less crystals, m.p. 92–96°, $[\alpha]^{20}D$ −37.1° (*c* 6.13 in chloroform). Two recrystallizations from methanol gave the analytical sample, m.p. 95.5–97.0°, $[\alpha]^{20}D$ −62.8° (*c* 2.88 in chloroform). Major bands of the infrared absorption spectrum in chloroform solution: 3.46vw, 5.83vs, 6.25w, 6.32vw, 6.72vw, 6.91w, 7.27vw, 7.44vw, 7.64m, 7.88–8.45vs, 9.05s, 9.15s, 9.38m, 9.77w, 10.16 vw and 10.41 vw. The spectrum was identical in every respect with that of the dibenzoate of D,L-*erythro*-1-phenyl-1,2-propanediol (m.p. 103.0–104.5°) described in the following paper.

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.88; H, 5.58.

D-*threo*-1-Phenyl-1,2-propanediol (VII) Dibenzoate from Acid-catalyzed Hydrolysis of D-*erythro*-1-Phenyl-1,2-epoxypropane (IV).—A mixture of 1.00 g. of pure *cis*-epoxide, 50 ml. of water and 5 drops of perchloric acid (60%) was stirred vigorously at room temperature. After 40 minutes much unchanged starting material remained, so 25 ml. of water and 3 drops of perchloric acid (60%) were added. After another 20 minutes of stirring, the mixture became a clear solution and was stirred for an additional two hours. The solution was then saturated with sodium chloride, treated with excess sodium bicarbonate and extracted with ether. The ethereal extracts were washed with saturated sodium chloride solution, dried and evaporated. The residue was 1.04 g. of a colorless liquid which could not be crystallized. The crude product in 5 ml. of pyridine, cooled in an ice-bath, was benzoylated with 1.91 g. of benzoyl chloride. The product was combined with the crude benzoylation product obtained *via* hydrolysis and benzoylation of 1.5 g. more of *cis*-epoxide in the same way. Crystallization from methanol yielded a first crop of 2.88 g. (42.9% based on epoxide) of colorless crystals, m.p. 85–91°, $[\alpha]^{20}D$ 0.0° (*c* 3.24 in chloroform). Two recrystallizations from methanol yielded the analytical sample, m.p. 89.5–91.0°, $[\alpha]^{20}D$ 0.0° (*c* 6.7 in chloroform). Major bands in the infrared absorption spectrum (chloroform): 3.39vw, 5.81vs, 6.23w, 6.30vw, 6.71vw, 6.89w, 7.25vw, 7.39w, 7.62m, 7.84–8.40vs, 9.02s, 9.12s, 9.37m, 9.76m, 9.99vw and 10.20w.

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.94; H, 5.62.

D-*threo*-1-Phenyl-1,2-propanediol (VII).—In order to regenerate the glycol 0.50 g. of the dibenzoate (m.p. 89.5–91.0°) in 6 ml. of methanol was treated with 0.16 g. of potassium hydroxide in 3 ml. of water. Slight warming in a water-bath yielded a solution which was allowed to stand at room temperature for 24 hours. Then it was diluted with 15 ml. of water and saturated with sodium chloride. The resulting mixture was extracted with ether, and the ethereal extracts were washed with saturated sodium chloride solution, combined, dried and evaporated. The residue was a viscous oil, $[\alpha]^{20}D$ −64.4° (*c* 0.82 in chloroform), which crystallized after thorough drying and two weeks of standing at room temperature. Recrystallization from ether–ligroin (66–68°) yielded the analytical sample, m.p. 61–62°, $[\alpha]^{20}D$ −60.6° (*c* 0.94 in chloroform). Major bands of the infrared absorption spectrum (chloroform): 2.82m, 2.95w, 3.38w, 3.48w, 6.71w, 6.89m, 7.19m, 7.32m, 7.60w, 7.98–8.43m, 8.95s, 9.03m, 9.36m, 9.67s, 9.86s, 10.97w, 11.57w and 12.06w.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.76; H, 7.97.

D-*erythro*-1-Phenyl-1,2-propanediol (VI) Dibenzoate from the Mother Liquors of the Dibenzoate of the D-*threo*-Glycol VII.—Concentration of the first mother liquor of the D-*threo*-dibenzoate yielded colorless crystals, m.p. 85–96°. Recrystallization from methanol yielded 0.36 g. of crystals, m.p. 90–96° and further recrystallization yielded crystals, m.p. 95.0–97.0°, $[\alpha]^{20}D$ −60.9° (*c* 0.46 in chloroform). Rotation, mixed melting point determination and infrared spectra established the identity with the dibenzoate of the hydrolysis product of the *trans*-epoxide III.

