pared against hydrogen peroxide. The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$; the intensity of each band is given in parenthesis: 3400 (8), 2990 (4), 2980 (3.5), 2800 (2.5), 1610 (2.5), 1460 (4.5), 1365 (8.5), 1340 (5.5), 1255 (5.5), 1195 (5.5), 1160 (8.5), 1035 (2.5), 940 (3), 875 (4), 830 (7.5).

Anal. Calcd. for $C_3H_8O_4$: (O), 29.60; mol. wt., 108.1. Found: (O), 29.10 (KI + CH_3COOH method); mol. wt., 115 (in exaltone).

Using the procedure of Brewster and Cotte[8] the bis-*p*-nitrobenzoate was prepared, m.p. 129–130° dec., from methyl alcohol.

Anal. Calcd. for $C_{17}H_{14}O_{10}N_2$: C, 50.25; H, 3.47; N, 6.89. Found: C, 50.33; H, 3.46; N, 6.68.

When the reaction between acetone and hydrogen peroxide was carried out at room temperature for 24 hr., the product contained over 95% of peroxide I and traces of peroxide III. Paper chromatograms taken daily of this reaction mixture showed a consistent increase of peroxide III in the mixture. After seven days the chromatogram began to show, in addition to peroxides I and III, traces of two new peroxides the R_f's of which were 0.110 and 0.168, respectively. Since the amounts of these peroxides were too small and their R_f's too close to the R_f of peroxide III, it was difficult to separate and identify them.

Decomposition of Peroxide I at 30–32°.—In a tube attached to a closed system similar to that used for the decomposition of 3,3-dihydroperoxypentane was placed 0.1264 g. of pure 2,2-dihydroperoxypropane (I) and the tube covered with aluminum foil and kept in an oil-bath at 30–32° for 500 hr. A small amount of gas which proved to be oxygen was evolved, but the loss of weight of the sample was negligible. A paper chromatogram of the residue showed four spots: one, the most intense, was attributed to the original peroxide I; another of lower intensity with an R_f of 0.052 due to peroxide III; and two others of slightly higher R'_fs present in traces. These results show that the main decomposition product is peroxide III.

2,2'-Dihydroperoxy-2,2'-diisopropylperoxide (III).—When the hydrogen peroxide–acetone mixture described above was allowed to stand at room temperature for ten days, it had produced about 20% of peroxide III estimated by means of paper chromatography. An equal volume of water was then added to the mixture and the solution extracted with pentane, dried and the pentane concentrated in vacuum to one fourth of its original volume. This was cooled in Dry Ice and the crystals separated and recrystallized several times at low temperatures from pentane; m.p. 35°, lit.[5b] 34–35°. A paper chromatogram showed a single spot with an R_f of 0.052. The infrared spectrum was identical with that reported by Criegee and Metz.[5b]

1,1,4,4,7,7-Hexamethyl-1,4,7-cyclononatriperoxane (II).—To 11.3 cc. (0.2 mole) of 50% hydrogen peroxide cooled to 0° was added with stirring 2.6 cc. (0.05 mole) of concd. sulfuric acid. To this solution was added dropwise at 0° with stirring 14.7 cc. (0.2 mole) of acetone in the course of one hr. Stirring was continued at 0° for three additional hr., then the mixture was extracted with 200 cc. of pentane, the extract washed 2 × 50 cc. of saturated ammonium sulfate solution followed by 3 × 50 cc. of water and dried over magnesium sulfate. The solution was filtered and analyzed by means of paper chromatography. When the chromatogram was sprayed with the hydrogen iodide–acetic acid reagent four spots appeared with R_f's at 0.052, 0.110, 0.168 and 0.918 with the last spot being very intense representing more than 90% of the total mixture. All of peroxide I went into the aqueous layer since it is insoluble in pentane; it was extracted from the aqueous layer with ether and when tested on paper it gave a single spot with an R_f of 0.01 and was identical with peroxide I.

The pentane layer was cooled to −10° and the colorless crystals which separated were recrystallized several times at −10° from pentane; m.p. 96°, lit.[5b] 98°. A paper chromatogram showed a single spot with an R_f of 0.918 when sprayed with the hydrogen iodide–acetic reagent. It does not react with potassium iodide–acetic acid mixture. This peroxide is unusually volatile and sublimes readily at room temperature. In fact, it is difficult to detect it on a paper chromatogram unless the spraying is done immediately after development. The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 2990 (3), 2900 (3), 1460 (3.5), 1370 (6.5), 1360 (7.5), 1270 (3.5), 1225 (4), 1175 (9), 1000 (2), 940 (6), 885 (6.5), 840 (3).

