3. The method is rapid. The apparatus can be cleaned easily. Non-transparent liquids can be used, likewise liquids of any density. The apparatus can be placed in a water thermostat and kept at constant temperature while readings are being made.

4. In constructing this apparatus, it is not essential that the diameter of the capillary be strictly uniform throughout. Calibration of capillary radius is necessary only for a given point on the capillary tube; also for work of ordinary accuracy no capillary corrections for meniscus height readings are necessary.

5. Results which have been obtained show a close agreement with what are believed to be the most accurate interfacial tension data available in the literature.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

SYNTHESIS OF HEPTANE DICARBOXYLIC ACID-1,5[1]

BY ALBERT S. CARTER

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Perkin[2] attempted to prepare heptane dicarboxylic acid-1,5 through the condensation of diethyl ethyl malonate with trimethylene bromide and subsequent condensation with diethyl malonate to yield heptane tetracarboxylic ester-1,1,5,5. This was hydrolyzed and partially decarboxylated with the formation of an acid which seemed to be ethyl pimelic acid (heptane dicarboxylic acid-1,5). This product could not be purified to yield a solid acid, such as might be expected from the melting points of the other isomers of azelaic acid, consequently Perkin expressed doubt as to the purity of his product. This work was repeated with the utmost care and it was found that the results duplicated those obtained by Perkin. It was found, however, that small amounts of nonane tetracarboxylic ester-3,3,7,7 could be isolated from the reaction product and it was thought probable that the corresponding diethyl pimelic acid might be the impurity which inhibited the crystallization of the product.

The use of trimethylene chlorobromide or the addition of the sodium derivative of ethyl malonic ester to trimethylene bromide instead of the addition of the bromide to the sodium derivative would decrease the tendency to form the nonane tetracarboxylic acid (the former was tried by Perkin), but neither of these methods would insure that none of the second-

[1] From an investigation carried out under the direction of Professor Richard Fischer which constituted a part of a thesis presented by A. S. Carter to the Graduate School Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Perkin, *J. Chem. Soc.*, **65**, 991 (1894).

ary product would be formed. The idea of adding the sodium derivative to the bromide in order to have constantly an excess of the bromide present was tried without success.

To avoid completely the condensation of two molecules of the malonic ester with trimethylene bromide, a synthesis involving the use of phenoxypropyl bromide was carried out to yield phenoxypropylmalonic ester and phenoxyvaleric acid. This was hydrolyzed to form iodovaleric acid, esterified and condensed with diethyl malonate.

$$C_6H_5O(CH_2)_3Br \xrightarrow[C_2H_5ONa]{CH_2(COOC_2H_5)_2} C_6H_5O(CH_2)_3CH(COOC_2H_5)_2 \xrightarrow{H_2O}$$

$$C_6H_5O(CH_2)_3CH(COOH)_2 \longrightarrow C_6H_5O(CH_2)_4COOH \xrightarrow{HI} I(CH_2)_4COOH \xrightarrow[HCl]{C_2H_5OH}$$

$$I(CH_2)_4COOC_2H_5 \xrightarrow[NaOC_2H_5]{HCC_2H_5(COOC_2H_5)_2} C_2H_5OOC(CH_2)_4CC_2H_5(COOC_2H_5)_2 \xrightarrow[H_2O]{} \xrightarrow{Heat}$$

$$HOOC(CH_2)_4CH(C_2H_5)COOH$$

Experimental Part

δ-Phenoxypropyl Malonic Ester.—Following the general course of some work by Marvel and MacCorquodale,[3] phenoxypropyl malonic ester was prepared as follows: 32 g. of sodium was added to 500 cc. of absolute alcohol and to this was added 225 g. of diethyl malonate through a dropping funnel, with frequent shaking. During a period of about one hour, 325 g. of phenoxypropyl bromide was added to the reaction mixture, which was then refluxed for four hours. Most of the alcohol was distilled from the neutral product and it was shaken with water to remove the sodium bromide. The ester layer was collected in a little ether, separated from the water and dried over sodium sulfate. From this ether solution, phenoxypropyl malonic ester was obtained by fractionation under diminished pressure. The fraction containing the ester was collected at 228–235° (26 mm.); yield, 310 g. or 76%.

