



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.

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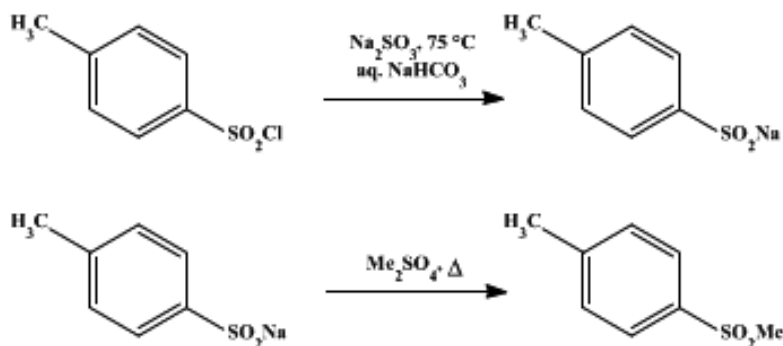
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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METHYL *p*-TOLYL SULFONE

[Sulfone, methyl *p*-tolyl]



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Checked by John C. Sheehan and M. Gertrude Howell.

1. Procedure

In a 4-l. beaker (Note 1) provided with a mechanical stirrer and thermometer are placed 600 g. (4.76 moles) of anhydrous sodium sulfite, 420 g. (5.0 moles) of sodium bicarbonate, and 2.4 l. of water. The mixture is heated on a hot plate at $70\text{--}80^\circ$ and is maintained at this temperature by switching the hot plate off occasionally, while 484 g. (2.54 moles) of *p*-toluenesulfonyl chloride (Note 2) is added in portions of 5–10 g., with stirring, during 3 hours. When addition is complete, the mixture is heated and stirred at $70\text{--}80^\circ$ for 1 hour (Note 3). The mixture is then removed from the hot plate and allowed to stand for 4 to (preferably) 10 hours.

The solid sodium *p*-toluenesulfinate which separates is collected by filtration and mixed with 400 g. (4.76 moles) of sodium bicarbonate and 490 g. (370 ml., 3.88 moles) of dimethyl sulfate (Note 4) in a 3-l. three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a 1-l. separatory funnel containing 925 ml. of water. Water (75–100 ml.) is added from the separatory funnel to make the mixture fluid enough for stirring. The remainder of the water is then added dropwise, with stirring, during 3 hours. The mixture is then heated under reflux for 20 hours.

After the mixture is cooled to 75° , 200 ml. of benzene (Note 5). The mixture is stirred briefly, and the liquid is decanted from the solid into a 5-l. separatory funnel. The aqueous layer is separated and extracted again with 200 ml. of benzene. The aqueous layer is then returned to the separatory funnel, and the solid in the reaction flask is washed in with it by means of 2 l. of water. The mixture is shaken with 200-ml. portions of benzene until all solid has dissolved (usually three portions of benzene suffice). All the benzene extracts are combined and dried with 20 g. of anhydrous calcium chloride. The drying agent is removed by filtration and washed with two 20-ml. portions of benzene. Benzene is removed from the filtrate by distillation under reduced pressure (Note 6), and the solid which separates is dried further at about 10 mm. and room temperature to constant weight. The yield (Note 2) of methyl *p*-tolyl sulfone is 298–317 g. (69–73%), m.p. $83\text{--}87.5^\circ$. Further purification is generally unnecessary, but, if desired, the product may be recrystallized from carbon tetrachloride or ethanol-water (1:1). The submitters state that the method may be extended to the preparation of methyl phenyl sulfone and, presumably, of methyl aryl sulfones generally (Note 7).

2. Notes

1. A porcelainized metal bucket is a convenient alternative.
2. The submitters used Eastman Kodak Company practical grade; although the solid is somewhat oily,

the m.p. is 66–68°. The checkers used *p*-toluenesulfonyl chloride purchased from Matheson, Coleman and Bell and obtained a yield of 78–82%.

3. The volume at the end of the heating period should not exceed 2.4 l. If, after 1 hour of heating, the volume exceeds 2.4 l., the mixture is heated longer.