Acknowledgment.—The authors are indebted to Dr. Nagy for all the combustion analyses, to Dr. Nelson and associates for the infrared spectra and to Lucidol Division of Wallace and Tiernan, Inc., for the financial support of this investigation.

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[8] J. H. Brewster and C. J. Cotte, Jr., THIS JOURNAL, **77**, 6214 (1955).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

The Stereochemistry of the Hydrogenolysis of 1,2-Diphenyl-1,2-propanediol

BY RODERICK A. BARNES AND BENEDICT R. JULIANO[1]

RECEIVED FEBRUARY 26, 1959

Optically active 1,2-diphenyl-1,2-propanediol (methylhydrobenzoin) has been hydrogenolyzed over copper chromium oxide at 200° to yield optically active 1,2-diphenylpropane. This reaction takes place with about 20% retention of configuration, which is less than in previously studied hydrogenolyses.

The reductive cleavage of a benzyl group linked to an oxygen, nitrogen or sulfur atom is a rather general reaction that can be effected by hydrogen in the presence of catalysts or by several chemical reducing agents. Previous work on atrolactic acid[2] and 2-phenyl-2-butanol[3] using a Raney nickel catalyst showed that replacement of the hydroxyl group by hydrogen proceeded predominately with retention of configuration.

The observation that *meso*-3,4-di-(*p*-hydroxyphenyl)-3,4-hexanediol reacted with hydrogen in the presence of copper–chromium oxide catalyst at 200° to yield *meso*-3,4-di-(*p*-hydroxyphenyl)-hexane (hexesterol)[4] suggested that a stereospecific process might be involved. Either retention or inversion of configuration at both centers could explain this result. Although retention would be expected by analogy with the previous results,[2,3] the differences in the structure of the molecule undergoing hydrogenolysis and the reaction condi-

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[1] Abstracted from a thesis presented to the Graduate School by B. R. Juliano for the Ph.D. degree, February, 1956.

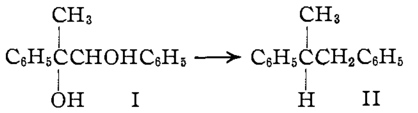
[2] W. A. Bonner, J. A. Zderic and G. A. Casaletto, THIS JOURNAL, **74**, 5086 (1952).

[3] D. J. Cram and N. L. Allinger, *ibid.*, **76**, 4516 (1954).

[4] The details of this reaction and related hydrogenolyses will be reported in a future communication.

tions are such that the possibility of an entirely different kind of process occurring, could not be discounted.

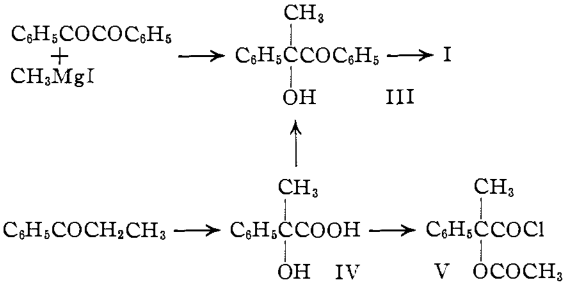
To determine the stereochemistry of this kind of hydrogenolysis, it was necessary to carry out the reaction on a molecule with a known configuration and then to determine the configuration of the product. 1,2-Diphenyl-1,2-propanediol (I) was chosen as a typical 1,2-diaryl-1,2-glycol which should yield a hydrogenolysis product (II) with a single asymmetric center.



$$C_6H_5\overset{CH_3}{\underset{OH}{C}}CHOHC_6H_5 \quad \text{I} \longrightarrow C_6H_5\overset{CH_3}{\underset{H}{C}}CH_2C_6H_5 \quad \text{II}$$

The preparation of optically active I has been previously attempted in several ways.[5-8] However the complete stereochemistry of the products was not clearly established, the yields were low, and there was disagreement among the various investigators as to the properties of the products.

