scribed but in neither case was any reaction observed, the amides being recovered unchanged.

N,N-Diethylcarbethoxyformamide was obtained as a colorless liquid (b.p. 137–138° (18 mm.), n^{20}D 1.4432) in 74% yield from the reaction of carbethoxyformoyl chloride (b.p. 134–135° (760 mm.), n^{29}D 1.4162), prepared by the method of Southwich,[25] and diethylamine in dry ether.

Anal. Calcd. for $C_8H_{15}O_3N$: N, 8.09. Found: N, 8.26.

N,N′-Tetraethyldiketosuccinamide was prepared in 31% yield from a acyloin reaction (16 hours at the temperature of refluxing benzene) of N,N-diethylcarbethoxyformamide. The orange oil boiled at 107° (0.002 mm.), n^{20}D 1.4780.

The dioxime, prepared in the usual manner, melted from 228–229° dec. after crystallization from dilute ethanol.

Anal. Calcd. for $C_{12}H_{22}O_4N_4$: C, 50.35; H, 7.41; N, 19.54. Found: C, 49.76; H, 7.02; N, 19.59.

N,N-Diethyl-β-phenyl-αβ-diketopropionamide was obtained in 7% yield from the mixed, acyloin reaction (16 hours at the temperature of refluxing benzene) between N,N-diethylcarbethoxyformamide and ethyl benzoate. The viscous yellow oil boiled at 107° (0.1 mm.), n^{20}D 1.5187.

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.95; H, 6.43; N, 6.00. Found: C, 67.60; H, 7.9; N, 6.60.

N,N-Diethyl-β-carbomethoxypropionamide was obtained as a colorless liquid (b.p. 107–110° (0.8 mm.), n^{20}D 1.4555) in 85% yield from the reaction of β-carbomethoxypropionyl chloride (b.p. 92–93° (18 mm.) which was prepared by Caxson's method,[26] and diethylamine in dry ether.

Anal. Calcd. for $C_9H_{17}O_3N$: N, 7.49. Found: N, 7.31.

N,N′-Tetraethyl-γ,δ-diketosuberamide was the product obtained from the acyloin reaction (one hour at the temperature of refluxing benzene) of N,N-diethyl-β-carbomethoxypropionamide in 16% yield. The yellow viscous oil was found to boil from 178–195° (0.05 mm.).

The 2,4-dinitrophenylosazone was prepared and after crystallization from ethyl acetate melted from 236–238° dec.

Anal. Calcd. for $C_{28}H_{36}O_{10}N_{10}$: N, 20.18. Found: N, 20.85.

N,N-Diethyl-δ-phenyl-γ,δ-diketovaleramide was obtained from the mixed acyloin reaction (two hours at the temperature of refluxing benzene) of N,N-diethyl-β-carbomethoxypropionamide and ethyl benzoate as a yellow oil boiling from 89–94° (0.1 mm.), n^{25}D 1.5284.

Anal. Calcd. for $C_{15}H_{19}O_3H$: C, 68.96; H, 7.27; N, 5.36. Found: C, 69.09; H, 7.03; N, 5.27.

The more volatile neutral fraction was separated from a considerable polymeric residue by use of a molecular still. Polymerization also occurred during the fractional distillation of this fraction which resulted in a yield of less than 1% of the desired product.

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[25] P. L. Southwick and L. L. Seivard, THIS JOURNAL, **71**, 2535 (1949).

[26] J. Caxson, "Organic Syntheses," **26**, 19 (1945).

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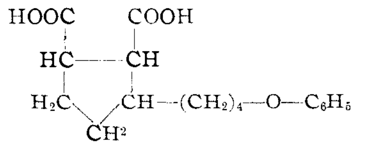
[CONTRIBUTION NO. 797 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Studies in the Cyclopentane Series. II.[1] The Synthesis of Two Isomeric 3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylic Acids

BY MILTON N. DONIN,[2] SHERMAN L. BURSON, JR.,[2] JOHANNES H. MÜLLER,[3] CHIADAO CHEN, WALTER E. BEHNKE[4] AND KLAUS HOFMANN[5]

The synthesis of two of the four theoretically possible racemic 3-(4-phenoxybutyl)-cyclopentane-1,2-dicarboxylic acids is described and their structures are partially established. An additional example of a hydrazine-catalyzed *cis–trans* inversion in the cyclopentane series is also presented.

