over 45 min. while maintaining the temperature below 10°. After standing overnight, the mixture was filtered and the filter cake washed with pentane. The pentane filtrate was stripped to an amber liquid which was distilled to give 1,1-dichloronorcarane[26]; 9.3 g., 40% yield; b.p. 80–81° (16 mm.) n_D^{21} 1.4990.

St. Louis 66, Mo.

[Contribution from Department of Chemistry, Duke University]

Conjugate Addition of Disodiophenylacetate to Ethyl Cinnamate to Form *erythro*- and *threo*-4-Carbethoxy-2,3-diphenylbutyric Acids

ROBERT B. MEYER[1] AND CHARLES R. HAUSER

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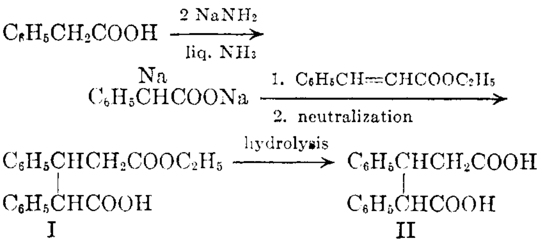
Disodiophenylacetate, prepared from phenylacetic acid and two molecular equivalents of sodium amide in liquid ammonia, underwent conjugate addition to ethyl cinnamate to form *erythro*- and *threo*-4-carbethoxy-2,3-diphenylbutyric acids in approximately equal amounts. The configurations of these isomers were established by hydrolysis and by esterification to the diacids and diethyl esters, respectively. The conjugate addition appeared to occur nonstereospecifically. The ester acids and also the monoethyl esters of glutaric and 3-phenylglutaric acids underwent rapid hydrolysis with excess sodium hydroxide solution at room temperature.

Disodiophenylacetate, prepared from phenylacetic acid and two molecular equivalents of sodium amide in liquid ammonia, has recently been observed[2] to undergo conjugate addition to ethyl cinnamate to form diacid II. Ester acid I was considered to be an intermediate (Equation 1).

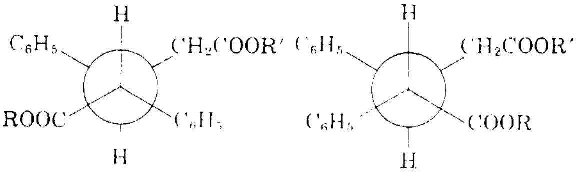


$$C_6H_5CH_2COOH \xrightarrow[\text{liq. } NH_3]{2\ NaNH_2} \overset{Na}{C_6H_5CHCOONa} \xrightarrow[\text{2. neutralization}]{\text{1. } C_6H_5CH{=}CHCOOC_2H_5} \underset{\text{I}}{\underset{C_6H_5CHCOOH}{C_6H_5CHCH_2COOC_2H_5}} \xrightarrow{\text{hydrolysis}} \underset{\text{II}}{\underset{C_6H_5CHCOOH}{C_6H_5CHCH_2COOH}} \qquad (1)$$

The stereochemistry of this reaction has not been studied. Neutralization of the reaction mixture in liquid ammonia with ammonium chloride afforded a 96% yield of a mixture of the diastereomers of ester acid I. The higher melting isomer of I was isolated in 49% yield and the lower melting isomer in 32% yield; most of the remaining 15% of the product was probably the latter isomer (see Experimental). Each of these isomers gave satisfactory analyses not only for carbon and hydrogen but also for the ethoxy group; moreover they gave acceptable neutralization equivalents. Their infrared spectra showed sharp peaks at 5.82 and 5.90 μ,[3] whereas the spectrum of each of the diastereomers of diacid II exhibited a single carbonyl peak at 5.88 μ.[3]

When the condensation was performed using potassium amide or lithium amide, similar results were obtained. However, in the latter case the yields were somewhat lower.