Since compound I could be readily prepared from benzil, an attempt was made to resolve it.



$$\begin{matrix} C_6H_5COCOC_6H_5 \\ + \\ CH_3MgI \end{matrix} \longrightarrow C_6H_5\overset{CH_3}{\underset{OH}{C}}COC_6H_5 \ \text{III} \longrightarrow \text{I}$$

$$C_6H_5COCH_2CH_3 \longrightarrow C_6H_5\overset{CH_3}{\underset{OH}{C}}COOH \ \text{IV} \ (\uparrow \text{III}) \longrightarrow C_6H_5\overset{CH_3}{\underset{OCOCH_3}{C}}COCl \ \text{V}$$

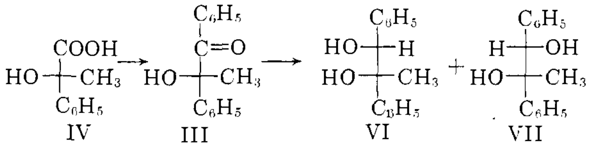
The reduction of 1,2-diphenyl-2-propanol-1-one (III) with lithium aluminum hydride produced a mixture of the two racemates of I and by fractional crystallization; the higher melting racemate was obtained in about 40% yield. The acid succinate and the acid phthalate of I were prepared, but were not successfully resolved by salt formation with the usual alkaloids.

The scheme which was finally successful for preparing optically active I started with propiophenone which was converted to atrolactic acid IV by the procedure of Levine and Stephens.[9] The next step, the conversion of IV to III, was first attempted by reaction of acid chloride V with phenylcadmium. This reaction failed, perhaps because of steric hindrance at the carbonyl group of V. However, the direct reaction of acid IV with phenyllithium proved to be a very efficient method for preparing III. The optical activity of III from resolved acid IV compared favorably with the value reported by McKenzie and Ritchie[8] for a sample of the ketone obtained in 6% yield by the reaction of the amide of acid IV with phenylmagnesium bromide.

The reduction of III with lithium aluminum hydride furnished I having a lower rotation than was reported[8] for the catalytic hydrogenation. Therefore the addition of hydrogen to the carbonyl group of III by lithium aluminum hydride was less stereospecific than by the catalytic method; the results with inactive III indicate that the hydride reduction produces the two racemates of I in about equal quantities.

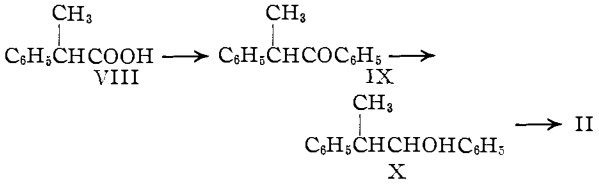
(−)-Atrolactic acid was first assigned the D-configuration by Freudenberg[10] using the method of "optical comparison" with corresponding derivatives of closely related mandelic and lactic acids. This assignment was also in harmony with the later results of Prelog.[11]

The preparation of optically active I for this study started with L(+)-atrolactic acid; therefore the sample of I obtained was actually a mixture of the two diastereomers represented by plane projection formulas VI and VII.



$$\begin{array}{c} COOH \\ HO-\!\!\!-\!\!\!\!\!\!\!\!\;CH_3 \\ C_6H_5 \\ \text{IV} \end{array} \longrightarrow \begin{array}{c} C_6H_5 \\ C{=}O \\ HO-CH_3 \\ C_6H_5 \\ \text{III} \end{array} \longrightarrow \begin{array}{c} C_6H_5 \\ HO-H \\ HO-CH_3 \\ C_6H_5 \\ \text{VI} \end{array} + \begin{array}{c} C_6H_5 \\ H-OH \\ HO-CH_3 \\ C_6H_5 \\ \text{VII} \end{array}$$

Since in the hydrogenolysis of VI and VII the secondary carbon becomes non-asymmetric, it is important only that the tertiary carbon have a single, known configuration. Hydrocarbon II, the expected product of the hydrogenolysis, was prepared in optically active form from resolved hydratropic acid (VIII).



$$C_6H_5\overset{CH_3}{C}HCOOH \ \text{VIII} \longrightarrow C_6H_5\overset{CH_3}{C}HCOC_6H_5 \ \text{IX} \longrightarrow C_6H_5\overset{CH_3}{C}HCHOHC_6H_5 \ \text{X} \longrightarrow \text{II}$$

Reaction of acid VIII with phenyllithium as in the preparation of III proceeded in 50% yield, but the ketone IX which resulted was 85% racemized.[12] The reaction of the acid chloride of VIII with diphenylcadmium has been reported[13] to yield ketone IX optically pure. However in several trials the ketonic product was always contaminated with an ester impurity (infrared band at 5.79 μ), believed to be ethyl hydratropate resulting from cleavage of diethyl ether in the presence of the acid chloride and the magnesium and cadmium halides.[14] Attempts to remove all of the ether used for preparation of the Grignard reagent by addition and distillation of benzene decreased the amount of ester but did not eliminate this by-product. Apparently ether cannot be separated from its complexes with the cadmium and magnesium atoms at the boiling point of benzene.

The direct reduction of ketone IX containing the impurity to hydrocarbon II with palladium-on-charcoal was a slow and incomplete reaction.