Four geometrical isomers of 3-(4-phenoxybutyl)-cyclopentane-1,2-dicarboxylic acid (I) may be expected. Two of these possess a *cis*, the other two a *trans* configuration of the carboxyl groups. The pairs differ in the orientation of the phenoxybutyl sidechain, which may bear either a *cis* or a *trans* relationship with respect to the carboxyl group in position 2. The present communication describes the preparation of two of these isomers.



I

Diethyl adipate was condensed with diethyl oxalate and the ensuing triester (II) converted into diethyl (3-carbethoxypropyl)-malonate (III) by heating in the presence of powdered glass. The structure of (III) followed from its conversion into adipic acid by hydrolysis and decarboxylation.

The alkylation with 4-phenoxybutyl iodide of (III) proceeded normally and the resulting disubstituted malonic ester (IV) was transformed into dimethyl 2-(4-phenoxybutyl)-adipate (V) by hydrolysis, decarboxylation and reësterification. Treatment with sodium methoxide in ether of the dimethyl ester (V) afforded methyl 5-(4-phenoxybutyl)-cyclopentanone-2-carboxylate (VI), which was purified through its copper chelate complex.

The cyclization of the dimethyl ester (V) may occur in two different ways, and, consequently, could lead to the formation of either methyl 5-(4-phenoxybutyl)-cyclopentanone-2-carboxylate (VI) or methyl 2-(4-phenoxybutyl)-cyclopentanone-2-carboxylate (VII). Although theoretical considerations favor the former possibility, it seemed desirable to establish the structure of the reaction product. This was done by comparing the properties of methyl 2-(4-phenoxybutyl)-cyclopentanone-2-carboxylate (VII), prepared by the alkylation with 4-phenoxybutyl iodide of methyl cyclopentanone-2-carboxylate, with those of the ketoester obtained from the Dieckmann cyclization of (V). The two ketoesters exhibited different properties, but both compounds on hydrolysis were converted into 2-(4-phenoxybutyl)-cyclopentanone (VIII). These

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[1] For Paper I see J. Müller, W. Behnke, M. Donin and K. Hofmann, THIS JOURNAL, **73**, 2487 (1951).

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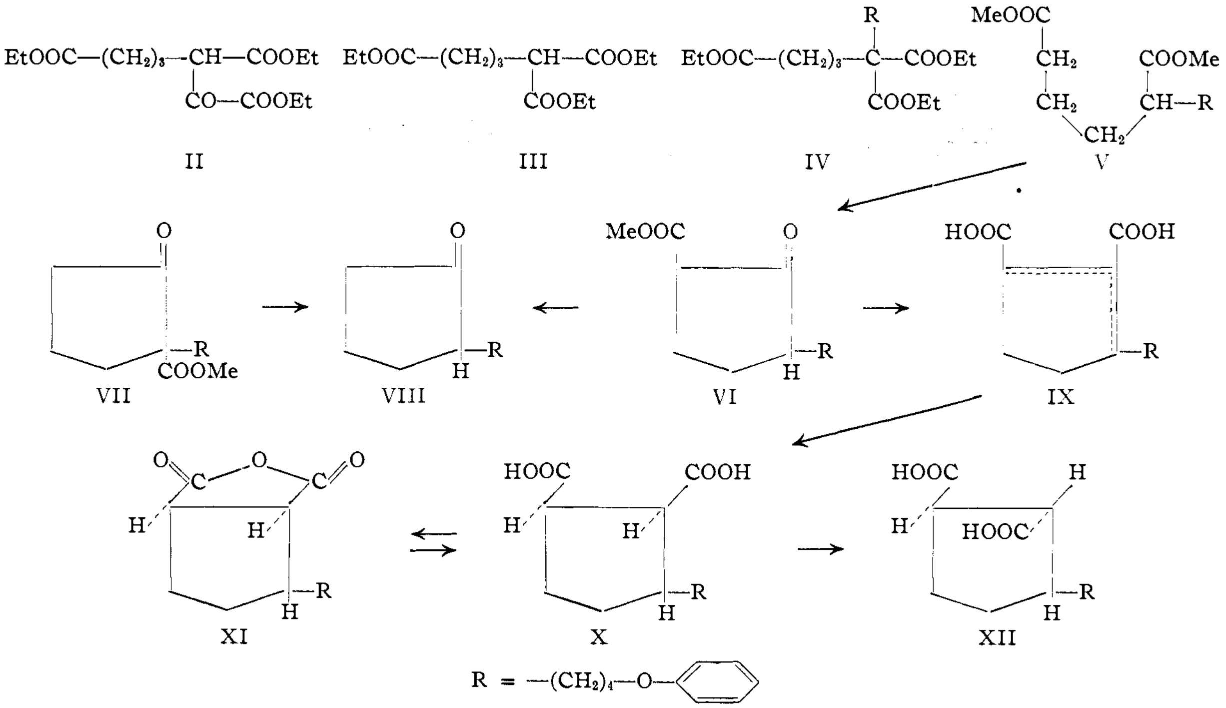
[5] The authors wish to express their appreciation to Ciba Pharmaceutical Products, Inc., Summit, New Jersey, for their generous support of this study.



