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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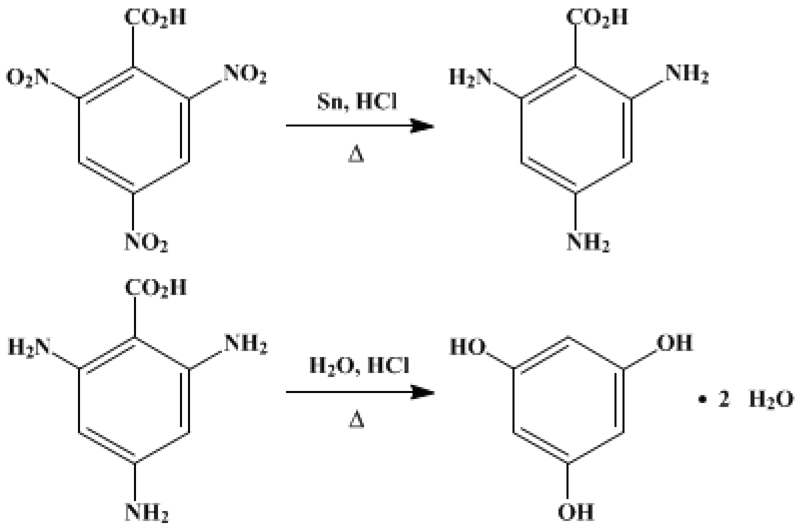
PHLOROGLUCINOL



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1. Procedure

To 225 g. (0.87 mole) of crude 2,4,6-trinitrobenzoic acid (p. 543) (Note 1) and (Note 2) is added 2100 g. (1800 cc., 19.6 moles) of concentrated hydrochloric acid (sp. gr. 1.17) in a 5-l. flask provided with a reflux condenser, the inner tube of which is 15–20 mm. in diameter. To this mixture is added 830 g. (7.0 atoms) of granulated tin in small portions, the reaction being started after the addition of 30–40 g. of the tin by immersing the flask in a hot-water bath (Note 3). The rest of the tin is added through the condenser at such a rate that the reaction proceeds briskly. It is advisable to carry out this reaction under a hood since hydrogen chloride is likely to escape at the beginning of the reaction. The mixture is finally heated on a steam bath for one hour in order to complete the reaction, and is then filtered hot through glass wool in order to remove unreacted tin.

The filtrate is made up to exactly 2 l., and a 50-cc. sample is titrated with sodium hydroxide solution of known concentration (35–40 per cent in a suitable strength). The volume of alkali necessary to produce a slight permanent precipitate is noted (it usually requires 6–8 cc. of 40 per cent alkali). More alkali is run in until the liquid is neutral to litmus paper: this second value represents the acid combined with tin. To the filtrate in the 5-l. flask are added 1 kg. of cracked ice and then sufficient alkali to neutralize the free acid as well as 60 per cent of that combined with the tin (about 800 cc. of 40 per cent sodium hydroxide is required). The mixture is diluted, without filtering, to 6 l. and boiled in a 12-l. flask under a reflux condenser in an atmosphere of coal gas (Note 4) for twenty hours. The precipitate is then filtered off and washed very thoroughly with boiling water (2–3 l. of water); the combined filtrates are concentrated to 3 l., then rendered slightly acid to litmus with hydrochloric acid, and chilled to 0°, when crystals of phloroglucinol separate. This crop is filtered off; it should weigh 70–80 g. It is then dissolved in 700 cc. of hot water, filtered, and allowed to crystallize at 0°. In this way 65–75 g. (46–53 per cent of the theoretical amount) of almost colorless (Note 5) phloroglucinol dihydrate melting at 217–218° is obtained.

2. Notes

1. It is unnecessary to remove the small amount of trinitrotoluene with which the crude trinitrobenzoic acid is contaminated, since it has been found that no trace of the methyl homologue of phloroglucinol is obtained on treating trinitrotoluene in the above manner.

2. An equivalent quantity of 1,3,5-trinitrobenzene (p. 541) may be employed in place of trinitrobenzoic acid with exactly the same result; but, as the most convenient method of preparing trinitrobenzene in the laboratory is through trinitrobenzoic acid, nothing is gained by the substitution.

3. In carrying out the reduction, care must be taken that not more than 5 per cent of the tin is added before the reaction starts; otherwise the interaction begins with such violence that the product may be lost. The reaction may be readily checked by immersion of the flask in water. The application of wet towels to the upper half of the flask is often of great assistance to condensation though only slightly checking the reaction itself.

4. Coal gas is recommended as being the most convenient inert gas in which to carry out the hydrolysis; carbon dioxide or nitrogen should serve equally well.

5. If it is found impossible to obtain a white product by crystallization, purification may be effected by dissolving the phloroglucinol dihydrate in four times its weight of boiling water and passing in sulfur dioxide until no further bleaching effect is observed (about one-half minute is usually sufficient).

3. Discussion

Phloroglucinol can be prepared by the following fusion reactions: resorcinol with sodium hydroxide;[1] 1,3,5-benzenetrisulfonic acid with sodium hydroxide;[2] and 3,5-dibromophenol with potassium hydroxide.[3] Better yields, however, are obtained by boiling a dilute solution of triaminobenzene hydrochloride[4] or triaminobenzoic acid hydrochloride[5] with water.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 522

References and Notes

1. Barth and Schreder, Ber. **12**, 503 (1879).
2. Barth and Schreder, Ber. **12**, 422 (1879).
3. Blau, Monatsh. **7**, 632 (1886).
4. Weidel and Pollak, ibid. **21**, 20 (1900).
5. Cassella and Co., Ger. pat. 102,358 [Frdl. **5**, 156 (1897–1900)].

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

methyl homologue of phloroglucinol

hydrogen chloride,
hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

sulfur dioxide (7446-09-5)

nitrogen (7727-37-9)

tin (7440-31-5)

carbon dioxide (124-38-9)

potassium hydroxide (1310-58-3)

1,3,5-Trinitrobenzene (99-35-4)

Phloroglucinol (108-73-6)

2,4,6-Trinitrobenzoic acid (129-66-8)

phloroglucinol dihydrate (6099-90-7)

trinitrotoluene (118-96-7)

trinitrobenzoic acid

trinitrobenzene

resorcinol (108-46-3)

1,3,5-benzenetrisulfonic acid

3,5-dibromophenol

triaminobenzene hydrochloride

triaminobenzoic acid hydrochloride