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(5) A. McKenzie and H. Wren, *J. Chem Soc.*, **97**, 473 (1910).

(6) C. Neuberg and H. Ohle, *Biochem. Z.*, **127**, 335 (1922).

(7) R. Roger, *ibid.*, **230**, 320 (1930).

(8) A. McKenzie and A. Ritchie, *Ber.*, **70B**, 23 (1937).

(9) R. Levine and J. R. Stephens, THIS JOURNAL, **72**, 1642 (1950).

(10) K. Freudenberg, J. Todd and R. Seidler, *Ann.*, **501**, 200 (1933).

(11) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).

(12) K. Mislow and J. Brenner, THIS JOURNAL, **75**, 2318 (1953), have observed 10% racemization in the reaction of methyllithium with acid VIII.

(13) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5846 (1947).

(14) Ethyl hydratropate has also been observed (see ref. 12) as a product of the reaction of hydratropyl chloride and dimethylcadmium; see also J. Cason, *Chem. Revs.*, **40**, 15 (1947).

However, after saponification to remove the ester impurity some of hydrocarbon II was obtained ([α]D − 59.5°). A sample with a slightly higher rotation ([α]D − 63.5°) resulted when recrystallized alcohol X from the catalytic hydrogenation was hydrogenolyzed over copper–chromium oxide. Since the rotation of alcohol X was the same as that reported for optically pure product[13] and since the hydrogenolysis does not involve the asymmetric carbon, this hydrocarbon is believed to be optically pure. Racemization in the presence of the catalyst might be possible by dehydrogenation–hydrogenation mechanism: higher temperatures would be expected to favor such a process. A comparison of the results of the low temperature palladium hydrogenolysis and the higher temperature copper–chromium oxide reaction seems to indicate that this process is not an important one.

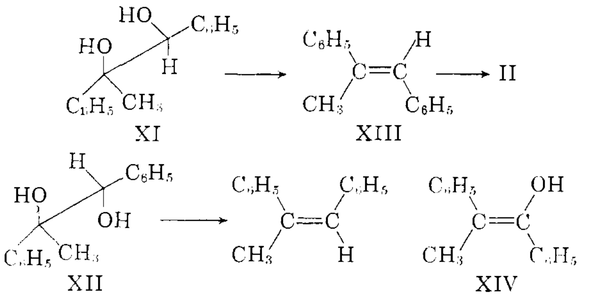
The hydrogenolysis of the optically active glycol I over copper–chromium oxide at 200° yielded the optically active hydrocarbon II in 58% yield. Since II was a liquid it was desirable to convert it to a solid derivative in which purity was more readily demonstrable. This was achieved by acetylating the phenyl groups of II with acetic anhydride and aluminum chloride: the diacetyl derivative was readily purified by recrystallization.

TABLE I

1,2-Diphenylpropane (II)	$[\alpha]^{20}\mathrm{D}$	Diacetyl derivative M.p., °C.	$[\alpha]^{20}\mathrm{D}$
d,l (synthetic)	.....	79–80	.....
(−)-Isomer from hydratropic acid	−63.5	91–92	−158.3
(+) Isomer from hydrogenolysis of I	+11.75	79–80	+ 35.3

Since the starting material (+)-hydratropic acid has the D-configuration,[15] the resulting (−)-1,2-diphenylpropane must have the same configuration. Therefore the isolation of L(+)-diphenylpropane by the hydrogenolysis of L(−)-1,2-diphenyl-1,2-propanediol demonstrates that the optically active product in the hydrogenolysis was formed with retention of configuration. The rotations for the hydrocarbons lead to the value of 18.1% retention and 81.9% racemization (59% retention, 41% inversion) and from the diacetyl derivatives the values 22.3% retention and 77.7% racemization (61.2% retention and 38.8% inversion) are obtained. The higher value for retention calculated from the diacetyl derivative could be due to separation of an impurity present in the liquid hydrocarbon or from fractionation in recrystallizing the derivative.

The amount of racemization observed in this hydrogenolysis is greater than with Raney nickel (10–36% racemization).[2,3] This could be due to differences in kinds of interactions on the two catalyst surfaces. Although it is not possible to suggest a detailed mechanism, it may be worthwhile to point out that for these 1,2-diaryl-1,2-glycols, simultaneous cleavage of both carbon–oxygen bonds at the catalyst surface could led to a racemic intermediate, α-methylstilbene.