4. Eastman Kodak Company practical grade was used, b.p. 69–70°/10 mm. Dimethyl sulfate is toxic and must be handled with caution. This part of the preparation should be run in a hood with provision for containing the contents should breakage occur. It is unlikely that any dimethyl sulfate survives the 20-hour reflux period however, and the submitters reported that no difficulty whatever was encountered in handling the mixture after this point without special precautions; nevertheless, they recommend that the possible presence of dimethyl sulfate be borne in mind. Ammonia is a specific antidote for dimethyl sulfate and should be at hand to destroy any accidentally spilled. A solution of a detergent in dilute ammonia water may be used to clean glassware used in transfers. The hazards associated with dimethyl sulfate are described by Sax.²

5. Extraction with benzene improves the yield somewhat but offers the more important advantage of permitting effective drying of the sulfone when it is to be used in metalation reactions. If this advantage is not sought, the reaction mixture simply can be allowed to cool to room temperature and to stand until crystallization is complete (2–3 hours). The solid is then collected by filtration and washed with water (about six 200-ml. portions) until the washings give no precipitate with barium chloride solution. The yield is 272 g. (63%); it can be increased by 12.6 g. (66%) by extraction of the mother liquor and wash water. The sulfone thus obtained contains only 0.25% of benzene-insoluble material and has m.p. 86.5–87.5°.

6. If the benzene is removed at a temperature not exceeding 50°, the sulfone is obtained as well-formed crystals.

7. According to the submitters, methyl phenyl sulfone³ is obtained similarly from benzenesulfonyl chloride in 66–69% yields, m.p. 86–88°.

3. Discussion

Methyl *p*-tolyl sulfone has been prepared by oxidation of methyl *p*-tolyl sulfide with hydrogen peroxide^{4,5} or ruthenium tetroxide,⁶ by alkylation of sodium *p*-toluenesulfinate with methyl iodide^{7,8} or with methyl potassium sulfate,⁹ by decarboxylation of *p*-tolylsulfonylacetic acid,⁷ by thermal decomposition of tetramethylammonium *p*-toluenesulfinate,¹⁰ by reaction of *cis*-bis-(*p*-tolylsulfonyl) ethene with sodium hydroxide (low yield),¹¹ by the reaction of methanesulfonyl chloride with toluene in the presence of aluminum chloride (mixture of isomers),¹² by reaction of alkali with 3-*p*-tolylsulfonyl-7-hydroxynaphtho- α -pyrone,¹³ by heating allyl *p*-tolyl sulfone with sodium hydroxide,¹⁴ and by the decomposition of sodium *p*-toluenesulfonyl-acetate.¹⁵

The method described here is that of Field and Clark.³ It involves preparation of sodium *p*-toluenesulfinate by the procedure of Oxley et al.⁸ and alkylation by modification of a method used by Baldwin and Robinson¹⁶ for the preparation of methyl phenyl sulfone.

References and Notes

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

3-p-tolylsulfonyl-7-hydroxynaphtho- α -pyrone

calcium chloride (10043-52-4)

ammonia (7664-41-7)

Benzene (71-43-2)

sodium sulfite (7757-83-7)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

carbon tetrachloride (56-23-5)

dimethyl sulfate (77-78-1)

barium chloride (10361-37-2)

Benzenesulfonyl chloride (98-09-9)

aluminum chloride (3495-54-3)

toluene (108-88-3)

hydrogen peroxide (7722-84-1)

Methyl iodide (74-88-4)

Methanesulfonyl chloride (124-63-0)

methyl potassium sulfate (562-54-9)

methyl phenyl sulfone (3112-85-4)

ruthenium tetroxide (20427-56-9)

p-Toluenesulfonyl chloride (98-59-9)

Sodium p-toluenesulfinate

Methyl p-tolyl sulfone,
Sulfone, methyl p-tolyl (3185-99-7)

methyl p-tolyl sulfide (623-13-2)

p-tolylsulfonylacetic acid (3937-96-0)

tetramethylammonium p-toluenesulfinate

cis-bis-(p-tolylsulfonyl)ethene

allyl p-tolyl sulfone (3112-87-6)

sodium p-toluenesulfonyl-acetate