meso and Racemic Forms of 2,4-Pentanedithiol[1]

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Received August 5, 1965

meso and racemic forms of 2,4-pentanedithiol have been separated from their mixture, *via* vapor phase chromatography, and their structure has been identified by an independent synthesis, starting from *meso* and racemic 2,4-pentanediol. The n.m.r. spectra of the two isomers serve as added proof of the assigned structures.

In earlier publications[2a–e] we have described the synthesis of a variety of mono- and polyfunctional mercaptans prepared for the investigation of structural effects on the rate of mercaptan oxidation. As part of this work, the stereoisomers of vicinal dithiols were synthesized[2f] in order to study the effects of configuration on the oxidation rates. As a continuation of this study, this paper describes the separation and identification of *meso* and racemic 2,4-pentanedithiol.

2,4-Disubstituted pentanes are often used as model compounds for the investigation of physical and chemical properties of vinyl polymers. *meso* and racemic 2,4-pentanedithiol can be used as models for the oxidation of isotactic and syndiotactic polyvinyl mercaptan, respectively, and their high-resolution n.m.r. spectra can serve as a means of determination of the polymer tacticity.

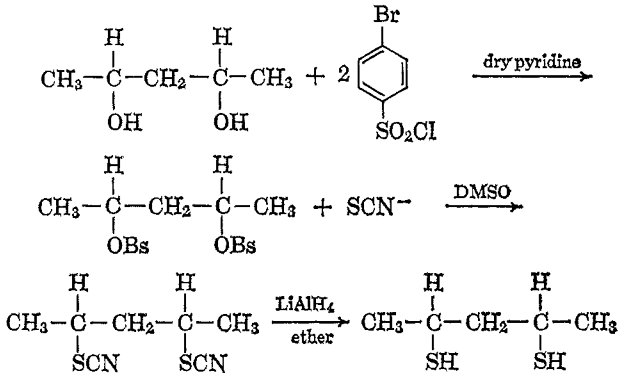
Results and Discussion

Separation and Characterization of *meso* and Racemic 2,4-Pentanedithiol.—Complete separation of the pure *meso* and racemic 2,4-pentanedithiol was achieved *via* vapor phase chromatography of the mixture of the two isomers. Best results were obtained on a 20 ft. × $^3/_8$ in. aluminum column packed with ethylene glycol succinate as a liquid phase on Chromosorb W. The chromatogram showed two peaks with retention times of 38 and 46 min. at 130° and a flow rate of 75 cc./min. No decomposition could be detected during the chromatographic separation, and the microanalysis of the collected fractions was in agreement with the theoretical values.

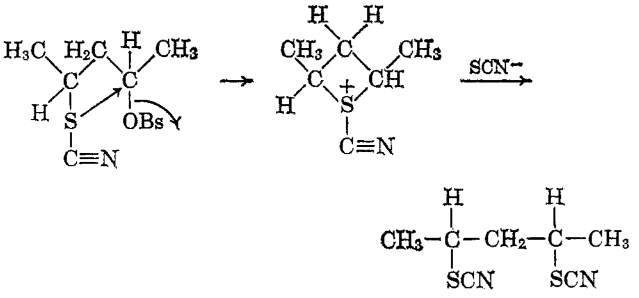
To elucidate the structure of the two fractions isolated, an independent synthesis of the isomeric dithiols was undertaken. The method adopted was similar to that used by Corey and Mitra for the synthesis of optically active 2,3-butanedithiol.[3] The last step, however, differs from the above procedure, and consists of direct reduction of the dithiocyanate to the dithiol. The synthesis is described in Scheme I. 2,4-Pentanediol was separated into its *meso* and racemic isomers by fractional distillation of their cyclic sulfite esters and subsequent hydrolysis.[4] The isomeric diols were converted to the dibromobenzenesulfonate esters by reaction with *p*-bromobenzenesulfonyl chloride in dry pyridine. No inversion of configuration is involved in this step. Thiocyanate ion was then allowed to react with the dibrosylate, in a nucleophilic displacement reaction, to yield the dithiocyanates.

