular nucleophilic displacement (SN2) resulting in an inversion of configuration.[3] However, examples of ring opening reactions which gave retention of configuration have been reported.[4,5] In order to shed additional light on the mechanism of epoxide openings, we have examined the reaction of an unsymmetrical oxide with a carboxylic acid in an aprotic solvent.

The reaction of benzoic acid with indene oxide in anhydrous chloroform formed a hydroxy benzoate which, upon saponification, yielded exclusively *trans*-1,2-dihydroxyindan (**4**); no *cis*-1,2-dihydroxyindan (**5**) was detected (Scheme I). To substantiate the reaction products, known derivatives were synthesized by previously established routes.

The reaction of indene oxide with aqueous acid was reported[6] to yield a mixture of trans (**4**) and cis (**5**) isomers where the proportion of isomers formed was

(1) Taken in part from the Master's thesis of A. Gagis, at Fairleigh Dickinson University, 1971.

(2) Inmont Corp., Hawthorne, N. J. 07506.

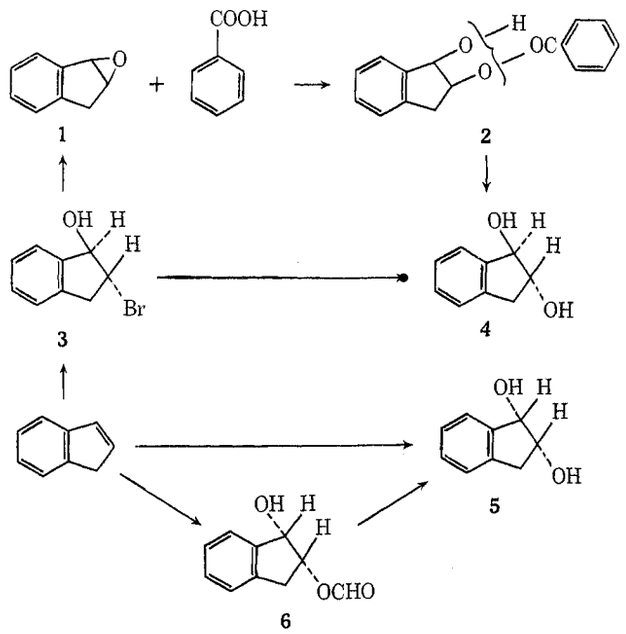
(3) (a) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); (b) S. Winstein and R. B. Henderson, "Hetrocyclic Compounds," Vol. 1, 27, R. C. Elderfield, Ed., Wiley, New York, N. Y.

(4) D. Y. Curtin, A. Bradley, and Y. Hendrickson, *J. Amer. Chem. Soc.*, **78**, 4064 (1956).

(5) J. H. Brewster, *ibid.*, **78**, 4061 (1956).

(6) J. Böeseken, *Recl. Trav. Chim. Pays-Bas*, **47**, 683 (1928).

SCHEME I



dependent on pH and temperature. Based on these results, Brewster[5] maintained the unfeasibility of the phenonium ion mechanism due to the geometry of indene oxide, instead postulating the "ion pair" mechanism. Berti and Bottari[7] supported the ion pair theory with their study of the cis addition of peracids to *trans*- and *cis*-stilbene to form hydroxy esters. The fact that the original work was performed in an aqueous rather than in a nonacidic, aprotic medium appears to have been overlooked.

In our work indene oxide was allowed to react with benzoic acid under the conditions recommended by Curtin[4] for the analogous reaction of *p*-methoxystilbene oxide. The latter proceeded through a cis addition (retention of configuration), while our product was the result of trans addition (inversion of configuration). Since the two reactions were performed under identical conditions, the only possible explanation for the pronounced stereochemical differences must be the position of the phenyl group. Unlike stilbene oxide, the structure of indene oxide does not permit the interaction of the phenyl group with the epoxide carbons to form the discrete phenonium ion intermediate. An ion pair mechanism proceeds with retention of configuration whether the phenyl group is free to migrate (as in stilbene oxide) or is held rigid (as in indene oxide). The possibility of an SN1 mechanism occurring is excluded on the basis of the bonds in a carbonium ion being coplanar, thus permitting attack from either side. This results in a mixture of cis and trans isomers.

The phenonium ion, "ion pair," or SN1 mechanisms are precluded by the absence of *cis* isomer (**5**). The results of our study therefore indicate that the ring opening of indene oxide by carboxylic acids in aprotic, nonacidic solvents proceeds with complete inversion of configuration. The reaction mechanism is of an SN2 order, which is considered the normal course for ring openings of epoxides.

(7) G. Berti and F. Bottari, *J. Org. Chem.*, **25**, 1286 (1960).

Experimental Section

All melting points were taken on a Fisher-Johns block apparatus and are uncorrected; boiling points are also uncorrected. Infrared spectra were recorded on a Beckman IR-5A spectrophotometer and were determined as Nujol mulls (unless otherwise stated). Nuclear magnetic resonance data were determined with a Varian T-60 using tetramethylsilane as an internal standard. Where "dried" is stated, magnesium sulfate was employed as the drying agent.