The configurations of each isomer of ester-acid I were determined by hydrolysis by means of dilute hydrochloric acid to form the diastereoisomers of diacid II, the configurations of which have been well established.[4,5] Thus, the higher melting ester-acid was assigned the *erythro* configuration Ia and the lower melting isomer the *threo* configuration Ib, since they gave the *erythro*- and *threo*-diacids IIa and IIb in yields of 99 and 79%, respectively. Furthermore, the higher and lower melting isomers of ester-acid I were esterified with ethanol to form the *erythro*- and *threo*-diethyl esters IIIa and IIIb in yields of 97 and 46%, respectively. Authentic samples of these diesters were prepared by esterification of the corresponding diacids.



erythro	*threo*
Ia. R = H, R′ = C_2H_5 (M.p. 189.5–190°)	Ib. R = H, R′ = C_2H_5 (M.p. 104–105°)
IIa. R = R′ = H (M.p. 230–231°)	IIb. R = R′ = H (M.p. 212–213°)
IIIa. R = R′ = C_2H_5 (M.p. 92.5–93°)	IIIb. R = R′ = C_2H_5 (M.p. 76–76.5°)
IVa. R = R′ = CH_3 (M.p. 142–142.5°)	IVb. R = R′ = CH_3 (M.p. 85–86°)

Although the acid-catalyzed hydrolyses and esterifications mentioned above involved refluxing aqueous or ethanolic solutions or suspensions for several hours, little if any epimerization appeared to occur. Certainly complete epimerization in each reaction, which would have to be assumed if the

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[1] American Cyanamid Co. Fellow, 1959–1960.

[2] C. R. Hauser and M. T. Tetenbaum, *J. Org. Chem.*, **23**, 1146 (1958).

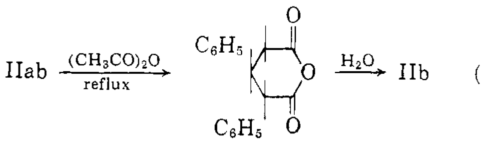
[3] See L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1958, pp. 161, 178.

[4] S. Avery and W. D. Maclay, *J. Am. Chem. Soc.*, **51**, 2833 (1929).

[5] D. Lednicer and C. R. Hauser, *J. Am. Chem. Soc.*, **80**, 6364 (1958).

reverse configurations were to be assigned, seems improbable.

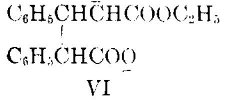
The *erythro*-diacid IIa employed in the preparation of the authentic *erythro*-diethyl ester IIIa was readily obtained in 50% yield by fractional crystallization of the mixture of diacids produced as represented in equation 1. The *threo*-diacid IIb was isolated in only 17% yield by fractional crystallization of the mixture of isomers but it was obtained in 64% yield by refluxing the mixture with acetic anhydride and hydrolyzing the resulting *threo*-anhydride V (Equation 2). Under these conditions the *erythro*-diacid IIa isomerizes to IIb.[4,6]



V (2)

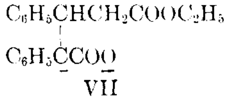
The highest yield of the *erythro*-ester acid Ia or the *erythro*-diacid IIa that has been isolated from the product of the conjugate addition of disodiophenylacetate to ethyl cinnamate (Equation 1) was approximately 50%. Although lower yields (17–32%) of the *threo*-ester acid or *threo*-diacid were isolated, more of this isomer appeared to be present in the mixture; the yield by difference amounts to about 50%. Moreover, esterification of the mixture of diacids obtained according to Equation 1 with methanol followed by fractional crystallization produced the *erythro*-dimethyl ester in 48% yield and, presumably, the *threo*-dimethyl ester (as an oil) in about the same yield (see Experimental).

These results indicate that the conjugate addition occurs nonstereospecifically. The mechanism of the reaction appears to involve the intermediate formation of the two diastereomeric forms of of dianion VI in roughly equal amounts, from which Ia and Ib are obtained on acidification.



$$\begin{array}{l} C_6H_5CH\bar{C}HCOOC_2H_5 \\ \quad | \\ C_6H_5CHCOO^- \end{array}$$

VI



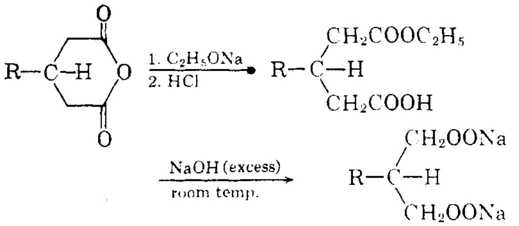
$$\begin{array}{l} C_6H_5CHCH_2COOC_2H_5 \\ \quad | \\ C_6H_5\underset{-}{C}COO^- \end{array}$$