SCHEME I

THE CONVERSION OF *meso* AND RACEMIC 2,4-PENTANEDITHIOL TO THE CORRESPONDING DITHIOLS



N.m.r. spectra showed that each dithiocyanate was somewhat contaminated with the other isomer. This contamination may be explained as follows: at the stage of 2-SCN monosubstituted 4-bromobenzenesulfonate an internal nucleophilic displacement might occur, through a four-membered sulfonium ion ring, thus causing double inversion on one of the asymmetric carbons, and leading to an inversion from one configuration to the other.[4]



Pure racemic dithiocyanate, however, was isolated in small quantities, as a white crystalline solid of low melting point. The n.m.r. spectrum confirmed its isomeric purity and was consistent with the predicted spectra of racemic 2,4-disubstituted pentanes (see n.m.r. discussion). The *meso* isomer failed to crystallize.

The dithiocyanates (crude oil) were reduced with lithium aluminum hydride to the corresponding dithiols.

This step does not involve any change in configuration, since the C–S bond is untouched. Both vapor phase chromatographs of the two dithiols showed two peaks: a major peak and a minor peak, with retention times identical with those of the pure isomers. The *major*

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[1] This paper comprises a portion of a dissertation to be submitted by T. Kurtz in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[2] (a) C. G. Overberger and J. J. Ferraro, *J. Org. Chem.*, **27**, 3539 (1962); (b) C. G. Overberger, J. J. Ferraro, and F. W. Orttung, *ibid.*, **26**, 3458 (1961); (c) C. G. Overberger and H. Aschkenasy, *ibid.*, **25**, 1648 (1960); *J. Am. Chem. Soc.*, **82**, 4357 (1960); (d) C. G. Overberger and P. V. Bonsignore, *ibid.*, **80**, 5427, 5431 (1958); (e) C. G. Overberger and A. Lebovits, *ibid.*, **78**, 4792 (1956); (f) C. G. Overberger and A. Drucker, *J. Org. Chem.*, **29**, 360 (1964).

[3] E. J. Corey and R. B. Mitra, *J. Am. Chem. Soc.*, **84**, 2938 (1962).

[4] J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

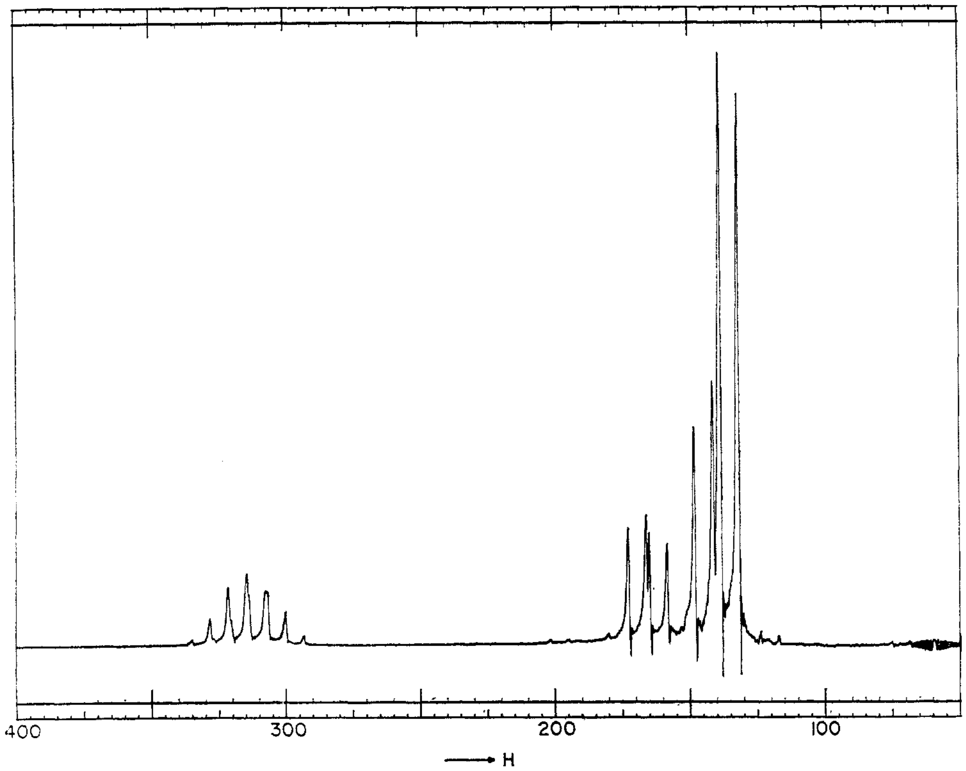

Figure 1.—Proton resonance spectrum at 100 Mc./sec. of racemic 2,4-pentanedithiol in deuterated chloroform (10% solution) (tetramethylsilane = 0 c.p.s.).

peak (81% of the integrated area) of the dithiol derived from the racemic diol had a retention time of 38 min. Therefore, the fraction isolated having this retention time is the racemic dithiol. The retention time of the *major* peak (73% of the integrated area), for the dithiol derived from the *meso* diol, is 46 min. Therefore, the fraction isolated at this retention time is the *meso* isomer.

