



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.

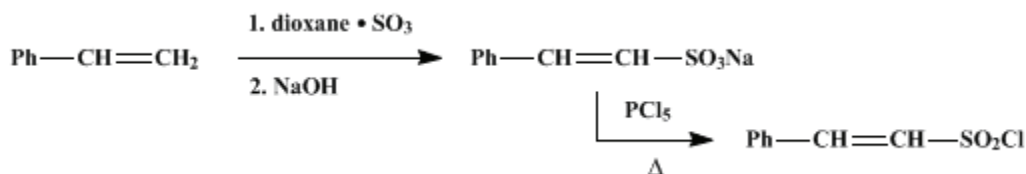
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.846 (1963); Vol. 34, p.85 (1954).*

# SODIUM $\beta$ -STYRENESULFONATE AND $\beta$ -STYRENESULFONYL CHLORIDE

**[Ethenesulfonic acid, 2-phenyl-, sodium salt]**

**[Ethenesulfonyl chloride, 2-phenyl-]**

Submitted by Christian S. Rondestvedt, Jr. and F. G. Bordwell<sup>†</sup>

Checked by T. L. Cairns and H. E. Winberg.

## 1. Procedure

A. *Sodium  $\beta$ -styrenesulfonate*. In a 3-l. three-necked flask, equipped with a drying tube, a sealed stirrer, and a ground-glass stopper, is placed 800 ml. of **ethylene chloride** (Note 1). The flask with fittings is weighed and then connected through the third neck to a **sulfur trioxide** distillation apparatus (Note 2). **Sulfur trioxide** is distilled into the flask until about 300 g. has been collected. During the distillation the flask is cooled with a large pan of cold water (Note 3). The distillation is stopped, the condenser is disconnected and replaced by the glass stopper, and the flask is again weighed.

The stopper is replaced by a thermometer, and the other side neck is equipped with a two-way adapter to hold a dropping funnel and a drying tube. The sulfur trioxide solution is cooled below  $-5^{\circ}\text{C}$ ; with an ice-salt bath, then an amount of dioxane (Note 4) equivalent to the sulfur trioxide is added slowly with vigorous stirring at such a rate that the temperature does not exceed  $5^{\circ}\text{C}$  (Note 5).

One molar equivalent of [styrene \(Note 6\)](#) dissolved in 2 volumes of [ethylene chloride](#) is added with stirring to the suspension of [dioxane sulfotrioxide](#). The temperature is maintained below 10° during the hour required for addition, during which the suspension of colorless solid changes to a milky tan solution. The cooling bath is removed, and stirring is continued for an additional hour. After standing overnight, the nearly clear yellow solution is heated under reflux for 2 hours on the steam bath. The solution, now dark brown, is allowed to cool, is poured into 3 l. of ice water, and is stirred or shaken to ensure transfer of the sulfonic acid to the water ([Note 7](#)). The emulsion is neutralized with [sodium hydroxide](#) solution ([Note 8](#)), the layers are separated, and the aqueous phase is extracted with two 500-ml. portions of [isopropyl ether](#) ([Note 9](#)).

Several crops of crystals are now taken by evaporating the aqueous solution to the saturation point on a hot plate with stirring, then cooling. Each crop is dried for 2 hours at 100° and analyzed for unsaturation by the bromate-bromide titration method (Note 10). The first two crops usually total about 380 g. (based on 300 g. of sulfur trioxide), 49% yield, and are about 95% pure by titration. They may be further purified by one recrystallization from water, with about 80% recovery of 99 + % pure salt.

The third crop generally weighs about 100 g. and is about 80% pure; the fourth crop weighs about 75 g., and is about 60% pure (Note 11). For purification, the third crop is recrystallized from the mother liquor resulting from the recrystallization of the combined first and second crops; the fourth crop is recrystallized from the third-crop mother liquor. An additional recrystallization from water is usually required to obtain material of 95 + % purity.

The total weight of 95 + % pure sodium  $\beta$ -styrenesulfonate from 300 g. of sulfur trioxide is 450–500 g. (58–65% yield) (Note 12) and (Note 13).

