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.

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.

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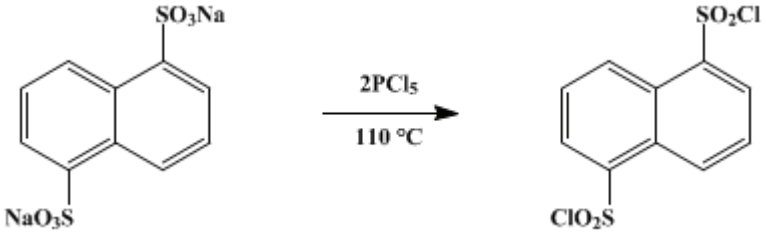
NAPHTHALENE-1,5-DISULFONYL CHLORIDE

[1,5-Naphthalenedisulfonyl chloride]



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1. Procedure

In a 1-l. round-bottomed flask is placed a mixture of 204.3 g. (1 mole) of finely divided phosphorus pentachloride and 132.8 g. (0.4 mole) of the disodium salt of naphthalene-1,5-disulfonic acid which has been dried previously at 140° for 48 hours (Note 1). The flask is provided with an air condenser which is fitted at the top with a calcium chloride drying tube. It is then placed in an oil bath which is heated to 110°, and the mixture is maintained at that temperature for 1 hour. The condenser is removed for brief intervals now and then during the heating period, and the reactants are stirred by means of a glass rod. At the end of the heating period, the product is a thick paste.

The flask and contents are placed on a steam cone and heated for 2 hours under vacuum (furnished by a water aspirator) (Note 2) in order to remove the phosphorus oxychloride formed in this process as well as most of the unreacted phosphorus pentachloride. The dry cake is pulverized in a mortar and transferred to a 4-l. beaker. To this is added 750 ml. of distilled water and 2 l. of chloroform. The mixture is placed on a steam bath, heated to boiling, and stirred vigorously until nearly all the solid dissolves. By means of a separatory funnel the layers are separated while still hot. The chloroform solution is again heated to boiling and filtered through a large fluted filter into an Erlenmeyer flask.

After sufficient chloroform has been evaporated to give a solution volume approximating 250 ml., the solution is cooled in an ice bath and the crystalline product collected on a filter. By further concentration of the mother liquor, an additional quantity of naphthalene-1,5-disulfonyl chloride is obtained. A total yield of 85–115 g. (65–88%) of recrystallized material results; m.p. 181–183°.

2. Notes

1. The powdered solids should be thoroughly mixed before heating. This may be done by inserting a rubber stopper into the neck of the reaction flask and shaking vigorously for about 2 minutes. However, an appreciable pressure develops in the flask and care must be taken in removing the stopper.
2. The reaction flask should be connected to the receiver by a tube of large bore and equipped, preferably, with ground-glass fittings. Two traps between the receiver and the aspirator are desirable to assure no contact between the phosphorus chlorides and water.

3. Discussion

Naphthalene-1,5-disulfonyl chloride has been prepared by the reaction of naphthalene with chlorosulfonic acid; [2,3,4,5,6,7] however, the yields are generally poor and the conditions difficult to reproduce. It also has been obtained by treating disodium 1,5-naphthalene-disulfonate with chlorosulfonic acid.[8] The present method has been published.[9]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 695

References and Notes

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

chlorosulfonic acid (7790-94-5)

phosphorus pentachloride (10026-13-8)

chloroform (67-66-3)

Phosphorus Oxychloride (21295-50-1)

Naphthalene (91-20-3)

Naphthalene-1,5-disulfonyl chloride,
1,5-Naphthalenedisulfonyl chloride (1928-01-4)

disodium 1,5-naphthalene-disulfonate,
disodium salt of naphthalene-1,5-disulfonic acid