

To this in suspension conc. hydrogen peroxide<sup>3</sup> is added and hydrogen chloride is bubbled through simultaneously in such manner that the bubbles keep the platinum black well agitated. After the flow of gas and of peroxide have been properly regulated, the process needs very little attention and solution is complete in the course of some hours, the time depending on the amount of platinum black to be dissolved.

The solution thus obtained is treated with the necessary amount of pure potassium chloride and the potassium chloroplatinate crystals are filtered off, dried and added to the stock of pure chloroplatinate on hand.

From a weighed amount of this stock the reagent is prepared by reduction with alkaline sodium formate, washing the platinum black obtained and dissolving it as described above. This solution is then made up to the proper volume as calculated from the weight of chloroplatinate taken, so that 10 cc. of the reagent contains 1 g. of metallic platinum, as required by the official methods of the A.O.A.C.<sup>4</sup>

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**FRIEDEL AND CRAFTS' REACTION. SOME SUBSTITUTED  
PHTHALIC ANHYDRIDES WITH TOLUENE AND  
ALUMINUM CHLORIDE.**

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As pointed out in a previous paper<sup>1</sup> an unsymmetrical phthalic anhydride with benzene and aluminum chloride may give two acid products. In some of the reactions described in this paper two acid products were obtained, in others only one. With the symmetrical tetrahalogenophthalic anhydrides only one acid product was obtained as was to be expected.

The physical properties of the toluyl-nitrobenzoic acids are very similar

<sup>3</sup> The conc. hydrogen peroxide should be freshly prepared immediately before use. Commercial peroxide, free from preservatives, is concentrated by distillation at reduced pressure to  $\frac{1}{10}$  its volume. The reservoir of commercial peroxide is connected to a Pyrex distilling flask, holding about twice the volume of conc. peroxide to be prepared, and the initial volume in the flask, which is the final volume desired, is maintained. The distillation is carried on under a pressure of 50 mm. of mercury or less and the bath is kept at a temperature 5° to 10° higher than the boiling point of water at the pressure in the flask.

Hydrogen chloride is prepared in the usual manner by adding conc. sulfuric acid to conc. hydrochloric acid in a suitable generator.

<sup>4</sup> Official Methods, A.O.A.C., 1920, p. 12.

<sup>1</sup> Lawrance, *THIS JOURNAL*, 42, 1871 (1920).

to those of the benzoyl-nitrobenzoic acids. They are brownish amorphous powders which do not have a sharp melting point and decompose on melting and while somewhat more soluble in hot than in cold alcohols, they do not crystallize from these solvents.

In all the acids obtained the toluene is represented as entering the reaction at the position *para* to the methyl group. The sodium, potassium and ammonium salts of all the toluyl-tetrahalogeno-benzoic acids are only slightly soluble in water. A small quantity of each of the benzoyl-tetrahalogeno-benzoic acids described by Alice Hofmann<sup>2</sup> was prepared and it was found that their alkali salts are also only slightly soluble in cold water.

**General Procedure.**—The derivative of the phthalic anhydride was treated with aluminum chloride and excess of toluene in the proportion of two mol. wts. of aluminum chloride to one mol. wt. of the anhydride. In most of the experiments about 9 g. of aluminum chloride was used and 45 to 50 cc. of toluene. After heating until hydrogen chloride ceased to come off, 10% hydrochloric acid was added, the contents of the flask were shaken and the excess of toluene distilled with steam. The residue was filtered, washed and boiled with a saturated solution of sodium carbonate. The alkaline solution was filtered and the filtrate acidified slowly with 10% hydrochloric acid.

**3-Nitrophthalic Anhydride with Toluene and Aluminum Chloride.**—The yield was 51%, calculated on the anhydride. The two isomeric acids in this precipitate have no marked solubility differences, but a somewhat unsatisfactory separation was effected by methyl alcohol.

*Identification of the Acid Less Soluble in Methyl Alcohol.*—This acid is very soluble in acetone, moderately soluble in ethyl alcohol, less soluble in methyl alcohol and almost insoluble in ether and ligroin; m. p. 262–5° (decomp.).

