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FRIEDEL AND CRAFTS' REACTION. THE CARBOMETHOXY-BENZOYL CHLORIDES WITH AROMATIC HYDROCARBONS AND ALUMINUM CHLORIDE.

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Roser¹ obtained the amyl ester of benzoyl-formic acid from the acid chloride of mono-amyl oxalate, benzene and aluminum chloride. This preparation suggested the use of the acid chlorides of the mono-alkyl esters of the phthalic acids for the preparation of various keto acids.

The isophthalic acid and the terephthalic acid were prepared by the oxidation of commercial xylene, which had been fractionated with a 150cm. column, by Professor Kenrick in this laboratory. It was found that the fraction boiling at 138.2° to 138.4° gave the largest yield of terephthalic acid.

Oxidation of the Xylene.—Fifty g. of xylene, b. p. 138.2° to 138.4°, 5 liters of water and 30 g. of sodium hydroxide were heated to 90° in a 10-liter can which had a tight-fitting cover containing openings for condenser, mechanical stirrer and thermometer. All the openings were made steam tight. To the mixture was added 300 g. of potassium permanganate in 4 equal portions at half-hour intervals. After 19 hours' heating at 85° to 95° the solution was decolorized with methyl alcohol, cooled, filtered and the filtrate acidified. The precipitate dried at 110° weighed 60 g.

Separation of the Acids.—This product was found to be practically free from phthalic acid which is soluble 0.58 g. in 100 g. of water at 20°. The isophthalic acid and terephthalic acid were separated by means of their barium salts. The solubility of barium terephthalate and barium isophthalate, determined by evaporating a saturated solution and drying the residue at 200° for 8 hours, was found to be approximately 0.5 g. and 14.0 g. respectively in 100 g. of water at 20°. Fittig² using this method boiled the acids with barium carbonate but this is not convenient when using large quantities.

Sixty g. of the mixed acids was made into a paste with water and warmed with 125 cc. of conc. ammonia on a water-bath for 20 minutes; more water was then added to dissolve the ammonium salts, and the solution was boiled to expel the excess of ammonia. When nearly neutral, the volume was made up to 350 cc. and a hot solution of 40 g. of barium chloride in 70 cc. water added. After shaking for one hour and standing for 12 hours the barium terephthalate was filtered off, washed, and digested on a water-bath for 6 hours with 100 cc. of 15 % hydrochloric acid; yield

¹ Roser, *Ber.*, **14**, 940 (1881).

² Fittig, *Ann.*, **153**, 269 (1870).

of terephthalic acid 11.5 g. The combined filtrates were acidified affording 47 g. of isophthalic acid.

Further purification of the acids was effected by recrystallization of the dimethyl esters. Twenty g. of isophthalic acid and 150 cc. of methyl alcohol saturated with hydrogen chloride on standing for 36 hours gave 19 g. of dimethyl isophthalate, m. p. 66° to 67°. Ten g. of terephthalic acid boiled for 7 hours with 150 cc. of methyl alcohol and 15 cc. of conc. sulfuric acid gave 8 g. of dimethyl terephthalate, m. p. 141°.

***o*-Carbomethoxy-benzoyl Chloride with Benzene and Aluminum Chloride.**—Six g. of *o*-carbomethoxy-benzoyl chloride was dissolved in 80 cc. of benzene, cooled to 10°, and 10 g. of aluminum chloride added gradually with shaking. After standing for one hour at room temperature the mixture was kept at 80° for 7 hours and then poured into 100 cc. of 10% hydrochloric acid. After distilling off the benzene the ester was hydrolyzed with alcoholic potassium hydroxide, water was added and the solution was acidified with hydrochloric acid. The precipitate when recrystallized from ethyl alcohol gave 4.7 g. of *o*-benzoylbenzoic acid.

***m*-Carbomethoxyl-benzoyl Chloride with Benzene and Aluminum Chloride.**—Five g. of *m*-carbomethoxy-benzoyl chloride was dissolved in 90 cc. of benzene and 9 g. of aluminum chloride added. The mixture was kept at 45° to 50° for 5 hours and then at 80° for 7 hours. After hydrolysis of the ester and recrystallization from dilute alcohol the yield of *m*-benzoyl-benzoic acid, m. p. 161–162°, was 3.9 g.

Silver salt. Calc. for $C_{14}H_9O_3Ag$: Ag, 32.4. Found: 31.9.

This acid had previously been prepared by Doebner³ from benzoic anhydride, benzoyl chloride and zinc chloride, by Ador⁴ as a by-product in the preparation of isophthalophenone, and by Senff⁵ who oxidized benzyl-toluol. None of these methods give nearly as good a yield as was obtained above.