transformations offer unequivocal proof for the course of this Dieckmann condensation and establish the structure of compound (VI).

The second carboxyl group was incorporated into methyl 5-(4-phenoxybutyl)-cyclopentanone-2-carboxylate by means of a cyanohydrin synthesis. The cyanohydrin of (VI) was dehydrated and the resulting unsaturated ester nitrile hydrolyzed to give a 3-(4-phenoxybutyl)-cyclopentene-1,2-dicarboxylic acid. The double bond in this compound may occupy either of the two positions indicated in structure (IX). The possibility also cannot be excluded that the substance may represent a mixture of these two acids.

Catalytic hydrogenation transformed the acid (IX) into a 3-(4-phenoxybutyl)-cyclopentane-1,2-dicarboxylic acid of melting point 119–122°. Conversion of this acid into its anhydride (XI) and hydrolysis of the latter with dilute acetic acid regenerated the original compound. On the other hand, the refluxing of its dimethyl ester with sodium methoxide in methanol, followed by hydrolysis of the resulting ester yielded an isomeric acid of melting point 136–139°.

These experiments establish the structure of the acid of m.p. 119–122° as one of the two possible forms of (X), while the inverted acid of melting point 136–139° must be represented by one of the possible structures of (XII). It is well established that the exposure to alkali alkoxides of esters of alicyclic *cis*-1,2-dicarboxylic acids results in an inversion to the thermodynamically more stable *trans*-isomer.[6,7] Similar inversions may be brought about by hydrazine.[1] Attempts to convert the *cis*-diacid (X) into the corresponding *cis*-dihydrazide were unsuccessful. Treatment of the dimethyl ester of (X) and (XII) with hydrazine hydrate under a variety of conditions afforded the same dihydrazide, which must possess a *trans* configuration. These experiments support the assigned *cis* configuration of the acid (X) and represent an additional example of a hydrazine catalyzed *cis–trans* inversion in the cyclopentane series.[1]

Experimental[8,9]

Diethyl (3-Carbethoxypropyl)-malonate (III).—A suspension of sodium ethoxide in ether was prepared from powdered sodium (69 g.), anhydrous ether (500 ml.) and anhydrous ethanol (100 ml.). This suspension was cooled in an ice-bath and a mixture of ethyl adipate (575 g.) and ethyl oxalate (415 g.) was added slowly (two hours) with stirring. Following this addition, the solvents were removed by distillation under anhydrous conditions and 33% acetic acid (600 ml.) added to the viscous residue. The resulting slurry was added to concentrated hydrochloric acid (300 ml.) and cracked ice (300 g.), and the mixture extracted with ether. The ethereal extract was washed with 10% sodium bicarbonate, water and saturated sodium chloride solution, dried over sodium sulfate, and the ether removed by distillation. The residue was heated at 190–200° in the presence of powdered soft glass (3 g.) until the evolution of carbon monoxide subsided, and distilled to give a fraction boiling at 165–175° at 12 mm. Redistillation gave a fraction boiling at 155–162° at 0.6 mm., which represented the desired ester; yield 257.0 g. (33%).

Anal. Calcd. for $C_{13}H_{22}O_6$: C, 56.9; H, 8.1. Found: C, 56.9; H, 7.8.

A sample of the ester (III) was refluxed for three hours with 6 *N* hydrochloric acid and the solvent removed *in vacuo*. Recrystallization of the residue from a mixture of ether and benzene gave adipic acid, m.p. 151–152°, which was identified by a mixed melting point with an authentic sample.

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.3; H, 6.9. Found: C, 49.7; H, 6.7.