Acknowledgment.—We are greatly indebted to Dr. J. W. Pratt for assistance in nomenclature.

BETHESDA, MARYLAND

CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH]

The Stereochemistry of the 1-Phenyl-1,2-propanediols and of α-Isoephedrine

BY CALVIN M. FOLTZ AND BERNHARD WITKOP

RECEIVED MAY 3, 1956

cis-β-Methylstyrene (II), obtained by stereospecific reduction of phenylmethylacetylene (I) with Lindlar catalyst, was oxidized by potassium permanganate to D,L-*erythro*-1-phenyl-1,2-propane (V), m.p. 93.5–95°, dibenzoate IV m.p. 103.5–104.5°, and by the silver benzoate iodine complex (Prévost reaction) to the dibenzoate VII of D,L-*threo*-1-phenyl-1,2-propanediol (VI), m.p. 77–78.5°, free glycol m.p. 55–57°. The acid-catalyzed hydrolysis of D,L-*cis*-β-methylstyrene oxide (III), after benzoylation, yielded the dibenzoates VII and IV of the expected *threo*-(VI) as well as of the *erythro*-glycol V, suggestive of normal bimolecular *trans*- as well as of *quasi*- unimolecular racemic opening of the epoxide. The comparison of the infrared spectra of the *rac*-glycols and dibenzoates with the D-*threo* and *erythro*-glycols from ephedrine, ψ-ephedrine and isoephedrine allowed final assignments of configurations.

The structural assignments for the simple disecondary glycols with symmetric substituents, such as *meso*- and *rac*-2,3-butane- or -stilbene are well established.[1,2] The configurations of the two optically inactive diastereoisomers of 1-phenyl-1,2-propanediol[3] are not known.

There are three reasons for this failure of stereochemical assignments in this series: (i) an internally compensated *meso*-form does not exist; (ii) all synthetic procedures[3,4] started out with mixtures of *cis*- and *trans*-propenylbenzene[5] and the intermediate epoxide[6,21] and dibromide[3] were sterically inhomogeneous and invariably led to mixtures of 1-phenyl-1,2-propanediols ("α-form," m.p. 56–57°, "β-form," m.p. 101°); (iii) even with the sterically pure *cis*- or *trans*-β-methylstyrene oxides of known configuration available, acid-catalyzed hydrolysis did not lead to pure *threo*- or *erythro*-glycols but to mixtures.[7]

Pure *cis*-propenylbenzene recently has been prepared by catalytic reduction of 1-phenyl-1-propyne

(1) *Cf.* C. E. Wilson and H. J. Lucas, THIS JOURNAL, **58**, 2396 (1936).

(2) *Cf.* J. Read and I. G. M. Campbell, *J. Chem. Soc.*, 2377 (1930).

(3) Th. Zincke and K. Zahn, *Ber.*, **43**, 849 (1910).

(4) J. Lévy and M. Dvoleitzka-Gombinska, *Bull. soc. chim.*, [4] **49**, 1765 (1931).

(5) A. Klages, *Ber.*, **36**, 621 (1903).

(6) *Cf.* E. Forneau and G. Benoit, *Bull. soc. chim.*, **12**, 985 (1945).

(7) B. Witkop and C. M. Foltz, THIS JOURNAL, **79**, 197 (1957).