VII

The predominant formation of one of the diastereoisomers of VI followed by isomerization through dianion VII to give an equal mixture of the two isomers seems less likely. In fact evidence was obtained against such an isomerization. Thus pure Ia or Ib failed to undergo appreciable isomerization with two molecular equivalents of sodium amide or sodium triphenylmethide (with Ia) in liquid ammonia under similar conditions. The red color of the latter reagent was discharged indicating that dianion VI was formed. A similar lack of appreciable isomerization of the isomers of 2,3-diphenylbutyric acid with sodium amide in liquid ammonia was observed recently.[7]

In the earlier work on the conjugate addition (Equation 1),[2] the liquid ammonia was replaced by ether, and the resulting ethereal suspension of the reaction product was shaken with cold water and sodium hydroxide solution. Since the diacid II was obtained on acidification, the intermediate ester acid I was indicated to undergo hydrolysis with remarkable ease. This has now been confirmed. Thus, each isomer of ester acid I was hydrolyzed completely on extracting ethereal solutions of them with 10% sodium hydroxide solution at room temperature even though the alkaline extracts were acidified within five minutes. Isomer Ia was also completely hydrolyzed on standing at room temperature with two molecular equivalents of sodium hydroxide solution for several hours. After standing under similar conditions with only one equivalent of sodium hydroxide, however, ester acid Ia or Ib was recovered unchanged; this shows that the monoacid salts of these isomers are relatively stable. Similarly ester acids of Ia and Ib were recovered after standing in solution with excess sodium bicarbonate at room temperature for several hours.

Likewise the mono ethyl esters of glutaric and 3-phenylglutaric acids, which were prepared from the corresponding anhydrides, underwent hydrolysis on extracting ethereal solutions of them with excess 10% sodium hydroxide solution at room temperature (Equation 3). The mechanism of such hydrolyses may involve a cyclic intermediate.[8]



(3)

EXPERIMENTAL[9]

Condensation of disodiophenylacetate with ethyl cinnamate. (A) *Isolation of ester acids* I. To a stirred suspension of 0.10 mole of sodium amide in 300 ml. of commercial, anhydrous liquid ammonia[10] was added 6.8 g. (0.050 mole) of solid phenylacetic acid. The resulting green solution was stirred

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(6) G. M. Badger and J. W. Cook, *J. Chem. Soc.*, 1084 (1949)

(7) C. R. Hauser, D. Lednicer, and W. R. Brasen, *J. Am. Chem. Soc.*, **80**, 4345 (1958).

(8) For a discussion of the alkaline hydrolysis of certain related ester acids, see M. L. Bender, *Chem. Rev.*, **60**, 80–82 (1960); E. Gaetjens and H. Morawetz, *J. Am. Chem. Soc.*, **82**, 5328 (1960).

(9) Melting points and boiling points are uncorrected. Melting points were taken on a Fisher-Johns melting point apparatus. Elemental analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich., unless otherwise indicated. Infrared spectra were taken on a Perkin-Elmer Infracord by the potassium bromide method.

(10) See. C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **VIII**, 122 (1954).

for 15 min., and a solution of 8.8 g. (0.050 mole) of ethyl cinnamate in 25 ml. of anhydrous ether was added during 4 min. The color faded, and a white precipitate formed. After stirring for 30 min., solid ammonium chloride (6 g.) was added. The liquid ammonia was evaporated and an equal volume of ether was added. The resulting ethereal suspension was poured into 100 ml. of 3*N* hydrochloric acid, and the layers were separated. After being combined with three ether washings of the aqueous solution, the ethereal solution was dried over Drierite, filtered, and the solvent was distilled leaving the crude ester acids I (15 g., 96%).

The mixture of ester acids I was dissolved in 200 ml. of boiling benzene and allowed to crystallize. Filtration gave 7.6 g. (49%) of *erythro*-4-carbethoxy-2,3-diphenylbutyric acid (Ia), m.p. 188–189° and at 189.5–190° after recrystallization from benzene.