The infrared and n.m.r. spectra of the predominantly racemic and *meso* isomers obtained by synthesis were in very good agreement with the spectra of the pure isomers and confirmed the assigned structure.

Infrared Spectra.—The infrared absorption peaks of the *meso* and racemic 2,4-pentanedithiols are listed in Table I.

N.m.r. Spectra.—The 100 Mc./sec. n.m.r. spectra of the thiols in deuterated chloroform are given in Figures 1 and 2.

The n.m.r. spectra of some 2,4-disubstituted pentanes were calculated theoretically and used as a means of identification of the two isomers.[3,5–8]

Four main groups of peaks, which are centered at 135, 145, 170, 315 c.p.s. from the tetramethylsilane peak, are observed in the spectra of the dithiols. From the position and intensities of these groups, the doublet at 135 c.p.s. has been assigned to the methyl protons, the doublet at 145 c.p.s. to the thiol protons, the multiplet at 170 c.p.s. to methenyl protons, and the multiplet at 315 c.p.s. to methinyl protons.

TABLE I

INFRARED ABSORPTION PEAKS (CM.$^{-1}$) OF *meso* AND RACEMIC 2,4-PENTANEDITHIOL

meso	Racemic
	2965 (sh)
	2955 (s)
2920 (s)	2910 (s)
2885 (s)	2890 (s)
	2860 (s)
2800 (w–m)	2810 (m)
2508 (w)	2570 (w–m)
1435 (s)	1445 (s)
1710 (sh)	1423 (sh)
1359 (s)	1373 (s)
	1310 (w)
	1280 (sh)
1255 (m)	1260 (s)
1210 (m)	1270 (sh)
1178 (w–m)	
1112 (m)	1122 (m)
1077 (w)	1095 (sh)
1050 (w)	
	1017 (m)
995 (w–m)	1000 (sh)
970 (w)	980 (w)
	970 (w–m)
860 (w)	890 (w–m)
835 (w)	870 (m)

The methyl proton spectrum displays a doublet (J = 6.8 and 6.6 c.p.s. for the racemic and *meso* isomers, respectively) owing to coupling of the methyl protons to the adjacent methinyl protons. The thiol proton spectrum also displays a doublet (J = 6.9 and 6.5 c.p.s. for the racemic and *meso* isomers, respectively) owing to coupling of the thiol protons with the adjacent methinyl protons, and the methinyl proton spectrum has a septet owing to coupling of the methinyl protons to the methyl, methenyl, and thiol protons with similar coupling constants. This is true for both the racemic and *meso* isomers.

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(5) Y. Fujimara and S. Fujiwara, *Bull. Chem. Soc. Japan*, **37**, 1005 (1964).

(6) D. Doskočilová and B. Schneider, *Collection Czech. Chem. Commun.*, **29**, 2290 (1964).

(7) D. Doskočilová and B. Schneider, *J. Polymer Sci.*, **B3**, 213 (1965).

(8) P. E. McMahon and W. C. Tincher, *J. Mol. Spectr.*, **16**, 180 (1965).