*Hydrolysis.*—A solution of 2 g. of the acid and 10 g. of potassium hydroxide was heated in a nickel crucible to about 215° for 20 minutes. When cold the mass was dissolved in water, filtered, acidified and the precipitate dried. When heated for several hours on the water-bath the sublimate was *p*-toluic acid and the residue was *o*-nitrobenzoic acid.

*Synthesis.*—Nine g. of 2-carbethoxy-3-nitrobenzoyl chloride<sup>3</sup> was dissolved in 45 cc. of toluene and 9.5 g. of powdered aluminum chloride slowly added. The mixture became warm and large quantities of hydrogen chloride were given off. When the initial reaction was over the mixture was heated on the water-bath for 8 to 9 hours, acidified and the excess of toluene removed. The product, a tarry viscous oil, was hydrolyzed with alcoholic potassium hydroxide, the potassium salt dissolved in water and the solution acidified. The acid was purified by dissolving in hot alcohol and allowing the solution to cool, when a light brown amorphous powder was obtained which melted

<sup>2</sup> Hofmann, *Monatsh.*, 36, 805 (1915).

<sup>3</sup> In my previous paper it was stated that the carbethoxy-nitrobenzoyl chlorides from 3-nitrophthalic acid had not previously been described. Since publication I have found that they had been described by Cohen, Woodroffe and Anderson, *J. Chem. Soc.*, 109, 234 (1916).

with decomposition at 262-5°; yield about 53%. This product, therefore, is 6-*p*-toluyl-2-nitro-benzoic acid.

*Analysis.*—Calc. for  $C_{15}H_{11}O_5N$ : N, 4.91. Found: 4.72.

*Identification of the Acid More Soluble in Methyl Alcohol.*—From a hot saturated solution of the acid in methyl alcohol a small quantity of a light brown amorphous powder was obtained which darkened at 105-7° and decomposed at 122-6°.

*Hydrolysis.*—Fusion with potassium hydroxide gave two products which were separated by sublimation. They were identified as *p*-toluic acid and *m*-nitrobenzoic acid.

*Synthesis.*—Nine g. of 6-carbomethoxy-2-nitrobenzoyl chloride was dissolved in 45 cc. of toluene and 9.5 g. of aluminum chloride added slowly. The reaction began in the cold and no heat was applied for one hour. The mixture was then heated on the water-bath for 9 hours, cooled, acidified and the toluene distilled. The viscous, black, oily ester was hydrolyzed with 8% alcoholic potassium hydroxide. The acid so prepared darkened at 106-9° and decomposed at 123-6°. This product is, therefore, 2-*p*-toluyl-3-nitrobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{11}O_5N$ : N, 4.91. Found: 4.71.

**4-Nitrophthalic Anhydride with Toluene and Aluminum Chloride.**—The precipitate obtained by acidifying the sodium carbonate solution was found to consist almost altogether of an acid soluble in ethyl alcohol and melting with decomposition at 100-105° but there was a small quantity of material less soluble in ethyl alcohol melting with decomposition at 211-18°.

*Identification of the Acid Melting with Decomposition at 100-105°.*—This acid is soluble in methyl alcohol, ethyl alcohol and acetone, slightly soluble in ether and benzene and insoluble in ligroin.

*Hydrolysis.*—Fusion with potassium hydroxide for 20-25 minutes at 210-20° gave *p*-toluic acid and *p*-nitrobenzoic acid.

*Synthesis.*—Ten g. of 6-carbo-methoxy-3-nitrobenzoyl chloride was dissolved in 50 cc. of toluene and 9 g. of powdered aluminum chloride slowly added. The reaction began vigorously in the cold, and after standing for one hour the mixture was heated on the water-bath for 6-7 hours. The black viscous product obtained after acidification and removal of the toluene was hydrolyzed with 8% alcoholic potassium hydroxide redissolved in sodium carbonate solution, precipitated by acid, washed and dried; m. p. 101-5° with decomposition; yield, 55%.

This acid is, therefore, 2-*p*-toluyl-4-nitrobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{11}O_5N$ : N, 4.91. Found: 4.77.