Anal.[11] Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45; C_2H_5O, 14.42; neut. equiv., 312. Found: C, 72.85; H, 6.41; C_2H_5O, 14.29; neut. equiv., 308.

The benzene was evaporated from the filtrate, and the residual oil was crystallized very slowly from 350 ml. of ligroin (b.p. 90–120°) to give 5.0 g. (32%) of *threo*-4-carbethoxy-2,3-diphenylbutyric acid (Ib), m.p. 104–105°. The melting point was not altered by recrystallization.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45; C_2H_5O, 14.42; neut. equiv., 312. Found: C, 73.08; H, 6.47; C_2H_5O, 14.33; neut. equiv., 309.

The infrared spectrum of each isomer showed carbonyl absorption[3] at 5.82 and 5.90 μ.

Similar results were obtained when the reaction mixture was poured into a suspension of ammonium chloride in liquid ammonia (inverse neutralization) or when the liquid ammonia was replaced by ether and the resulting etheral suspension poured into dilute hydrochloric acid. The latter experiment gave crude ester acids I in 88% yield, from which the *erythro* and *threo* isomers were isolated in yields of 49% and 7%, respectively.

(B) *Isolation of diacids* II. The white suspension of the reaction product obtained as described above under (A) was stirred for 1 hr., and the liquid ammonia was then replaced by ether (without adding ammonium chloride). The resulting ethereal suspension was refluxed for 30 min., cooled, and shaken with ice water essentially as described previously.[2] The etheral layer was extracted twice with 5% sodium hydroxide solution at room temperature, and the combined alkaline extracts (after filtering) were acidified to precipitate a mixture of isomeric diacids II in 90–95% yield. Crystallization from ethanol gave *erythro*-2,3-diphenylglutaric acid (IIa), m.p. 225–228° in 50% yield. Recrystallization from ethanol raised the melting point to 230–231°. Reported m.p. 226–228°[4] and 230–231°.[6]

The filtrates were concentrated, filtered, and the solid crystallized from dilute acetic acid to give *threo*-2,3-diphenylglutaric acid (IIb), m.p. 206–209° in 17% yield; reported[4] m.p. 208–210°.

The infrared spectrum of each isomer showed carbonyl absorption[3] at 5.88 μ.

(C) *Conversion of the mixture of diacids* II *to dimethyl esters.* The mixture of isomeric diacids II obtained as described under (B) was refluxed for 18 hr. with 150 ml. of absolute methanol containing 5 ml. of concd. sulfuric acid. The excess methanol was distilled, and the residue was dissolved in ether. The ethereal solution was washed with water followed by 10% sodium bicarbonate solution and dried over magnesium sulfate. After filtering, the solvent was removed to leave a mixture of isomeric dimethyl esters IV in 96% yield (based on the diacids). Crystallization of the mixture from absolute methanol afforded *erythro*-dimethyl 2,3-diphenylglutarate (IVa), m.p. 142–143° in 48% yield, reported[4] m.p. 143°. No depression in melting point was observed on admixture with an authentic sample of the *erythro* isomer prepared as described below. Evaporation of the methanolic filtrate left an oil which was presumably the *threo*-dimethyl ester IVb.

Configurations of ester acids I. (A) *By hydrolysis.* A suspension of 1.0 g. of the higher melting ester acid Ia in 30 ml. of 1:1 hydrochloric acid was refluxed for 24 hr., cooled, and filtered to give 0.90 g. (99%) of *erythro*-2,3-diphenylglutaric acid (IIa), m.p. 227–229°. Admixture with authentic *erythro*-diacid IIa produced no depression in melting point but admixture with authentic *threo*-diacid IIb depressed the melting point to 202–213°.

Similar treatment of the lower melting ester acid Ib gave, after crystallization from dilute acetic acid, *threo*-2,3-diphenylglutaric acid (IIb), m.p. 205–209° and 207–210° when mixed with authentic diacid IIb.