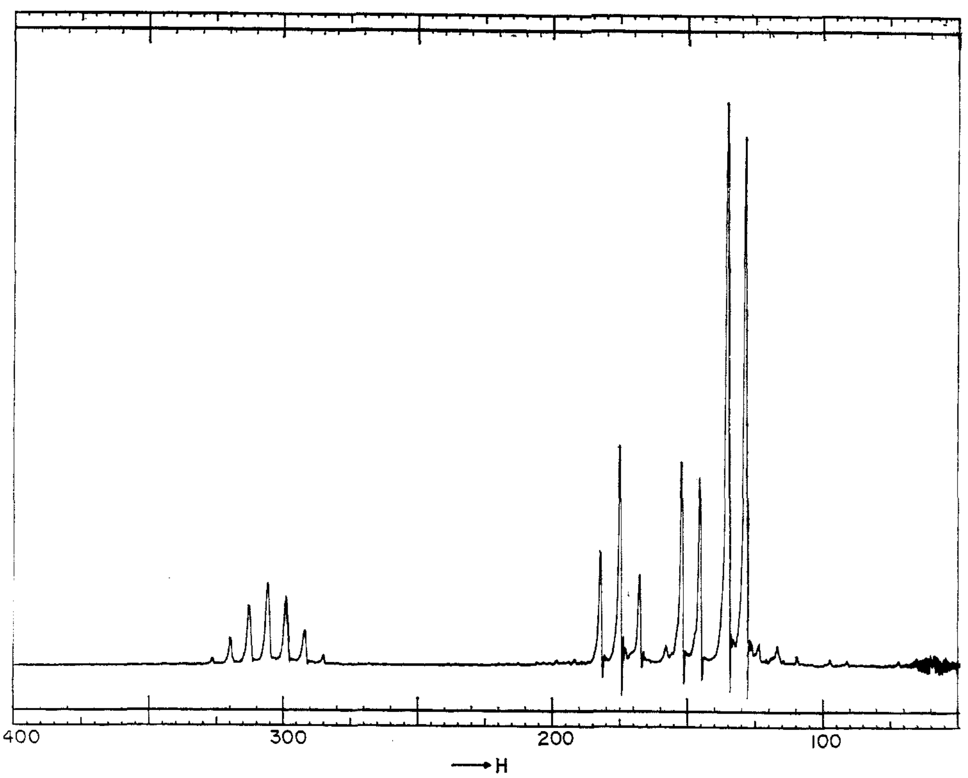

Figure 2.—Proton resonance spectrum at 100 Mc./sec. of *meso*-2,4-pentanedithiol in deuterated chloroform (10% solution) (tetramethylsilane = 0 c.p.s.).

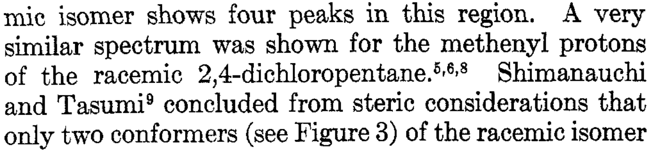

Figure 3.—Stable conformers of racemic 2,4-disubstituted pentanes.

The significant difference is between the spectra of the methylene protons of the two isomers. The racemic isomer shows four peaks in this region. A very similar spectrum was shown for the methenyl protons of the racemic 2,4-dichloropentane.[5,6,8] Shimanauchi and Tasumi[9] concluded from steric considerations that only two conformers (see Figure 3) of the racemic isomer are stable at reasonable temperatures. McMahons and Tincher[8] calculated the conformational energie for several 2,4-disubstituted pentanes and verified this conclusion. The methenyl protons are equivalent in all conformations, but the coupling constants between the methenyl and methinyl protons are nonequivalent because of unequal population of the conformers. This system leads to the observed spectrum of the racemic isomers. The n.m.r. spectrum of the racemic dithiocyanate also showed this characteristic spectrum.

The methenyl proton spectrum of the *meso* isomer was somewhat surprising. In all cases of *meso* 2,4-disubstituted pentanes reported up to now[5-8] the two methenyl protons were nonequivalent as was concluded from their complex multiplet spectra. The n.m.r. spectrum of the *meso* dithiol, however, showed an almost symmetrical triplet in the ratio 1:2:1 and with a separation of 7.3 c.p.s. A similar phenomenon was reported by Ramey and Field[10] concerning the n.m.r. spectrum of poly(vinyl trifluoroacetate): where an AB quartet should appear in the decoupled spectrum of the methenyl protons because of appreciable amounts of isotactic segments, only a single peak is observed. This result suggests that in these particular cases the methenyl protons are accidently equivalent and are coupled almost equally to the methinyl protons. In contrast, the n.m.r. spectrum of the precursor *meso* dithiocyanate (73%) showed the expected complex multiplet for the methenyl protons.

Experimental Section

Separation of the 2,4-Pentanedithiol Mixture.—2,4-Pentanedithiol, prepared according to the procedure of Overberger, Ferraro, and Orttung,[2b] was separated into the *meso* and racemic isomers by means of vapor phase chromatography. The apparatus used to obtain the separation was an Aerograph Autoprep Model A-700 (Wilkens Instrument and Research). The column used was a 20 ft. × $^3/_8$ in. o.d. aluminum column packed with 20% by weight of ethylene glycol succinate on 60–80 mesh Chromosorb W.