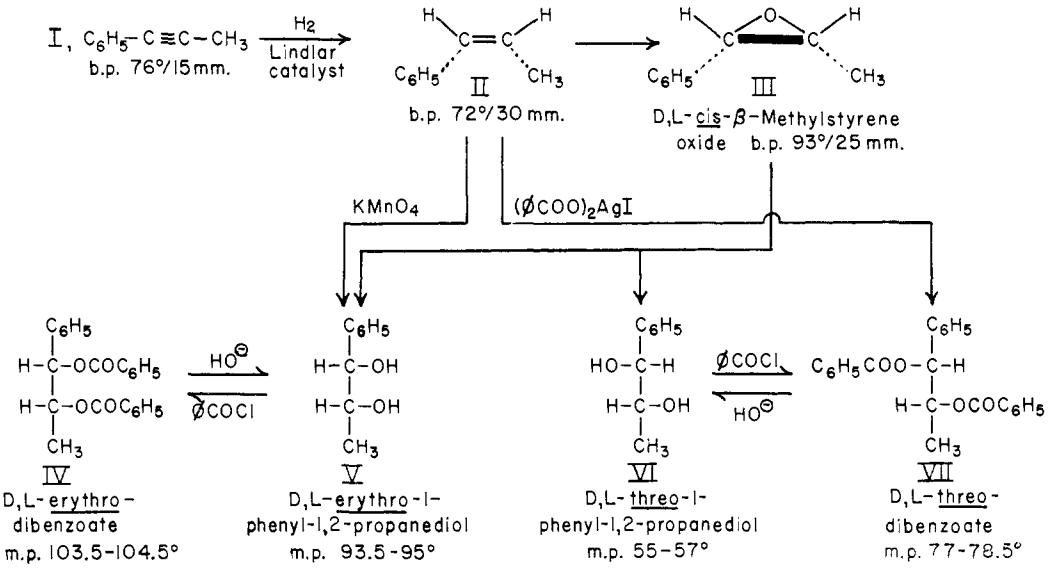


Chart I.—Preparation of the racemic *erythro*- and *threo*-1-phenyl-1,2-propanediols from *cis*-β-methylstyrene by *cis*-glycolization ($KMnO_4$) and *trans*-benzoyloxylation (Prévost reaction). Only the D-forms of the racemic compounds are pictured here.

with palladium-on-Norite in ether.[8,9] By the use of Lindlar catalyst[10] the reduction of the acetylene precursor was even more stereospecific. The ethylene II obtained after hydrogenation was of high purity and had a constant boiling point throughout.

The *cis*-glycolization of the pure *cis*-propenylbenzene (II) should lead to the *erythro*-glycol V. This reaction was achieved by potassium permanganate in neutral aqueous solution. The glycol was obtained in good yield and high purity. It had m.p. 93.5–95°. Zincke's high melting "β-form"[3] must therefore be D,L-*erythro*-glycol V.

The way to the *threo*-glycol *via* the *cis*-epoxide III was not feasible for reasons given in the preceding paper.[7] For confirmation and completion sake we prepared (Chart I) the D,L-*cis*-epoxide by oxidation of *cis*-β-methylstyrene with perbenzoic acid for the first time in a sterically pure form.[6,21] Figure 1 shows the infrared spectra of (+)-*trans*-β-methylstyrene oxide from (−)-ephedrine, of (+)-*cis*-β-methylstyrene oxide from (+)-ψ-ephedrine. The spectra of the D- and D,L-*cis*-β-methylstyrene oxides are identical in all respects. In addition to other significant differences they show the band associated with the epoxide ring at a longer wave length (11.74 μ) than the diastereoisomeric oxide (11.63 μ). This is in agreement with the observation that *cis*-epoxides in general have this band at longer wave length than *trans*-epoxides.[11]

As expected[7] the acid-catalyzed opening of the epoxide III led to a non-crystallizable mixture of glycols.[12] Crystallization and partial separation was possible *via* the dibenzoates. About 60% of the epoxide was found again as the dibenzoate VII of the *threo*-glycol VI. The mother liquors contained higher-melting dibenzoate IV. These findings confirm the importance of the contribution of an intermediate open carbonium ion to the transition state composed of the conjugate acid of the epoxide and of the positively charged addition product of water to the open carbonium ion.[13] Only the carbonium ion will add water in a sterically unselective manner to give *erythro*-glycol V in addition to *threo*-glycol VI.

A direct correlation of *cis*-β-methylstyrene with the *erythro*-series was possible through the Prévost reaction.[14] By reaction of II with the complex of silver benzoate with iodine in benzene suspension a 65% yield of the pure dibenzoate VII and, by alkaline hydrolysis, the glycol VI, m.p. 55–57° were obtained. Zincke's low-melting "α-form," therefore, is the *threo*-glycol VI.

The comparison of the infrared spectra (Fig. 2) of the synthetic glycols and dibenzoates with the D-compounds from ephedrine showed complete identity for the *threo* and *erythro* derivatives, respectively, and confirms the assignments made in the preceding paper.[7]

It is now possible to go backward from the D,L-phenyl-1,2-propanediol obtained by Emde and Runne[15] and to arrive at the configuration of their starting material. Their glycol was crystalline and apparently homogeneous. According to the melting point of 94° it was D,L-*erythro*-glycol V formed by the action of water (no acid catalysis!)

(8) R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, THIS JOURNAL, **75**, 4094 (1953).

(9) *cis*-Propenylbenzene is also formed in minor amounts by the pyrolysis of 1-phenyl-1-ethylcarbinol acetate [C. G. Overberger and D. Tanner, *ibid.*, **77**, 369 (1955)]. The refractive index and the ultraviolet data of a lower boiling fraction of β-methylstyrene agree well with the constants for the *cis*-ethylene reported in ref. 8.