(B) *By esterification.* A solution of 1.0 g. of the higher melting ester acid Ia in 25 ml. of absolute ethanol was saturated with hydrogen chloride and refluxed for 4.5 hr. After cooling, the solution was poured into water, and the resulting suspension was made slightly alkaline by the addition of 10% sodium hydroxide solution. Filtration of the alkaline suspension afforded the crude diester (97%), m.p. 89.5–90.5°. Crystallization from dilute ethanol gave *erythro*-diethyl 2,3-diphenylglutarate (IIIa), m.p. 92–92.5°, which was not depressed on admixture with an authentic sample prepared as described below.

The lower melting ester acid Ib was esterified similarly. After cooling, the ethanolic solution was poured into 100 ml. of water, and the resulting aqueous suspension was extracted three times with ether. The combined extract was washed with two 50-ml. portions of 5% sodium bicarbonate solution, and dried over Drierite. After filtering, the solvent was distilled to leave an oily residue (0.93 g.) which slowly solidified (m.p. 65–73°). Recrystallization from 95% ethanol afforded 0.50 g. (46%) of *threo*-diethyl 2,3-diphenylglutarate (IIIb), m.p. 73–75°, which was not depressed on admixture with an authentic sample prepared as described below.

Preparation of threo-diacid IIb *through anhydride* V. A mixture of the isomeric 2,3-diphenylglutaric acids (II) (27.1 g., 0.095 mole) was refluxed for 17 hr. with 150 ml. of freshly distilled acetic anhydride according to the procedure of Badger and Cook.[6] The acetic acid and excess acetic anhydride were distilled, and the residue was crystallized from chloroform–petroleum ether (b.p. 30–60°) to give 16.2 g. (64%) of 2,3-diphenylglutaric anhydride (V), m.p. 126.5–127°. Reported, m.p. 125–126°[6] and 126.5°.[4]

The infrared spectrum of this compound showed carbonyl absorption[12] at 5.54 and 5.66 μ.

A mixture of 5.0 g. (0.018 mole) of this anhydride and 50 ml. of 10% sodium carbonate solution was refluxed for 30 min. After cooling and filtering, the solution was acidified with cold 3*N* hydrochloric acid to precipitate 5.3 g. (99%) of *threo*-2,3-diphenylglutaric acid, m.p. 207–213°. Two crystallizations from dilute acetic acid raised the melting point to 212–213° (sealed tube), reported,[4] m.p. 208–210°.

Esterification of erythro- and threo-diacids II. (A) *with ethanol to form IIIa and* IIIb. A solution of 1.0 g. of *erythro*-2,3-diphenylglutaric acid (IIa) in 25 ml. of absolute ethanol was saturated with hydrogen chloride and refluxed for 6 hr. The solution was poured into 100 ml. of water, cooled, made alkaline with 10% sodium hydroxide solution, and filtered to give *erythro*-diethyl 2,3-diphenylglutarate (IIIa) (1.15 g., 96%), m.p. 90–91°. Crystallization from aqueous ethanol raised the melting point to 92.5–93°. Reported[4] m.p. 93.3°.

Similar treatment of *threo*-2,3-diphenylglutaric acid (IIb) gave *threo*-diethyl 2,3-diphenylglutarate (IIIb) (96%), m.p. 76–76.5°, reported[4] m.p. 76°.

The infrared spectrum of the *erythro* isomer showed carbonyl absorption[3] at 5.80 μ and of the *threo* isomer at 5.78 μ.

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(11) Carbon and hydrogen analysis by Galbraith Laboratories, Knoxville, Tenn.

(12) See ref. 3, p. 127.

(B) *With methanol to form* IVa *and* IVb. A solution of 1.0 g. of *erythro*-diacid IIa, 0.5 ml. of concd. sulfuric acid, and 25 ml. of absolute methanol was refluxed for 10.5 hr. After cooling, the solution was poured into 150 ml. of ice water, and made alkaline with 10% sodium carbonate solution. The resulting suspension was filtered to give *erythro*-dimethyl 2,3-diphenylglutarate (IVa) (95%), m.p. 138–140°. Two crystallizations from methanol raised the melting point to 142–142.5°, reported[4] m.p. 143°.

The *threo*-diacid IIb was esterified similarly. After the treatment with sodium bicarbonate solution, the suspension was extracted with ether. There was isolated from the ethereal extract *threo*-dimethyl 2,3-diphenylglutarate (IVb) (87%), m.p. 85–86° (recrystallized from petroleum ether, b.p. 30–60°), reported,[4] m.p. 87°.