Operational details of the separation were as follows: carrier gas (helium) inlet pressure, 28 p.s.i.g.; approximate low rate, 75 cc./min.; injection port temperature, 160°; column temperature, 130°; detector block temperature, 190°; and filament current, 150 ma. Portions of the mixture (0.1 ml.) were injected at 25-min. intervals and collected in receivers cooled by a Dry Ice–acetone mixture. Retention times for the racemic and *meso* isomers are 38 and 46 min., respectively. Racemic dithiol had n^{25}D 1.5020; *meso* dithiol, n^{25}D 1.5052.

Anal. Calcd. for $C_5H_{12}S_2$: C, 44.06; H, 8.87; S, 47.05. Found for racemic isomer: C, 44.05; H, 8.78; S, 46.90. Found for *meso* isomer: C, 44.16; H, 8.82; S, 47.17.

N.m.r. Spectroscopy.—Samples of each isomeric form of 2,4-pentanedithiol in deuterated chloroform (10% solution) were sealed in thin-walled tubes 13 × 0.5 cm. in diameter. Spectra were run at 35° on a Varian HA-100, operating at 100 Mc./sec., machine. Tetramethylsilane served as internal reference and its signal was scaled at zero.

***meso*-2,4-Pentanediol Di-*p*-bromobenzenesulfonate.**—*meso*-2,4-Pentanediol (18 g., 0.173 mole) in 20 ml. of dry pyridine was

(9) T. Shimanauchi and M. Tasumi, *Spectrochim. Acta*, **17**, 755 (1961).

(10) K. C. Ramey and N. D. Field, *J. Polymer Sci.*, **3**, 63 (1965).

added gradually to a stirred mixture of 95.5 g. (0.375 mole) of technical grade *p*-bromobenzenesulfonyl chloride in 200 ml. of dry pyridine, cooled in an ice bath. The mixture was allowed to stir overnight at room temperature. An ice–water mixture (500 ml.) was added to the reaction flask, which was then stoppered and shaken vigorously to prevent lump formation. Gradually, a fine crystalline suspension separated. The mixture was stirred for an additional 2 hr. and then poured, with rapid stirring, into a mixture of 140 ml. of concentrated hydrochloric acid and 200 g. of crushed ice. The resulting slurry was filtered, washed thoroughly with water, and dried under vacuum at room temperature to give 81.9 g. (89.6%) of product. A small sample (0.5 g.) was dissolved in tetrahydrofuran and chromatographed on a deactivated alumina column with benzene as eluent. Recrystallization from benzene gave a white, crystalline solid, m.p. 146–147° dec. (lit.[11] m.p. 145–146°).

Anal. Calcd. for $C_{17}H_{18}Br_2O_6S_2$: C, 37.67; H, 3.35. Found: C, 37.68; H, 3.29.

Racemic 2,4-Pentanediol Di-*p*-bromobenzenesulfonate.—Starting from racemic 2,4-pentanediol, the method used for the synthesis of the *meso* isomer was applied. The racemic dibrosylate was obtained in 84% yield. Treatment of an analytical sample as described above yielded white crystals, m.p. 116.5–117°.

Anal. Found: C, 37.77; H, 3.30.

Reaction Product of *meso* 2,4-Pentane Di-*p*-bromobenzenesulfonate with Potassium Thiocyanate.—The dibrosylate, 25 g., was added to a solution of 62.5 g. of dry potassium thiocyanate in 120 ml. of dimethyl sulfoxide, and the reaction mixture was stirred under nitrogen for 50 hr. at 70–75° bath temperature. The reaction mixture was diluted with water to 1 l. and divided into two 500-ml. portions. Each portion was extracted with five 100-ml. portions of 3:1 pentane–methylene chloride. The organic extracts were combined, filtered to remove some insoluble yellow material, washed with water, dried, and concentrated to give a crude yellow oil 5.89 g. (68%). Distillation at 98° (0.2 mm.) yielded a pale yellow oil, $n^{25.5}D$ 1.5313.

Anal. Calcd. for $C_7H_{10}N_2S_2$: C, 45.12; H, 5.41. Found: C, 45.22; H, 5.21.

Racemic 2,4-Dithiocyanopentane.—Starting from the racemic dibrosylate, the method used for the synthesis of the *meso* isomer was applied. The crude yellow oil was obtained in 67% yield. A small sample was distilled at 104–105° (bath) (0.35 mm.) to give a water-white oil which crystallized on standing. Two recrystallizations from ether–petroleum ether (b.p. 30–60°) yielded white crystals of racemic 2,4-dithiocyanopentane, m.p. 42.5–44°.

Anal. Found: C, 45.01; H, 5.70.

