Tetrahydrofuran Compounds. III. Some Acid Derivatives

By Richard D. Kleene[1]

For the preparation of the following esters, Eastman Kodak Co. furoic acid was used. Tetrahydrofuroic acid was obtained by hydrogenation of furoic acid with a nickel catalyst according to the directions of Paul and Hilly.[2]

Phenacyl ester of furoic acid and the following esters were prepared according to the directions of Shriner and Fuson.[3] The ester was twice recrystallized from water–alcohol solutions; small cream-colored needles, m. p. 85–86°.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.82; H, 4.35. Found: C, 67.96; H, 4.59.

No solid phenacyl ester was obtained from tetrahydrofuroic acid.

***p*-Phenylphenacyl ester of furoic acid** was recrystallized from water and alcohol; crystalline white powder, m. p. 110–111°.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.51; H, 4.57. Found: C, 74.35; H, 4.63.

***p*-Phenylphenacyl ester of tetrahydrofuroic acid** was recrystallized from water and alcohol; m. p. 100.5°.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.55; H, 5.81. Found: C, 73.50; H, 5.59.

***p*-Phenylphenacyl Ester of β-Tetrahydrofurylpropionic Acid.**—The acid was obtained by hydrogenation of ethyl β-furylacrylate, followed by saponification with aqueous sodium hydroxide. The derivative was obtained as glistening white needles, recrystallized from water and alcohol; m. p. 97–98°.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.55; H, 6.52. Found: C, 74.86; H, 6.57.

The analyses were performed by Dr. T. S. Ma.

---

[1] Formerly 1st Lt. CWS, Army of the United States.

[2] Paul and Hilly, *Compt. rend.*, **208**, 359 (1939).

[3] Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, New York, 1940, p. 132.

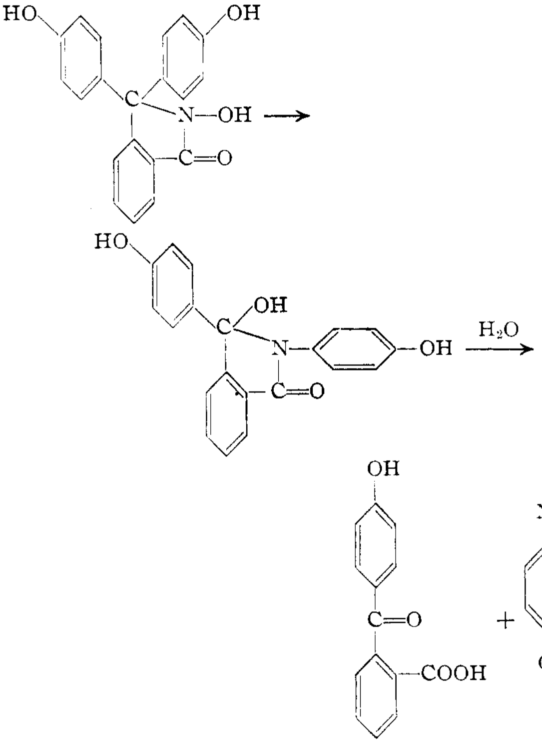
2211 Burling Street
Chicago, Illinois

Received December 26, 1945

The Preparation of 2-(4-Hydroxybenzoyl)-benzoic Acid

By M. H. Hubacher

In the synthesis of various phthaleins, a relatively large quantity of 2-(4-hydroxybenzoyl)-benzoic acid was needed. This acid has been prepared by heating 2-(4-halobenzoyl)-benzoic acid with sodium hydroxide,[1] or 2-(4-methoxybenzoyl)-benzoic acid with hydrobromic acid.[2] It has also been shown that when a solution of phenolphthalein in 0.2 *N* sodium hydroxide is slowly oxidized by air, then the 2-(4-hydroxybenzoyl)-benzoic acid is obtained in a yield of 41–46%.[3] Ullmann and Schmidt produced 2-(4-hydroxybenzoyl)-benzoic acid by treating phthalic anhydride with an excess of phenol in *s*-tetrachloroethane in the presence of aluminum chloride[4]; some 2-(2-hydroxybenzoyl)-benzoic acid and phthalein are also formed in this reaction. By the same method, Blicke and Weinkauff obtained a yield of 55% based on the phthalic anhydride,[5] a figure confirmed in this Laboratory. The best method, however, for the production of this acid is clearly that discovered by Friedlaender, who found that the "phenolphthalein oxime" could easily be split into 2-(4-hydroxybenzoyl)-benzoic acid and *p*-aminophenol.[6] The mechanism of this somewhat unusual reaction was cleared up by Orndorff, Murray and Yang[7]; first a rearrangement of the "oxime" takes place and then a splitting



The Friedlaender method was thoroughly investigated and the following procedure evolved, which was found to give consistent and almost quantitative yields of an acid of high purity.

Phenolphthalein Oxime.—Into a 500-ml. three-necked round-bottom flask fitted with a stirrer and a thermometer are placed 31.8 g. (0.10 mole) of phenolphthalein (m. p. 259–263°) and 160 ml. (0.40 mole) of 2.5 *N* sodium hydroxide. The mixture is heated to 65° and as soon as the phenolphthalein has dissolved, the flame is removed and a solution of 7.6 g. (0.105 mole) of hydroxylamine hydrochloride (96%) or 9.0 g. of hydroxylamine sulfate (95–98%) in 30 ml. of water is added in one portion. The temperature will go up from 65° to 72–79° within two and one-half to three minutes and the color will change from distinct red to a brownish red. The solution is stirred for an additional fifteen minutes at 75–80° and then poured, while still warm, into 690–710 ml. of 0.5 *N* sulfuric acid. The yellow precipitate is filtered off, using

---

[1] I. Gubelmann, H. J. Weiland and O. Stallmann, U. S. Patent 1,654,289 [*C. A.*, **22**, 788 (1928)].

[2] L. C. Kin, *Ann. chim.*, **13**, 332 (1940).

[3] M. H. Hubacher, This Journal, **65**, 2097 (1943).

[4] F. Ullmann and W. Schmidt, *Ber.*, **52**, 2107 (1919).

[5] F. F. Blicke and O. J. Weinkauff, This Journal, **54**, 1450 (1932).

[6] P. Friedlaender, *Ber.*, **26**, 174 (1893).

[7] W. R. Orndorff and R. R. Murray, This Journal, **39**, 679 (1917); W. R. Orndorff and S. T. Yang, *ibid.*, **45**, 1926 (1923).