Anal. Subs., 0.2000: CO_2, 0.4770; H_2O, 0.1334. Calcd. for $C_{16}H_{22}O_5$: C, 65.30; H, 7.48. Found: C, 65.05; H, 7.41.

δ-Phenoxypropyl Malonic Acid.—One liter of 20% sodium hydroxide and 300 g. of phenoxypropyl malonic ester were refluxed for about five hours. The resulting solution was cooled and acidified with dilute sulfuric acid. The precipitated phenoxypropyl malonic acid was filtered off and recrystallized from hot water; yield, 218 g. or 90%; m. p. 72–78° with some decomposition. The melting point is given in the literature[4] as 75–80°.

δ-Phenoxypropyl Valeric Acid.—Two hundred g. of the malonic acid derivative was decarboxylated by heating in a 2-liter flask in an oil-bath at 175° until the evolution of carbon dioxide was complete. The product was cooled and recrystallized from petroleum ether, giving 147 g. (90%) of the phenoxypropyl valeric acid; m. p. 55–56° (Gabriel gives 65–66°). The silver salt of this acid was prepared by crystallization from a hot solution of the ammonium salt by the addition of silver nitrate.

Anal. Subs., 0.2000: AgCl, 0.0957. Calcd. for $C_{11}H_{13}O_3Ag$: Ag, 35.85. Found: Ag, 36.01.

δ-Iodovaleric Acid.—One hundred g. of phenoxyvaleric acid was refluxed for four

[3] Marvel and MacCorquodale, THIS JOURNAL, **46**, 2838 (1924).

[4] Gabriel, *Ber.*, **25**, 418 (1892).

hours with 400 cc. of hydriodic acid (sp. gr. 1.70) and the mixture was diluted with several times its volume of water and extracted with ether. To separate the iodovaleric acid from phenol, the ether solution was extracted with saturated sodium carbonate from which the acid was precipitated with hydrochloric acid, filtered and dried. This crude product was partly purified by dissolving in 75% alcohol and pouring over ice. After drying and recrystallization from warm petroleum ether, white needles were obtained, melting at 54–56°, which agrees with the melting point previously reported;[5] yield, 80 g. or 68%. An attempt to prepare bromovaleric acid in a similar manner using 48% hydrobromic acid gave poor yields.

Ethyl δ-Iodovalerate.—A mixture containing 100 g. of the iodovaleric acid in 500 g. of a 5% solution of dry hydrogen chloride in absolute alcohol was refluxed for four hours and then the greater part of the alcohol and hydrogen chloride was removed by distillation. The solution was diluted with an equal volume of water, the ester layer extracted with ether and the ether solution washed with saturated sodium carbonate to remove free acid. The ether solution of the ester was dried over sodium sulfate and distilled under diminished pressure; the ester was collected in the fraction boiling from 108 to 118° (20 mm.); yield, 68 g., representing 61% of the theoretical (this is almost 90% if corrected for the acid reclaimed from the carbonate extract of the reaction product).

Anal. Subs., 0.5000: AgI, 0.4490. Calcd. for $C_7H_{13}O_2I$: I, 49.61. Found: I, 48.54.

Triethyl Ester of Heptane Tricarboxylic Acid-1,5,5.—Four g. of sodium was dissolved in 50 cc. of absolute alcohol and to this was added 34 g. of diethyl ethylmalonate followed by 44.1 g. of ethyl iodovalerate. The reaction mixture was worked up in the same manner as in the preparation of phenoxypropyl malonic ester, the product being obtained in a fraction boiling between 195 and 200° at 20 mm.

Heptane Tricarboxylic Acid-1,5,5.—As in the case of phenoxypropyl malonic acid, 31.5 g. of the tricarboxylic acid ester was hydrolyzed with 150 cc. of 20% sodium hydroxide to yield a product of oily crystals melting at 86–88° and decomposing with the evolution of carbon dioxide at temperatures above 140°.

