

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BARNARD COLLEGE.]

THE PREPARATION OF *o*-NITROBENZOIC ACID.

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The object of the work described in this paper was the preparation of pure *o*-nitrobenzoic acid. The method was the oxidation with potassium permanganate of the mixture of *o*- and *p*-nitrotoluenes formed by the nitration of toluene and the separation of the *o*- and *p*-nitrobenzoic acids thus formed. The usual slow oxidation in dilute solution and the laborious separation of the 2 acids by fractional crystallization of their barium salts¹ which gave an impure *o*-acid, was replaced by more rapid oxidation in concentrated solution and the separation of the 2 acids by fractional distillation of their methyl esters under diminished pressure. Thus much time was saved and pure *o*-nitrobenzoic acid obtained.

After working out the procedure with the product from the nitration of toluene, it was possible to prepare in a few hours by the same method pure *o*-nitrobenzoic acid from any one of a number of samples of *o*-nitrotoluene of various grades of purity which had been obtained on the market. Some *p*-nitrotoluene was present in every sample even in those which distilled within 0.1°.

The Oxidation of the Mixed *o*- and *p*-Nitrotoluenes.

The usual method is oxidation in dil. alkaline solution with potassium permanganate. The reaction is slow and a great deal of time is required for evaporation of the large volume of solution. An attempt was made to carry out the oxidation in a very concentrated solution of permanganate, the flask being heated on the water bath and the contents agitated by an electrical stirrer fitted with a mercury seal to avoid loss of substance. The oxidation was rapid but the yields of acid extremely poor.

While these experiments were in progress the paper of Bigelow² on the oxidation of the nitrotoluenes appeared. Our results with mixed *o*- and *p*-nitrotoluenes agree substantially with his.

The procedure finally adopted for rapid oxidation was as follows. Forty g. of mixed nitrotoluenes, 400 cc. of water and 25 cc. of 10% solution of sodium hydroxide were put into a 2-liter flask fitted with a return condenser and an inlet tube for steam. Forty-six g. of solid potassium permanganate, half the calculated quantity, were added, the flask heated on the water bath and steam passed in until the reaction was well started. The heat of reaction was then sufficient to keep the mixture boiling rapidly. At the end of an hour the rest of the permanganate was added. As soon as the boiling caused by the heat of reaction ceased, steam was again passed into the solution and this continued until the permanganate was

¹ Monnet, Reverdin, Noeltig, *Ber.*, 12, 443 (1879).

² Bigelow, *THIS JOURNAL*, 41, 1559 (1919).

entirely decolorized. The time for the oxidation was about 2 hours. The oxides of manganese were then filtered out by suction and washed repeatedly with boiling water. The combined filtrates were cooled and filtered through a folded filter paper. The unoxidized oil was held back completely by the filter paper and could be run out, dried and weighed. The yield of oxidation product could then be calculated from the amount of oil oxidized. The separation of the oil by filtration is an immense saving of time over the usual method of distillation with steam.

In no case was it found possible to oxidize all the oil, even when a large excess of permanganate was used, a fact noted by the early investigators. The incomplete reaction and low yield of product are due, as pointed out by Bigelow,¹ to the reduction of some of the permanganate by the oxides of manganese formed during the reaction and to the rapid and complete oxidation of some of the nitrobenzoic acids by the excess of permanganate. For this reason oxidation in concentrated solution gives a low yield of product, from 50 to 60% being obtained by following the above directions, while slow oxidation in very dilute solution gave yields as high as 87%. As it is possible, however, by the method described to obtain fair yields in less than $\frac{1}{4}$ the time required for oxidation in dilute solution the procedure is to be recommended.

The Partial Separation of *p*-Nitrobenzoic Acid from the Oxidation Mixture.

Although both the nitrobenzoic acids are soluble in water, the *p*-acid is far less soluble than the *ortho*. It was found that if the filtrates from the oxidation mixture were evaporated so that there was about 900 cc. of liquid for each 30 g. of oil oxidized, practically pure *p*-nitrobenzoic acid was precipitated on acidification of the cooled solution. If the solution were more concentrated, some *o*-acid separated with the *para* and was subsequently lost on crystallization of the latter acid from boiling water.

The filtrates from the precipitation were exactly neutralized with sodium carbonate, since *o*-nitrobenzoic acid is slightly volatile with water vapor, and evaporated to a small volume. From the cooled solution, hydrochloric acid precipitated a mixture of *o*- and *p*-nitrobenzoic acids melting at about 120–140°. The filtrate was extracted with ether, the ether evaporated, and the residue added to the precipitated mixed acids.

The Separation of *o*-Nitrobenzoic Acid from the Mixture of Acids.