B.  *$\beta$ -Styrenesulfonyl chloride*. One hundred grams of dry sodium  $\beta$ -styrenesulfonate (Note 14) is

placed in a 500-ml. round-bottomed flask and thoroughly mixed with 120 g. of powdered phosphorus pentachloride with vigorous shaking. The flask is attached to a reflux condenser capped with a drying tube and heated on the steam bath until the reaction mixture liquefies, then for an additional 4 hours. The phosphorus oxychloride is removed by distillation at reduced pressure (water aspirator) on the steam bath. The semisolid residue is extracted three times by boiling for 15 minutes with 100-ml. portions of chloroform. The residue in the flask is dissolved in 200 ml. of ice water and extracted with 100 ml. of chloroform. The combined chloroform solutions are washed with 200 ml. of water, two 100-ml. portions of 5% sodium bicarbonate, and finally with 100 ml. of water. After drying for 2 hours over calcium chloride, the solution is treated with 3 g. of Norit, filtered, and concentrated to 150 ml., and 200 ml. of 60–68° petroleum ether is added. On cooling, 81–86 g. (83–88% yield) of  $\beta$ -styrenesulfonyl chloride separates as colorless needles, m.p. 88–90°. Recrystallization raises the melting point to 89–90° (Note 15), (Note 16), and (Note 17).

## 2. Notes

1. A good grade of ethylene chloride is dried by slowly distilling a portion and rejecting the wet fore-run. Technical grade material should be carefully fractionated before use; the fraction boiling at 82.6–82.8° gives excellent results.
2. The apparatus for distillation of sulfur trioxide is constructed from a 500-ml. round-bottomed flask, connected by a ground joint to a 6-in. section of 20-mm. glass tubing. A safety tube (8-mm. tubing) reaching to the bottom of the flask is attached at the top by means of a ground joint; it is convenient to bend the top of the tube so that any acid drip can be caught in a beaker. A side arm, sealed in near the top of the wide tube, leads through a ground joint to an air condenser consisting of a 30-in. length of 12-mm. tubing, which terminates in a ground joint (with a drip tip) to fit the reaction flask. It is imperative that the apparatus be all glass, since sulfur trioxide rapidly attacks rubber or cork connections. Sulfur trioxide is distilled by heating 60% fuming sulfuric acid contained in the flask. Spent acid may be fortified with "Sulfan B," stabilized liquid sulfur trioxide obtainable from the General Chemical Company, 40 Rector St., New York. Undiluted Sulfan B solidifies in the flask after a few heatings, and subsequent reheating may be dangerous.
3. Only slight cooling is needed at this stage. Stirring may be intermittent, if more convenient. If the sulfur trioxide solidifies above the level of the ethylene chloride from excessive cooling, it may easily be melted by warming the flask with a soft flame.
4. Dioxane is purified by refluxing for 12 hours with an excess of sodium, then distilling. The fraction boiling at 99.6–99.8° is collected and stored over calcium chloride or, preferably, calcium hydride.
5. If the temperature is allowed to rise much above 5°, charring results and the product is discolored. A Dry Ice bath may be used to advantage. The reagent thus prepared should be used within a few hours, since dioxane is slowly attacked by sulfur trioxide.
6. Stabilized styrene of monomeric quality is used directly. The small amount of stabilizer does not interfere with the reaction.
7. In small runs, ether may be used to break the emulsion, thus permitting the separation of the layers before neutralization. In large runs, excessively large amounts of ether are required and it is preferable to neutralize first.
8. Methyl red serves as a convenient indicator. Slightly more than 1 mole of sodium hydroxide is required per mole of sulfur trioxide. Other metal salts can be prepared, using a suitable hydroxide or carbonate for the neutralization.
9. Ethyl ether may be substituted, but its greater water solubility is a disadvantage. Evaporation of the combined organic layers at reduced pressure below 40° leaves a residue of about 5% (based on sulfur trioxide) of 2,4-diphenylbutane-1,4-sultone, which may be purified (60% recovery) by recrystallization from acetone-water; m.p. 147–149°. The yield of sultone may be increased to about 25% of pure material by using 3 moles of styrene per mole of sulfur trioxide.
10. A sample (approximately 0.2 g.) is weighed accurately and dissolved in 25 ml. of water; then 25 ml. of 0.1N hydrochloric acid and 0.2 g. of potassium bromide are added. The solution is titrated with 0.07M potassium bromate until a permanent yellow color is produced. Potassium iodide (0.1 g.) is added, and the solution is backtitrated to a starch end point with 0.1N sodium thiosulfate. The blue color returns in about a minute since the high acidity promotes air oxidation of excess iodide. The accuracy is only slightly less if the appearance of a faint yellow bromine color is taken as the end point. One mole

of potassium bromate is equivalent to 3 of sodium  $\beta$ -styrenesulfonate.

