



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

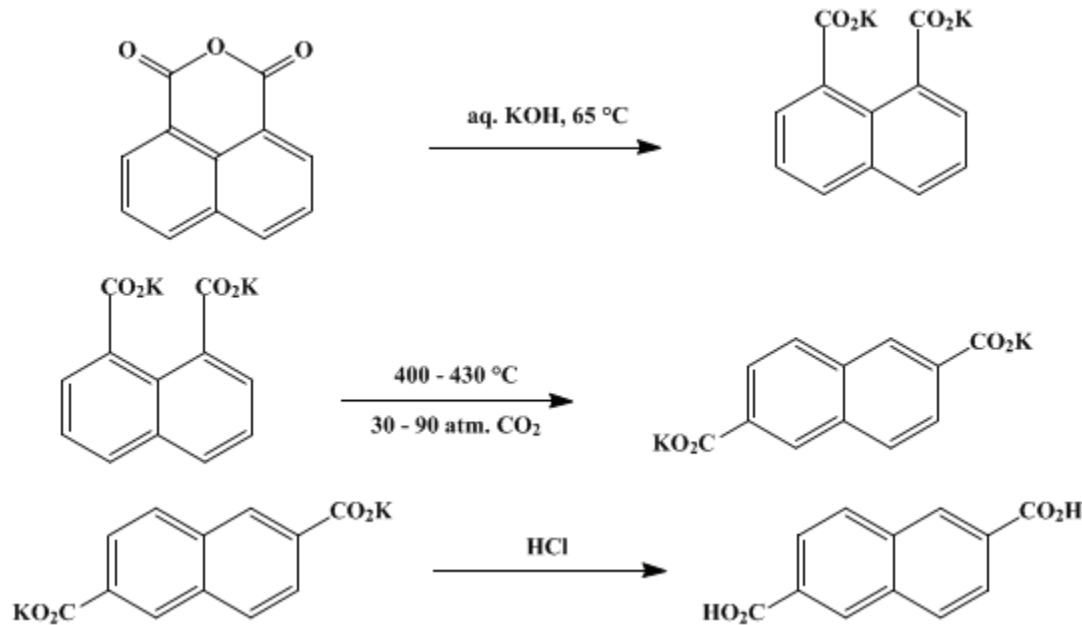
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.813 (1973); Vol. 40, p.71 (1960).

2,6-NAPHTHALENEDICARBOXYLIC ACID



Submitted by Bernhard Raecke and Hubert Schirp¹.
Checked by B. C. McKusick and P. E. Aldrich.

1. Procedure

A solution of 66.5 g. (1.01 moles) of 85% **potassium hydroxide** in 300 ml. of water in an 800-ml. beaker is heated to 60–70°, and 100 g. (0.505 mole) of commercial **1,8-naphthalic anhydride** (Note 1) is stirred in. The pH of the resultant deep-brown solution is adjusted to a value of 7 (Note 2) with 6*N* **hydrochloric acid** and 3*N* **potassium hydroxide**. It is treated with 10 g. of decolorizing **carbon** and filtered. This operation is repeated. The filtrate is concentrated in a 1.5-l. beaker on a steam bath to about 180 ml. The concentrate is cooled to room temperature, 800 ml. of **methanol** is added with vigorous stirring by hand, and the mixture is cooled to 0–5°. The precipitated **dipotassium naphthalate** is separated by filtration, washed with 150 ml. of **methanol**, and dried in a vacuum oven at 150°/150 mm. The dried cream-colored salt weighs 130–135 g. (88–92%).

A mixture of 100 g. of **dipotassium naphthalate** and 4 g. of anhydrous **cadmium chloride**² is ground in a ball mill for 4 hours. The mixture is placed in a 0.5-l. autoclave (Note 3) and (Note 4) that can be rocked, rolled, or shaken. The autoclave is evacuated, for **oxygen** lowers the yield of the product. The autoclave is then filled with **carbon dioxide** to a pressure of about 30 atm. The agitated autoclave is heated to an internal temperature of 400–430° in the course of 1–2 hours and is maintained at this temperature for 1.5 hours. The pressure rises to about 90 atm. in the course of the heating (Note 4).

The autoclave is cooled to room temperature, and the **carbon dioxide** is bled off. The solid reaction product is taken from the autoclave, pulverized, and dissolved in 1 l. of water at 50–60°. Ten grams of decolorizing **carbon** is added, and the mixture is stirred well and filtered to remove cadmium salts and **carbon**. The filtrate is heated to 80–90° and acidified with concentrated **hydrochloric acid** to pH 1 (Note 5). **2,6-Naphthalenedicarboxylic acid** precipitates. It is separated from the hot mixture by filtration. It is then suspended in 500 ml. of water at 90–95° (Note 5), separated by filtration, and washed successively with 300 ml. of water, 300 ml. of 50% **ethanol**, and 300 ml. of 90% **ethanol**. After being dried at 100–150°/150 mm. in a vacuum oven, the **2,6-naphthalenedicarboxylic acid** weighs 42–45 g. (57–61%). It decomposes on a heated block at 310–313°.