(10) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

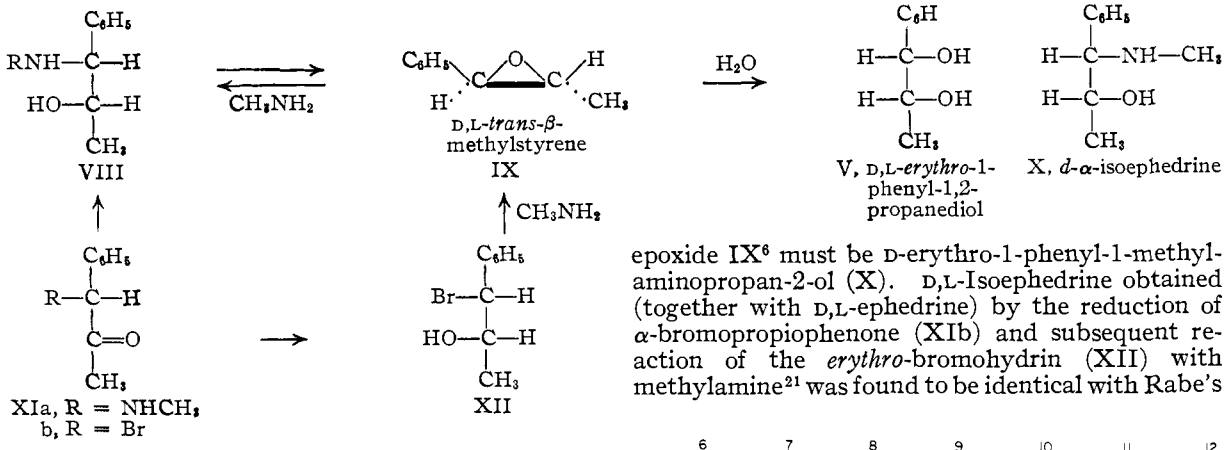
(11) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 277 (1951).

(12) *Cf.* A. McKenzie, E. M. Lewis and A. G. Mitchell, *Ber.*, **65**, 798 (1932).

(13) *Cf.* C. A. Stewart and C. A. VanderWerf, THIS JOURNAL, **76**, 1259 (1954); H. H. Wasserman and N. E. Aubrey, *ibid.*, **78**, 1726 (1956).

(14) C. Prévost, *Compt. rend.*, **106**, 1129 (1933); **197**, 1661 (1933).

(15) H. Emde and E. Runne, *Ber.*, **43**, 1727 (1910).



on the oxide,[16] which must be the *trans*-oxide IX if the opening, as is reasonable to assume, proceeded exclusively by Walden inversion. The epoxide in turn must come from the quaternary ammonium base of D,L-*erythro*-1-phenyl-1-amino-2-hydroxypropane (*nor*-iso-ephedrine, VIII, R = H, m.p. 85°).[17] The *erythro* assignment is in accordance with the exclusive formation of VIII in the reduction of α-amino-α-phenylacetone. It is comparable to the selective reduction of α-methylaminopropiophenone (XIa) to D,L-ephedrine.[18] The *erythro* configuration is also preferred in the catalytic reduction of 1-phenyl-1-hydroxyacetone which yields exclusively V.[19] This then makes possible the *erythro* assignment for D,L-α-isoephedrine (VIII, R = CH_3).[20]

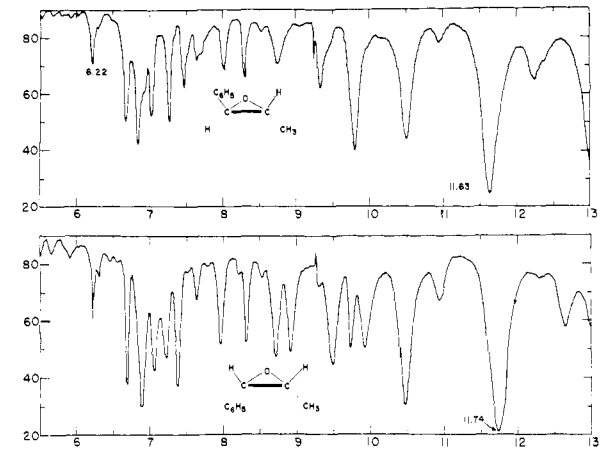


Fig. 1.—Infrared spectra of D-*threo*-1-phenyl-1,2-epoxypropane (from ephedrine) and of D-*erythro*-1-phenyl-1,2-epoxypropane (from ψ-ephedrine). The latter is identical with that of D,L-*erythro*-1-phenyl-1,2-epoxypropane (synthetic from *cis*-propenylbenzene), all in chloroform solution.