***p*-Carbomethoxy-benzoyl Chloride with Benzene and Aluminum Chloride.**—Five g. of *p*-carbomethoxy-benzoyl chloride, 50 cc. of benzene and 8.5 g. of aluminum chloride were heated at 45° to 50° for 5 hours and then on a boiling water-bath for 5 hours. After hydrolysis of the ester the *p*-benzoyl-benzoic acid was separated from terephthalic acid by dissolving in alcohol and recrystallized by the addition of water, m. p. 194°; yield, 4 g; terephthalic acid recovered, 2 g.

One g. of the acid dissolved in thionyl chloride and added to methyl alcohol gave after recrystallization from methyl alcohol 1 g. of methyl *p*-benzoyl-benzoate, m. p. 106–107°.

³ Doebner, *Ber.*, **14**, 647 (1881).

⁴ Ador, *ibid.*, **13**, 320 (1880).

⁵ Senff, *Ann.*, **220**, 236 (1883).

***o*-Carbomethoxy-benzoyl Chloride with Toluene and Aluminum Chloride.**—Five g. of *o*-carbomethoxy-benzoyl chloride, 50cc. toluene, and 8.5 g. of aluminum chloride were heated at 45° to 50° for 5 hours and then on a boiling water-bath for 7 hours. After addition of hydrochloric acid and removal of the toluene the reaction product was separated by the addition of ether, hydrolyzed with alcoholic potassium hydroxide and recrystallized from dil. alcohol, m. p. 96–100°; dried in a vacuum at 80°, m. p. 138° to 40°. The acid was fused with potassium hydroxide for 20 minutes at 200° and gave a mixture of benzoic acid and *p*-toluic acid. As it was not easy to separate these acids the mixture was boiled for 3 hours with alkaline permanganate solution, acidified and the product esterified with methyl alcohol. The ester recrystallized from alcohol melted at 140°. This identifies it as dimethyl terephthalate and identifies the product of hydrolysis as *p*-toluic acid. The original acid is, therefore, *p*-toluyl-*o*-benzoic acid. This acid has been prepared from phthalic anhydride, toluene and aluminum chloride by Limpricht⁶ and others.

***m*-Carbomethoxy-benzoyl Chloride with Toluene and Aluminum Chloride.**—Five g. of *m*-carbomethoxy-benzoyl chloride was dissolved in 60 cc. of benzene and, after cooling the solution to 10°, 9 g. of aluminum chloride was added gradually. After standing at room temperature for one hour, the mixture was heated on a water-bath for 10 hours. The product was hydrolyzed with alcoholic potassium hydroxide and the acid obtained was recrystallized from hot methyl alcohol. Yield, 4.0 g.; m. p. 172°.

Silver salt. Calc. for $C_{13}H_{11}O_3Ag$: Ag, 31.1. Found: 30.8.

On fusion with potassium hydroxide and oxidation of the acid product with potassium permanganate, terephthalic acid, identified by its methyl ester, was obtained. The method of preparation and the product of hydrolysis identify the product of this reaction as *p*-toluyl-*m*-benzoic acid, not previously described.

One g. of *p*-toluyl-*m*-benzoic acid was dissolved in thionyl chloride, the excess of thionyl chloride removed and 25 cc. of methyl alcohol added. After the reaction ceased the solution was poured into cold water and the ester recrystallized from methyl alcohol, m. p. 108°. Yield of methyl *p*-toluyl-*m*-benzoate, 0.9 g.

***p*-Carbomethoxy-benzoyl Chloride with Toluene and Aluminum Chloride.**—Five g. of *p*-carbomethoxy-benzoyl chloride, 60 cc. of toluene, and 9 g. of aluminum chloride were heated for 9 hours at 40–50° and then for 2 hours on a boiling water-bath. After washing the reaction product with dil. sodium hydrogen carbonate solution, it was hydrolyzed with alcoholic potassium hydroxide and the acid recrystallized from methyl alcohol; m. p. 228°; yield 4.4 g. The methyl ester was prepared; m. p.

⁶ Limpricht, *Ann.*, 299, 300 (1898).

126°. *p*-Toluy-*p*-benzoic acid had previously been prepared by Limp-richt⁷ by oxidizing *p,p*-ditolyl ketone.

***o*-Carbomethoxy-benzoyl Chloride with *m*-xylene and Aluminum Chloride.**—Five g. of *o*-carbomethoxy-benzoyl chloride and 50 cc. of *m*-xylene were cooled to 10° and 8.5 g. of aluminum chloride was added gradually. After the initial reaction had ceased the mixture was warmed on a water-bath until hydrogen chloride ceased to come off. After acidification and removal of the *m*-xylene the reaction product was extracted with chloroform, hydrolyzed with alcoholic potassium hydroxide and recrystallized from benzene as fine needles; m. p. 139–140°; yield, 3.5 g.