Reduction of the Dithiocyanate Obtained from the *meso* Dibrosylate.—The dithiocyanate, 9 g., in 45 ml. of ether was added dropwise to a stirred slurry of 3.69 g. of lithium aluminum hydride in 225 ml. of dry ether, cooled in an ice bath. The reaction mixture was heated to reflux for 2.5 hr., cooled to 0°, treated dropwise with water, and then acidified with 6 *N* hydrochloric acid until it became clear. The ether layer was separated, and the aqueous acid layer was extracted with four 100-ml. portions of ether. The ethereal solutions were combined, washed with a saturated salt solution, dried, and distilled under vacuum to give the dithiol, 4.88 g. (74%), as a slightly yellow oil, b.p. 74.5 (12 mm.).

Anal. Calcd. for $C_5H_{12}S_2$: C, 44.06; H, 8.88; S, 47.06. Found: C, 43.96; H, 8.81; S, 46.95.

Reduction of the Dithiocyanate Obtained from the Racemic Dibrosylate.—The above method was employed giving the dithiol in 83.3% yield as a pale yellow oil, b.p. 65° (11 mm.).

Acknowledgment.—The authors wish to thank Mr. R. Pitcher, Varian Associates at Pittsburgh Airport, for carrying out the 100 Mc./sec. n.m.r. spectra. Financial assistance from the Socony-Mobil Oil Company is also gratefully acknowledged.

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[11] H. B. Henbest and B. B. Millwood, *J. Chem. Soc.*, 3575 (1960).

The Diastereomers of 1,3-Diphenyl-1,2-propanediol

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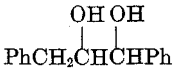
Received August 9, 1965

cis- and *trans*-1,3-diphenylpropene (I) isomers have been subjected to stereoselective hydroxylation reactions to determine the configurations of the diastereomeric 1,3-diphenyl-1,2-propanediols (II) resulting therefrom. *trans* benzoylation of *trans*-I, after saponification of the di-O-benzoate product, afforded *erythro*-II, m.p. 82–84°. *cis* hydroxylation of *cis*-I gave the same *erythro*-II isomer, while *cis* hydroxylation of *trans*-I produced *threo*-II, m.p. 62–64°. The diastereomeric diols obtained have been characterized both in the free state and as their di-O-benzoyl derivatives, with which they proved readily interconvertible. Stereochemical aspects of the production of the diastereomers of II by catalytic hydrogenations of phenylbenzylglyoxal and of benzalacetophenone oxide are briefly discussed.

In connection with another problem we have recently had occasion to prepare and characterize the *cis* and *trans* isomers of 1,3-diphenylpropene[2] (I). The same problem required a clean and quantitative method for degrading I into PhC- and $PhCH_2C$–fragments. As an approach to the latter objective we have undertaken a study of the hydroxylation of *cis*- and *trans*-I to 1,3-diphenyl-1,2-propanediol (II), with the idea that the latter might be quantitatively cleaved with periodic acid into benzaldehyde and phenylacetaldehyde.

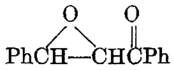
$PhCH_2CH{=}CHPh$

I



$$PhCH_2\underset{}{\overset{OH}{\overset{|}{C}}}H\overset{OH}{\overset{|}{C}}HPh$$

II



III

We wish now to report the results of these hydroxylation experiments and the bearing they have on establishing the configurations of the diastereomers of II.

1,3-Diphenyl-1,2-propanediol has been reported in several isomeric forms. One form, m.p. 63–64°, was obtained by Levy[3] on hydrolysis of 1,3-diphenyl-1,2-dibromopropane (m.p. 110°, from 1,3-diphenylpropene[4]) with aqueous sodium carbonate. The same form, m.p. 65–66°, was obtained by Ruggli and Lutz by the Raney nickel catalyzed hydrogenation of phenylbenzylglyoxal,[5] and also by Trevoy and Brown[6] on lithium aluminum hydride reduction of benzalacetophenone oxide (III). The latter investigators confirmed the skeletal structure of their II product by periodate cleavage into benzaldehyde and phenyl-

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[1] National Science Foundation Science Teaching Faculty Fellow, 1962–1963.

[2] E. K. Raunio and W. A. Bonner, *J. Org. Chem.*, in press.

[3] J. Levy and Dvoleitzka-Gombinska, *Bull. soc. chim. France*, [4] **49**, 1765 (1931).

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[5] P. Ruggli and A. H. Lutz, *Helv. Chim. Acta*, **30**, 1070 (1947).

[6] L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949).