6,8-Dinitroimidazo[1,2-a]pyridin-3(2H)-one was obtained, according to Knott,[9] in the following manner. Dinitro-2-pyridylalanine (10 g) and phosphorus trichloride (50 ml) were heated under reflux on a steam bath for 15 min. The solid slowly dissolved and a transitory yellow-brown coloration occurred; the mixture was then allowed to cool at room temperature and the product was completely precipitated by addition of ether (100 ml). The solid was filtered off, dissolved in methyl ethyl ketone, and precipitated with ether; the yellow grains were difficult to purify.

Anal. Calcd for $C_8H_6N_4O_5$: C, 40.33; H, 2.52; N, 23.52. Found: C, 39.97; H, 2.40; N, 23.28.

Kinetics of Hydrolysis.—The kinetics of hydrolysis of I and II were determined (a) by following the appearance of glycine and (b) by observing the intermediate at or very nearly its absorption maximum.

Rate of Appearance of Glycine.—Aqueous solutions of substrate (2×10^{-3} *M*) were diluted to two volumes with appropriate NaOH solutions; the hydrolysis experiments were performed in a thermostated water bath whose temperature was held constant to ±0.05°, and 1.0-ml portions were withdrawn for analysis at predetermined times. The extent of hydrolysis was measured by analysis of samples neutralized by 30% acetic acid, according to the ninhydrin procedure of Moore and Stein.[10] Portions of each hydrolysis mixture were subjected to complete hydrolysis by heating in 1.0 *M* NaOH for 1 hr at 60°. Spectrophotometric readings were made with a Beckman Model DU spectrophotometer at wavelength 570 mμ.

Rate of Change of Intermediate.—The stock solutions of I and sodium hydroxide for all runs were equilibrated in a water bath (±0.05°) prior to mixing; the temperature of the thermostated compartment of the Beckman DU spectrophotometer was maintained to within 0.1° by circulating water from a constant-temperature bath. The following general procedure was used in the kinetic determinations. To 50 μl of 2×10^{-3} *M* aqueous solution of I placed in the cell was rapidly added 3.0 ml of NaOH solution. The time lapse between removal of the alkali solution from the water thermostat and placement in the spectrophotometer was never longer than a few seconds. The reactions were followed by continuous recording of the optical density at 440 mμ.

Beer's law was found to be obeyed within the concentration and wavelength range employed.

Acknowledgments.—Many thanks are due to Professor A. Indelli and Professor E. Scoffone for helpful discussions and to Dr. A. Fotia for competent technical assistance.

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Optical Resolution and Absolute Configuration of *trans*-β-Phenylglycidic Acid[1,2]

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β-Phenylglycidic acid prepared by the Darzens' method was resolved by the use of (*S*)-(−)- and (*R*)-(+)-methylbenzylamine. The ammonolysis of these resolved (−)- and (+)-β-phenylglycidic acids resulted in mixtures of *erythro*-(+)-phenylserine and *erythro*-(+)-phenylisoserine and of *erythro*-(−)-phenylserine and *erythro*-(−)-phenylisoserine. The configurations of (−)- and (+)-glycidic acid were identified as follows: (−) isomer, (2*R*),(3*S*); (+) isomer, (2*S*),(3*R*). The configurations of (+)- and (−)-phenylisoserine were determined as follows: (+) isomer, (2*R*),(3*R*); (−) isomer, (2*S*),(3*S*). The ethyl β-phenylglycidate, prepared by the Darzens' method, was confirmed as being mostly or entirely composed of the *trans* isomer. The SN2 reaction in the ammonolysis of glycidic acid is discussed.

Many studies have been made on the chemistry of epoxides. These have been reviewed by Winstein and Henderson[3] and by Parker and Isaacs.[4] The Darzens' reaction in the synthesis of the glycidic acids has been reviewed.[5] Several ammonolysis and aminolysis reactions of the glycidic acids have been reported.[6-15]

A previous study[16] showed that ammonolysis of potassium (±)-β-phenylglycidate yielded a mixture of *erythro*-β-phenylserine and β-phenylisoserine (low melting point) in a ratio of 25:75.

