Organic Syntheses

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.

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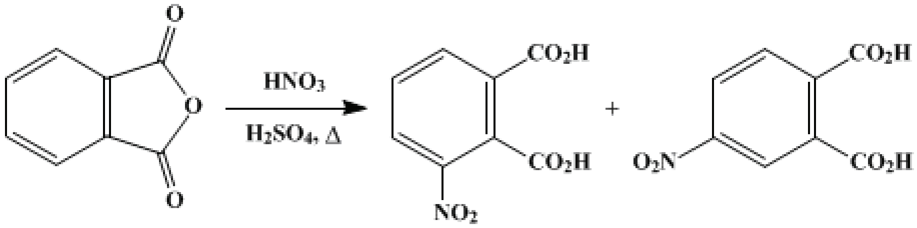
Organic Syntheses, Coll. Vol. 1, p.408 (1941); Vol. 7, p.70 (1927).

3-NITROPHTHALIC ACID

[Phthalic acid, 3-nitro-]



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1. Procedure

A 2-l. beaker placed on a piece of board in the bottom of a 4-l. (1-gallon) crock is fitted with a mechanical stirrer (Note 1). In the beaker are placed 650 cc. of commercial sulfuric acid (sp. gr. 1.84) and 500 g. (3.4 moles) of technical phthalic anhydride. The mixture is stirred, and steam is passed into the crock. When the mixture reaches 80°, the steam is shut off and 210 cc. of fuming nitric acid (sp. gr. 1.51) is added slowly from a separatory funnel at such a rate as to maintain the temperature of the stirred mixture at 100–110°. The addition requires one to two hours. After the fuming acid has been added, 900 cc. of concentrated nitric acid (sp. gr. 1.42) is added as rapidly as possible without causing the temperature to rise above 110° (Note 2). The mixture is then stirred and heated by passage of steam into the crock for two hours longer.

The mixture is allowed to stand overnight and then poured into 1.5 l. of water in a 4-l. (1-gallon) crock. After cooling, the solid mixture of 3- and 4-nitrophthalic acids is filtered by suction through a Büchner funnel without a filter paper (Note 3) or through a filtros plate (p. 11). The wet cake is returned to the crock and stirred thoroughly with 200 cc. of water, which dissolves a large amount of the 4-nitrophthalic acid. The mixture is again filtered by suction (Note 4), and the wet cake is dissolved by boiling with 200–300 cc. of water (Note 5). The solution is filtered hot and stirred mechanically until crystallization starts. It is then allowed to stand overnight, as the crystallization is slow. The crystals are filtered by suction and air-dried. The product melts at 205–210° in a sealed tube. The yield is 200–220 g. (28–31 per cent of the theoretical amount) (Note 6). Recrystallization of 200 g. of the crude acid from 300 cc. of water gives 170 g. of acid melting at 215–218° (capillary tube sealed 2 cm. from bottom). The washings and mother liquor from the crystallization may be saved for the recovery of 4-nitrophthalic acid (Note 7).

2. Notes

1. A large steam bath may be used instead of the crock. A motor should not be placed directly above the nitration mixture because of the fumes evolved. The motor should be connected with the stirrer by a belt, or, better still, a stirrer of the wind turbine type should be used. If a hood is not available, a 3-l. three-necked flask provided with a glass tube to conduct the fumes outside has been found satisfactory. When a beaker is used, it is recommended that two rectangular glass plates be placed across the top to reduce the danger of acid spattering.
2. The indicated proportions of fuming nitric acid and concentrated acid give as good results as fuming acid alone. The addition of the concentrated acid first does not work well.
3. The filtrate is repeatedly poured through the filter until clear. The mother liquor containing sulfuric acid and nitric acid cannot be worked up profitably for the recovery of the nitrophthalic acids.
4. The mother liquor is saved for the recovery of 4-nitrophthalic acid (Note 7). The product, if air-dried at this point, weighs about 500 g.
5. The amount of water needed depends on the dryness of the cake of crude acids.

6. The yields may be increased by various refinements, but the cost of the 3-nitrophthalic acid obtained is also increased. Because of the extreme cheapness of phthalic anhydride, it is inadvisable to increase the labor cost unduly in order to improve the yield. If a purer product is desired, crystallization from acetic acid will give 3-nitrophthalic acid melting at about 217° (closed tube).

7. The washings and mother liquors from crystallizations may be evaporated and esterified to separate the isomeric acids.[1]

About 370 g. of air-dried solid material may be recovered from the mother liquors and washings. Care must be exercised in concentrating these solutions, as the solid material chars readily when the solution becomes concentrated.

3. Discussion

3-Nitrophthalic acid can be prepared by the oxidation of nitronaphthalene,[2] and by the nitration of phthalic acid in a variety of ways.[3] The procedure described is based on that of Bogert and Boroschek[1] and of Lawrance.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 56
- Org. Syn. Coll. Vol. 1, 410
- Org. Syn. Coll. Vol. 2, 457
- Org. Syn. Coll. Vol. 3, 656

References and Notes

1. Bogert and Boroschek, J. Am. Chem. Soc. **23**, 743 (1901).
2. Beilstein and Kurbatow, Ann. **202**, 217 (1880); de Aguiar, Ber. **5**, 899 (1872)
3. Faust, Ann. **160**, 57 (1871); Miller, Ann. **208**, 224 (1881); Kenner and Mathews, J. Chem. Soc. **105**, 2476 (1914); Cohen, Woodroffe, and Anderson, ibid. **109**, 232 (1916); Littmann, J. Am. Chem. Soc. **47**, 1980 (1925).
4. Lawrance, ibid. **42**, 1872 (1920).

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

3- and 4-nitrophthalic acids

nitrophthalic acids

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

nitric acid (7697-37-2)

3-Nitrophthalic acid,
Phthalic acid, 3-nitro- (603-11-2)

phthalic anhydride (85-44-9)

4-nitrophthalic acid (610-27-5)

nitronaphthalene (86-57-7)

phthalic acid (88-99-3)