4-Phenoxybutyl Iodide.—A solution of 4-phenoxybutyl chloride[10] (46 g.) and sodium iodide (46 g.) in anhydrous acetone (150 ml.) was refluxed under anhydrous conditions for five hours, and filtered. The filtrate was concentrated

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(6) W. Hückel and E. Goth, *Ber.*, **58**, 447 (1925).

(7) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 74 (1948).

(8) The melting points were determined with short-stem Anschütz thermometers, and are uncorrected.

(9) The microanalyses were performed in our microanalytical laboratories by Mr. George L. Stragand.

(10) J. Lohmann, *Ber.*, **24**, 2631 (1841).

to a volume of 100 ml. *in vacuo;* water (100 ml.) was added, and the mixture placed in a refrigerator for 12 hours. The resulting crystals of the iodide were collected, washed with water, and dried. Distillation of the dried, crude material gave a fraction, boiling at 123–125° at 0.1 mm., which solidified; m.p. 38–41°; yield 51.0 g. (74%).

Anal. Calcd. for $C_{10}H_{13}OI$: I, 45.9. Found: I, 45.1.

Diethyl (4-Phenoxybutyl)(3-carbethoxypropyl)-malonate (IV).—A solution of the sodio derivative of (III) was prepared by adding this ester (635 g.) to a cooled solution of sodium (53.4 g.) in absolute ethanol (1160 ml.). 4-Phenoxybutyl iodide (638.9 g.) in benzene (1160 ml.) was added to this solution, and the mixture refluxed for 26 hours. The mixture was then concentrated to a small volume *in vacuo* and extracted with ether. The ethereal solution was washed with water and saturated sodium chloride solution, dried over sodium sulfate, and the ether removed *in vacuo*. Distillation of the residue gave the desired ester as an oil boiling at 200–215° at 0.4 mm.; yield 420.0 g. (43%). A sample for analysis was redistilled at 191–192° at 0.1 mm.

Anal. Calcd. for $C_{23}H_{34}O_7$: C, 65.4; H, 8.1. Found: C, 65.4; H, 8.1.

(4-Phenoxybutyl)(3-carboxypropyl)-malonic Acid.—The ester (IV) (1.0 g.) was hydrolyzed by refluxing for ten hours with a mixture of 5 *N* sodium hydroxide (30 ml.) and ethanol (5 ml.), and the acid isolated in the usual manner. Recrystallization from a mixture of acetone and benzene gave crystals of m.p. 143–144°.

Anal. Calcd. for $C_{17}H_{22}O_7$: C, 60.4; H, 6.6. Found: C, 60.1; H, 6.7.

2-(4-Phenoxybutyl)-adipic Acid.—A sample of the above malonic acid (1.0 g.) was heated at 160° until the evolution of carbon dioxide ceased; the residue was recrystallized from a mixture of acetone and benzene; m.p. 137–138°.

Anal. Calcd. for $C_{16}H_{22}O_5$: C, 65.3; H, 7.5. Found: C, 65.3; H, 7.5.

Dimethyl 2-(4-Phenoxybutyl)-adipate (V).—A solution of (IV) (48.5 g.) and potassium hydroxide (200 g.) in water (500 ml.) and ethanol (50 ml.) was refluxed for 18 hours. The mixture was acidified to congo red with concentrated hydrochloric acid and extracted with ether. The ethereal extracts were washed with water and saturated sodium chloride solution, dried over sodium sulfate and the ether removed by distillation. The residue was heated at 160° until the evolution of carbon dioxide ceased. The resulting acid was dissolved in dry methanol (120 ml.); concentrated sulfuric acid (1 ml.) was added and the solution refluxed for five hours. Isolation in the usual manner gave an oil which was distilled. The fraction boiling at 181–190° at 0.3 mm. was collected; yield 31.0 g. (84%).

Anal. Calcd. for $C_{18}H_{26}O_5$: C, 67.1; H, 8.1. Found: C, 67.6; H, 8.4.

Methyl 5-(4-Phenoxybutyl)-cyclopentanone-2-carboxylate (VI).—A solution of the dimethyl ester (V) (242 g.) in anhydrous ether (820 ml.) was added to a suspension of sodium methoxide in ether, prepared in the usual manner from powdered sodium (34.3 g.) and methanol (50 ml.) in anhydrous ether (820 ml.); the mixture was refluxed for six hours, and kept at room temperature for an additional 12 hours. The mixture was cooled in an ice-bath and acidified to congo red with ice-cold concentrated hydrochloric acid. The ethereal solution was washed with 10% sodium bicarbonate, water and saturated sodium chloride solution, dried over sodium sulfate, and the ether evaporated. A solution of cupric acetate (230 g.) in water (4200 ml.) was added with vigorous stirring to the resulting oily residue. The mixture was placed in a refrigerator for 12 hours, the solid chelate collected and washed with ice-water. The crude chelate was resuspended in ether, ground with ether in a mortar, filtered, washed with additional cold ether, and dried; m.p. 118–120°, yield 199.0 g. (82%). A sample for analysis was recrystallized from ether.

