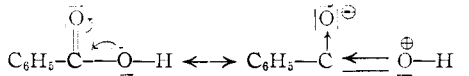
The negative ρ-value means that the reaction rate is increased by the substitution of groups which increase the electron density on the diazocarbon. It is interesting to note[2] that the rate is also increased by the substitution of electron-withdrawing groups on the benzoic acid.

In the five cases where the effect of a substituent on one ring was compared to the effect of two of the same substituents on different rings, it was found that the σ-values are satisfactorily additive.[3a] The good correlation for 3-nitro-4'-methyldiphenyldiazomethane, where the nitro group with a strong deactivating effect and the methyl group with a moderate activating effect are both influencing the same reaction center, offers striking proof of the additive principle of substituent effects.

The results show that an increase in the electron density on the diazocarbon increases the rate of the reaction. This fact is consistent with either of the mechanisms shown in Fig. 1. However, consideration of resonance in the carboxyl group of benzoic acid, and the resulting partial positive charge on



the hydroxyl oxygen and partial negative charge on the carbonyl oxygen indicates that mechanism II, involving a simultaneous attack of hydroxyl oxygen and of hydroxyl hydrogen, is more probable since the more positive of the two oxygens is more likely to attack the nucleophilic diazocarbon.

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COLLEGE STATION, TEXAS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

The Stereochemistry of the Ivanov and Reformatsky Reactions. I

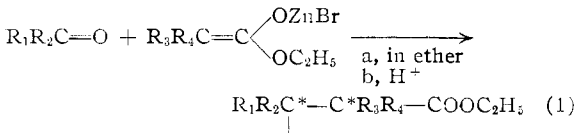
BY HOWARD E. ZIMMERMAN AND MARJORIE D. TRAXLER

RECEIVED NOVEMBER 1, 1956

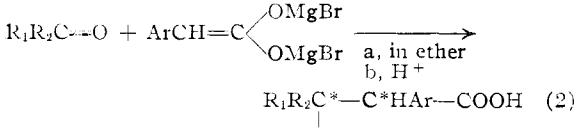
The stereochemistry of the reaction of benzaldehyde with the magnesium enolate of phenylacetic acid has been studied. In addition to the known 178° isomer of 2,3-diphenyl-3-hydroxypropionic acid, its diastereomer, m.p. 144°, was isolated as a minor product. By means of a stereospecific degradation the former was shown to be the *threo* isomer while the latter was found to have the *erythro* configuration. The ratio of the diastereomeric reaction products was determined and a hypothesis advanced to account for the preferential formation of the *threo* isomer.

The Reformatsky reaction has been known for over sixty years; its synthetic utility is undisputed. Nevertheless, little is known about its stereochemistry. Similarly, the stereochemical course of the mechanistically analogous but more recent Ivanov reaction has not been investigated.

Thus, in the reaction of an aldehyde or unsymmetrically substituted ketone with an unsymmetrically substituted Reformatsky reagent (equation 1) or Ivanov reagent (equation 2), no theory



$$R_1R_2C(OH)-C^*R_3R_4-COOC_2H_5 \quad (1)$$



$$R_1R_2C(OH)-C^*HAr-COOH \quad (2)$$

exists for predicting whether both possible diastereomers will be formed and, if so, which will predominate. Such information would be not only of synthetic but also of intrinsic mechanistic interest. The present paper relates efforts directed toward an elucidation of the stereochemistry of these reactions, efforts which began with study of an example of the Ivanov reaction.

Perusal of the literature[1] on the Ivanov reaction showed that almost without exception[2] only one diastereomer[3] had been obtained in situations where two might have been expected. Thus it appeared that a stereospecific reaction was involved.

The present work began with the Ivanov condensation of benzaldehyde with phenylacetic acid. Previously this reaction had been reported by Ivanov[1a] to yield 2,3-diphenyl-3-hydroxypropionic acid, m.p. 175°, in 60% yield; the same product, reported as melting at 173–174°, was isolated by Blicke[1c] in an 80% yield.

