



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.112 (1943); Vol. 19, p.29 (1939).

***n*-BUTYL SULFITE**



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1. Procedure

In a 2-l. three-necked flask, fitted with a mercury-sealed stirrer, thermometer, condenser, and dropping funnel, is placed 684 g. (845 cc., 9.2 moles) of dry *n*-butyl alcohol (Note 1). The condenser is connected to a trap for absorbing hydrogen chloride, and 500 g. (305 cc., 4.2 moles) of thionyl chloride (Note 2) is added over a period of two hours, with stirring. The reaction mixture is kept at 35–45°, by immersing the flask in ice water, during the addition of the first half of the thionyl chloride (Note 3). After evolution of hydrogen chloride begins, the water bath is removed and a small flame applied to maintain this temperature. After all the thionyl chloride has been added the temperature is raised gradually to the boiling point, over a period of thirty minutes, to complete the reaction and remove the remainder of the hydrogen chloride. The reaction mixture is then transferred to a 1-l. modified Claisen flask with a 25-cm. fractionating side arm, and fractionated under diminished pressure. After a fore-run consisting largely of unchanged alcohol, there is obtained 625–689 g. (77–84 per cent of the calculated amount) of *n*-butyl sulfite, b.p. 109–115°/15 mm. Refractionation gives 585–674 g. (72–83 per cent) of a product distilling at 109–112° at 14 mm. (Note 4).

2. Notes

1. Commercial *n*-butyl alcohol was dried by distillation through a column; the fore-run and a small fraction collected after the vapors reached 117° were discarded.
2. Commercial thionyl chloride was redistilled, and the fraction boiling at 78–80° was employed.
3. Considerable heat is evolved until gas evolution begins, after which heat is absorbed.
4. The submitters report that *n*-propyl sulfite is obtained from *n*-propyl alcohol in somewhat smaller yields, by the same procedure.

3. Discussion

n-Butyl sulfite has been prepared from butyl alcohol and thionyl chloride by the method described,¹ and using anhydrous ether as a solvent together with dry pyridine to take up the hydrogen chloride evolved.² The pyridine method has been checked, but its advantages do not offset the extra expense of the ether and pyridine used. Butyl sulfite has also been made by the action of sulfur chloride on butyl alcohol.³

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 2, 111*

References and Notes

1. Voss and Blanke, *Ann.* **485**, 258 (1931); Barkenbus and Owen, *J. Am. Chem. Soc.* **56**, 1204 (1934).
 2. Gerrard, *J. Chem. Soc.* **1939**, 99.
 3. Bert, *Compt. rend.* **178**, 1827 (1924).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

hydrogen chloride (7647-01-0)

ether (60-29-7)

thionyl chloride (7719-09-7)

butyl alcohol,
n-butyl alcohol (71-36-3)

pyridine (110-86-1)

n-propyl alcohol (71-23-8)

sulfur chloride

Butyl sulfite,
n-butyl sulfite (626-85-7)

n-propyl sulfite