The optical resolution of the glycidic acids has not been studied and their absolute configuration has not yet been directly clarified. Therefore it seemed worthwhile to resolve the glycidic acids and to characterize their optically active isomers stereochemically (Scheme I).

In this study, ethyl β-phenylglycidate was synthesized by the Darzens' method, and the ester was converted to its potassium salt (I) by treatment with alcoholic potassium hydroxide. The salt was liberated and the resulting unstable free β-phenylglycidic acid (II) (G acid) was resolved by (*S*)-(−)- and (*R*)-(+)-methylbenzylamine [(−)-amine, (+)-amine][17,18] in an ether solution. (−)-Amine and (±)-G acid resulted in crystallization of (−)-amine–(−)-G acid salt (IIIa). The mother liquor was treated with an equimolar proportion of hydrochloric acid and the free G acid was crystallized by addition of (+)-amine to form (+)-amine–(+)-G acid salt (IIIb). These amine salts

(1) Stereochemistry of Glycidic Acid. I.

(2) Aided by Grant No. NsG-689 of the National Aeronautics and Space Administration. Contribution No. 053 of the Institute of Molecular Evolution, University of Miami.

(3) S. Winstein and R. B. Henderson in Heterocyclic Compounds," Vol. I, R. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p 22.

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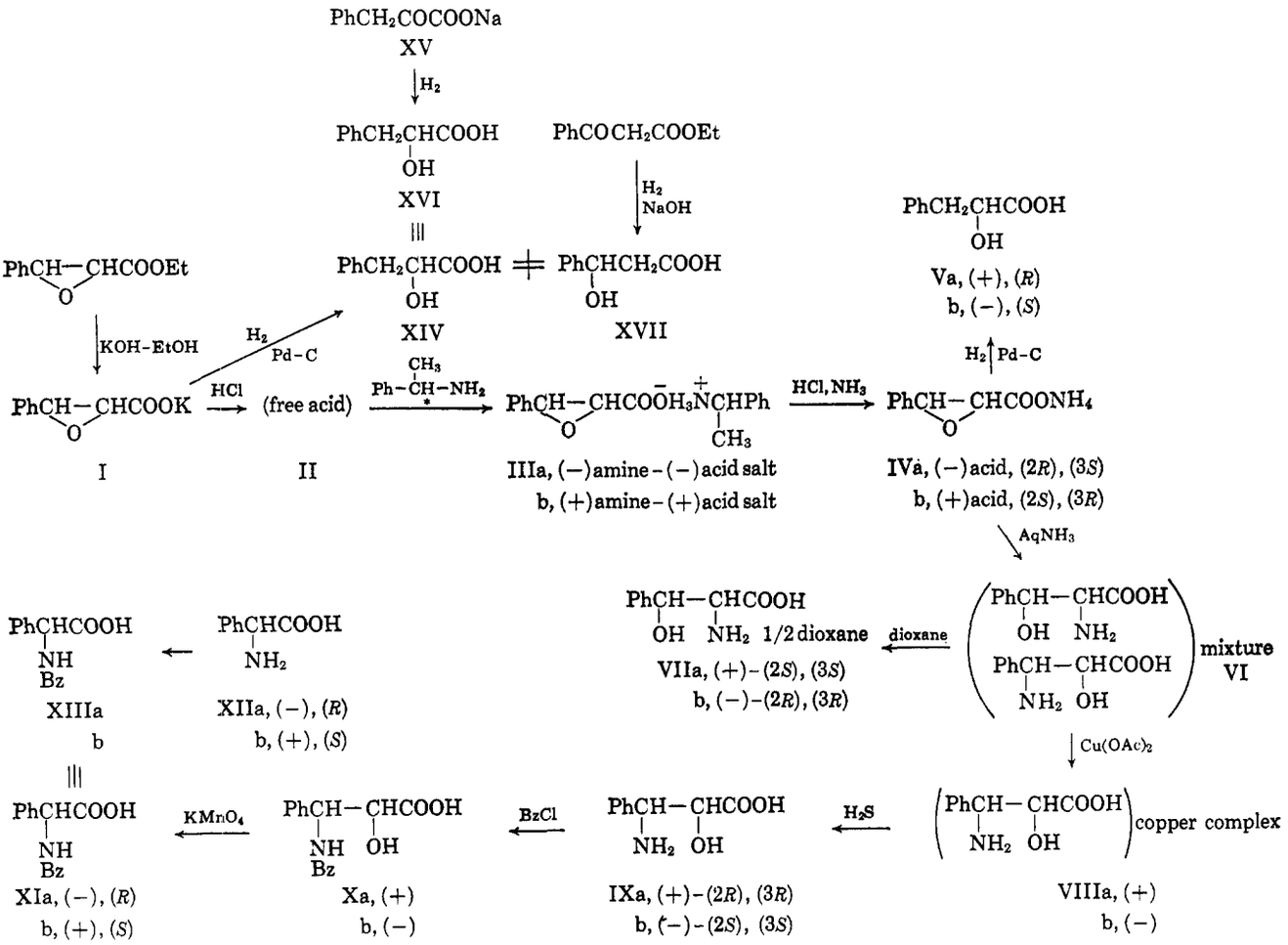
SCHEME I



