## 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

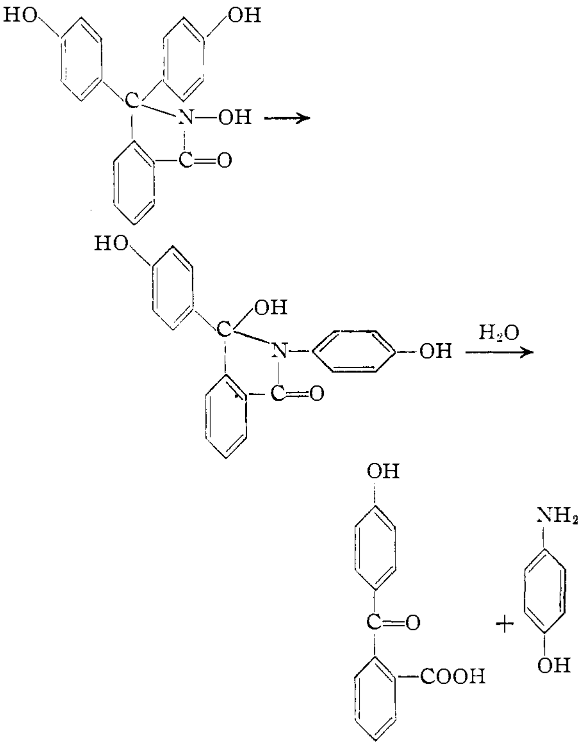
Received December 26, 1945

---

## 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).

a hardened filter paper or a funnel with a sintered glass disc, washed with water, and pressed in order to squeeze out most of the water. It is not necessary to wash it free from $SO_4^{=}$. For the subsequent step, the wet cake, weighing from 109–143 g., is used.

**2-(4-Hydroxybenzoyl)-benzoic Acid.**—The wet, yellow cake of "phenolphthalein oxime" is placed into a flask or a beaker of 500 ml., fitted with a stirrer and a thermometer. One-hundred ml. 5 *N* of sulfuric acid, prewarmed to 90–104°, is then added in such a way as to wash down any oxime adhering to the neck of the flask or the side of the beaker. The stirrer is started and the yellow slurry rapidly heated. Within three minutes after the temperature has reached 96–102°, a dark yellow solution is formed. After one to three minutes from this point on, the solution first becomes turbid and then crystals of the acid appear. The reaction mixture is stirred for an additional ten minutes at 97–103°, gradually becoming brown. After cooling to 20°, the sandy crystals of 2-(4-hydroxybenzoyl)-benzoic acid are filtered off and washed with three portions of 20 ml. of water. After drying at 100–120°, the acid, of moderate greenish yellow color, weighs from 22.1–23.0 g. and melts at 209–213° cor. (sl. dec.); (yield 91.3–95.0% based on the phenolphthalein).

If a purer product is required, 20 g. of the acid, 0.5 g. of decolorizing carbon (Norit-A) and 1 liter of water are refluxed for fifteen minutes, filtered through a preheated funnel and the filtrate cooled to 5°. From 18.0–18.4 g. of acid, which melts at 211–215° cor. (sl. dec.), is obtained. This purified acid dissolves in ethanol (1 g. in 20 ml.) with but faint yellow color; its solution in 0.1 *N* sodium hydroxide (0.2 g. in 20 ml.) is clear and either light yellowish or faintly red.

From the filtrate of the acid, together with 75 ml. of wash-water, there can be obtained, after neutralization with 80 ml. of 5 *N* sodium hydroxide and about 60 ml. of 20% sodium sulfite solution and subsequent extraction with ether, 8.6–9.6 g. of *p*-aminophenol (m. p. 182–187°).

Equally good yields are obtainable with batches from 0.5 to 1.0 mole of phenolphthalein.