Isomer XI of the glycol would be expected to react most rapidly by this mechanism, forming the more stable *trans*-α-methylstilbene. An additional possibility is that at 200° dehydration precedes hydrogenolysis. This process also should be faster for isomer XI, with inactive XIV as the product.[16]

Experimental[17]

d,l-**1,2-Diphenyl-1,2-propanediol** (I).—Methylbenzoin (37.3 g.), prepared in 47% yield by the reaction of benzil with methylmagnesium iodide,[8] was dissolved in ether (130 ml.) and added to a suspension of lithium aluminum hydride (6.3 g.) in ether (250 ml.). The reaction mixture was stirred for three hours and then treated with water and dilute hydrochloric acid. The ether layer was separated and the aqueous solution extracted with ether. The combined ether solution was washed with sodium bicarbonate solution, dried and concentrated to yield an oil (38.4 g.). Crystallization of this material from benzene-ligroin yielded a solid which melted at 70–90° (mixture of racemates); however, slow crystallization from a minimum of hot benzene produced 15 g. (40%) of the higher melting isomer, m.p. 103–104° (reported[18] 104°). The lower melting racemate could not be obtained in pure form.

The reaction of α-methylstilbene (4 g.) with silver benzoate (10 g.) and iodine (5.25 g.) in benzene (150 ml.) according to the directions of Prevost[19] produced an oily product (7 g.). After several months there was crystallization of a small amount (0.38 g., 4.5%) of the total product. This substance was recrystallized from benzene, m.p. 195–196°; it is believed to be the dibenzoate of I.

Anal. Calcd. for $C_{29}H_{24}O_4$: C, 79.78; H, 5.54. Found: C, 79.79; H, 5.68.

Attempted Resolution of I.—The hydrogen phthalate of methylhydrobenzoin was prepared by heating I (1 g.) and phthalic anhydride (1.3 g.) in pyridine at 90° for 45 hours. The crude product was obtained by pouring the reaction mixture into ice, and 10% hydrochloric acid. Purification was effected by dissolving the crude precipitate in ether and extracting the acid phthalate with dilute potassium carbonate solution. The basic solution was acidified and the precipitate recrystallized three times from benzene to yield 1.07 g. (46%) of the desired half-ester which melted at 181–183°.

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 73.39; H, 5.36. Found: C, 73.39; H, 5.40.

A solution of this substance was combined with a solution containing an equivalent of brucine, quinine, cinchonine or 1-phenylethylamine. However, in none of the experiments were crystalline alkaloid salts formed using any of a variety of solvents and solvent mixtures.

The hydrogen succinate of I resulted in 81% yield from I (1 g.), succinic anhydride (0.88 g.) and pyridine (10 ml.) at

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(15) H. I. Bernstein and F. C. Whitmore, THIS JOURNAL, **61**, 7324 (1939), and K. Mislow and M. Heffler, *ibid.*, **74**, 3668 (1952).

(16) It is interesting to note that if XI reacted exclusively by one of these mechanisms, the observed retention for isomer XII would be 44.6% which is comparable with the values observed using Raney nickel. This follows from the fact that XI and XII are present in approximately equal amounts.

(17) Melting points were determined using the Kofler micro-hot-stage. Analyses were by W. Manswer, Zurich, Switz., and G. Robertson, Florham Park, N. J.

(18) M. Tiffeneau and H. Dorlencourt, *Compt. rend.*, **143**, 127 (1906), prepared this substance by the addition of methylmagnesium iodide to benzoin.

(19) C. Prevost, *Compt. rend.*, **196**, 1129 (1933); **197**, 1661 (1933).

90° for 18 hours. Three recrystallizations from benzene yielded a product which melted at 154–156°.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 69.40; H, 6.18. Found: C, 69.50; H, 6.14.

Attempts to obtain crystalline alkaloid salts with strychnine, quinine, brucine, cinchonidine, cinchonine and 1-phenylethylamine were fruitless.

L(+)-Atrolactic Acid (IV).—Racemic atrolactic acid was prepared in 60% yield from propiophenone (53.6 g.), bromine (64 g.) and sodium hydroxide (400 g.) by the procedure of Levine and Stephens.[9] The resolution was carried out essentially as described by McKenzie and Clough.[20] After eight recrystallizations from ethanol the quinine salt melted at 225° and had $[\alpha]^{20}_{\rm D}$ −109° (*c* 0.54, ethanol). The atrolactic acid regenerated from the salt had $[\alpha]^{20}_{\rm D}$ +35.3° (*c* 2.53, ethanol); the reported value is $[\alpha]_{\rm D}$ +37.3° (ethanol).