In the present investigation it was found that by crystallization 53% of 2,3-diphenyl-3-hydroxypropionic acid, m.p. 177.0–178.0°, could be isolated without difficulty. Further quantities could be isolated, however, with more difficulty. By means of systematic recrystallization small quantities of a stereoisomer melting at 142.0–143.5° were isolable. With much less difficulty these acids could be separated by silica gel chromatography; in fact, it was found that this procedure could be utilized

(1) (a) D. Ivanov and N. Nicoluff, *Bull. soc. chim.*, **51**, 1325 (1932), and earlier references cited therein; (b) A. Weston and R. DeNet, THIS JOURNAL, **73**, 4221 (1951); (c) F. Blicke and H. Raffelson, *ibid.*, **74**, 1730 (1952); (d) F. Blicke and R. Cox, *ibid.*, **77**, 5401 (1955); (e) F. Blicke and H. Zinnes, *ibid.*, **77**, 6247 (1955); (f) C. Rondestvedt and E. Rowley, *ibid.*, **78**, 3804 (1956).

(2) Ivanov (ref. 1a) reported a major and a minor product from the reaction of phenylacetic acid and isobutyraldehyde. The yield was not reported and more recent workers (ref. 1c) have been unable to isolate the minor product and to reproduce the melting point of the major product. Recently (ref. 1f) two sets of diastereomers have been reported; however, in each case the total yield was below 25% with no indication of the proportion of the isomers.

(3) The reported yields vary from much below 50% to considerably above this. In the latter situation there is a suggestion of stereospecificity; in the former case no conclusion can be drawn from isolation of only one isomer.

analytically as well as preparatively. In this fashion it was ascertained that the 178° acid constituted 76% of the hydroxyacid product *versus* 24% for the 143° acid. The total yield was 91%.

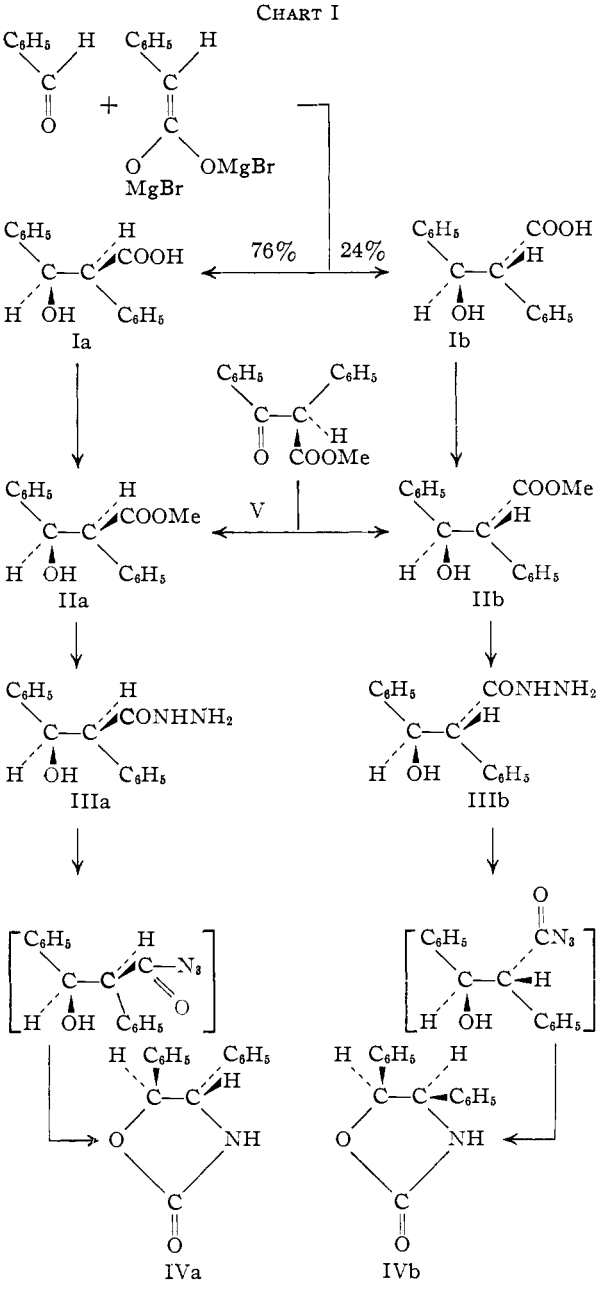
The higher melting diastereomer having thus been shown to be the preferred reaction product, it was necessary to determine its configuration in order to uncover the reason for the observed stereospecificity. Conversion of each of the hydroxyacid diastereomers Ia and Ib, to their methyl esters IIa and IIb, respectively, was effected under Fischer conditions. That no epimerization had occurred was evidenced by the isolation of different products and by the observation that the same product (IIa) resulted by diazomethane methylation of Ia as under Fischer conditions. Each methyl ester was converted to its respective hydrazide (IIIa) and IIIb) under mild conditions, and each of these was subjected to the Curtius rearrangement. From the hydrazide IIIa of the 178°-hydroxyacid there was obtained *trans*-4,5-diphenyl-2-oxazolidone,[4] m.p. 161–162°, which proved identical with an authentic sample.[5] From the Curtius degradation of IIIb there was obtained *cis*-4,5-diphenyl-2-oxazolidone,[5] m.p. 193.5–194.5° (reported[5] 193.5–195.0°). The entire degradative scheme[6] is illustrated in Chart I.