2. Notes

1. Suitable 1,8-naphthalic anhydride, m.p. 274–275°, is obtainable from Coaltar Chemicals Corp., 420 Lexington Ave., New York, N. Y.
2. Bromothymol blue or commercial universal indicator pH paper (graduated in 0.2-pH units) may be used as external indicators.
3. A 150-ml. shaking Hastelloy-C autoclave, manufactured by the Haynes Stellite Division of Union Carbide Co., Kokomo, Indiana, was used by the checkers. The approximate composition of the alloy is: Cr, 15.5–17.5%; Mo, 16–18%; Fe, 4.5–7%; W, 3.7–4.75%; and the remainder, Ni. Because their autoclave had only three-tenths the capacity of that used by the submitters, the checkers used three-tenths the quantities of materials given here.
4. The line to the pressure gauge tends to become clogged during the reaction.
5. Heat conduction in the heavy slurry that is formed is poor, and bumping may occur if the mixture is overheated. Efficient mechanical stirring aids this operation.

3. Discussion

2,6-Naphthalenedicarboxylic acid has been prepared by fusing dipotassium 2,6-naphthalenedisulfonate with potassium cyanide to give the corresponding dinitrile, which is hydrolyzed;³ by oxidation of 2-methyl-6-acetylnaphthalene with dilute nitric acid at 200°;⁴ by the thermal disproportionation of potassium α - or β -naphthoate to dipotassium 2,6-naphthalenedicarboxylate and naphthalene;⁵ and by the present method.⁶ The present method is much more convenient than earlier methods, if a suitable autoclave is available.

The present method for preparing aromatic dicarboxylic acids has been used to convert phthalic or isophthalic acid to terephthalic acid (90–95%); 2,2'-biphenyldicarboxylic acid to 4,4'-biphenyldicarboxylic acid; 3,4-pyrroledicarboxylic acid to 2,5-pyrroledicarboxylic acid; and 2,3-pyridinedicarboxylic acid to 2,5-pyridinedicarboxylic acid.⁷ A closely related method for preparing aromatic dicarboxylic acids is the thermal disproportionation of the potassium salt of an aromatic monocarboxylic acid to an equimolar mixture of the corresponding aromatic hydrocarbon and the dipotassium salt of an aromatic dicarboxylic acid. The disproportionation method has been used to convert benzoic acid to terephthalic acid (90–95%); pyridinecarboxylic acids to 2,5-pyridinedicarboxylic acid (30–50%); 2-furoic acid to 2,5-furandicarboxylic acid; 2-thiophenecarboxylic acid to 2,5-thiophenedicarboxylic acid; and 2-quinolinecarboxylic acid to 2,4-quinolinedicarboxylic acid.⁷ One or the other of these two methods is often the best way to make otherwise inaccessible aromatic dicarboxylic acids. The two methods were recently reviewed.⁷

References and Notes

1. Henkel & Cie. GmbH, Post Box 1100, Düsseldorf, Germany.
 2. J. Cason and F. S. Prout, *Org. Syntheses*, Coll. Vol. **3**, 603 (1955).
 3. R. Ebert and V. Merz, *Ber.*, **9**, 604 (1876).
 4. G. E. Tabet, U. S. pat. 2,644,841 (1953) [*C.A.*, **48**, 6469 (1954)].
 5. B. Raecke and H. Schirp, Ger. pat. 953,072 (1955) [*C.A.*, **53**, 1289 (1959)].
 6. B. Raecke, W. Stein, and H. Schirp, Ger. pat. 949,652 (1953) [*C.A.*, **52**, 20106 (1958)].
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Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Bromothymol blue
potassium α - or β -naphthoate
phthalic or isophthalic acid
ethanol (64-17-5)
hydrochloric acid (7647-01-0)
methanol (67-56-1)
nitric acid (7697-37-2)
oxygen (7782-44-7)
potassium cyanide (151-50-8)
Benzoic acid (65-85-0)
carbon dioxide (124-38-9)
carbon (7782-42-5)
potassium hydroxide (1310-58-3)
Naphthalene (91-20-3)
2-Furoic acid (88-14-2)
cadmium chloride (10108-64-2)
Terephthalic acid (100-21-0)
2,6-Naphthalenedicarboxylic acid (1141-38-4)
1,8-naphthalic anhydride (81-84-5)
dipotassium naphthalate
dipotassium 2,6-naphthalenedisulfonate
2-methyl-6-acetylnaphthalene
dipotassium 2,6-naphthalenedicarboxylate
3,4-pyrroledicarboxylic acid
2,5-pyrroledicarboxylic acid
2,3-pyridinedicarboxylic acid (89-00-9)

2,5-pyridinedicarboxylic acid (100-26-5)

2,5-furandicarboxylic acid (3238-40-2)

2-thiophenecarboxylic acid (527-72-0)

2,5-thiophenedicarboxylic acid (4282-31-9)

2-quinolinecarboxylic acid (93-10-7)

2,4-quinolinedicarboxylic acid

2,2'-biphenyldicarboxylic acid (482-05-3)

4,4'-biphenyldicarboxylic acid