The optically active *d*-isoephedrine obtained from the reaction of methylamine on the D-*trans*-epoxide IX[6] must be D-erythro-1-phenyl-1-methylaminopropan-2-ol (X). D,L-Isoephedrine obtained (together with D,L-ephedrine) by the reduction of α-bromopropiophenone (XIb) and subsequent reaction of the *erythro*-bromohydrin (XII) with methylamine[21] was found to be identical with Rabe's

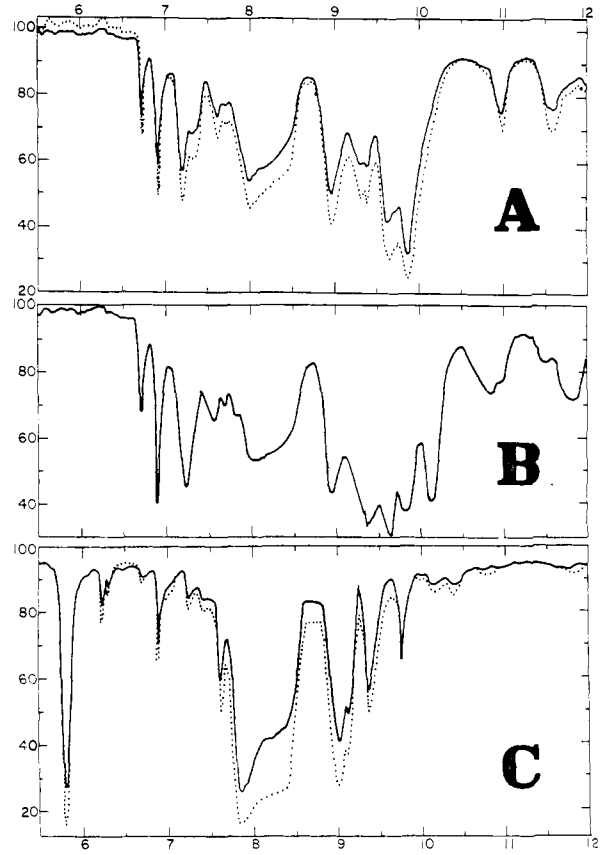
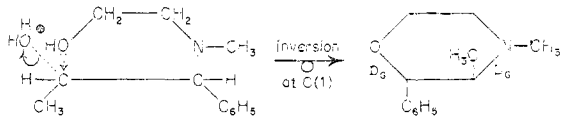


Fig. 2.—Infrared spectra (in chloroform) of: A, D-*threo*-1-phenyl-1,2-propanediol from ψ-ephedrine (solid line) and of synthetic D,L-*threo*-1-phenyl-1,2-propanediol (VI, dotted line); B, synthetic D,L-*erythro*-1-phenyl-1,2-propanediol (V); C, D-*erythro*-1-phenyl-1,2-propanediol dibenzoate from ephedrine (solid line) and synthetic D,L-*erythro*-1-phenyl-1,2-propanediol dibenzoate (IV, dotted line).

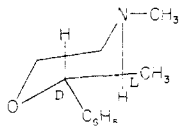
D,L-α-isoephedrine. Apparently there are two Walden inversions in this sequence: the bromohydrin with base will first give the *trans*-epoxide IX which is opened by methylamine to ephedrine as well as isoephedrine, both having *erythro* configurations. So far the *threo* isomer, D,L-ψ-α-isoephedrine, which

(16) P. Rabe and J. Hallensleben, *Ber.*, **43**, 2622 (1910).
(17) H. Emde, *Arch. Pharm.*, **247**, 130 (1909).
(18) S. Kanao, *J. Pharm. Soc. Japan*, **540**, 102 (1927); *cf.* H. K. Müller, *Ann.*, **598**, 70 (1956).
(19) I. Hirao, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 265 (1953); *C. A.*, **48**, 10534 (1954).
(20) H. Emde and E. Runne, *Arch. Pharm.*, **249**, 371 (1911).
(21) P. G. Stevens, O. C. W. Allenby and A. S. DuBois, THIS JOURNAL, **62**, 1424 (1940). The term used there for D,L-α-isoephedrine is "*d,l*-pseudoisoephedrine."

should correspond to ψ-ephedrine, has not been observed in a pure state.[6,22]



XIII XIV



XV

The ring-closure of N-hydroxyethylephedrine (XIII) to the morpholine derivative XIV[23] proceeds with retention at C(2) and inversion at C(1). This is the stereochemical reversal of the Hofmann degradation in which the configuration at C(1) is retained and inverted at C(2). The action of strong acid leads to ether formation by either a concerted process or *via* a benzylcarbonium ion with inversion of configuration at C(1). Since only one product is observed it must be the thermodynamically more stable *trans*-disubstituted morpholine XIV with the methyl and phenyl groups *trans* and equatorial as expressed in XV. The correct name for the dextrorotatory XIV is then L-*threo*-2-phenyl-3,4-dimethyl-1,4-tetrahydroöxazine; it is a derivative of ψ-ephedrine.