The formation of the *trans*-oxazolidone IVa from the 178°-hydroxyacid Ia and the *cis*-oxazolidone IVb from Ib allows Ia to be identified as *threo*-2,3-diphenyl-3-hydroxypropionic acid and Ib, the minor product, to be assigned the *erythro* configuration as shown in Chart I.

Furthermore it was found that the diastereomeric methyl esters (IIa and IIb) could be obtained by the sodium borohydride reduction of methyl 2-benzoylphenylacetate (V). In this case, however, the *erythro* product predominated, constituting 83% of the hydroxyester product. The preferential formation of the *erythro* isomer is consonant with Cram's rule of asymmetric induction[8a,b]; hence, depending on one's viewpoint, this might be considered to be either a further example in support of Cram's rule or additional evidence for the *erythro* configuration of IIb.

Configurations having been assigned to the major and minor products of the Ivanov condensation, it is of interest to consider whether the observed stereochemistry is consistent with a reasonable condensation mechanism. It is clear that the reaction involves σ-bond formation by overlap of the electron rich p-orbital of the Ivanov reagent[9] with

CHART I



the electron-deficient p-orbital of the benzaldehyde with gradual change in hybridization from p to sp^3. In addition, it is reasonable to expect the benzaldehyde carbonyl group to be polarized by coördination with magnesium.

It is suggested that this coördination is intramolecular, for such an assumption allows prediction of the observed stereochemistry. Of the several possible transition states VI and VII it may be seen that VIa, leading to *threo* product, involves the lowest energy approach for bonding; in all the alternate transition states (for example VIb, leading to the *erythro* isomer) serious phenyl–phenyl interaction develops.[10]

(4) M. Newman and A. Kutner, THIS JOURNAL, **73**, 4199 (1951).

(5) Kindly supplied by Dr. M. Newman.

(6) The proof of configuration depends on the assumption that the migrating group retains its configuration in the Curtius rearrangement. This point has been discussed in an earlier paper (ref. 7), in which a similar degradative scheme was employed.

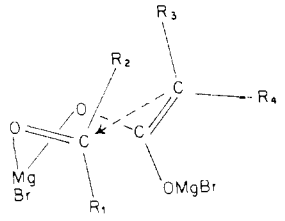
(7) H. Zimmerman and J. English, Jr., THIS JOURNAL, **76**, 2291 (1954).

(8) (a) D. Cram and F. Abd Elhafez, *ibid.*, **74**, 5828 (1952). (b) The *erythro*-hydroxy ester, IIb, is predicted by the rule as follows: with the carbonyl oxygen of V oriented *trans* to the phenyl group on carbon 2 as shown in Chart I, attack of hydride should occur from the least hindered side of the molecule, as determined by the smaller size of H at C_2 compared to COOMe.

