0.1223. Calcd. for $C_{19}H_{36}O_2$: mol. wt., 296.3; C, 76.95; H, 12.24. Found: mol. wt., 297.9; C, 77.08; H, 12.25.

Summary

The syntheses of κ-cyclohexyl-undecanoic acid and μ-cyclohexyl-tridecanoic acid have been completed. These acids are homologs of dihydrochaulmoogric and dihydrohydnocarpic acids in which the cyclohexyl group has replaced the cyclopentyl group.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE PREPARATION OF ORTHO-PHTHALALDEHYDIC ACID

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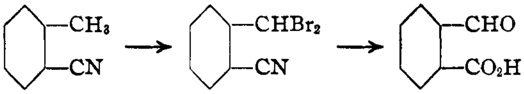
In connection with the preparation of certain substituted phenylparaconic acids used in a study of the structure of naphthalene[2] it was necessary to prepare considerable quantities of *o*-phthalaldehydic acid. Although several methods for the preparation of this compound are given in the literature none of them proved to be entirely satisfactory for its preparation in the desired quantity. It was, therefore, decided to study the various methods and to try to develop a procedure which would give satisfactory and consistent results. This paper is a report of the results of this study and comprises not only improved directions for the preparation of *o*-phthalaldehydic acid but also certain theoretical points of interest in connection with the preparation.

In the first method to be tried *o*-tolunitrile was the starting material. This was converted into the *o*-cyanobenzal bromide (I) by bromination and from the latter compound *o*-phthalaldehydic acid (II) was formed by hydrolysis. The synthesis is represented by the following scheme.



I II

The method proved to be unsatisfactory because of the great difficulty encountered in introducing the second bromine atom into *o*-tolunitrile. The yields were small and the preparation of *o*-phthalaldehydic acid in this way was abandoned.

Gilliard, Monnet and Cartier[3] prepared the compound from phthalonic acid obtained by oxidation of naphthalene with potassium permanganate. The directions for this procedure, which are to be found only in the patent

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[1] National Research Fellow in Chemistry.

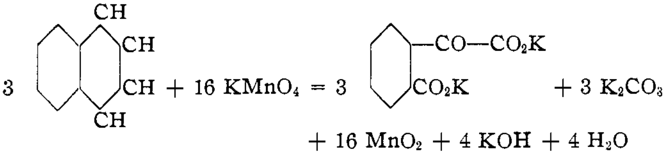
[2] Fuson, THIS JOURNAL, **46,** 2784 (1924); **47,** 516 (1925).

[3] Gilliard, Monnet and Cartier, Ger. pat. 97,241 (1897). See also Friedländer, "Fortschritte der Teerfarbenfabrikation," **5,** 139 (1897–1900).

literature, were proved to be inadequate and much trouble was encountered in attempting to use them. Moreover, one step (2) in the preparation is very obscure. Nevertheless, this method seemed decidedly more promising than any of the others and was, accordingly, chosen for the present study.

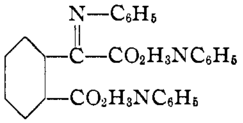
The starting material for the preparation is naphthalene and the process consists of four steps: (1) the oxidation of naphthalene to phthalonic acid by means of alkaline permanganate solution; (2) the conversion of phthalonic acid into its aniline derivative; (3) the decomposition of the aniline derivative to form *o*-carboxybenzylidene aniline; (4) the hydrolysis of the latter to *o*-phthalaldehydic acid.

The Oxidation of Naphthalene.—The oxidation of naphthalene by an alkaline solution of potassium permanganate proceeds chiefly according to the equation

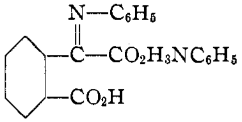


The reaction has frequently been used in preparing phthalonic acid,[4] the yield being 55–60%. Although this yield is good considering the type of the reaction, it seemed probable from the results of Daly[5] that it could be improved by carrying out the oxidation in a solution of about 0.5 *N* alkali and in which the concentration of permanganate as well as that of the phthalonic acid remained nearly constant throughout the reaction. The directions given in the experimental part were worked out to fulfil these requirements. The method does, in fact, give better yields and it has the additional advantages that it lessens the time required for the oxidation and that it practically eliminates "bumping."

The Aniline Derivative of Phthalonic Acid.—When an aqueous solution of phthalonic acid is treated with an excess of aniline an insoluble derivative is formed to which Gilliard, Monnet and Cartier assigned Formula III.



III



IV

Analysis, however, shows this formula to be incorrect inasmuch as the salt contains but two aniline residues. In analogy with the aniline deriva-

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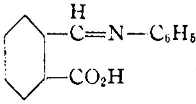
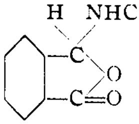
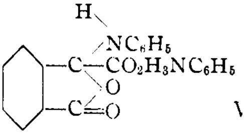
[4] Tcherniac, Ger. pats. 79,693 (1895), 86,914 (1896); *J. Chem. Soc.*, **109**, 1236 (1916). Graebe and Trümpy, *Ber.*, **31**, 369 (1898).

[5] Daly, *J. Phys. Chem.*, **11**, 93 (1907).

tive of benzoylformic acid, the formula would be IV. According to Gilliard, Monnet and Cartier, when this salt is heated it gives aniline, carbon dioxide and *o*-carboxybenzylidene aniline. The latter compound, however, is insoluble in carbonate solutions and therefore probably has the constitution VI instead of V.