Experimental[24]

cis-**Propenylbenzene** (I).—A solution of 19.7 g. of 1-propenylbenzene (b.p. 75–76° (15 mm.), $n^{20}D$ 1.5638) was hydrogenated in 50 ml. of cyclohexane over 2 g. of Lindlar catalyst[10] at atmospheric pressure and room temperature. At the end of one hour somewhat more than the calculated amount of hydrogen had been consumed and the hydrogenation was terminated. The mixture was freed of catalyst by filtration, and of cyclohexane by distillation at reduced pressure. The residue was distilled *in vacuo* using a 15-cm. Vigreux column and yielded 6.1 g. of a colorless liquid, b.p. 69.0° (28 mm.), $n^{20}D$ 1.5285[25] (fraction I) and 7.4 g., b.p. 69.0–69.5° (28 mm.), $n^{20}D$ 1.5363 (fraction II). Both fractions (67.3% yield) were used in subsequent syntheses; a sample of the second fraction was analyzed.

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.44; H, 8.67.

D,L-*erythro*-1-**Phenyl-1,2-propanediol** (V).—A vigorously stirred solution of 4.0 g. of *cis*-propenylbenzene in 50 ml. of acetone, cooled in an ice-bath, was treated dropwise with a solution of 4.72 g. of potassium permanganate in 480 ml. of water at such a rate that the temperature of the mixture remained between 4 and 5°. After the addition of the oxidant which required 45 minutes, the mixture was stirred vigorously for 15 minutes, allowed to stand overnight in an ice-bath and then filtered free of manganese dioxide. The manganese dioxide was washed thoroughly with hot water. The combined aqueous filtrates were adjusted to *p*H 7.0–7.5 with hydrochloric acid and concentrated at reduced pressure on a water-bath to a volume of 50 ml. This solution was extracted with ethyl acetate. The extracts were washed with water, combined, dried and freed of solvent at reduced pressure. The residue weighed 1.83 g. (41.5%) and crystallized in platelets, m.p. 91.0–93.5°. Recrystallization from acetone–ligroin (66–68°) yielded the analytical sample, m.p. 93.5–95.0°. Major bands in the infrared absorption spectrum (chloroform); 2.81m, 2.93w, 3.38w, 3.48w, 6.71w, 6.90m, 7.23m, 7.56w, 7.70w, 8.02–8.47m, 8.95m, 9.36s, 9.65s, 9.83s, 10.14m, 10.85w, 11.50vw and 11.82 w.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.92. Found: C, 70.79; H, 7.96.

D,L-*erythro*-1-**Phenyl-1,2-propanediol Dibenzoate** (IV).—A solution of 0.40 g. of the synthetic *erythro*-1-phenyl-1,2-propanediol in 4 ml. of pyridine was benzoylated with 0.74 g. of benzoyl chloride at 0–4°. The dibenzoate was recrystallized from methanol to obtain the analytical sample, m.p. 103.0–104.5°. Major bands in the infrared absorption spectrum (chloroform): 3.43vw, 5.81vs, 6.23w, 6.30vw, 6.71vw, 6.89w, 7.25vw, 7.42vw, 7.63m, 7.85–8.40 vs, 9.03s, 9.14s, 9.38m, 9.77w, 9.99vw, 10.15 vw and 10.83 vw.

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.50; H, 5.64.

D,L-*threo*-1-**Phenyl-1,2-propanediol Dibenzoate** (VII).—A suspension 15.6 g. of thoroughly dried, freshly prepared silver benzoate in 150 ml. of dry benzene was treated with 8.6 g. of iodine. The mixture was refluxed for 30 minutes, 4.00 g. of *cis*-propenylbenzene in 25 ml. of benzene added and the mixture refluxed with vigorous stirring for 24 hours. The silver iodide was collected and washed with benzene. The combined filtrate and washings were washed with water, 5% sodium bicarbonate solution, 1% sodium thiosulfate solution, and water, and dried. The benzene was distilled from the solution at reduced pressure. The residue was a yellow oil which from methanol yielded 7.87 g. (64.2%) of colorless crystals, m.p. 75.0–77.5°. Recrystallization from methanol yielded the analytical sample, m.p. 77.0–78.5°. Major bands in the infrared absorption spectrum (chloroform): 3.43v, 5.81v, 6.23w, 6.30vw, 6.71vw, 6.90w, 7.26vw, 7.40w, 7.62m, 7.84–8.40vs, 9.03s, 9.13s, 9.38m, 9.77m, 9.99v and 10.21w.