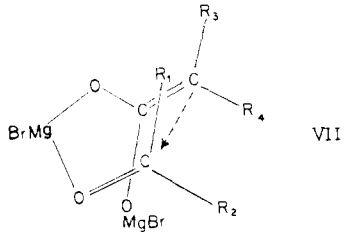
(9) The Ivanov reagent is pictured as a true enolate rather than as a carboxylate salt with magnesium bonded to the α-carbon atom. Which is actually the correct ground state is not necessarily relevant in deciding which is the reactive species.

(10) These are drawn from Fisher–Hirshfelder models in which carbon was used for tetrahedral magnesium and imine nitrogen for the coördinated carbonyl oxygen. A similar conclusion is reached on the basis of the product (*i.e.*, as magnesium salt) stability.

Further research is in progress in order to test these concepts. For example, the degree of specificity should be a function of the relative bulk of R_1 and R_2 as well as of R_3 and R_4; also under consideration is the effect of changing the metal involved in coördination.



VIa, R_1, R_3 = C_6H_5; R_2, R_4 = H
VIb, R_1, R_4 = C_6H_5; R_2, R_3 = H
VIc, R_2, R_3 = C_6H_5; R_1, R_4 = H



VII

Experimental[11]

Ivanov Condensation of Benzaldehyde and Phenylacetic Acid; *erythro-* and *threo*-2,3-Diphenyl-3-hydroxypropionic Acids.—To 0.50 mole of isopropylmagnesium bromide in 200 ml. of ether in a liter flask equipped with Hershberg stirrer, dropping funnel, reflux condenser and drying tube was added 27.25 g. (0.20 mole) of phenylacetic acid in 75 ml. of anhydrous ether dropwise with stirring over 1 hr. and 50 minutes. The mixture was then stirred at room temperature for 15 hr. At the end of this time a dark lower layer of viscous magnesium enolate could be discerned below a clear ether layer. To the flask was added dropwise with stirring 21.22 g. (0.20 mole) of benzaldehyde dissolved in 50 ml. of anhydrous ether; the addition required 70 minutes after which the mixture was refluxed for 5 hr. Then 167 ml. of 6 *N* hydrochloric acid was added slowly with stirring followed by 100 ml. of water. A total of 1300 ml. of ether was required to extract the white solid which separated. The ether phase was then extracted with a solution of 30 g. of anhydrous sodium carbonate in 600 ml. of water. The aqueous extract was acidified to a congo red end-point, and the solution was filtered to yield 2,3-diphenyl-3-hydroxypropionic acid as a mixture of stereoisomers.

Several crystallizations from ethyl acetate–ligroin (b.p. 86–100°) gave a total of 26.18 g. of essentially pure *threo*-2,3-diphenyl-3-hydroxypropionic acid, m.p. 177–178°. The combined filtrates were concentrated and subjected to chromatography on a silica gel column (Davidson 40–200 mesh, 33 × 700 mm.). Eight 250-ml. fractions were collected by elution with 1:1 ether–hexane as follows: The first fraction was empty. Fraction 2 contained 5.21 g., m.p. 126–134°. Fraction 3 yielded 6.78 g., m.p. 130–151°, while 4 gave only 2.13 g., m.p. 126–147°; 5 contained 4.57 g., m.p. 174–176°; 6 gave 1.28 g., m.p. 175–176°. From 7 only 0.53 g. of solid, m.p. 173–174°, was obtained; 8 was void of material. Fractions 2 and 3 after recrystallization from ethyl acetate–ligroin yielded a total of 8.59 g. of pure *erythro*-2,3-diphenyl-3-hydroxypropionic acid, m.p. 142.0–143.5°. Fractions 5–7 represented reasonably pure *threo*-acid. The filtrates from the recrystallization of the *erythro*-acid together with fraction 4 were combined and concentrated *in vacuo* to leave 5.16 g. of solid. This was subjected to silica gel chromatography as described above, yielding 2.10 g. of *erythro*-acid and 758 mg. of *threo*-acid. The total yield of *erythro*-2,3-diphenyl-3-hydroxypropionic acid, m.p. 142.0–143.5°, was 10.69 g. (22%), while that of the *threo* isomer, m.p. 177.0–178.0° (reported[1a,c] 173–174°, 175°), was 33.32 g. (69%); the total yield was thus 91%.