were quite stable, although the ammonium salts of (−)- and (+)-G acid were not stable enough to keep for long periods of time.

The ammonium salt of (−)- or (+)-G acid was treated with concentrated ammonia (28%) for 6 days. The reaction products were found to be a mixture (VI) of *erythro*-phenylserine and *erythro*-phenylisoserine, as was observed in the ammonolysis of sodium (±)-phenylycidate.[16] Absence of *threo*-phenylserine was confirmed by paper chromatography with the use of the Shaw–Fox solvent.[19] The resulting optically active *erythro*-phenylserines (VIIa and b) were each isolated as dioxane adduct[19,20] from the reaction mixture. (−)-G acid gave optically pure (+)-*erythro*-phenylserine (VIIa), and (+)-G acid gave optically pure (−)-*erythro*-phenylserine (VIIb). The absolute configurations of *erythro*-phenylserine were already known[20,21] as (+) isomers, (2*S*),(3*S*), and (−) isomer, (2R),(3*R*).

Optically active phenylisoserine was isolated as a copper complex (VIIIa and b) from the reaction mixture from which optically active *erythro*-phenylserine had already been isolated. Free phenylisoserine (IXa and b) was prepared by treatment with hydrogen sulfide. (−)-G acid resulted in (+)-phenylisoserine (IXa), and (+)-G acid gave (−)-phenylisoserine (IXb).

The configuration determinations of (+)- and (−)-phenylisoserine (IXa and b) were carried out as follows.

A. Configuration of α-Carbon.—(−)-G acid (IVa) could be converted exclusively to (+)-β-phenyllactic acid (2*R*, Va) upon hydrogenation by the use of palladium on charcoal. In the same way (+)-G acid (IVb) gave (−)-β-phenyllactic acid (2*S*, Vb). Thus, the configurations of the α-carbons of (+)- and (−)-phenylisoserine (IXa and b) are *R* and *S*, respectively.

B. Configuration of β-Carbon.—The β-amino group of (+)- or (−)-phenylisoserine (IXa and b) was benzoylated and the resulting (+)- and (−)-N-benzoyl β-phenylisoserine (Xa and b) were each oxidized by potassium permanganate. (+)-N-Benzoyl-β-phenylisoserine (Xa) gave optically pure (−)-N-benzoylphenylglycine (2*R*, XIa), and (−)-N-benzoyl-β-phenylisoserine (Xb) gave optically pure (+)-phenylglycine (2*S*, XIb) upon oxidation. Therefore, the configurations of the β-carbon atoms of (+)- and (−)-phenylisoserine (IXa and b) were identified as *R* and *S*, respectively.

Consequently, the configuration of the original G acid is now known from the data above. The configurations of the α-carbons of (−)- and (+)-G acid are *R* and *S*, respectively, as was mentioned earlier in the study of hydrogenation of these glycidic acids. The configurations of the β-carbons of (−)- and (+)-G acid are identical with the configurations of the β-carbons of (+)- and (−)-*erythro* β-phenylserine (VIIa and b), *S* and *R*, respectively. Therefore, (−)-G acid has a

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(20) T. Kaneko and K. Harada, *Bull. Chem. Soc. Japan*, **34**, 1314 (1961).
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configuration of (2*R*),(3*S*) and (+)-G acid has a configuration of (2*S*),(3*R*). These results show that resolved (−)- and (+)-G acids are each optically pure *trans* isomers.