Silver salt. Calc. for $C_{10}H_{13}O_3Ag$: Ag, 29.9. Found: 30.2.

On fusion of the acid with potassium hydroxide for 30 minutes at 160° to 170°, and sublimation of the acid product, benzoic acid and 2,4-dimethylbenzoic acid, m. p. 124° to 126°, were identified. The acid is therefore 2,4-dimethylbenzoyl-*o*-benzoic acid and is identical with the acid prepared by Meyer⁸ from phthalic anhydride, *m*-xylene and aluminum chloride. Meyer gave no melting point.

***m*-Carbomethoxy-benzoyl Chloride with *m*-xylene and Aluminum Chloride.**—Five g. of *m*-carbomethoxy-benzoyl chloride, 40 cc. of *m*-xylene and 8.5 g. of aluminum chloride were kept at 20° for 5 hours and then on a boiling water-bath for 6 hours. After acidification and removal of the *m*-xylene the reaction product was extracted with chloroform, washed with dil. sodium hydrogen carbonate solution, hydrolyzed with alcoholic potassium hydroxide and acidified; yield of crude acid, 6.0 g. Recrystallized from hot methyl alcohol the acid melted at 168°; yield, 4.0 g.

Silver salt. Calc. for $C_{16}H_{13}O_3Ag$: Ag, 29.9. Found: 30.0.

On fusion of the acid with potassium hydroxide for 20 minutes at 170° to 80° and sublimation of the acid products the sublimate contained benzoic acid and 2,4-dimethylbenzoic acid, m. p. 126°, and the residue from the sublimation was isophthalic acid, identified by the formation of its methyl ester. The greater part of the acid decomposes into isophthalic acid and *m*-xylene, but part of it gives benzoic acid and 2,4-dimethylbenzoic acid. The acid is, therefore, 2,4-dimethylbenzoyl-*m*-benzoic acid.

One g. of 2,4-dimethylbenzoyl-*m*-benzoic acid was warmed with thionyl chloride until the reaction ceased and the resulting acid chloride was poured into methyl alcohol. The ester was precipitated by adding water and recrystallized from methyl alcohol, giving small needles; m. p. 73°.

***p*-Carbomethoxy-benzoyl Chloride with *m*-xylene and Aluminum Chloride.**—Five g. of *p*-carbomethoxy-benzoyl chloride, 40 cc. of *m*-

⁷ Limpriht, *Ann.*, **312**, 92 (1900).

⁸ Meyer, *Ber.*, **15**, 636 (1882).

xylene and 8.5 g. of aluminum chloride were kept at 45° to 50° for 5 hours and then at 80° for 7 hours. The acid product was obtained as in the previous experiment and after recrystallization from methyl alcohol melted at 184° to 5°; yield, 4.5 g.

Silver salt. Calc. $C_{16}H_{18}O_3Ag$: Ag, 29.9. Found: 30.0.

Fusion with potassium hydroxide gave benzoic acid, 2,4-dimethylbenzoic acid, and terephthalic acid, identified by the formation of its dimethyl ester. In this case, again, part of the acid decomposed to benzoic acid and 2,4-dimethylbenzoic acid and part to *m*-xylene and terephthalic acid. The acid is, therefore, 2,4-dimethylbenzoyl-*p*-benzoic acid.

The methyl ester of 2,4-dimethylbenzoyl-*p*-benzoic acid prepared from the acid chloride by adding methyl alcohol and recrystallizing from methyl alcohol was obtained as long, colorless needles; m. p. 59°.

Summary.

1. A method has been described of preparing isophthalic acid and terephthalic acid from commercial xylene.

2. The reaction of each of the carbomethoxy-benzoyl chlorides with aluminum chloride and benzene, toluene, and *m*-xylene, respectively, has been studied. In each case, the reaction with toluene takes place in the *para* position to the methyl group, and with *m*-xylene in the *para* position to one of the methyl groups.

3. New and improved methods of preparing *m*-benzoylbenzoic acid, *p*-benzoylbenzoic acid and some of their derivatives have been given.

4. The following new compounds have been prepared: *p*-toluyl-*m*-benzoic acid, m. p., 172°; methyl-*p*-toluyl-*m*-benzoate, m. p., 108°; 2,4-dimethylbenzoyl-*m*-benzoic acid, m. p. 168°; methyl-2,4-dimethylbenzoyl-*m*-benzoate, m. p. 73°; 2,4-dimethylbenzoyl-*p*-benzoic acid, m. p. 185°; methyl-2,4-dimethylbenzoyl-*p*-benzoate, m. p. 59°.

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