(11) All melting points were taken using a Fisher–Johns block checked with known compounds.

A small sample of the crude product was subjected to chromatography on a 20 × 490 mm. silica gel column. Eleven 50-ml. fractions were collected using 1:1 ether–hexane. Only fractions 7–9 contained material, and from these there was obtained a total of 16.9 mg. of slightly impure *erythro*-acid, m.p. 135–137°. Fractions 12–15, each 50 ml., were eluted with pure ether; fraction 16 was eluted with ethyl acetate. Fractions 13–16 contained solid, which when combined weighed 52.8 mg. and melted at 176–179°, being reasonably pure *threo*-acid. Thus the ratio of *threo*-2,3-diphenyl-3-hydroxypropionic acid to the *erythro*-isomer was 3.12.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found for *threo* isomer: C, 74.45; H, 5.68. Found for *erythro* isomer: C, 74.60; H, 5.78.

2-Benzoylphenylacetonitrile.—This was prepared essentially by the method described by Levine and Hauser[12] for acetylphenylacetonitrile, except that 69.0 ml. (0.60 mole) of phenylacetonitrile, 79.0 ml. (0.60 mole) of methyl benzoate, 13.8 g. (0.60 g. atom) of sodium and 300 ml. of liquid ammonia were used. The crude product was recrystallized from ethanol to give 56.2 g. of 2-benzoylphenylacetonitrile, m.p. 96–97° (reported[13] 89–90°).

Methyl 2-Benzoylphenylacetate.—The method described by Howk and McElvain[13] for the preparation of the ethyl ester was followed except for the substitution of methanol. The product, crystallized from ethanol, melted at 70.0–70.5° (reported[14] 75°).

Sodium Borohydride Reduction of Methyl 2-Benzoylphenylacetate; *erythro-* and *threo*-2,3-Diphenyl-3-hydroxypropionic Acids.—A solution of 0.38 g. (0.01 mole) of sodium borohydride in 50.0 ml. of methanol (reagent) was added dropwise to a stirred, ice-cooled suspension of 2.54 g. (0.01 mole) of 2-benzoylphenylacetate in 50.0 ml. of methanol. The temperature was kept between 5 and 10° during the addition which required 15 minutes. The mixture was then stirred at the same temperature for an additional 90 minutes; at the end of the first 15 minutes the solid had dissolved. Finally, 10 ml. of acetic acid was added followed by 500 ml. of water. The mixture was ether extracted and the extracts were dried over sodium sulfate. By concentration an oil was obtained; this solidified, giving m.p. 63–66°. Crystallization from ether–hexane afforded 1.41 g., m.p. 79–84°. Another crystallization brought the m.p. to 86.5–87.5° with negligible loss to the filtrate; this represented essentially pure methyl *erythro*-2,3-diphenyl-3-hydroxypropionate.

The combined filtrates were chromatographed on silica gel (20 × 460 mm., packed with 1:9 ether–hexane and washed with hexane). Nine 100-ml. fractions were collected, the first two by elution with 1:9 ether–hexane and the rest with 1:4 ether–hexane. Fractions 5–7 contained a total of 403 mg. of *erythro*-ester (m.p. 71–75°, 84–86°, 83–86°, respectively; m.p. 87.5–88.5° after crystallization). Fraction 9 contained 361 mg. of solid, m.p. 87–92°. One crystallization from hexane–ethyl acetate gave m.p. 96–98°. After another crystallization the m.p. was brought to 98.0–99.5°, wt. 248 mg. This material was identical with methyl *threo*-2,3-diphenyl-3-hydroxypropionate prepared by the esterification of the *threo*-acid. The infrared spectra of the isomeric methyl esters in chloroform were similar but exhibited differences above 7 μ.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found for *erythro* isomer: C, 74.98; H, 6.11. Found for *threo* isomer: C, 75.07; H, 6.29.