Discussion

Phenylglycidic acid prepared by the Darzens' reaction has been considered to be *trans*.[22] This can be explained by the overlap control theory.[23] In this investigation, the ammonium β-phenylycidates (IVa and b) were characterized as pure *trans* isomers as will be shown in the Experimental Section. However, the original (±)-ethyl β-phenylglycidate might have contained a small amount of the *cis* isomer. The *cis* isomer might be fractionated in each of two ways in this study: (1) fractionation during the formation of potassium phenylglycidate (I); (2) fractionation during the optical resolution. The ammonolysis product of potassium (±)-β-phenylglycidate, however, showed only (±)-*erythro*-β-phenylserine which would be expected from *trans* glycidate by an SN2 reaction. Fractionation (2) is accordingly not likely but (1) is a possibility if a small amount of *cis* isomer is in the original ethyl β-phenylglycidate.

As described in the Experimental Section, (−)- and (+)-G acid (IVa and b) [(−) isomer, (2*R*),(3*S*); (+) isomer, (2*S*),(3*R*)] were converted to pure (+)- and (−)-*erythro*-phenylserine (VIIa and b), and no *threo* isomer was identified. This was confirmed by paper chromatography before isolation of VIIa and b. The facts indicate that the nucleophilic attack of ammonia on the α-carbon atom proceeds in a typical SN2 reaction accompanied by a complete Walden inversion. During the reaction no racemization, which would have resulted in *threo*-phenylserine as a reaction product, took place. The ammonolysis of IVa and b also resulted in formation of *erythro*-(+)- and (−)-phenylisoserine [(+) isomer, (2*R*),(3*R*); (−) isomer, (2*S*),(3*S*)]. This fact indicates that the nucleophilic attack of ammonia on the β-carbon atom accompanies a Walden inversion. A small amount of *threo*-phenylisoserine might be formed by an incomplete SN2 reaction or racemization. However, because of a lack of a sensitive identification method for the *threo*-phenylisoserine (such as paper chromatography), it might be overlooked.

Experimental Section[24]

Ethyl (±)-β-Phenylglycidate.—Ethyl β-phenylglycidate was synthesized by Darzens' method from ethyl chloroacetate and benzaldehyde: yield 73%, bp 162–164° (18 mm).

Potassium (±)-β-Phenylglycidate (I).—Ethyl (±)-β-phenylglycidate (100 g) in 200 ml of ethanol was mixed slowly, while being cooled, with a solution of potassium hydroxide (50 g) in 300 ml of ethanol. Precipitated potassium salt was filtered and washed with ethanol repeatedly. A weight of 97 g of I was obtained. This material was used without further purification.

Optical Resolution of β-Phenylglycidic Acid.—Potassium β-phenylglycidate (I, 16.2 g) was dissolved in 100 ml of water. Crushed ice and 80 ml of ether were added to the solution. To this mixture, 80 ml of 1 *N* HCl was added and the liberated free G acid was extracted with ether. Two additional ether extractions (two 50-ml portions) were carried out. The ether solutions were combined and dried with anhydrous sodium sulfate. To the dried ether solution, 9.70 g (0.08 mole) of (−)-amine, $[\alpha]^{27}D$ −40.6° (benzene), was added. The precipitated oil was crystallized by rubbing with a glass rod. After 2 hr, the crystals were collected by filtration. Uncrystallized oily materials [diastereomeric salt (−)-amine–(+)-acid salt] passed through the filter paper. The crystals were washed with acetone. (−)-Amine–(−)-acid salt IIIa (8.5 g) was obtained, mp 157–158° dec. This was recrystallized by dissolving in 34 ml of ethanol and by precipitating with 60 ml of acetone: yield 6.80 g, mp 161–162° dec, $[\alpha]^{25}D$ −125.4° (*c* 0.95, absolute EtOH).

Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.82; H, 6.69; N, 4.88.