11. Further crops may be taken, but the recovery of pure material from them is not worth the time required. They consist mainly of sodium 2-phenyl-2-hydroxyethane-1-sulfonate along with some sodium sulfate.

12. The procedure may be modified to prepare sodium 2-phenyl-2-hydroxyethane-1-sulfonate. The temperature during the addition of styrene is maintained below 0°. After 30 minutes of additional stirring at 0°, the mixture is hydrolyzed in ice water without heating. The crops of salts are analyzed, and those that are low in unsaturation are recrystallized from 70% aqueous ethanol. The more unsaturated crops are recrystallized from the mother liquors. The yield is 45–50% of material with less than 5% unsaturation.

13. Since the sodium sulfonates have no definite melting points, they may be converted to crystalline benzylthiuronium, *p*-chlorobenzylthiuronium, aniline, or *p*-toluidine salts for characterization.<sup>2</sup>

14. The salt is dried at 100° for 4 hours, then powdered.

15. An additional 6–7 g. of product, m.p. 88–89°, may be obtained by evaporation of the mother liquors and distillation of the residue as rapidly as possible at 2 mm. (bath temperature 120–140°). The total yield is thus 88–92%; in smaller runs, yields up to 96% are frequently obtained. Large batches cannot be distilled satisfactorily.

16. Carbon tetrachloride may also be used as a recrystallization solvent. The product should be stored in a tightly closed brown bottle to retard its slow decomposition.

17. The checkers used one-third quantities throughout both parts of this preparation with comparable results.

### 3. Discussion

Salts of  $\beta$ -styrenesulfonic acid have been prepared by the sulfonation of styrene with dioxane sulfotrioxide,<sup>2</sup> by heating styrene with ammonium sulfamate,<sup>3</sup> by the reaction of styrene with sodium bisulfite in the presence of oxygen,<sup>4</sup> and by the sulfonation of styrene with pyridine sulfotrioxide.<sup>5</sup>

---

### References and Notes

1. Joint contribution from Northwestern University, Evanston, Illinois, and the University of Michigan, Ann Arbor, Michigan.
  2. Bordwell, Suter, Holbert, and Rondestvedt, Jr., *J. Am. Chem. Soc.*, **68**, 139 (1946); Bordwell and Rondestvedt, Jr., *J. Am. Chem. Soc.*, **70**, 2429 (1948).
  3. Quilico and Fleischner, *Atti acad. Lincei*, **7**, 1050 (1928) [*C. A.*, **23**, 1628 (1929)].
  4. Kharasch, Schenck, and Mayo, *J. Am. Chem. Soc.*, **61**, 3092 (1939).
  5. Terent'ev and Dombrovskii, *Zhur, Obshchei Khim. (J. Gen. Chem.)*, **20**, 1875 (1950) [*C. A.*, **45**, 2892 (1951)]; Terent'ev, Gracheva, and Shcherbatova, *Doklady Akad. Nauk S.S.S.R.*, **84**, 975 (1952) [*C. A.*, **47**, 3262 (1953)].
- 

### Appendix

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

petroleum ether

Methyl Red

benzylthiuronium, *p*-chlorobenzylthiuronium, aniline, or *p*-toluidine salts

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether,  
ethyl ether (60-29-7)

sodium hydroxide (1310-73-2)

phosphorus pentachloride (10026-13-8)

sulfur trioxide (7446-11-9)

chloroform (67-66-3)

sodium bicarbonate (144-55-8)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

carbon tetrachloride (56-23-5)

potassium iodide (7681-11-0)

sodium thiosulfate (7772-98-7)

ethylene chloride (107-06-2)

sodium bisulfite (7631-90-5)

Norit (7782-42-5)

Phosphorus Oxychloride (21295-50-1)

potassium bromate (7758-01-2)

sodium (13966-32-0)

potassium bromide (7758-02-3)

styrene (100-42-5)

dioxane (123-91-1)

isopropyl ether (108-20-3)

$\beta$ -Styrenesulfonyl chloride,  
Ethenesulfonyl chloride, 2-phenyl- (4091-26-3)

Ethenesulfonic acid, 2-phenyl-, sodium salt,  
Sodium  $\beta$ -styrenesulfonate (2039-44-3)

dioxane sulfotrioxide

2,4-diphenylbutane-1,4-sultone

sodium 2-phenyl-2-hydroxyethane-1-sulfonate

ammonium sulfamate (7773-06-0)

pyridine sulfotrioxide

calcium hydride (7789-78-8)