



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](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.

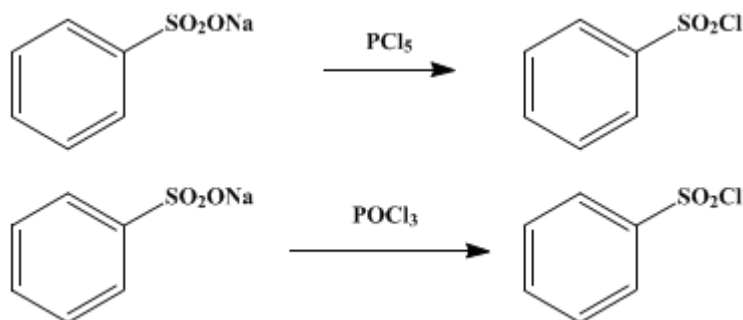
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 1, p.84 (1941); Vol. 1, p.21 (1921).*

## BENZENESULFONYL CHLORIDE

[(A) and (B) (from *Sodium Benzenesulfonate*)]



Submitted by Roger Adams and C. S. Marvel.

Checked by H. T. Clarke and W. W. Hartman.

### 1. Procedure

(A) *Phosphorus Pentachloride Method.*—In a 2-l. round-bottomed flask is placed a mixture of 250 g. (1.2 moles) of finely divided phosphorus pentachloride and 450 g. (2.5 moles) of sodium benzenesulfonate which has previously been dried for three hours at  $140^\circ$ . The mixture is heated in an oil bath at  $170$ – $180^\circ$  (Note 1) for fifteen hours (Note 2). It is advisable to have a reflux condenser attached to the flask, although very little active refluxing takes place. Every four hours during the heating period, the flask should be removed from the oil bath, cooled for fifteen minutes, stoppered and shaken thoroughly until the mass becomes pasty (sometimes ten to fifteen minutes are required to accomplish this). At the end of the heating period, the mixture is cooled and 1 l. of water with 1 kg. of cracked ice are added. Benzenesulfonyl chloride sinks to the bottom, is separated, washed once with water, filtered if necessary, and distilled under reduced pressure for purification. The forerun, consisting of a little chlorobenzene, water, and a little benzenesulfonyl chloride, is discarded and the fraction boiling between  $145$ – $150^\circ$  /45 mm. is collected. This weighs 330–360 g. (75–80 per cent of the theoretical amount) (Note 3).

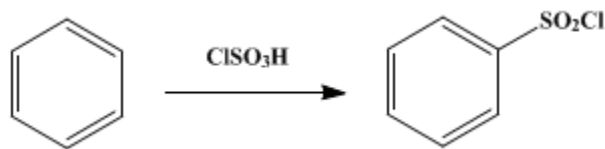
The yields in this procedure are likely to vary widely on account of the variability in the different samples of sodium benzenesulfonate. With certain samples a solid impurity is left as a residue from the distillation of the crude benzenesulfonyl chloride.

(B) *Phosphorus Oxychloride Method.*—Benzenesulfonyl chloride may be prepared by the same procedure described above from a mixture of 270 g. (1.5 moles) of sodium benzenesulfonate and 180 g. (1.17 moles) of phosphorus oxychloride. It is advisable to observe the same precaution of shaking every few hours. The yield of product boiling at  $145$ – $150^\circ$  /45 mm. is 195–230 g. (74–87 per cent of the theoretical amount) (Note 3).

### 2. Notes

1. The temperature must be maintained between  $170$ – $180^\circ$ . A lower temperature does not give so good a yield.
  2. It is advisable to heat the mixture as long as fifteen hours to be certain that the reaction is complete. The reaction is chiefly over, however, at the end of ten hours.
  3. If a means of mechanical stirring were provided, the yields would undoubtedly be much better, and the time required shorter. The mixtures, however, are so thick that in the laboratory mechanical stirring is impracticable.
- Experiments using a larger excess of phosphorus pentachloride or phosphorus oxychloride were made but no particular advantage was so obtained.

[(C) (from *Benzene*)]



Submitted by H. T. Clarke, G. S. Babcock, and T. F. Murray.  
Checked by Frank C. Whitmore and A. M. Griswold.

## 1. Procedure

In a 5-l. flask, fitted with stirrer, separatory funnel, exit tube, and thermometer, is placed 3.5 kg. (2 l., 30 moles) of chlorosulfonic acid (Note 1), and to it is slowly added, with continuous stirring, 780 g. (888 cc., 10 moles) of benzene (Note 2), keeping the temperature between  $20^\circ$  and  $25^\circ$  by means of cold water. The hydrogen chloride which is evolved is led to a hood or absorbed in water (Fig. 7, p. 97). The addition requires two to three hours; when this is complete, the mixture is stirred for one hour, and poured upon 6–7 kg. of crushed ice (Note 3). One liter of carbon tetrachloride is then added, the oil is separated as soon as possible (Note 4), and the watery layer is shaken with 500 cc. of carbon tetrachloride. The combined extracts are washed with dilute sodium carbonate, and the bulk of the carbon tetrachloride is distilled under atmospheric pressure (Note 5); the pressure is then reduced (Note 6) and the benzenesulfonyl chloride collected at  $113\text{--}115^\circ / 10$  mm. ( $118\text{--}120^\circ / 15$  mm.). The yield is 1320–1360 g. (75–77 per cent of the theoretical amount) of a colorless liquid which on cooling sets to a crystalline solid melting at  $13\text{--}14^\circ$ .