The infrared spectrum of the *erythro* isomer showed carbonyl absorption[3] at 5.79 μ and of the *threo* isomer at 5.77 μ.

Failure of ester-acid Ia *or* Ib *to isomerize.* (A) *With sodium amide.* To a stirred suspension of 0.022 mole of sodium amide in 200 ml. of liquid ammonia[10] was added 3.4 g. (0.011 mole) of *erythro*-ester acid Ia. After stirring for 30 min., ammonium chloride was added. The ammonia was replaced by ether, and the etheral suspension was poured into dilute hydrochloric acid. Four crops of ester acid Ia were recovered in yields of 37%, 13%, 7%, and 3% melting at 186–187°, 181–183°, 177–179°, and 164–170°, respectively. There was also isolated diacid IIa in 21% yield, m.p. and mixed m.p. with an authentic sample 226–229°. The total recovery of *erythro*-ester acid or diacid amounts to 80%. None of the *threo* isomers Ib or IIb was found.

The *threo*-ester acid Ib was treated similarly with sodium amide in liquid ammonia. There was recovered 66% of crude ester acid, 89% of which consisted of the starting isomer Ib, m.p. 101–104° (recrystallized from ligroin, b.p. 90–120°). None of the *erythro*-ester acid Ia was found.

(B) *With sodium triphenylmethide.* To a stirred suspension of 0.012 mole of sodium amide in 300 ml. of liquid ammonia[10] was added 3.0 g. (0.012 mole) of triphenylmethane. The deep red solution was stirred for 15 min., and 2.0 g. (0.0064 mole) of *erythro*-ester acid Ia was added. The color slowly faded. After stirring for 45 min., the suspension was neutralized by the addition of excess ammonium chloride. The ammonia was replaced by ether, and the etheral suspension was poured into 100 ml. of 3*N* hydrochloric acid. The layers were separated, and the ethereal solution was extracted with three 100-ml. portions of 5% sodium bicarbonate solution. On acidification and filtration of the alkaline solution there was recovered 1.30 g. (65%) of *erythro*-ester acid Ia, m.p. 185–188°. Also there was isolated from the filtrate *erythro*-diacid IIa in 6% yield, m.p. 223–225°. None of the *threo* isomers Ib or IIb was found.

Rapid alkaline hydrolysis of ester acids Ia *and* Ib. A solution of 0.50 g. of *erythro*-ester acid Ia in 20 ml. of ether was extracted with two 10-ml. portions of 10% sodium hydroxide solution. After standing at room temperature (about 25°) for 5 min., the combined alkaline extracts were poured into excess 3*N* hydrochloric acid to precipitate evidently a mixture of *erythro*- and *threo*-diacids IIa and IIb, m.p. 208–218° in 99% yield.

Similarly an ethereal solution of 0.30 g. of *threo*-ester acid Ib was extracted with 10% sodium hydroxide solution. Acidification of the alkaline extract produced *threo*-diacid IIb, m.p. 205–207° in 99% yield.

A solution of 0.395 g. (1.26 mmole) of *erythro*-ester acid Ia in 42.6 ml. of 0.0592 *N* sodium hydroxide solution (2.52 mmoles) was allowed to stand at room temperature for 7 hr. The solution was then poured into 10 ml. of 3*N* hydrochloric acid to precipitate a mixture of diacids IIa and IIb, m.p. 205–215°. The infrared spectrum of the mixture showed only one carbonyl peak[3] at 5.88 μ.

A solution of 0.568 g. (1.82 mmoles) of *erythro*-ester acid Ia in 30.7 ml. of 0.592*N* sodium hydroxide solution (1.82 mmoles) was allowed to stand at room temperature for 7 hr. The solution was then poured into 10 ml. of 3*N* hydrochloric acid to precipitate the starting *erythro*-ester acid Ia, m.p. 183–184°.

On similar treatment of *threo*-ester acid Ib (0.887 mmole) with sodium hydroxide solution (0.888 mmole) the *threo*-ester acid Ib, m.p. 101.5–102.5°, was recovered.

