



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.

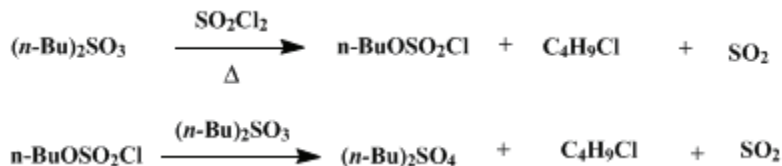
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

Organic Syntheses, Coll. Vol. 2, p.111 (1943); Vol. 19, p.27 (1939).

n-BUTYL SULFATE



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1. Procedure

In a 2-l. three-necked flask, fitted with a dropping funnel, mercury-sealed stirrer, and condenser, is placed 625 g. (3.2 moles) of *n*-butyl sulfite (p. 112). The condenser is connected to a gas absorption trap, and 217 g. (131 cc., 1.6 moles) of sulfuryl chloride (Note 1) is added over a period of thirty minutes, with rapid stirring and cooling with tap water. The dropping funnel is then replaced by a thermometer dipping into the liquid, and the flask is heated slowly, with stirring, until the refluxing of the butyl chloride becomes vigorous (about 100–110°). Sulfur dioxide is evolved copiously during this time. The condenser is replaced with a 40-cm. Vigreux column and downward condenser; the temperature is gradually raised to 130–135° and kept there until no more sulfur dioxide or butyl chloride distils. The heating and distillation require about two hours. The residue of crude *n*-butyl sulfate is cooled to room temperature, and 100 cc. of saturated sodium carbonate solution is added. The mixture is stirred for about ten minutes, poured into a separatory funnel, and let stand for thirty minutes to allow the layers to separate. The upper layer is dried with calcium chloride, at least overnight, and then allowed to stand over 15 g. of anhydrous sodium or potassium carbonate for a day, with occasional shaking. The product is filtered into a 500-cc. modified Claisen flask with a 25-cm. fractionating side arm, and distilled from an oil bath. The first distillation gives 250–280 g. (74–83 per cent of the calculated amount) of *n*-butyl sulfate, b.p. 110–114°/4 mm., which has a sharp odor. Redistillation gives a pure material with a slight ester odor, boiling at 109–111° at 4 mm., with only a small mechanical loss (Note 2).

2. Notes

- Commercial sulfuryl chloride was redistilled and the fraction boiling at 69–70° was used.
- The submitters report that *n*-propyl sulfate may be prepared in similar fashion, the yield being about 66–70 per cent. The second distillation in this case should be done through a short column to remove higher-boiling material; *n*-propyl sulfate distils at 88–91° at 4 mm.

3. Discussion

n-Butyl sulfate has been prepared by the action of *n*-butyl chlorosulfonate upon *n*-butyl orthoformate or *n*-butyl sulfite.¹ It has been obtained also by oxidation of *n*-butyl sulfite with potassium permanganate in glacial acetic acid solution.² The method described above appears to be the most satisfactory for laboratory-scale preparations.

References and Notes

- Levaillant, Compt. rend. **197**, 648 (1933); Barkenbus and Owen, J. Am. Chem Soc. **56**, 1204 (1934).
 - Evans, Ph.D. Dissertation, Northwestern University, 1935.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

acetic acid (64-19-7)

potassium permanganate (7722-64-7)

sodium carbonate (497-19-8)

sulfur dioxide (7446-09-5)

sulfuryl chloride (7791-25-5)

sodium (13966-32-0)

Butyl chloride (109-69-3)

n-butyl sulfite (626-85-7)

n-BUTYL SULFATE (15507-13-8)

n-propyl sulfate

n-butyl chlorosulfonate

n-butyl orthoformate