A small amount (50–100 g.) of higher-boiling material remains in the flask. This is mainly diphenyl sulfone, which may be isolated by distillation under reduced pressure (b.p.  $225^\circ / 10$  mm.) and recrystallization from methyl alcohol. It forms colorless crystals which melt at  $128^\circ$ .

## 2. Notes

1. If less than 50 per cent excess of chlorosulfonic acid is taken, the yield of diphenyl sulfone increases at the expense of the sulfonyl chloride.
2. A good commercial grade of benzene, boiling over a  $1^\circ$  range, is satisfactory. The benzene must be added to the acid (not vice versa); otherwise, a larger proportion of sulfone is formed.
3. The benzenesulfonyl chloride separates at first as a crystalline solid which melts as the temperature rises. It was found impracticable to filter off this solid, owing to its tendency to melt on the funnel.
4. The sulfonyl chloride should be removed from the water as soon as possible; otherwise, the yield falls, owing to hydrolysis. In one run in which the mixture was allowed to stand overnight before separating, only 1220 g. (69 per cent) was obtained. If difficulty is experienced in the separation, owing to the presence of suspended solid matter, the oil may first be filtered with suction through a hardened paper or felt cloth. As a rule, it is merely necessary to filter the sludgy layer lying between the oil and the water.
5. The carbon tetrachloride vapor carries with it any moisture that may be present. If this were not removed at a relatively low temperature, hydrolysis of the chloride would take place, with the formation of sulfonic acid which would promote decomposition of the sulfonyl chloride during its distillation.
6. The pressure should be reduced gradually, and the first runnings, mainly carbon tetrachloride, collected separately.

## 3. Discussion

Benzenesulfonyl chloride can be prepared by the action of phosphorus pentachloride on benzenesulfonic acid or its salts;<sup>1</sup> by the action of phosphorus oxychloride upon the salts of benzenesulfonic acid;<sup>2</sup> by the action of chlorosulfonic acid on benzene<sup>3</sup> or sodium benzenesulfonate;<sup>4</sup> and by the action of sulfonyl chloride on benzene in the presence of anhydrous aluminum chloride.<sup>5</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 504](#)
- [Org. Syn. Coll. Vol. 3, 159](#)

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## References and Notes

1. Gerhardt and Chiozza, *Ann.* **87**, 299 (1853); Vogt, *Ann.* **119**, 143 (footnote) (1861); Otto, *Z. Chem.* **106** (1866); Barbaglia and Kekulé, *Ber.* **5**, 876 (1872); Bourgeois, *Rec. trav. chim.* **18**, 432 (1899); Mohrmann, *Ann.* **410**, 379 (1915); Rosenmund and Struck, *Ber.* **54**, 439 (1921).
2. Gerhardt and Chancel, *Compt. rend.* **35**, 690 (1852).
3. Knapp, *Z. Chem.* **41** (1869); Pummerer, *Ber.* **42**, 1802, 2274 (1909); Ullmann, *Ber.* **42**, 2057 (1909); Saccharinfabrik A.-G., *Ger. pat.* 224,386 [Frdl. **10**, 114 (1913)].
4. Heumann and Köchlin, *Ber.* **15**, 1118 (1882).
5. Böeseken, *Rec. trav. chim.* **30**, 382 (1911).

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## Appendix

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

sulfonyl chloride

[hydrogen chloride \(7647-01-0\)](#)

[Benzene \(71-43-2\)](#)

[methyl alcohol \(67-56-1\)](#)

[chlorosulfonic acid \(7790-94-5\)](#)

[phosphorus pentachloride \(10026-13-8\)](#)

[sodium carbonate \(497-19-8\)](#)

[sulfone \(7446-09-5\)](#)

[carbon tetrachloride \(56-23-5\)](#)

[Benzenesulfonyl chloride \(98-09-9\)](#)

[Sodium Benzenesulfonate \(515-42-4\)](#)

[chlorobenzene \(108-90-7\)](#)

[Phosphorus Oxychloride \(21295-50-1\)](#)

[diphenyl sulfone \(127-63-9\)](#)

[benzenesulfonic acid \(98-11-3\)](#)

sulfuryl chloride (7791-25-5)

aluminum chloride (3495-54-3)

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