Anal. Calcd. for $C_{34}H_{42}O_8Cu$: C, 63.6; H, 6.6. Found: C, 63.7; H, 6.7.

The ketoester was regenerated as follows: The copper chelate (199 g.) was suspended in ether (1200 ml.); chipped ice and 2 *N* sulfuric acid (300 ml.) were added, and the mixture shaken until the green color of the chelate disappeared from the ethereal solution, which was then separated, washed with sodium bicarbonate, water and saturated sodium chloride solution, and dried over sodium sulfate. The ether was removed and the residue placed in a refrigerator where crystallization soon occurred; yield 162.0 g. (90%). A sample for analysis was recrystallized from a mixture of ether and petroleum ether (b.p. 30–60°); m.p. 51–53°.

Anal. Calcd. for $C_{17}H_{22}O_4$: C, 70.3; H, 7.6. Found: C, 70.4; H, 7.7.

The ketoester distils at 184–186° at 0.6 mm. with decomposition. It is not advisable to distil a large quantity of the compound since considerable loss due to decomposition seriously impairs the yield. A crystalline semicarbazone could not be prepared.

Oxime.—To a solution of the ketoester (VI) (2.0 g.) in 95% ethanol (10 ml.) was added a solution of hydroxylamine hydrochloride (1.0 g.) and potassium acetate (1.4 g.) dissolved in water (4 ml.), and the mixture refluxed for three hours. The solution was evaporated to dryness *in vacuo*, the residue extracted with ether, and the ethereal solution washed with water, dried over sodium sulfate, and the ether evaporated. Distillation of the residue gave a fraction boiling with decomposition at 175–180° at 0.01 mm.; yield 760 mg. (58%).

Anal. Calcd. for $C_{17}H_{23}O_4N$: N, 4.6. Found: N, 4.7.

Methyl Cyclopentanone-2-carboxylate.—This compound was prepared according to the procedure of reference 11 from dimethyl adipate (52.2 g.) and powdered sodium (10 g.) in anhydrous benzene (250 ml.). The ester boiled at 117–120° at 19 mm.; yield 24.2 g. (57%).

Methyl 2-(4-Phenoxybutyl)-cyclopentanone-2-carboxylate (VII).—Dimethylethylcarbinol (15.1 g.) was added to a suspension of powdered potassium (6.17 g.) in anhydrous xylene (130 ml.), and the reaction mixture refluxed under nitrogen until all of the potassium had disappeared. The mixture was cooled to 60°; methylcyclopentanone-2-carboxylate (24.4 g.) was added, followed by a solution of 4-phenoxybutyl iodide (38.8 g.) in dry xylene (45 ml.), and the mixture heated at 110° under nitrogen for 45 hours. The reaction mixture was cooled, poured on cracked ice, acidified to congo red with 6 *N* hydrochloric acid and extracted with ether. The ethereal solution was washed with 5% sodium carbonate and water, dried over sodium sulfate, and the solvents removed *in vacuo*. Distillation gave an oil which boiled at 178–181° at 0.08 mm.; yield 27.5 g. (67%).

Semicarbazone.—The semicarbazone was prepared in the usual manner and was recrystallized from methanol; m.p. 138–141°.

Anal. Calcd. for $C_{18}H_{25}O_4N_3$: C, 62.2; H, 7.3; N, 12.1. Found: C, 62.3; H, 7.0; N, 11.8.

2-(4-Phenoxybutyl)-cyclopentanone (VIII). (a) From Methyl 5-(4-Phenoxybutyl)-cyclopentanone-2-carboxylate (VI).—A solution of the ketoester (VI) (1.78 g.) in concentrated hydrochloric acid (20 ml.) and glacial acetic acid (40 ml.) was refluxed for 20 hours, and the solvents removed *in vacuo*. The residue was dissolved in ether, the ethereal solution washed with 5% sodium carbonate and water, dried over sodium sulfate and the ether removed *in vacuo*. Distillation of the residue gave a main fraction boiling at 118–122° at 0.01 mm.; yield 1.02 g. (72%), $n^{25}\text{D}$ 1.5196.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.6; H, 8.7. Found: C, 77.2; H, 8.5.