**3-Acetyl-amino-phthalic Anhydride with Toluene and Aluminum Chloride.**—The solution obtained by using cold sodium carbonate on acidification gave an acid which on purification melted at 256-7°. The residue from the sodium carbonate solution after washing with cold benzene gave an acid which on further purification melted at 206°.

*Partial Identification of the Acid Melting at 256-7°.*—This acid is not very soluble in water but small quantities of very pure crystals may be obtained by making a saturated solution in hot water, allowing the solution to cool, and repeating this once or twice. It is soluble in ethyl and methyl alcohol. Yield about 20%, calculated on the anhydride.

*Hydrolysis.*—When fused with potassium hydroxide for 20 minutes at 200-215° and acidified only *p*-toluic acid and benzoic acid were recognized. This indicates that the aminobenzoic acid was converted into benzoic acid during the fusion.

Reduction of the *p*-toluyl-nitrobenzoic acids by ferrous sulfate and also by zinc and acetic acid was attempted, but the results were unsatisfactory, due in part to the limited amount of pure acids available.

This acid is, therefore, 2- or 6-*p*-toluyl-3- or 2-aminobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{12}O_3NAg$ : Ag, 29.8. Found: 30.0.

*Partial Identification of the Acid Melting at 206°.*—This acid is not very soluble in cold sodium carbonate solution but is somewhat soluble in the hot solution. The alkaline solution was acidified and the precipitate dried; yield about 40% calculated on the anhydride used. It was recrystallized twice from ethyl alcohol. It is soluble in acetone, slightly soluble in ether and insoluble in benzene.

*Hydrolysis.*—Fusion with potassium hydroxide at 210–20° for 20 minutes gave a product from which *p*-toluic acid and a small amount of benzoic acid were obtained.

This acid is, therefore, 2- or 6-*p*-toluyl-3- or 2-aminobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{12}O_3NAg$ : Ag, 29.8. Found: 29.65.

**4-Acetyl-amino-phthalic Anhydride with Toluene and Aluminum Chloride.**—The precipitate consists principally of one acid; only a small quantity of the second acid was found; yield, 62%.

*Partial Identification of the Acid Melting at 135–6°.*—The precipitate from the carbonate solution was dissolved in alcohol and water added until a faint cloudiness appeared. On standing for several hours a small quantity of gum separated; the alcohol which still contained the bulk of the material was poured off and allowed to slowly evaporate at room temperature. The second deposit was still gummy but on drying was easily powdered. Repeating this operation gave a product melting at 135–6°. It is soluble in ethyl alcohol, methyl alcohol and acetone, slightly soluble in benzene and insoluble in ether.

*Hydrolysis.*—Fusion with potassium hydroxide at 205–215° for 25 minutes gave a product from which *p*-toluic acid and a small quantity of benzoic acid were obtained.

This acid is, therefore, 2- or 6-*p*-toluyl-4- or 3-aminobenzoic acid.

*Analysis.* Calc. for  $C_{15}H_{12}O_3NAg$ : Ag, 29.8. Found: 29.7.

The small quantity of material which separated first from the alcohol solution was dried *in vacuo*, dissolved in sodium carbonate solution, precipitated with acid, washed and dried; m. p. 180–3°. It is soluble in acetone and almost insoluble in benzene or ether. It is probably the isomeric acid, but sufficient quantity for identification was not obtained.

**Tetrachloro-phthalic Anhydride with Toluene and Aluminum Chloride.**—The dried product weighed 12.4 g. corresponding to a 94% yield. When recrystallized from alcohol it melted at 174.5° corr. This acid is soluble in alcohol, ether or acetone. It may be recrystallized from benzene. The sodium, potassium and ammonium salts are only slightly soluble in water.

*Hydrolysis.*—Fusion with potassium hydroxide at 210–5° for 15 minutes gave a product from which *p*-toluic acid and a small quantity of 2,3,4,5-tetrachloro-benzoic acid were obtained.

It is, therefore, 6-*p*-toluyl-2,3,4,5-tetrachloro-benzoic acid.<sup>4</sup>

*Analysis.* Calc. for  $C_{15}H_8O_3Cl_4$ : Cl, 37.5. Found: 37.1.