RESEARCH LABORATORY
EX-LAX, INC.
BROOKLYN 17, N. Y.
RECEIVED JANUARY 3, 1946

---

## Habit Modification of Ammonium Oxalate Monohydrate Crystals During Growth from Solution

BY HARRY J. KOLB[1] AND JOSEPH J. COMER[2]

In a previous paper,[3] the habit modification of ammonium dihydrogen phosphate was described. Additional investigations on the habit modification of ammonium oxalate monohydrate are presented here.

**Procedure.**—Ammonium oxalate monohydrate crystals were grown in the large water-bath described previously.[3] Each of the tanks was filled with 7.5 liters of ammonium oxalate solution saturated at 40°. Two crystal seeds, about 0.3 sq. cm. in the *z*-plane and 2 cm. along the *z*-axis, were suspended in each tank and grown, as before, by reduction of the temperature in the thermostat until the seeds were 4-cm. long. The cations which were added to the saturated oxalate solution containing the growing crystals are the eight listed in Table I. The concentrations of the cations were 0.1 g./liter of solution. Modification tests were also made at the following concentrations of magnesium ion: 0.001, 0.005, 0.01, 0.03, 0.05, 1.0, 2.0, 5.0 g./liter.

**Results.**—The ammonium oxalate monohydrate crystals normally show the (001), (110) and (010) planes. The modifications of the growing crystal by the cations are listed in Table I, *i. e.*, development of (021), (110) and (111) planes.

TABLE I

| Development of planes | $Zn^{++}$ | $Cu^{++}$ | $Mg^{++}$ | $Sc^{+++}$ | $Co^{++}$[a] | $Ni^{++}$[a] | $Cd^{++}$ | $Mn^{++}$ |
|---|---|---|---|---|---|---|---|---|
| (110) | + | 0 | 0 | 0 | 0 | 0 | + | + |
| (111) | + | + | + | + | 0 | 0 | 0 | 0 |
| (021) | + | + | + | + | + | + | 0 | 0 |

[a] Crystal tapered toward *z*-axis, obscuring the identity of individual planes.

In the series of experiments using magnesium ion, the (021) and $(0\bar{2}1)$ planes became more fully developed as the metal ion concentration increased until the (001) plane was finally eliminated. At the magnesium ion concentration of 5 g./liter, the growth of the crystal seed was completely inhibited.

The habit modification may be due to adsorption of foreign metal ions at the crystal–solution interface. This adsorption with subsequent habit modification could be explained by the insolubility interpretation (oxalate in this case) suggested in the previous paper.[3]

The oxalate reticular densities of the crystal planes were calculated and found to be (110), 3.54; (010), 2.87; (111), 1.83; (021), 1.71; (001), 1.06. All are relative to the (011) plane as 1.00. Thus, the appearance of the (021) plane rather than the (011) plane could be accounted for by the density sequence. The removal of the (001) plane could also be explained. In cases where the (110) plane was not developed (given in the table), no growth was noted on either the (110) or (010) planes. The cessation of all growth at high foreign cation concentrations supports a strongly adsorbed ion interpretation. However, it must be stated that we have no direct evidence of an adsorbed metal ion layer.

NAVAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND INVENTION
WASHINGTON, D. C.
RECEIVED SEPTEMBER 24, 1945

---

[1] Present address: E. I. du Pont de Nemours and Company, Rayon Dept., Pioneering Research, Buffalo, N. Y.

[2] Present address: Pennsylvania State College, State College, Pa.

[3] Kolb and Comer, THIS JOURNAL, **67**, 894 (1945).

---

## The Molecular Structure of Trimethyl Silicon Chloride

BY R. L. LIVINGSTON[1] AND L. O. BROCKWAY

The silicon–carbon bond distances have been determined in several compounds and found to be less than the value of 1.93 Å. obtained for tetramethyl silicon.[2] For example, in hexamethyl disilicon[3] and in SiC,[4] the silicon–carbon distance

---

[1] Present address: Department of Chemistry, Purdue University, West Lafayette, Indiana.

[2] L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936).

[3] L. O. Brockway and N. R. Davidson, *ibid.*, **63**, 3287 (1941).

[4] Ewald and Hermann, "Structurbericht," Akademische Verlagsgesell., 1931, 146.