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.80; H, 5.66.

D,L-*threo*-1-**Phenyl-1,2-propanediol** (VI).—A solution of 1.5 g. of the *threo*-glycol dibenzoate in 8 ml. of warm methanol was treated with a solution of 0.33 g. of sodium hydroxide in 2 ml. of water. The mixture warmed up and gave a clear solution after one minute. After 30 minutes the reaction mixture was taken up with water and ether. The ethereal solution was washed with water, dried and evaporated. Crystallization of the residue from ether–ligroin (66–68°) yielded the analytical sample, m.p. 55.0–57.0°. Major bands in the infrared absorption spectrum (chloroform): 2.82m, 3.38w, 3.48w, 6.72w, 6.90m, 7.19m, 7.60w, 7.71w, 7.99m, 8.95s, 9.29m, 9.36m, 9.63s, 9.86vs, 10.97w, 11.57w and 12.06w.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.99; H, 8.08.

cis-1-**Phenyl-1,2-epoxypropane** (II).—In a 500-ml. volumetric flask 11.82 g. of *cis*-propenylbenzene was treated with a slight excess of perbenzoic acid in benzene and the mixture brought to 500 ml. with benzene. The mixture was allowed to stand overnight at room temperature. Titrations then indicated that perbenzoic acid was no longer being consumed. The mixture was washed twice with 10% sodium hydroxide solution and with water and dried. The solvent was removed from the solution at reduced pressure, and the residue distilled using a 15-cm. Vigreux column. The product was 6.96 g. (51.9%) of a colorless liquid, b.p. 92.0–93.0° (25 mm.), $n^{20}D$ 1.5202; $\lambda_{max}^{isooctane}$ 249, 254, 260 and 267 mμ (log ε 2.12, 2.22, 2.31 and 2.18). Major bands in the infrared absorption spectrum (thin film of pure liquid): 3.39m, 6.23w, 6.68m, 6.90m, 7.07w, 7.23w, 7.39m, 7.65vw, 7.97w, 8.32w, 8.72m, 8.93w, 9.49m, 9.74w, 9.93w, 10.48m, 10.96vw, 11.74m, 12.65w, 13.13m, 13.49s and 14.31s.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.58; H, 7.73.

(22) The properties of the glycol, m.p. 57°, $[\alpha]D$ −18°, obtained as a by-product of the *trans*-epoxide (D-form of IX) from *l*-ephedrine,[6] are close to those of D-threo-1-phenyl-1,2-propanediol,[7] m.p. 62°, $[\alpha]D$ −60°; however, the D-*erythro*-glycol would be expected on the base-catalyzed hydrolysis of the *trans*-epoxide. The preparation of the free D-*erythro*-glycol, now in progress, will settle this remaining question.

(23) *Cf. Angew. Chem., Nachr. Chem. Techn.*, **22**, 221 (1955); W. G. Otto, *Angew. Chem.*, **68**, 181 (1956).

(24) All melting points are corrected, all boiling points are uncorrected. The analyses were performed by Dr. W. C. Alford and his associates, Analytical Service Laboratory of the National Institutes of Health.

(25) The low refractive index points to the presence of 1-phenylpropane, $n^{20}D$ 1.4925, since somewhat more than one mole of hydrogen was consumed. This saturated contaminant would not interfere with the preparation of pure derivatives of *cis*-propenylbenzene.

D,L-*threo*-1-Phenyl-1,2-propanediol Dibenzoate (VII) from D,L-*cis*-1-Phenyl-1,2-epoxypropane by Acid Hydrolysis.—A mixture of 3.00 g. of D,L-*cis*-1-phenyl-1,2-epoxypropane and 75 ml. of water was stirred vigorously for five minutes and then treated with 5 drops of perchloric acid (60%). After one hour of vigorous stirring at room temperature much unchanged starting material remained, so 50 ml. of water and 8 drops of perchloric acid were added to the mixture. One hour later, the mixture was only slightly turbid but a strong odor of epoxide was still noticeable. The mixture was stirred for two more hours and was allowed to stand overnight. The following morning the mixture was still turbid and the odor of starting material pronounced. Four drops of perchloric acid was added to the mixture and stirring was resumed for several hours. At the end of that period the mixture was still slightly turbid, but the odor of starting material weak. The mixture was saturated with sodium chloride, treated with excess sodium bicarbonate and extracted with ether. The ethereal extracts were washed with saturated sodium chloride solution, dried and evaporated. The residue was 3.57 g. of a colorless, viscous liquid, $\lambda_{max}^{CHCl_3}$ 2.81s, 2.94m, 5.85w. Attempts to crystallize the residue were unsuccessful.