Fischer Esterification of *erythro*-2,3-Diphenyl-3-hydroxypropionic Acid; Methyl *erythro*-2-Diphenyl-3-hydroxypropionate.—A solution of 2.84 g. (0.02 mole) of *erythro*-2,3-diphenyl-3-hydroxypropionic acid, m.p. 142.0–143.5°, and 0.08 ml. of concd. sulfuric acid in 50 ml. of methanol reagent was refluxed for 5 hr., cooled and poured into 150 ml. of water to yield 2.38 g. of solid, m.p. 84–85°. One crystallization brought the melting point to 87–88°. This product did not depress the melting point of pure methyl *erythro*-2,3-diphenyl-3-hydroxypropionate obtained from the borohydride reduction, while the m.p. on admixture with the *threo* isomer was depressed to 73–78°.

(12) R. Levine and C. Hauser, THIS JOURNAL, **68**, 760 (1946).
(13) B. Howk and S. McElvain, *ibid.*, **54**, 286 (1932).
(14) E. Kohler, *ibid.*, **46**, 1743 (1924).

erythro-**2,3-Diphenyl-3-hydroxypropionhydrazide.**—A mixture of 2.00 g. of methyl *erythro*-2,3-diphenyl-3-hydroxypropionate (m.p. 87–88°), 2.00 ml. of abs. ethanol and 2.50 ml. of 85% hydrazine hydrate was kept at 22° for 7 hr.; at the end of the first hour the mixture was clear. Then the mixture was concentrated at room temperature under oil-pump vacuum, finally reaching 0.05 mm. The solid residue was taken up in hot chloroform and treated with hexane. On cooling, the solution yielded 2.20 g., m.p. 164–167°. Crystallization from 80 ml. of chloroform gave 1.65 g., m.p. 166.0–167.5°.

Anal. Calcd. for $C_{15}H_{16}O_2N_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.31; H, 6.26; N, 11.09.

When the reaction was run at higher temperatures, the yield was markedly decreased with formation of benzalazine and phenylacethydrazide.

Curtius Degradation of *erythro*-2,3-Diphenyl-3-hydroxypropionhydrazide to Yield *cis*-4,5-Diphenyl-2-oxazolidone.—To a slurry of 513 mg. (0.0020 mole) of *erythro*-2,3-diphenyl-3-hydroxypropionhydrazide in 0.37 ml. (0.0022 mole) of 6 *N* hydrochloric acid plus 5.0 ml. of water was added 4.0 ml. of ether. The magnetically stirred mixture was cooled to 5° and a solution of 138 mg. (0.0020 mole) of sodium nitrite in 2.0 ml. of water was added over two minutes. The reaction was noticeably exothermic, but the temperature was kept below 10°. At the end of the addition the reaction mixture was immediately ether extracted and the extract washed once with water and dried over sodium sulfate for 15 minutes; 20 ml. of benzene was added and the ether removed by distillation. The benzene solution was then refluxed for 30 minutes and finally concentrated *in vacuo* to leave 481 mg. of solid, m.p. 131–133°. This was dissolved in ether and chromatographed on silica gel (19 × 500 mm.). The column having been washed first with 400 ml. of 1:1 ether–hexane without elution of material, five 50-ml. fractions were collected by eluting with ether. Fraction 1 contained 1.0 mg., m.p. 177–189°; 2 gave 227 mg., m.p. 192–193°. Fraction 3 yielded 118 mg., m.p. 130–139°, and from 4, 52 mg., m.p. 128–140°, was obtained. No other material was eluted. Recrystallization of fraction 2, using ethyl acetate–hexane, brought the melting point to 193.5–194.5° (reported[4] for *cis*-4,5-diphenyl-2-oxazolidone 193.5–195.0°). The infrared spectrum of this compound contained a carbonyl absorption band at 5.66 μ; while the spectrum was similar to that of *trans*-4,5-diphenyl-2-oxazolidone below 7 μ, it exhibited differences above this wave length.

One crystallization of the combined fractions 3 and 4 from chloroform–hexane brought the melting point to 147–148°; after another crystallization this material melted at 148.0–149.0°. The infrared spectrum of this compound possessed absorption bands at 2.98, 3.12, 6.08 and 6.17 μ. The yield of this compound was increased at the expense of *cis*-oxazolidone by a slower addition of the aqueous sodium nitrite.