2-Acetoxy-2-phenylpropionic Acid.—*d,l*-Atrolactic acid (2.53 g.) was dissolved in dry pyridine (20 ml.) and treated at 0° with acetyl chloride (2.2 ml.). The reaction mixture was stirred at this temperature for an hour, the temperature was allowed to rise to 25° and then water and benzene were added. The benzene layer was washed with dilute hydrochloric acid and water, then dried and concentrated. The residual oil (2.8 g.) was crystallized from benzene–ligroin to yield 1.55 g. (50%) of product which melted at 107–109°.

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 63.45; H, 5.81. Found: C, 63.43; H, 5.94.

This acid was converted with thionyl chloride to the acid chloride which was freed from volatile materials and treated with diphenylcadmium. Chromatography of the product of this reaction produced none of the desired α-methylbenzoin.

L(−)-1,2-Diphenyl-2-propanol-1-one (III).—A solution of L(+)-atrolactic acid (16 g.) in anhydrous ether was added to a solution of phenyllithium prepared from lithium (10.5 g.), bromobenzene (110 g.) and dry ether (500 ml.). The reaction mixture was refluxed for 95 hours, cooled and decomposed with cold dilute hydrochloric acid. The ether layer was separated and the aqueous layer extracted with ether. The combined ether extract was washed with sodium carbonate solution and water, then dried and concentrated. The residue was distilled to yield 12.5 g. (55%) of III which boiled at 115–130° (0.005 mm.). The separate fractions containing the ketone had rotations $[\alpha]^{20}_{\rm D}$ −156° (*c* 3.54, ethanol) to −178° (*c* 2.30, ethanol) (reported[8] −176.6° in ethanol). This product could not be obtained in crystalline form.

A similar procedure starting with *d,l*-atrolactic acid and with stirring at room temperature for 40 hours, yielded after crystallization from benzene–ligroin only 24% of *d,l*-α-methylbenzoin, m.p. 63–65°.

L(−)-1,2-Diphenyl-1,2-propanediol (I).—A solution of L(−)-1,2-diphenyl-2-propanol-1-one (1.45 g.) having $[\alpha]^{20}_{\rm D}$ −178° was added to a slurry of lithium aluminum hydride (0.25 g.) in ether (10 ml.). The mixture was stirred at room temperature for three hours and then decomposed with water followed by dilute hydrochloric acid. The product was extracted with ether; evaporation of the ether extract left an oil (1.26 g., 85%) which had $[\alpha]^{17}_{\rm D}$ −2.43° (*c* 3.48, ethanol) and $[\alpha]^{17}_{\rm D}$ −8.06° (*c* 3.05, chloroform) (reported[8] $[\alpha]^{18}_{\rm D}$ −33° in ethanol, for a sample prepared by catalytic reduction). The infrared spectrum for this substance showed that the reduction was complete (no absorption in the carbonyl region).

D(+)-Hydratropic Acid (VIII).—*d,l*-Hydratropic acid was prepared according to the directions of Eliel and Freeman[21]; from hydratropic aldehyde (59 g.) there was obtained 72.5% (48 g.) of acid VIII which boiled at 119° (0.4 mm.) and had $n^{25}_{\rm D}$ 1.5220.

The resolution was accomplished by means of the strychnine salt.[22] The salt was recrystallized five times from 75% ethanol and then reconverted to hydratropic acid which had $[\alpha]^{19.5}_{\rm D}$ −93.0° (*c* 1.35 benzene), reported[23] $[\alpha]^{20}_{\rm D}$ +92.5° in benzene.

D(+)-1,2-Diphenyl-1-propanone (IX). **A.**—A solution of D(+)-hydratropic acid (3.33 g.) in ether (15 ml.) was added to a solution of phenyllithium prepared from bromobenzene (20.5 g.) and lithium (1.84 g.) in anhydrous ether (100 ml.). The mixture was stirred at reflux temperature for 90 hours. The cold reaction mixture was decomposed with ice and the product removed by ether extraction. Evaporation of the ether and distillation of the residue furnished 2.1 g. (45%) of ketone IX which was largely racemized, $[\alpha]^{20}_{\rm D}$ + 30° in chloroform (reported[13] $[\alpha]^{23}_{\rm D}$ + 202° in chloroform).

B.—The procedure of Cram and Abd Elhafez[13] yielded distilled product, b.p. 63–70° (0.005 mm.), which had $[\alpha]^{20}_{\rm D}$ +65° (*c* 2.7, chloroform) and +100° (*c* 2.85, chloroform) in two separate experiments. In addition to the carbonyl absorption band at 5.95 there was an intense peak at 5.79 μ. In subsequent experiments the solution of diphenylcadmium in ether was distilled on the steam-bath until no more ether remained. Next, benzene was added and distilled until half had been removed; finally, hydratropyl chloride in benzene was added. The products from two such experiments had $[\alpha]^{20}_{\rm D}$ + 120° (*c* 2.1, chloroform) and + 160° (*c* 1.8, chloroform); the intensity of the infrared absorption at 5.79 μ was considerably reduced in these samples.