Two grams of the crude glycol in 9 ml. of pyridine, cooled in an ice-bath, was benzoylated with 3.68 g. of benzoyl chloride. Crystallization of the product from methanol yielded 2.64 g. (58.4% yield based on epoxide) of the *threo*-dibenzoate, m.p. 75.0–78.0°. Recrystallization from methanol afforded the analytical sample, m.p. 76.0–78.0°.

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.49; H, 5.70.

The compound was identical with the dibenzoate of VI according to mixed melting point determination and infrared spectrum.

Concentration of the mother liquor from the recrystallization of the dibenzoate (m.p. 75.0–78.0°) yielded 0.66 g. of colorless crystals, m.p. 68–103°.

D,L-*erythro*-1-Phenyl-1,2-propanediol Dibenzoate (IV) from *cis*-Propenylbenzene (II).—Careful fractionation of the mother liquors from the dibenzoate VII of the *threo*-glycol VI eventually led to pure dibenzoate IV of the *erythro*-glycol V. It was obtained from methanol as rosettes of short needles, m.p. 103–104°. The identity with IV was established by mixed melting point determination and by the infrared spectrum.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Chemistry of 1,4-Dithiadiene. III.[1] Preparation and Decomposition of Sulfoxides

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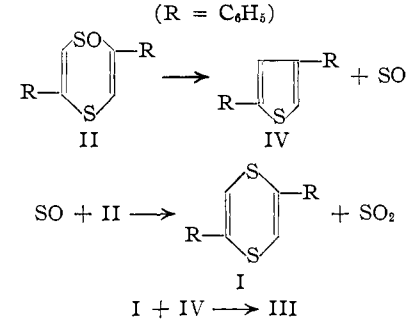
The monosulfoxides of 2,5-diphenyl-1,4-dithiadiene (I) and of the 3-nitro-, 3-bromo- and the 3-bromo-6-nitro derivatives of I were prepared. The sulfoxides are rather unstable and decompose to give substituted thiophenes. Possible mechanisms of the decomposition of the sulfoxide of I are suggested.

One of the remarkable reactions of 2,5-diphenyl-1,4-dithiadiene (I) and its derivatives is the formation of thiophenes during partial oxidation reactions. Parham[2] originally concluded that the formation of thiophenes proceeds by the loss of sulfur dioxide from an intermediate monosulfone of I. However, the thermal stability of the monosulfones of I[1] and of 2,5-diphenyl-3-bromo-1,4-dithiadiene[3] contradicts this conclusion. In our preceding publication[1] it was suggested that the monosulfoxide of I is the species which undergoes decomposition to a thiophene, and this paper provides experimental proof for this reaction path.

The preparation of the monosulfoxide of I (II) requires carefully controlled conditions because of the ease with which II is further oxidized and in view of its inherent instability. The use of peracetic acid and of a reaction time of two minutes permits the preparation of II in good yields (82%). The reduction of II by means of zinc yielded I, and the oxidation of II by peracetic acid gave a 72% yield of the monosulfone of I. The latter reaction is of interest since it indicates that the sulfoxide function of the heterocyclic ring of I is more susceptible to oxidation than the sulfide function.

The white crystals of II are rapidly discolored when exposed to light. Solutions of II were found to give upon heating either the molecular complex[1] III of I and 2,4-diphenylthiophene (IV) or only IV. The interesting feature in the formation of III is the apparent disproportionation of the sulfoxide. While the details of the mechanism of the decomposition of II are being currently investigated, we wish to suggest two possible paths by which II may produce either III or IV.

The first path may involve the loss of sulfur monoxide from II; the subsequent reduction of another molecule of II by the transient sulfur monoxide could produce I.



The second possible path of the decomposition of II is visualized to proceed by way of a bimolecular complex of two sulfoxide molecules[4] and is represented symbolically as

(1) For preceding paper see THIS JOURNAL, **78**, 1064 (1956).

(2) W. E. Parham and V. J. Traynelis, *ibid.*, **76**, 4960 (1954); **77**, 68 (1955).

(3) W. E. Parham, I. Nicholson and V. J. Traynelis, *ibid.*, **78**, 850 (1956).

(4) Association of sulfoxides was suggested by D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949), to explain the differences in the infrared spectra of sulfoxides in solution and in the solid state; see also J. Cymerman and J. B. Willis, *ibid.*, 1332 (1951). F. G. Bordwell and B. M. Pitt, THIS JOURNAL, **77**, 572 (1955), suggest an association of sulfoxides with thionyl chloride (an inorganic "sulfoxide") during the reaction leading to the formation of a chloro sulfide and sulfur dioxide.