To the mother liquor, 100 ml of ice–water and 40 ml of 1 *N* hydrochloric acid were added. Liberated G acid (II) was extracted with ether three times and the combined ether solution was dried with anhydrous sodium sulfate. To the dried ether solution, (+)-amine, 4.85 g (0.04 mole), $[\alpha]^{27}D$ +39.3° (benzene), was added. Crystallization of (+)-amine–(+)-acid salt IIIb began after 1 min.: yield 8.90 g, mp 156–157° dec. This was recrystallized from ethanol and acetone: yield 6.90 g, mp 161–162° dec, $[\alpha]^{25}D$ +125.5° (*c* 0.96, absolute EtOH).

Anal. Found: C, 71.67; H, 6.83; N, 4.93.

Ammonium (−)- and (+)-β-Phenylglycidate (IVa and b).—(−)-Amine–(−)-acid salt (2.0 g) was dissolved in 40 ml of water and cooled to 5°. To this, 20 ml of 1 *N* hydrochloric acid was added. Precipitated free (−)-G acid was extracted with ether and dried with anhydrous sodium sulfate. Dry ammonia gas was introduced to precipitate (−)-G acid ammonium salt (IVa): 1.05 g, $[\alpha]^{25}D$ −154.0° (*c* 1.03, H_2O).

(+)-G acid ammonium salt (IVb) was prepared in the same way: $[\alpha]^{25}D$ +153.5° (*c* 1 10, H_2O).

Ammonolysis of (−)- and (+)-G Acid (IVa and b) and Isolation of (+)- and (−)-*erythro*-Phenylserine (VIIa and b).—(−)-G acid ammonium salt IVa (10.0 g) was dissolved in 500 ml of 28% concentrated ammonia solution. The solution was kept at room temperature for 6 days. The reaction mixture was evaporated under reduced pressure to dryness. The residual mixture was examined paper chromatographically by the use of the Shaw–Fox solvent.[19] *erythro* Phenylserine and phenylisoserine were identified; however, *threo*-phenylserine and glycine were not found. The latter compound may form from β-phenylserine by cleavage of the α–β bond. *erythro*-Phenylserine had R_f 0.26; *threo*-phenylserine, 0.42; and phenylisoserine, 0.18.

The residue was dissolved in 70 ml of hot water and filtered. To this solution, 100 ml of hot dioxane was added. (+)-*erythro*-Phenylserine–dioxane adduct was crystallized from the solution. The suspension was kept in a refrigerator overnight and filtered. The crystals were washed with a mixture of water and dioxane (1:1): yield 2.85 g, mp 192° (no clear melting point). This was recrystallized by dissolving in 20 ml of hot water and precipitating with 20 ml of hot dioxane. A weight of 2.50 g of (+)-*erythro*-phenylserine–dioxane adduct (VIIa) was obtained: mp 192° dec, $[\alpha]^{25}D$ +66.0° (*c* 1.07, 5 *N* HCL).[25] By paper chromatography[24] the material was identified as pure *erythro*-phenylserine.

Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.65; H, 6.71; N, 6.22. Found: C, 58.61; H, 6.72; N, 6.11.

In the same way, 10.0 g of (+)-G acid (IVb) was treated with concentrated ammonia solution for 6 days. The reaction mixture was treated as described above. The (−)-*erythro*-phenylserine–dioxane adduct (VIIb), 2.45 g, was obtained after recrystallization: $[\alpha^{25}D$ −66.5° (*c* 1.07, 5 *N* HCl).[27] This was pure by paper chromatography.

Anal. Found: C, 58.75; H, 6.72; N, 6.16.

Isolation of (+)- and (−)-Phenylisoserine Copper Complex (VIIIa and b).—The mother liquor from which (+)-*erythro*-phenylserine was isolated was evaporated to dryness under reduced pressure. This was dissolved in 50 ml of water and filtered. To this was added a solution of 5.0 g of cupric acetate in 70 ml of water. (+)-Phenylisoserine copper complex (VIIIa) began to crystallize by rubbing with a glass rod. This crystalline mixture was kept at room temperature overnight. A yield of 5.30 g of (+)-phenylisoserine copper complex (VIIIa) was obtained. From the mother liquor an additional 1.2 g of copper complex was isolated by adjusting the pH to about 6.0 with sodium hydrogen carbonate: total weight 6.5 g.

