



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.

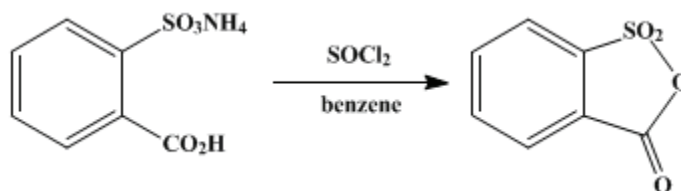
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.495 (1941); Vol. 9, p.80 (1929).*

## ***o*-SULFOBENZOIC ANHYDRIDE**

**[Benzoic acid, *o*-sulfo-, cyclic anhydride]**



Submitted by H. T. Clarke and E. E. Dreger.

Checked by Henry Gilman and J. E. Kirby.

### **1. Procedure**

In a 2-l. flask fitted with a mechanical stirrer, a separatory funnel, and an efficient reflux condenser are placed 219 g. (1 mole) of finely powdered acid ammonium *o*-sulfobenzoate (p. 14) and 200 cc. of dry benzene (Note 1). To this is added with stirring 145 g. (86.3 cc., 1.22 moles) of thionyl chloride (b.p. 76–78°). A tube is connected to the upper end of the reflux condenser which passes into an ice-cooled flask; from this another tube is provided to carry off the hydrogen chloride and sulfur dioxide generated during the reaction (Fig. 7, p. 97). The mixture is gently warmed on a steam bath in such a way that gases are evolved fairly briskly (Note 2); continuous stirring is essential. The bulk of the entrained benzene and thionyl chloride is condensed in the ice-cooled receiver; the condensate is returned periodically to the reaction mixture through the separatory funnel. After about fifteen hours' heating, the evolution of gases slackens; an additional 400 cc. of dry benzene is then added and the heating continued until the evolution of gases ceases; this requires about five hours longer.

The hot mixture is then filtered (Note 3) with suction into a 2-l. flask, and the solid material, consisting of ammonium chloride, is washed with 100 cc. of hot benzene. This solid is then returned to the 2-l. flask and boiled with stirring for one hour with 300 cc. of dry benzene; the mixture while hot is then filtered with suction into the same 2-l. flask. The combined filtrates and washings are then distilled until about 300 cc. of benzene has been removed, after which the solution is cooled in an ice bath; this causes the greater part of the sulfobenzoic anhydride to crystallize. The benzene mother liquor is decanted from these crystals and the bulk of the solvent removed by distillation.

The flask containing the crystals is attached to a condenser and heated until the solid has completely melted; the adhering solvent is then removed from the liquid by slightly reducing the pressure. The clear residue is poured into a dish and allowed to cool. The product thus obtained melts at 121–123°. The residue from the mother liquor, being as a rule somewhat dark in color, is preferably distilled under reduced pressure (Note 4), the flask being heated in a metal bath. The anhydride distils at 184–186°/18 mm. The second crop may have a slightly lower melting point. The total yield of *o*-sulfobenzoic anhydride, which is of sufficient purity for the preparation of sulfonephthaleins, amounts to 118–121 g. (64–66 per cent of the theoretical amount) (Note 5). In order to convert this into a product melting at 126–127° (Note 4), it is recrystallized from three times its weight of dry benzene.

### **2. Notes**

1. The benzene is most satisfactorily dried by distillation, the moist forerun being rejected.
2. The reaction may become so vigorous that it is necessary to interrupt the heating for a short time.
3. The filtration should be carried out under a hood, on account of the presence of some unchanged thionyl chloride.
4. It is stated in the literature that the pure compound melts at 128°. It is very sensitive to moist air, which converts it into the free acid.
5. With larger quantities the yields are significantly increased; the submitters of these directions

obtained 74–81 per cent of the theoretical amount with runs of 7.5 moles.

### 3. Discussion

*o*-Sulfobenzoic anhydride can be prepared from the free acid by heating alone or with phosphorus pentoxide<sup>1</sup> and by treating it with acetyl chloride;<sup>2</sup> from the neutral potassium salt by warming with phosphorus pentachloride;<sup>2</sup> from the acid potassium salt by warming with phosphorus pentachloride<sup>3</sup> or thionyl chloride,<sup>4</sup> and by heating it with phosphorus pentoxide to 400°. <sup>5</sup> The procedure described is a modification of that of White and Acree<sup>6</sup> who heated the acid ammonium salt with an excess of thionyl chloride and extracted the product with benzene.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 14](#)

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### References and Notes

1. Remsen and Dohme, *Am. Chem. J.* **11**, 343 (1889).
  2. Fahlberg and Barge, *Ber.* **22**, 757 (1889).
  3. Sohon, *Am. Chem. J.* **20**, 258 (1898).
  4. Cobb, *ibid.* **35**, 499 (1906).
  5. Heitman, *J. Am. Chem. Soc.* **34**, 1594 (1912).
  6. White and Acree, *J. Am. Chem. Soc.* **41**, 1197 (1919).
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### Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sulfonephthaleins

ACID AMMONIUM *o*-SULFOBENZOATE

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

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

[ammonium chloride](#) (12125-02-9)

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

[acetyl chloride](#) (75-36-5)

[thionyl chloride](#) (7719-09-7)

[sulfur dioxide](#) (7446-09-5)

[sulfobenzoic anhydride,  
\*o\*-Sulfobenzoic anhydride,  
Benzoic acid, \*o\*-sulfo-, cyclic anhydride](#) (81-08-3)

phosphorus pentoxide (1314-56-3)

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