V

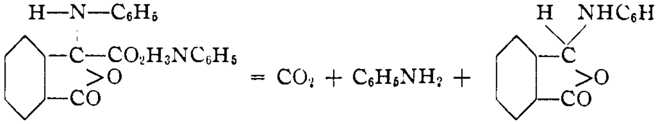

VI


VII

From this it appears probable that the aniline derivative is not IV but VII.[6]

Decomposition of the Aniline Derivative V

According to the general method of Bouveault[7] the aniline derivative (VII) would be expected to decompose under the influence of heat, giving carbon dioxide, aniline and (VI). Gilliard, Monnet and Cartier attempted to apply Bouveault's method to this case obtaining, however, no *o*-carboxybenzylidene aniline "but only high-melting substances which could not be changed into phthalaldehydic acid." However, they succeeded in preparing the desired aldehyde by suspending the aniline derivative in five times its weight of boiling xylene under which conditions it decomposed quantitatively according to the equation



In using the method it was found that the aniline derivative often failed entirely to decompose when suspended in boiling xylene, while in other cases under apparently identical conditions it decomposed with the utmost ease. Investigation has shown that the decomposition is inhibited by the presence of a trace of water in the xylene. Whereas in perfectly dry xylene (distilled from sodium) the salt decomposes in a few minutes, in xylene containing only 0.4% of water the salt remains wholly unchanged even after hours of boiling. The yield of *o*-carboxybenzylidene aniline is practically quantitative.

Experimental Part

The Oxidation of Napthhalene.—Thirty-two g. of naphthalene is placed in a 3-liter flask equipped with a reflux condenser, a dropping funnel and a very efficient mechanical stirrer. It is best to use a wide Liebig condenser and to introduce the solutions through it. One-half liter of 0.5 *N* sodium hydroxide solution is run in and the mixture heated to boiling over a free flame. A solution of 212 g. of potassium permanganate in 1.5 liters of hot water is added gradually to the reaction mixture over a

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[6] Compare Kuroda and Perkin, *J. Chem. Soc.*, **123**, 2094 (1923).

[7] Bouveault, *Bull. soc. chem.*, [3] **15**, 1020 (1896).

period of two and a half hours. To prevent the permanganate from crystallizing in the dropping funnel the solution is kept nearly boiling and is added to the funnel in small portions which can be run into the flask before they become cold enough to deposit the salt. The reaction mixture is kept boiling throughout the oxidation and is continually agitated. The stirring must be very vigorous to avoid difficulty from "bumping" caused by the accumulation of manganese dioxide as the oxidation proceeds. After all of the permanganate has been added the heating and stirring are continued for a half hour and finally any remaining permanganate is eliminated by the addition of a few cubic centimeters of ethyl alcohol to the hot mixture. The amount of unchanged naphthalene is very small. When the mixture is cold the manganese dioxide and the excess of naphthalene are filtered off, and to the clear colorless filtrate is added 140 cc. of concd. hydrochloric acid. Following the plan of Gilliard, Monnet and Cartier, the phthalonic acid is not isolated but its aniline derivative is prepared directly from the aqueous solution.

The Aniline Derivative of Phthalonic Acid.—The aqueous solution of phthalonic acid from the oxidation is concentrated to a volume of about 500 cc., cooled and filtered from precipitated inorganic salts. It is then diluted somewhat, 100 g. of aniline is added and the solution heated on the steam-bath. After a few minutes crystals begin to form and soon the whole becomes a mass of crystals. After an hour the mixture is cooled and filtered; yield of crude salt, 18–19 g., or 80–85%. After recrystallization from alcohol the salt melts at 165°.

Anal. Calcd. for $C_{21}H_{18}O_4N_2$: C, 69.6; H, 5.0; N, 7.7. Found: C, 69.8; H, 5.4; N, 7.7.

***o*-Phthalaldehydic Acid.**—*o*-Phthalaldehydic acid is obtained from the benzylidene aniline in the usual way by hydrolyzing with 10% hydrochloric acid. The yield of acid, m. p. 96.5–97°, is about 80% of the calculated amount based on the crude benzylidene aniline and about 65% of that required based on the amount of naphthalene used.

***o*-Cyanobenzal Bromide.**—Fifty-four g. of *o*-tolunitrile was placed in a brominating flask exposed to sunlight and kept at 180–200°. Into it was dropped 148 g. of bromine, the addition requiring one and a quarter hours. The reaction mixture was refluxed for four hours with a mixture of 75 g. of calcium carbonate and 175 cc. of water and subsequently steam distilled. The *o*-cyanobenzal bromide solidified in the receiver. It crystallized from alcohol in colorless, columnar crystals 2.5 cm. long; m. p., 62–63°.

Anal. Calcd. for $C_8H_5NBr_2$: Br, 58.1. Found: 57.8.

Hydrolysis.—The compound was boiled for four hours with dil. sulfuric acid (two parts of concd. acid to one of water). The nitrile dissolved gradually. The solution was cooled, diluted with water and extracted with ether. From the ether was obtained nearly pure *o*-phthalaldehydic acid.

Summary

An improved method is given for the oxidation of naphthalene to phthalonic acid and for the preparation of *o*-phthalaldehydic acid from the latter.

The aniline derivative of phthalonic acid is characterized and its structure discussed.

Its decomposition is found to be inhibited by the presence of a trace of water.

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