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(23) H. E. Zimmerman and L. Ahramjian, *ibid.*, **82**, 5459 (1960).

(24) All temperature measurements are uncorrected. All optical rotation measurements were carried out by the use of the Rudolph Model 80 polarimeter with PEC-101 photometer.

(25) The reported specific rotation of (−)-*erythro*-phenylserine–dioxane adduct is $[\alpha]^{25}D$ −53.7° (2 *N* HCl), $[\alpha]^{27}D$ −64.7° (6 *N* HCl).[20]

(−)-Phenylisoserine copper complex was obtained in the same way as described above: total yield 6.3 g.

(+)- and (−)-*erythro*-β-Phenylisoserine (IXa and b).—(+)-*erythro*-β-Phenylisoserine copper comples (VIIIa), 3.0 g, was dissolved in 60 ml of 10% acetic acid. Hydrogen sulfide gas was passed through the solution at room temperature. Precipitated copper sulfide was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in a minimum amount of water and filtered. By the addition of ethanol, 1.73 g of IXa was obtained: mp 243–244° dec. The crystals were purified by dissolving in 5 ml of water and precipitating with 20 ml of ethanol: yield 1.40 g, mp 243–244° dec (the decomposition point varied depending on heating rate), $[\alpha]^{25}D$ +58.6° (*c* 1.09, H_2O).

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.88; H, 6.10; N, 7.55.

(−)-*erythro*-Phenylisoserine (IXb) was prepared the same way as described above. From 3.0 g of VIIIb, 1.42 g of recrystallized IXb was obtained: mp 244–245° dec, $[\alpha]^{25}D$ −58.2° (*c* 1.02, H_2O).

(+)- and (−)-N-Benzoylphenylisoserine (Xa and b).—(+)-N-Benzoylphenylisoserine was prepared by the usual Schotten–Baumann method. From 1.0 g of IXa, a weight of 1.50 g of crude Xa was obtained: mp 180–181.5°. This was recrystallized from 16 ml of a mixture of ethanol and water (3:7): yield 1.17 g, mp 184–185°, $[\alpha]^{25}D$ +15.3° (*c* 1.12, absolute EtOH).

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.31; H, 5.40; N, 4.74.

(−)-*N*-Benzoylphenylisoserine.—From 1.0 g of IXb, 1.13 g of purified Xb was obtained: mp 183–185°, $[\alpha]^{25}D$ −15.1° (*c* 1.26, absolute EtOH).

Anal. Found: C, 67.43; H, 5.60; N, 4.85.

Oxidation of (+)- and (−)-N-Benzoylphenylisoserine (Xa and b).—A weight of 0.85 g of Xa was dissolved in a mixture of 3 ml of 1 *N* sodium hydroxide and 5 ml of water. To this, 0.948 g of powdered potassium permanganate was added slowly in a period of 35 min with stirring and cooling. After an additional 15 min of stirring, 50 mg of sodium hydroxide sulfite was added and the reaction mixture was stirred for 10 min. Then the reaction mixture was filtered and the MnO_2 was washed with 0.5 *N* sodium hydroxide. The combined filtrate was acidified to a pH of about 2 by addition of 6 *N* hydrochloric acid. Precipitated oil crystallized. The crystals were filtered, dried, and sublimed at 90° *in vacuo* to eliminate contaminated benzoic acid: yield 188 mg, mp 177–184°. The crude material was recrystallized three times from a mixture of ethanol and water (6:4). Pure N-benzoylphenylglycine, (2*R*), 85 mg, was obtained: mp 196–197°, $[\alpha]^{25}D$ −121.3° (*c* 0.98, absolute EtOH).

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49; neut equiv, 255. Found: C, 70.42; H, 5.28; N, 5.58; neut equiv,[26] 255.

Oxidation of Xb was carried out as described above. Xb (0.51 g) was oxidized with 0.53 g of potassium permanganate and 120 mg of crude XIb was obtained: mp 192–194°. After recrystallization, pure XIb was obtained: mp 196–197°, $[\alpha]^{25}D$ +120.2° (*c* 1.34, absolute EtOH).