Heptane Dicarboxylic Acid-1,5.—Decarboxylation of 20 g. of the tricarboxylic acid between 140 and 180° gave 16 g. of yellow oil which was distilled under diminished pressure from a Claisen flask carrying a modified arm. Upon fractionation almost the entire product was collected at 218–223° at 17 mm. (Perkin records 260° at 82 mm.) The fraction was a thick, colorless oil which seemed to resist all attempts to obtain a crystalline product from it, but after standing as a liquid for several days, it suddenly completely crystallized. This crystalline material melted at 41.5–43.0° and was soluble in hot water, alcohol and hot benzene. The silver salt was prepared by dissolving in dilute ammonium hydroxide, boiling out the excess ammonia and precipitating from the cooled solution of the ammonium salt by adding silver nitrate solution.

Anal. Subs., 0.3000: AgCl, 0.2125. Calcd. for $C_9H_{14}O_4Ag_2$: Ag, 53.68. Found: Ag, 53.32.

These analyses, while slightly low for silver, considered with the method of preparation, indicate that the product is heptane dicarboxylic acid-1,5.

Summary

Heptane dicarboxylic acid-1,5 has been synthesized through the following steps: trimethylene bromide, phenoxypropyl bromide, phenoxypropyl malonic ester, phenoxyvaleric acid, iodovaleric acid, heptane tricarboxylic acid-1,5,5 and heptane dicarboxylic acid-1,5.

[5] Cloves, *Ann.*, **319**, 367, 388 (1901).

Heptane dicarboxylic acid-1,5 has been obtained as a solid.

In the course of the synthesis, the following new compounds were prepared: ethyl δ-iodovalerate, triethyl ester of heptane tricarboxylic acid-1,5,5, heptane tricarboxylic acid-1,5,5 and the silver salt of heptane dicarboxylic acid-1,5.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMCIAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE USE OF PLATINUM-OXIDE PLATINUM BLACK IN THE CATALYTIC REDUCTION OF AROMATIC HYDROCARBONS. XVII[1]

BY ROGER ADAMS AND J. R. MARSHALL[2]

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One of the few classes of reducible compounds which does not lend itself readily to reduction under ordinary laboratory conditions is the aromatic hydrocarbons. These compounds have frequently been reduced at high temperatures, using nickel or other metals as a catalyst, but no satisfactory method is available for their reduction under such conditions as are most conveniently used in a scientific laboratory, namely, room temperature or slightly above, atmospheric pressure or pressures not over two or three atmospheres and readily prepared catalyst. The reactions should be comparatively rapid and it should be possible to reduce large enough quantities to be sufficient for ordinary research purposes. The success of platinum-oxide platinum black as a catalyst for the addition of hydrogen to many unsaturated compounds, as compared with other forms of catalytic platinum, led to a study of its use in the reduction of aromatic hydrocarbons.

Willstätter[3] and his associates report the hydrogenation of benzene and toluene at ordinary pressures and temperatures by means of hydrogen and platinum black prepared by the reduction of chloroplatinic acid and formaldehyde. However, the large amount of catalyst needed compared with the amount of material to be reduced renders the method impractical for ordinary work. For the reduction of 3.0 g. of benzene in 13 cc. of glacial acetic acid with 0.1 g. of platinum black, six hours was required; for 1.8 g. of toluene in 3 g. of acetic acid with 0.5 g. of platinum black, three and one-half hours; for 6 g. of xylene in 4 g. of acetic acid with 0.9 g. of platinum

[1] The previous article in this field is by Bray and Adams, THIS JOURNAL, **49**, 2101 (1927). Reference to the other work will be found in this article.

[2] This communication is an abstract of a thesis submitted by J. R. Marshall in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

[3] (a) Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 113 (1912); (b) Willstätter and Hatt, *ibid.*, **45**, 1471 (1921).