Semicarbazone.—The semicarbazone was prepared in the usual manner and was recrystallized from methanol; m.p. 176–178°.

Anal. Calcd. for $C_{16}H_{23}O_2N_3$: N, 14.5. Found: N, 14.5.

(b) From Methyl 2-(4-Phenoxybutyl)-cyclopentanone-2-carboxylate (VII).—Hydrolysis of the ketoester (VII) (5 g.) with concentrated hydrochloric acid (50 ml.) and glacial acetic acid (65 ml.) in the manner described above afforded a fraction boiling at 121–122° at 0.01 mm.; yield 1.98 g. (50%), $n^{25}\text{D}$ 1.5198.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.6; H, 8.7. Found: C, 77.0; H, 8.6.

Semicarbazone.—The semicarbazone was prepared in the usual manner and, following recrystallization from methanol, melted at 176–178°. No depression of the melting point was observed when this semicarbazone was mixed with the semicarbazone obtained according to (a) above.

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(11) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 119.

Anal. Calcd. for $C_{16}H_{23}O_2N_3$: N, 14.5. Found: N, 14.5.

1-Carbomethoxy-2-cyano-3-(4-phenoxybutyl)-cyclopentene.—Potassium cyanide (26 g.) and glacial acetic acid (26 ml.) were added to a solution of the ketoester (VI) (11.6 g.) in anhydrous ethanol (120 ml.), and the mixture was refluxed for 45 minutes. The mixture was poured on cracked ice, extracted with ether, and the ethereal solution washed and dried in the usual manner. Evaporation of the ether gave the oily cyanohydrin, which was dissolved in anhydrous pyridine (120 ml.); phosphorus oxychloride (50 ml.) was added slowly, and the solution refluxed for 45 minutes under anhydrous conditions. The dark reaction mixture was carefully poured on a mixture of cracked ice and concentrated hydrochloric acid (120 ml.), and the organic layer extracted with a mixture of ether (70 parts) and ethanol (30 parts). The ether extract was washed and dried in the usual manner, and the ether evaporated. Distillation gave a viscous, yellow oil, boiling at 187–195° at 0.2 mm.; yield 7.4 g. (62%).

Anal. Calcd. for $C_{18}H_{21}O_3N$: C, 72.2; H, 7.1; N, 4.7. Found: C, 72.1; H, 6.9; N, 4.5.

3-(4-Phenoxybutyl)-cyclopentene-1,2-dicarboxylic Acid (IX).—A suspension of the above ester nitrile (13.5 g.) in 5 *N* potassium hydroxide (250 ml.) was refluxed for 26 hours at a bath temperature of 160–170°. The cooled solution was extracted with ether, the aqueous layer acidified with concentrated hydrochloric acid and the acid isolated in the usual manner; yield 6.0 g. (44%), m.p. 137–140°. Several recrystallizations from aqueous ethanol raised the melting point to 154–156°.

Anal. Calcd. for $C_{17}H_{20}O_5$: C, 67.1; H, 6.6. Found: C, 67.1; H, 6.4.

Dianilide.—The acid (IX) (600 mg.) was suspended in ether (10 ml.), and phosphorus pentachloride (920 mg.) added with shaking to the cooled suspension. Shaking was continued at room temperature until most of the phosphorus pentachloride had disappeared. The solution was filtered and concentrated to dryness *in vacuo* under anhydrous conditions. Benzene (10 ml.) was added to the residue, then removed *in vacuo* at a bath temperature of 50°. This process was repeated twice more. The ensuing acid chloride was dissolved in ether (10 ml.) and a solution of aniline (1.3 g.) in ether (10 ml.) added slowly. Isolation in the usual manner gave the dianilide, which melted at 139–140° following recrystallization from methanol; yield 500 mg. (56%).

Anal. Calcd. for $C_{29}H_{30}O_3N_2$: C, 76.6; H, 6.7; N, 6.2. Found: C, 77.1; H, 6.9; N, 6.5.

