



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.

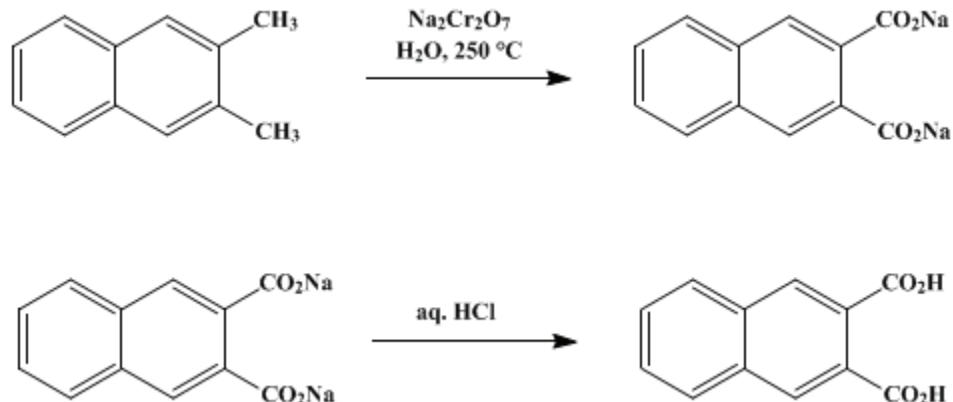
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.810 (1973); Vol. 43, p.80 (1963).

2,3-NAPHTHALENEDICARBOXYLIC ACID



Submitted by Lester Friedman¹

Checked by G. A. Boswell and B. C. McKusick.

1. Procedure

An autoclave (Note 1) is charged with 200 g. (1.28 moles) of 2,3-dimethylnaphthalene (Note 2), 940 g. (3.14 moles, 23% excess) of sodium dichromate dihydrate, and 1.8 l. of water. The autoclave is closed, heated to 250° , and shaken continuously at this temperature for 18 hours. The autoclave is cooled with continued agitation (Note 3), the pressure is released, and the autoclave is opened. The contents are transferred to a large vessel (Note 4). To effect complete transfer, the autoclave is rinsed with several 500-ml. portions of hot water. Green hydrated chromium oxide in the reaction mixture is separated on a large Büchner funnel and washed with warm water until the filtrate is colorless. The combined filtrates (7–8 l.) are acidified with 1.3 l. of 6*N* hydrochloric acid. The acidified mixture is allowed to cool to room temperature overnight. The 2,3-naphthalenedicarboxylic acid that has precipitated is collected on a large Büchner funnel, washed with water until the filtrate is colorless, and dried to constant weight in a vacuum oven at $50^\circ/20$ mm. or by long standing in air. The 2,3-naphthalenedicarboxylic acid is a white powder; m.p. $239\text{--}241^\circ$; weight 240–256 g. (87–93%).

2. Notes

1. An autoclave fitted for stirring or shaking is essential for good yields. The submitter used a hydrogenation autoclave of the type supplied by the American Instrument Company, catalog No. 406-21, having a capacity of 3.2 l. The autoclave is shaken by means of a "Bomb Shaker" in which it is placed. If a stirred autoclave or "Magne-Dash" is used, the reaction time can be shortened to 3–5 hours. At 250° the gauge pressure is about 600 lb./in.². The checkers' yield was 92% in a shaker tube, but only 75% in a rocker tube; the latter yield was raised to 82% by extending the reaction time to 40 hours. This oxidation does not poison the autoclave for subsequent hydrogenations.
2. Material produced by Ruetgerswerke A. G. is satisfactory. This can be obtained in the United States from Terra Chemicals Inc., New York, New York; Aldrich Chemical Co., Milwaukee 10, Wisconsin; and K and K Laboratories Inc., Jamaica 33, New York.
3. It is convenient to empty the autoclave while the contents are still warm.
4. Commercially available 10-quart polyethylene pails are very satisfactory.

3. Discussion

2,3-Naphthalenedicarboxylic acid has been prepared by the present method² and by hydrolysis of 3-cyano-2-naphthoic acid, which is obtainable from 3-amino-2-naphthoic acid by the Sandmeyer reaction.³

4. Merits of the Preparation

This procedure illustrates a general method for the preparation of aromatic carboxylic acids by oxidation of the corresponding alkylarenes.² For example, 2-naphthoic acid (360 g., 93% yield; m.p. 184–185°) was obtained from 2-methylnaphthalene (320 g., 2.25 moles), sodium dichromate (975 g., 3.26 moles, 45% excess), and water (1.8 l.).

2,3-Naphthalenedicarboxylic acid is useful in the synthesis of linear polyacenes,³ 3-halo-2-naphthoic acids,⁴ and 3-amino-2-naphthoic acid.⁴

References and Notes

1. Chemistry Department, Case Institute of Technology, Cleveland, Ohio.
 2. L. Friedman, D. L. Fishel, and H. Shechter, *J. Org. Chem.*, **30**, 1453 (1965).
 3. H. Waldmann and H. Mathiowetz, *Ber.*, **64**, 1713 (1931).
 4. L. Friedman, unpublished data.
-

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

hydrochloric acid (7647-01-0)

sodium dichromate (7789-12-0)

2-Naphthoic acid (93-09-4)

2-methylnaphthalene (91-57-6)

sodium dichromate dihydrate (10588-01-9)

3-Amino-2-naphthoic acid (5959-52-4)

chromium oxide (1308-38-9)

2,3-Naphthalenedicarboxylic acid (2169-87-1)

2,3-dimethylnaphthalene (581-40-8)

3-cyano-2-naphthoic acid