Reaction of Indene Oxide with Benzoic Acid in Chloroform (2).—A solution of 5.0 g of indene oxide in 60 ml of dried chloroform was allowed to stand for 3 days with benzoic acid. The solution was then washed with a 5% sodium carbonate solution and then with water, dried, and concentrated to yield 8.0 g (83%) of an oily liquid which proved difficult to crystallize: ir ($CHCl_3$) 3450 (OH), 1700 (C=O), 1265 (benzoate CO), 1050 (ether CO), 745 cm^{-1} (*o*-phenylene). This material was used directly without purification in the saponification step.

***trans*-1-Hydroxy-2-bromoindan (3).**—This bromo glycol was prepared in 60% yield according to the method of Suter and Milne:[8] mp on recrystallization from 95% ethanol, 129–130.5°; ir 725 cm^{-1} (*o*-phenylene); nmr ($CDCl_3$) δ 5.25 (m, 1, ArCH), 4.23 (m, 1, CHCH), 3.42 (q, 1, J = 15, 8.5 Hz, $ArCH_2$), 3.27 (q, 1, J = 16, 8 Hz, $ArCH_2$), 2.59 (s, 1, OH).

Indene Oxide (1).—To 400 ml of 13 *N* potassium hydroxide was added, with rapid agitation, 67.0 g of **3**. After stirring for 0.5 hr, a precipitate formed. The reaction mixture was poured into cold water, decanted, and extracted with ether. The ethereal extract was dried, concentrated, and distilled under reduced pressure to yield 22.4 g (53.8%) of epoxide **1**: bp 107–108° (8 mm); mp 30° (lit. mp 31°); ir ($CHCl_3$) 1240 cm^{-1} (epoxide); nmr ($CDCl_3$) δ 4.25 (d, 1, J = 3.5 Hz, ArCH), 4.02 (m, 1, CHCH), 3.10 (d, 1, J = 5 Hz, $ArCH_2$), 3.03 (d, 1, J = 3 Hz, $ArCH_2$).

***trans*-1,2-Dihydroxyindan (4).**—To a solution of 48.5 g of sodium carbonate in 725 ml of water was added 41.5 g of **3**, heated to reflux (102°) and held for 3.5 hr. The reaction solution was filtered and allowed to stand overnight at room temperature. The crystals that precipitated were filtered and dried *in vacuo* to yield 8.5 g (25%) of **4**. The crude product was stirred with toluene and then recrystallized twice from ethyl acetate: mp 157–159° (lit. mp 158.5–159.5°); ir 3300 (OH), 745 cm^{-1} (*o*-phenylene); nmr (pyridine) δ 5.52 (d, 1, J = 5 Hz, ArCH), 4.83 (m, 1, CHCH), 3.28 (q, 1, J = 16, 5 Hz, $ArCH_2$), 3.18 (q, 1, J = 16, 8 Hz, $ArCH_2$).

Osmium Tetraoxide Oxidation of Indene to *cis*-1,2-Dihydroxyindan (5).—A solution of 28.0 g of indene in 15 ml of ether and 1 ml of pyridine was added to a solution of 0.5 g of osmium tetraoxide in 15 ml of ether. The solution turned dark immediately; after 16 hr of stirring at room temperature, crystals were collected and washed with ether. They were dissolved in 20 ml of chloroform; the solution was stirred with 0.5 g of KOH in 40 ml of water containing 2.0 g of mannitol. Separation, decolorization with "Nuchar," and concentration yielded 0.29 g (67%) of **5**, mp 94–96°. Repeated recrystallizations did not raise the melting point above 98°: ir 3150 (OH), 745 cm^{-1} (*o*-phenylene); nmr (pyridine) δ 4.85 (d, 1, J = 5 Hz, ArCH), 4.59 (m, 1, CHCH), 3.09 (d, 1, J = 4 Hz, $ArCH_2$), 3.02 (d, 1, J = 5 Hz, $ArCH_2$).

Saponification of Glycol Ester (2).—To a solution of 25.0 g of 95% ethanol and 25.0 g of 6 *N* sodium hydroxide was added 6.0 g of **2**. The reaction mixture initially turned brown and then a deep violet. The solution was heated to reflux and held for 2.5 hr, cooled to 25°, and extracted with 5 × 50 ml portions of ether. The extract was washed with water, dried, and concentrated to yield 2.9 g (80%) of an oil which solidified on standing overnight. An ir spectrum of the oil prior to solidification was shown to be identical with that of authentic **4**. Addition of chloroform caused a precipitate to form which was filtered and dried *in vacuo*, mp 156–157°, ir spectrum identical with that of **4**. Recrystallization from ethyl acetate gave mp 156–157°. A mixture melting point with authentic **4** showed no depression.

Registry No.—**1**, 768-22-9; **3**, 10368-44-2; **4**, 4647-43-2; **5**, 4647-42-1; benzoic acid, 65-85-0.

(8) C. M. Suter and H. B. Milne, *J. Amer. Chem. Soc.*, **62**, 3473 (1940).