D(−)-1,2-Diphenyl-1-propanol (X).—The ketone–ester mixture (0.9 g.) from the preceding experiment was reduced with hydrogen in the presence of 10% palladium-on-charcoal using acetic acid (50 ml.) as the solvent. The hydrogenation was continued for three days with two additions of fresh catalyst. The catalyst was filtered and the acetic acid distilled *in vacuo;* the last traces were removed by washing an ether solution of the product with sodium bicarbonate solution. The oil (0.73 g.) remaining after evaporation of the ether no longer had the infrared absorption band due to the ketone but the ester band was still present. This mixture was saponified by refluxing for 4 hours with potassium hydroxide in aqueous methanol. Separation of the acidic and neutral substances yielded *ca.* 0.1 g. of acidic material with the characteristic odor of hydratropic acid. The neutral product in pentane was chilled overnight to yield 60 mg. of crystalline 1,2-diphenyl-1-propanol which melted at 70° and had $[\alpha]^{19}_{\rm D}$ −68.5° (*c* 1.2, chloroform) (reported[18] m.p. 71.5° and $[\alpha]^{22}_{\rm D}$ −67.8°). Chromatography on alumina separated the mother liquors into 1,2-diphenylpropane (II) and an additional quantity (132 mg.) of the alcohol, m.p. 71° and $[\alpha]^{19}_{\rm D}$ −67° in chloroform.

D(−)-1,2-Diphenylpropane (II). **A.**—The chromatography on alumina of the mother liquors after crystallization of 1,2-diphenylpropanol (preceding experiment) yielded 240 mg. of II with $[\alpha]^{19.5}_{\rm D}$ −59.5° (*c* 1.15, chloroform).

B.—1,2-Diphenyl-1-propanol (140 mg.) in ethanol (25 ml.) and in the presence of copper–chromium oxide catalyst[24] was heated in a high pressure bomb at 200° with hydrogen at 3150 p.s.i. for 7 hours. The catalyst was filtered, the solvent evaporated and the crude product chromatographed on alumina to yield 63 mg. of II with $[\alpha]^{19}_{\rm D}$ −63.5° (*c* 2.34, chloroform).

***d,l*-1,2-Diphenylpropane** (II). **A.**—Hydratropic acid (1 g.) was reduced to 2-phenyl-1-propanol using lithium aluminum hydride as in the preparation of I. There was obtained 0.82 g. (90% of alcohol which boiled at 65° (0.5 mm.) and had $n^{25}_{\rm D}$ 1.522 (reported[15] b.p. 105° (11 mm.) and $n^{25}_{\rm D}$ 1.523).

The alcohol (0.8 g.) and *p*-toluenesulfonyl chloride (1.1 g.) in pyridine (10 ml.) were allowed to stand overnight at 0° and then poured into cold dilute hydrochloric acid. The crude product was extracted with carbon tetrachloride, the extract dried over potassium carbonate and concentrated. The oily residue crystallized after several days at 0°. Trituration with cold ligroin yielded 2.34 g. (71%) of the tosylate which melted at 48–50°. Recrystallization from acetone–hexane raised the melting point to 50–51°.

Anal. Calcd. for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.24. Found: C, 66.29; H, 6.37.

The reaction of this tosylate (0.8 g.) with phenylmagnesium bromide, prepared from magnesium (0.073 g.) and bromobenzene (0.47 g.), at reflux temperature for two hours yielded only 17.5 mg. (1.8 %) of II, identified by its infrared spectrum.

B.—α-Methylstilbene (20 g.) and copper–chromium oxide catalyst (3 g.) in ethanol (150 ml.) were heated at 180° with hydrogen at 1300 p.s.i. for four hours. Processing as in the preparation of optically active II yielded II which boiled at

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(20) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **97**, 1019 (1910).

(21) E. L. Eliel and J. P. Freeman, THIS JOURNAL, **74**, 923 (1952).

(22) H. S. Raper, *J. Chem. Soc.*, 2558 (1923).

(23) C. L. Arcus and J. Kenyon, *ibid.*, 918 (1939).

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150° (16 mm.) and had n^{25}_{D} 1.5540 (reported[25] b.p. 127–130° (8 mm.) and n^{20}_{D} 1.5585). The infrared spectrum of this product was identical with the product of part A and also with the spectra of the optically active samples of II.