The crude mixed acids were dried, dissolved in 10 times their weight of methyl alcohol that had been saturated with hydrochloric acid, and boiled for 2 hours. The alcohol was then completely distilled off, and the residue cooled in a freezing mixture. Crystals of *p*-nitro ester separa-

¹ *Loc. cit.*

ted and were filtered out by suction. The oil remaining, consisting of *o*-nitro ester in which some *p*-nitro ester was dissolved, was washed with dil. sodium carbonate solution, extracted with ether, the solution dried, the ether distilled off, and the residue repeatedly fractioned under diminished pressure. The boiling points of the purified products were, 160° (14 mm.), 162° (16 mm.), 167° (21 mm.). Fractions of slightly higher boiling point, on cooling, usually deposited a few crystals of *p*-ester. These were filtered out and the liquid fractioned until it had a constant boiling point.

The methyl ester of *o*-nitrobenzoic acid is a pale yellow mobile liquid. In spite of a constant boiling point it may still contain traces of *p*-ester. It is possible to get rid of this by saponification in an alcoholic solution of definite concentration. For each g. of ester, one g. of potassium hydroxide in 16 cc. of cold absolute alcohol was used. In less than a minute, shining crystals of the potassium salt of the *o*-acid began to form. The mixture was allowed to stand an hour, and the mass of pearly crystals then filtered out by suction and washed with a small quantity of cold absolute alcohol. More than 90% of the acid separated out as the potassium salt. From the concentrated aqueous solution of this salt, hydrochloric acid precipitated pure *o*-nitrobenzoic acid as a snow-white solid, melting at 147–147.5°. The filtrate from the separation of the potassium salt gave an acid of considerably lower melting point.

The melting points of *o*-nitrobenzoic acid given in the literature are 140°,¹ 141°,² 145°,³ 147°.⁴ The cause of this wide variation in melting points is, undoubtedly, admixture of *p*-nitrobenzoic acid. The effect of various amounts of *p*-acid on the melting point of the *o*-acid, is shown in the following table:

<i>p</i> -Nitro-benzoic acid with <i>o</i> -acid. %	° C. at which substance begins to soften.	° C. at which substance melts.
20	127	138–142
15	131	139–144
10	132	139–144
5	135	140–145
0 (pure <i>o</i> -acid)	145	147–147.5
100 (pure <i>p</i> -acid)	...	239–240

Mixtures with 20% and with 15% of *p*-acid are almost completely melted at 140°. Thus a very impure *o*-acid gives a fair melting point. It is not possible to purify this acid by repeated crystallization, as much of the very soluble *o*-acid remains in the filtrate, the percentage of *p*-acid

¹ Greiss, *Ann.*, 166, 132 (1873).

² Beilstein and Kuhlberg, *ibid.*, 163, 135 (1872).

³ Monnet, Reverdin, Noelting, *loc. cit.*

⁴ Windmrmn, *Ann.*, 193, 221 (1878).

increasing with each crystallization. By far the most rapid method of obtaining perfectly pure *o*-acid is by way of its methyl ester.

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MENTHOL AND PHENYLHYDRAZINE DERIVATIVES OF THE HIGHER FATTY ACIDS.

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The separation of the higher fatty acids, or their determination when several are present together is a matter of very considerable difficulty. In the hope of securing a simple and reliable method of separation or determination of these acids, the preparation and properties of their menthyl esters and their phenylhydrazids have been studied. Although in neither case was the hope of a quantitative identification realized, the compounds are of sufficient interest to merit description.

The menthol esters of lauric, myristic, palmitic, stearic, and arachidic acids were prepared by heating the acid chlorides with menthol. The acid chlorides were obtained by the action of phosphorus pentachloride and thionyl chloride on the fatty acids. It was found that the reaction with thionyl chloride was not only more nearly quantitative but also yielded a product freer from impurities. However, since even the thionyl chloride did not give a quantitative yield of the acid chlorides, it was not possible to utilize the optical rotation of these methyl esters for the estimation of the above mentioned acids in mixtures when only 2 of them were present.

The phenylhydrazine derivatives of several of these fatty acids were prepared by heating the acids with an excess of phenylhydrazine. Derivatives of palmitic, stearic, and arachidic acids were prepared and their solubilities in alcohol, which was found to be the most suitable solvent from which to crystallize them, was studied. It was found that they were only slightly soluble in cold alcohol and that with the increase of the molecular weight the solubility decreased, as was to be expected. However, there was not enough difference in their respective solubilities to enable the compounds to be utilized in the separation of these acids from each other by fractional crystallization.

Experimental Part.

Menthyl Laurate, $C_{22}H_{42}O_2$.—Equal weights of pure lauric acid and phosphorus pentachloride were heated on the steam bath. When the reaction was completed, the phosphorus oxychloride was removed by heating the mixture under 15 mm. pressure to 150°. Then the pressure