



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.

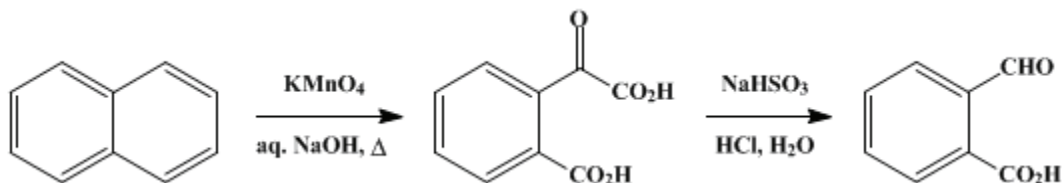
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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. 2, p.523 (1943); Vol. 16, p.68 (1936).

PHTHALALDEHYDIC ACID



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1. Procedure

In a 3-l. three-necked flask, provided with a liquid-sealed mechanical stirrer, a reflux condenser, and a dropping funnel, are placed 500 cc. of 0.5 *N* sodium hydroxide solution and 32 g. (0.25 mole) of pure naphthalene. The mixture is heated to boiling, and a boiling solution of 212 g. (1.34 moles) of potassium permanganate in 1.5 l. of water is added in small portions during one and one-half hours with vigorous stirring (Note 1). After the last addition, the mixture is boiled for thirty to forty-five minutes to complete the oxidation. Any unchanged permanganate is reduced by the addition of 20 cc. of alcohol, the flask is cooled to solidify the residual naphthalene, and the mixture is filtered.

The filtrate is acidified with 150 cc. (1.8 moles) of concentrated hydrochloric acid (sp. gr. 1.18), evaporated to 500 cc., cooled, and filtered. The filtrate is neutralized with 30 per cent sodium hydroxide solution (150–160 cc.), 50 g. (0.48 mole) of sodium bisulfite is added, and the mixture is evaporated to dryness on a steam bath. The residue is stirred with 100 cc. of concentrated hydrochloric acid and evaporated to dryness on a steam bath. The hydrochloric acid treatment and evaporation are repeated (Note 2).

The residue is extracted thoroughly with benzene in a large Soxhlet extractor (Note 3), and the benzene extract is evaporated to dryness. The crude product is dissolved in 50 cc. of hot water, the solution filtered, and the filtrate cooled in an ice bath with stirring (Note 4). The crystals are filtered with suction and dried in the air. The yield of slightly colored product melting at 94–95° 15–15.5 g. (40–41 per cent of the theoretical amount).

When this material is recrystallized from 40 cc. of water with 1 g. of decolorizing carbon, and the filtrate cooled to 0°, there is obtained 14–14.5 g. of white crystals melting at 96–96.5°.

2. Notes

1. During the addition of the hot permanganate solution no external heat is applied. From time to time steam is passed through the condenser jacket to return the sublimed naphthalene to the reaction flask.
2. The treatment with hydrochloric acid and the evaporation are repeated in order to decompose completely the phthalaldehydic acid bisulfite compound. Wegscheider and Bondi¹ state that it is necessary to heat the bisulfite compound on the water bath several days with a large excess of hydrochloric acid, but the treatment described above has been found adequate.
3. The material requires two extraction thimbles of the 45 by 125 mm. size, or four of the 30 by 75 mm. size. It is advantageous to use a modified Soxhlet extractor of the Clausnitzer type,² which allows the vapor of the boiling solvent to surround the extractor tube.
4. It is essential to control carefully the volume of water used in recrystallization. The crude acid contains considerable amounts of phthalic acid; too small a volume of water results in a contaminated product, and too large an amount causes a decided decrease in yield.

3. Discussion

Phthalaldehydic acid has been prepared by the hydrolysis of 2-bromo- or 2-chlorophthalide,³ of *o*-

trichloromethylbenzal chloride,⁴ of *o*-cyanobenzal chloride,⁵ and of *o*-dichloromethylbenzoyl chloride;⁶ by the ozonization of naphthalene;⁷ by the alkaline oxidation of naphthalene,⁸ or α -nitronaphthalene⁹ followed by the preparation and decomposition of the aniline condensation product¹⁰ or the bisulfite compound¹¹ of phthalonic acid; and by carbonating the reaction product of *o*-chlorobenzaldehyde and sodium.¹² Detailed directions for the preparation of phthalaldehydic acid by bromination of phthalide and hydrolysis of the bromination product are given in Volume 23 of this series.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 476](#)
- [Org. Syn. Coll. Vol. 3, 737](#)

References and Notes

1. Wegscheider and Bondi, *Monatsh.* **26**, 1055 (1905).
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5. Gabriel and Weise, *Ber.* **20**, 3197 (1887); Drory, *ibid.* **24**, 2571 (1891).
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10. Soc. Chim. des Usines du Rhône, *Ger. pat.* 97,241 [Frld. **5**, 139 (1897-1900)]; Fuson, *J. Am. Chem. Soc.* **48**, 1093 (1926).
11. Graebe and Trümpy, *Ber.* **31**, 369 (1898); Sidgwick and Clayton, *J. Chem. Soc.* **121**, 2263 (1922).
12. Morton, LeFevre, and Hechenbleikner, *J. Am. Chem. Soc.* **58**, 754 (1936).

Appendix

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

2-bromo- or 2-chlorophthalide

phthalonic acid

[alcohol \(64-17-5\)](#)

[hydrochloric acid \(7647-01-0\)](#)

[Benzene \(71-43-2\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[potassium permanganate \(7722-64-7\)](#)

[sodium bisulfite \(7631-90-5\)](#)

decolorizing carbon (7782-42-5)

sodium (13966-32-0)

Naphthalene (91-20-3)

α -nitronaphthalene (86-57-7)

phthalic acid (88-99-3)

Phthalaldehydic acid (119-67-5)

phthalaldehydic acid bisulfite

Phthalide (87-41-2)

o-chlorobenzaldehyde (89-98-5)

o-trichloromethylbenzal chloride

o-cyanobenzal chloride

o-dichloromethylbenzoyl chloride