*Methyl Ester.*—Five g. of the acid was boiled for 50 minutes with 50 cc. of methyl alcohol and hydrogen chloride. On cooling to 10° most of the ester crystallized out. On recrystallization from methyl alcohol the ester was colorless, m. p. 96–97° (corr.). It is soluble in ethyl alcohol and acetone and slightly soluble in ether and benzene.

**Tetrabromo-phthalic Anhydride with Toluene and Aluminum Chloride.**—The dried product weighed 10.7 g. which represents an 89% yield. When recrystallized from methyl alcohol the acid melts at 212° (corr.). It may also be recrystallized from

<sup>4</sup>Brit. pat. 8917(April 8, 1914) mentions this acid.

benzene or chloroform. It is soluble in acetone but insoluble in ether or water. The sodium, potassium and ammonium salts are only slightly soluble in water.

*Hydrolysis.*—Fusion with potassium hydroxide at 210–220° for 20 minutes gave a product from which *p*-toluic acid was isolated.

This compound is, therefore, 6-*p*-toluyl-2,3,4,5-tetrabromo-benzoic acid.

*Analysis.* Calc. for  $C_{15}H_8O_3Br_4$ : Br, 57.5. Found: 56.8.

*Methyl Ester.*—Five g. of the acid was dissolved in warm methyl alcohol containing hydrogen chloride and boiled for one hour. Most of the alcohol was then distilled off and the remainder poured into water. It was recrystallized from methyl alcohol, m. p. 162.5 (corr.). It is soluble in ethyl alcohol, benzene, ethyl acetate and ether.

**Tetra-iodo-phthalic Anhydride with Toluene and Aluminum Chloride.**—The dried product weighed 10.2 g., a 91% yield. When recrystallized from methyl alcohol or benzene it was pale yellow and melted at 266° (corr.). It is soluble in acetone and slightly soluble in water, ether and chloroform. Its sodium, potassium and ammonium salts are only slightly soluble in water.

*Hydrolysis.*—Fusion with potassium hydroxide at 200–215° for 30 minutes gave *p*-toluic acid and the acid is, therefore, 6-*p*-toluyl-2,3,4,5-tetra-iodo-benzoic acid.

*Analysis.* Calc. for  $C_{15}H_8O_3I_4$ : I, 68.25. Found: 67.9.

*Methyl Ester.*—Five g. of the acid was boiled for 1 hour with 50 cc. of methyl alcohol and hydrogen chloride and 1/2 of the alcohol was then distilled and the remainder poured into water. The ester when recrystallized from methyl alcohol was pale yellow and melted at 199° (corr.). It is soluble in alcohol, benzene and ethyl acetate and slightly soluble in ether.

### Summary.

1. The reaction of aluminum chloride and toluene with each of 7 derivatives of phthalic anhydride has been investigated.

2. Eleven new compounds have been prepared: 6-*p*-toluyl-2-nitrobenzoic acid, 262–5° (decomp.); 2-*p*-toluyl-3-nitrobenzoic acid, 123–6° (decomp.); 2-*p*-toluyl-4-nitrobenzoic acid, 101–5° (decomp.); 2- or 6-*p*-toluyl-3- or 2-aminobenzoic acid, 256–7°; 2- or 6-*p*-toluyl-3- or 2-aminobenzoic acid, 206°; 2- or 6-*p*-toluyl-4- or 3-aminobenzoic acid, 136–7°; methyl 6-*p*-toluyl-2,3,4,5-tetrachloro-benzoate, 96–7°; 6-*p*-toluyl-2,3,4,5-tetrabromo-benzoic acid, 212°; methyl 6-*p*-toluyl-2,3,4,5-tetrabromo-benzoate, 162.5°; 6-*p*-toluyl-2,3,4,5-tetra-iodo-benzoic acid, 266°; methyl 6-*p*-toluyl-2,3,4,5-tetra-iodo-benzoate, 199°.

3. The properties of 6-*p*-toluyl-2,3,4,5-tetrachloro-benzoic acid have been described.

This research was done under the direction of Professor F. B. Allan.

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