Anal. Calcd. for $C_{30}H_{28}O_4N_2$: C, 74.98; H, 5.87; N, 5.83. Found: C, 74.12; H, 6.18; N, 6.13.

Fischer Esterification of *threo*-2,3-Diphenyl-3-hydroxypropionic Acid; Methyl *threo*-2,3-Diphenyl-3-hydroxypropionate.—A solution of 5.00 g. of *threo*-2,3-diphenyl-3-hydroxypropionic acid and 0.15 ml. of concd. sulfuric acid in 100 ml. of methanol (reagent) was refluxed for 2.5 hr. The cooled solution was diluted with 250 ml. of water to yield a crystalline product, m.p. 88–90°, weighing 4.70 g. Two crystallizations from ethyl acetate–ligroin (b.p. 86–100°) brought the m.p. to 98.5–100.0°.

Diazomethane Preparation of Methyl *threo*-2,3-Diphenyl-3-hydroxypropionate.—A solution of diazomethane in 60 ml. of ether, prepared from 6.0 ml. of 40% potassium hydroxide and 2.0 g. of N-nitroso-N-methylurea, was added with swirling to 1.80 g. of *threo*-2,3-diphenyl-3-hydroxypropionic acid dissolved in 20 ml. of ether and 30 ml. of benzene. The mixture was allowed to stand at room temperature for 1 hr. and then was concentrated in the hood to yield large crystals, m.p. 95–100°. Crystallization from ethyl acetate–ligroin brought the melting point to 99.0–100.0°. This material was identical with that described earlier as methyl *threo*-2,3-diphenyl-3-hydroxypropionate.

threo-**2,3-Diphenyl-3-hydroxypropionhydrazide.**—A slurry of 200 mg. of finely powdered methyl *threo*-2,3-diphenyl-3-hydroxypropionate, 0.20 ml. of abs. ethanol and 0.25 ml. of 85% hydrazine hydrate was stirred magnetically at 22° for 6 hr. Ethanol and hydrazine were then removed at room temperature under oil-pump vacuum. The residue was dissolved in hot chloroform, in which it was only sparingly soluble. Three successive crops were obtained: 43 mg., m.p. 174–176°; 46 mg., m.p. 174–176°; 16 mg., m.p. 172–174°. Recrystallization brought the melting point to 175–176°.

Unlike the *erythro* isomer, the *threo*-hydrazide could be obtained from runs made at higher temperatures; however, the yield was poor. A solution of 5.12 g. of methyl *threo*-2,3-diphenyl-3-hydroxypropionate and 3.00 ml. of 85% hydrazine hydrate in 4.0 ml. of ethanol was refluxed for 2.5 hr. The solution was cooled, and a solid weighing 1.65 g. separated. Recrystallization from abs. ethanol gave 0.91 g., m.p. 175–177°.

Anal. Calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29. Found: C, 70.86; H, 6.73.

Curtius Degradation of *threo*-2,3-Diphenyl-3-hydroxypropionhydrazide to Yield *trans*-4,5-Diphenyl-2-oxazolidone.—A suspension of 470 mg. (0.0018 mole) of *threo*-2,3-diphenyl-3-hydroxypropionhydrazide in 5.0 ml. of water was stirred magnetically with cooling to 5°. To this was added 0.45 ml. (0.002 mole) of 6 *N* hydrochloric acid followed by 4.0 ml. of ether. A solution of 157 mg. (0.0023 mole) of sodium nitrite in 2.0 ml. of water was added during 5 minutes with the temperature being maintained at 5°. The solution was filtered and ether extracted. The extracts, to which 20 ml. of benzene had been added, were dried over sodium sulfate by brief swirling and the ether was removed by distillation. The remaining benzene solution was refluxed for 30 minutes and then concentrated *in vacuo* to leave 0.20 g. of crystalline solid, m.p. 145–155°. This on recrystallization melted at 161–162° (reported[4] 159.0–160.5°); a mixed melting point determination with authentic[5] *trans*-4,5-diphenyl-2-oxazolidone showed no depression.

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EVANSTON, ILLINOIS