Ethyl hydrogen glutarate and its rapid alkaline hydrolysis. Glutaric anhydride (22.4 g., 0.20 mole) was refluxed for 1 hr. with 0.20 mole of sodium ethoxide in 100 ml. of absolute ethanol. The ethanol was evaporated, and the residue was poured into 75 ml. of 3*N* hydrochloric acid. There was obtained 22.7 g. (71%) of ethyl hydrogen glutarate, b.p. 140–143° at 6 mm., reported[13] b.p. 143–145° at 7 mm.

The infrared spectrum of this compound, taken in carbon tetrachloride solution, showed carbonyl absorption[3] at 5.76 and 5.85 μ.

Crystallization of the pot residue from benzene afforded glutaric acid (11%), m.p. 98.5–99.5°, reported[14] m.p. 97.5°.

Extraction of a solution of 1.0 g. of ethyl hydrogen glutarate in 25 ml. of ether with two 25 ml. portions of 10% sodium hydroxide solution as described above for ester acid I produced glutaric acid, m.p. 98–99°, in 31% yield.

Ethyl hydrogen 3-Phenylglutarate and its rapid alkaline hydrolysis. To a cooled solution of 0.25 mole of sodium ethoxide in 100 g. of absolute ethanol was added 40 g. (0.25 mole) of diethyl malonate, followed by 44 g. (0.25 mole) of ethyl cinnamate according to the procedure of Michael.[15] After 5 days at room temperature, 500 ml. of water was added, and the resulting suspension was extracted with ether. There was obtained 57 g. (68%) of diethyl 2-carbethoxy-3-phenylglutarate, b.p. 160–163° at 1 mm., reported[15] b.p. 213–215° at 15 mm.

This triester (57 g., 0.17 mole) was refluxed for 11 hr. with 64 g. of potassium hydroxide in 80 ml. of water. After cooling, the mixture was poured into 200 ml. of 1:1 hydrochloric acid. The resulting tricarboxylic acid was isolated (ether extraction) and heated at 110–120° for 2 hr. (carbon dioxide evolved) and at 130° for 2 hr. The resulting 3-phenylglutaric acid (34 g., m.p. 123–135°) was heated on the steam bath with 75 ml. of acetyl chloride for 4 hr. The excess acetyl chloride was distilled, and the residue was stirred with petroleum ether (b.p. 30–60°) to give, on filtration, 21.3 g. (65%) of 3-phenylglutaric anhydride, m.p. 100–105°. Crystallization from benzene–petroleum ether (b.p. 30–60°) raised the melting point to 107–107.7°, reported,[16] m.p. 105°.

The infrared spectrum of this anhydride showed carbonyl absorption[12] at 5.50 and 5.67 μ.

This anhydride (5.7 g., 0.030 mole) was refluxed 1 hr. with 0.030 mole of sodium ethoxide in 50 ml. of absolute ethanol. The ethanol was evaporated, and the residue was dissolved in water. The resulting alkaline solution was washed with ether and acidified. There was isolated (ether extraction) 5.5 g. (80%) of ethyl hydrogen 3-phenylglutarate, m.p 57–59° (crystallized from petroleum ether, b.p. 30–60°). Several recrystallizations from petroleum ether raised the melting point to 59.5–60°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08, H, 6.83, C_2H_5O, 19.07, neut. equiv., 236. Found: C, 66.03, H, 6.84, C_2H_5O, 18.92, neut. equiv., 223.

The infrared spectrum of this ester acid showed carbonyl absorption[3] at 5.76 and 5.88 μ.

A solution of 0.40 g. of this ester acid in 10 ml. of ether was extracted with 10% sodium hydroxide solution as described above for ester acid I to give 3-phenylglutaric acid, m.p. 142–143°, in 68% yield, reported,[16] m.p. 140°.

DURHAM, N. C.

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(13) E. Fourneau and S. Sabetay, *Bull. soc. chim. France*, [4], **45**, 834 (1929).

(14) W. Markownikoff, *Ann.*, **182**, 324 (1876).

(15) A. Michael, *Am. Chem. J.*, **9**, 112 (1887).

(16) S. Avery and R. Bouton, *Am. Chem. J.*, **20**, 509 (1898).