Hydrogenolysis of L(−)-Methylhydrobenzoin (I).—A solution of the L(−)-methylhydrobenzoin (4 g.) in ethanol (50 ml.) was hydrogenolyzed for four hours at 200° with hydrogen at 1400 p.s.i. in the presence of copper–chromium oxide catalyst (2 g.). Processing yielded 1.5 g. of crude product and after distillation 0.87 g. (25%) of II which boiled at 54–58° (0.02 mm.) and had $[\alpha]^{20}_{D}$ 11.75° (*c* 2.1, chloroform). The infrared spectrum was identical with those of previous samples of II.

1,2-Bis-(4-acetylphenyl)-propane. A. *d,l*-Form.—Acetic anhydride (1.04 g.) was added during 15 minutes to a vigorously stirred mixture of *d,l*-1,2-diphenylpropane (1 g.), aluminum chloride (3.06 g.) and carbon bisulfide (10 ml.). The mixture then was refluxed for one hour and the solvent evaporated. The residue was treated with ice, hydrochloric acid and ether. Evaporation of the ether layer left a crystalline residue which was purified by five recrystallizations from pentane–benzene, m.p. 79–80°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.52; H, 7.40.

B. (+)-Form.—The reaction with the sample of (+)-1,2-diphenylpropane was carried out exactly as in part A. There was obtained after five recrystallizations, a product with m.p. 79–80° and $[\alpha]^{19}_{D}$ 35.3° (*c* 0.59, chloroform). The infrared spectrum of this product was identical with that of compound obtained in part A.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.46; H, 7.24.

C. (−)-Form.—The reaction with (−)-1,2-diphenylpropane from the hydrogenolysis of I was carried out as in part A. Five recrystallizations yielded a product with m.p. 91–92° and $[\alpha]^{19}_{D}$ −158.3° (*c* 0.55, chloroform), and with infrared spectrum identical with those of the other samples of this derivative.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.53; H, 7.32.

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(25) K. Serijan and P. H. Wise, THIS JOURNAL, **73**, 4766 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FORDHAM UNIVERSITY]

Ozonolysis of Polycyclic Aromatics. VI.[1] Benz[a]anthracene and Benz[a]anthracene-7,12-dione. Correlation of Quinone–Hydroquinone Oxidation–Reduction Potentials with the Positions of Predominant Ozone Attack[2]

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Benz[a]anthracene (I) and benz[a]anthracene-7,12-dione (II) absorb, respectively, three and two molar equivalents of ozone to yield an unstable, probably monomeric ozonide (IV) in inert solvents, and a methoxyperoxidic oil and solid (crude VIII) in methanol from which was isolated a dimethoxy peracetal (VIII); IV, the peroxidic oil, and crude VIII have been oxidized to 1,2-anthraquinonedicarboxylic acid (V) and reduced to 1,2-anthraquinonedicarboxaldehyde (IX) and the cyclic hydroxylactone of 1-(or 2)-formyl-2-(1)-anthraquinonecarboxylic acid (X). Since the positions of predominant ozone attack on unsubstituted, polycyclic aromatics can be correlated with the positions of lowest corrected oxidation–reduction potential of the appropriate quinone–hydroquinone system, it is concluded that ozone attacks predominantly in a 1,2- or 1,4-addition *via* a rate-controlling transition state whose geometry corresponds to the most stable dihydro compound. These oxidation–reduction potentials qualitatively assess the order of decreasing ease of ozonolysis in the series: naphthacene > anthracene > I > phenanthrene $\simeq$ dibenz[a,h]anthracene > pyrene > naphthalene > benzene.

Molecular orbital calculations predict that in the benz[α]anthracene molecule (I), the 7- and 12-carbon atoms have the lowest carbon localization energies[3a] (reactivity number),[3b] the 7,12-positions have the lowest paralocalization energy[3a,4a,5] and the 5,6-bond, the lowest bond localization energy[4b] (ortholocalization energy).[3a] Chemical evidence qualitatively supports this theory of chemical reactivity based on these three theoretical indices. Thus I undergoes substitution at the less sterically hindered 7-position[6] and addition at the 7,12-[7] and 5,6-positions.[8] Further, chromic acid,[9] perhydrol[10] and perbenzoic acid[11] oxidation of I gave benz[α]anthracene-7,12-dione (II) while oxidation with Milas reagent[12] gave a mixture of II and benz[α]anthracene-5,6-dione.[13]

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(5) E. C. Kooyman and J. A. A. Ketelaar, *Rec. trav. chim.*, **65,** 859 (1946).

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