***cis*-3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylic Acid (X).**—A solution of (IX) (10 g.) in 95% ethanol (200 ml.) was hydrogenated at room temperature and atmospheric pressure over a 5% palladium-on-charcoal catalyst[12] (10 g.). An amount of hydrogen equivalent to one mole was absorbed within two hours, when the hydrogenation came to an end. The hydrogenated acid was isolated in the usual manner and was recrystallized from 25% acetic acid; m.p. 119–122°, yield 9.5 g. (94%).

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.7; H, 7.3. Found: C, 67.0; H, 7.1.

Anhydride of *cis*-3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylic Acid (XI).—The acid (X) 10 g. was dissolved in propionic anhydride (210 ml.) and the mixture refluxed for three hours. The solvent was removed *in vacuo* and the residue distilled to give a fraction boiling at 184–186° at 0.3 mm.; yield 8.1 g. (85%). A sample of the anhydride (356 mg.) was refluxed for one hour with a mixture of glacial acetic acid (4 ml.) and water (5 ml.), and the solvents removed *in vacuo*. Recrystallization of the residue from 25% aqueous acetic acid gave an acid of m.p. 119–122°, which was identified with the *cis*-acid (X) by a mixed melting point determination.

***cis*-Dimethyl 3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylate.**—A solution of the anhydride (XX) (8.1 g.) in methanol (150 ml.) and acetyl chloride (2 ml.) was refluxed for eight hours and then evaporated *in vacuo*. The ester was isolated in the usual manner, and purified by distillation; b.p. 182–185° at 0.3 mm., yield 8.8 g. (95%). The ester was also prepared from the acid (X) (2.1 g.) and diazomethane in ether; b.p. 162–165° at 0.01 mm., yield 1.99 g. (95%), n^{26}D 1.5070.

Anal. Calcd. for $C_{19}H_{26}O_5$: C, 68.2; H, 7.8. Found: C, 68.3; H, 7.7.

Saponification of a sample of this *cis*-ester (269 mg.) with aqueous 2 *N* potassium hydroxide (14 ml.) for five hours, followed by recrystallization of the ensuing acid from 25% acetic acid gave the *cis*-acid (X) (yield 190 mg.).

***trans*-Dimethyl 3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylate.**—A solution of the *cis*-dimethyl ester (334 mg.) and sodium methoxide (108 mg.) in dry methanol (10 ml.) was refluxed for 16 hours under anhydrous conditions. The solution was concentrated to a small volume *in vacuo*, cooled, acidified to congo red with 2 *N* sulfuric acid, and the organic material dissolved in ether. The ethereal solution was washed with water and dried over sodium sulfate. Diazomethane was then added until the yellow color remained and the ether and excess diazomethane removed *in vacuo*. Distillation of the residue gave the *trans*-ester as an oil which boiled at 162–165° at 0.005 mm.; yield 290 mg. (87%), n^{26}D 1.5038.

Anal. Calcd. for $C_{19}H_{26}O_5$: C, 68.2; H, 7.8. Found: C, 68.4; H, 7.7.

***trans*-3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylic Acid (XII).**—Saponification of the *trans*-ester (163 mg.) gave the *trans*-acid (XII) which melted at 136–139° following recrystallization from 25% acetic acid.

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.7; H, 7.3. Found: C, 66.7; H, 7.3.

***trans*-3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylic Acid Dihydrazide. (a) From *trans*-Dimethyl 3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylate.**—A solution of the *trans*-ester (270 mg.) and hydrazine hydrate (850 mg.) in absolute ethanol (3 ml.) was refluxed for 42 hours. The solution was concentrated to half of its volume, cooled and the resulting hydrazide collected and recrystallized from absolute ethanol; yield 208 mg. (77%), m.p. 178–180°.

Anal. Calcd. for $C_{17}H_{26}O_3N_4$: C, 61.1; H, 7.8; N, 16.8. Found: C, 61.3; H, 8.1; N, 16.6.

(b) From *cis*-Dimethyl 3-(4-Phenoxybutyl)-cyclopentane-1,2-dicarboxylate.—The refluxing of a solution of the *cis*-ester (500 mg.) with hydrazine hydrate (1.5 g.) in absolute ethanol (5 ml.) for 42 hours gave 350 mg. (70%) of the *trans*-dihydrazide, m.p. 179–181°, which was identified with the above-described hydrazide by a mixed melting-point determination. The same hydrazide was obtained when the *cis*-dimethyl ester was refluxed with hydrazine hydrate.

PITTSBURGH, PENNA.

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[12] Obtained from the American Platinum Works, Newark, New Jersey.