Anal. Found: C, 70.52; H, 5.21; N, 5.32.

Authentic N-Benzoylphenylglycine.—(*R*)-Phenylglycine (XIIa) ($[\alpha]^{25}D$ −166.1 in 5 *N* HCl) and (*S*)-phenylglycine (XIIb) ($[\alpha]^{25}D$ +164.0 in 5 *N* HCl) were treated with benzoyl chloride in the usual Schotten–Baumann procedure. After recrystallizations, pure XIIIa (yield 73%) and XIIIb (yield 74%) were obtained. XIIIa had mp 195.5–196.5°, $[\alpha]^{25}D$ −120.7° (*c* 2.96, absolute EtOH). (*Anal.* Found: N, 5.44.) XIIIb had mp 195.5–196.5°, $[\alpha]^{25}D$ +120.5° (*c* 2.99, absolute EtOH). (*Anal.* Found: N, 5.32.)

Hydrogenation of (−)- and (+)-G Acid.—IVa (2.0 g) in 50 ml of water was hydrogenated with 1.50 g of 5% palladium on charcoal for 2 hr at room temperature. After the reaction was over, the catalyst was removed by filtration. The filtrate was acidified to a pH of 2.0 with 6 *N* hydrochloric acid and was extracted with ether three times. Then the ether was evaporated. The remaining oil was crystallized: yield 1.80 g, mp 121–123°. This was recrystallized from benzene. (+)-Phenyllactic acid (Va) was obtained: 1.40 g, mp 125°, $[\alpha]^{25}D$ +20.8° (*c* 2.15, H_2O).[27]

Anal. Calcd for $C_9H_{10}O_3$: C, 65.04; H, 6.07. Found: C, 65.04; H, 6.04.

Hydrogenation of IVb (2.2 g) was carried out in a similar way. (−)-β-Phenyllactic acid (Vb) was obtained: 1.42 g, mp 125°, $[\alpha]^{11}D$ −22.3° (*c* 1.97, H_2O).[28]

Anal. Found: C, 65.03; H, 6.18.

Hydrogenation of Potassium (±)-β-Phenylglycidate (I).—Compound I (3.0 g) was hydrogenated with palladium on charcoal in water. β-Phenyllactic acid (2.55 g, XIV) was obtained: mp 95.5–97°. After recrystallization from benzene, the melting point rose to 97–98°.

Anal. Found: C, 65.02; H, 6.07.

Hydrogenation of Sodium Phenylpyruvate (XV).—Sodium phenylpyruvate monohydrate (XV, 3.72 g) was hydrogenated in aqueous solution by 5% palladium on charcoal, The product, β-phenyllactic acid (XVI, 3.0 g) was obtained: mp 97–98°.

Anal. Found: C, 65.24; H, 6.25.

Hydrogenation of Ethyl Benzoylacetate.—Ethyl benzoylacetate (8.0 g) was hydrogenated in alcohol solution by the use of 5% palladium on charcoal. The hydrogenated products were hydrolyzed with sodium hydroxide in a mixture of alcohol and water (1:1) at room temperature. The alkaline solution was acidified and the alcohol was evaporated *in vacuo*. The resulting β-hydroxy-β-phenylpropionic acid (XVII) was isolated. After recrystallization from benzene, XVII melted at 92–93°.

Anal. Found: C, 65.09; H, 6.10.

Acknowledgment.—The author wishes to express his appreciation to Dr. H. P. Schultz for his valuable discussion and to Dr. S. W. Fox for his encouragement.

(26) The carboxyl group was titrated with 0.02 *N* sodium methoxide in dimethylformamide by the use of thymol blue as an indicator.

(27) F. Erlich and K. A. Jacobsen [*Ber.*, **44**, 894 (1911)] reported $[\alpha]^{20}D$ +22.2° (H_2O), mp 124°.

(28) H. D. Dakin and H. W. Dudley [*J. Biol. Chem.*, **18**, 46 (1914)] reported $[\alpha]D$ −13.3° (H_2O).