Organic Syntheses

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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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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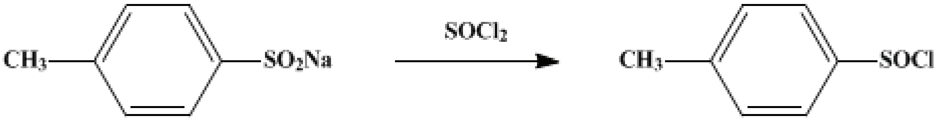
p-TOLUENESULFINYL CHLORIDE



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1. Procedure

Caution! This reaction should be conducted in a hood to avoid exposure to sulfur dioxide and hydrogen chloride.

To 179 g. (109 ml., 1.5 moles) of thionyl chloride (Note 1) contained in a 250-ml. round-bottomed flask, 42.8 g. (0.2 mole) of powdered sodium *p*-toluenesulfinate dihydrate[2] (Note 1) is added in portions at room temperature over a 10- to 15-minute period. A vigorous reaction occurs with the evolution of hydrogen chloride and sulfur dioxide. As the first portions of the sulfinate are added, the temperature of the reaction mixture rises, but it soon drops to approximately 0° as the addition proceeds (Note 2). The resulting reaction mixture, a clear yellow liquid containing a white opaque solid, is protected from atmospheric moisture by means of a calcium chloride drying tube and is set aside at room temperature for 1.5–2 hours. During this time slight effervescence continues (Note 3) and the white opaque suspended material gradually disintegrates to a finely divided translucent deposit.

The excess thionyl chloride is removed by distillation under reduced pressure (15–20 mm.) with the bath temperature below 50°, and the last traces are eliminated by one or two evaporations under reduced pressure after the addition of 50-ml. portions of anhydrous ether (Note 4). The residue consists of a viscous yellow oil containing a suspension of white granular inorganic solid. The crude sulfinyl chloride is readily dissolved by three successive treatments with portions of anhydrous ether (50, 30, and 30 ml., respectively) which are decanted without difficulty from most of the inorganic residue (Note 5). Removal of the solvent by distillation at reduced pressure leaves the sulfinyl chloride as a clear, pale, straw-yellow oil. The yield is 30–32 g. (86–92%) (Note 6). Distillation at reduced pressure (Note 5) yields *p*-toluenesulfinyl chloride as a deep yellow mobile oil, b.p. 113–115°/3.5 mm. or 99–102°/0.5 mm. (Note 7). The yield of redistilled material is 23–26 g. (66–74%). A small quantity (2–3 g.) of a dark tarry residue remains in the distilling flask.

2. Notes

1. Redistilled thionyl chloride is recommended. No difficulties were encountered when the color of the reagent was deep yellow. The sodium *p*-toluenesulfinate dihydrate should be thoroughly air-dried to remove mechanically bound water.
2. When smaller quantities are used the thionyl chloride may be added to the sulfinate in one portion. After an initial rise, the temperature drops to about 0°. With larger quantities this procedure is not practicable.
3. If the sodium *p*-toluenesulfinate is not finely powdered, reaction occurs more slowly with emission of slight crackling sounds.
4. The ether was dried over calcium chloride and finally over phosphorus pentoxide. The checkers found that after the ether evaporations the odor of thionyl chloride was still present. The last traces of thionyl chloride were best removed at a pressure of 1–2 mm. When free of thionyl chloride the residue no longer has the pungent odor of either hydrogen chloride or sulfur dioxide but has a faint odor typical of sulfonyl chlorides.
5. If it is desired to distil the sulfinyl chloride subsequently, any traces of suspended material must be removed by filtration of the ethereal solution through a small filter, preferably into the distilling flask. It

is advantageous to concentrate the ethereal solution to a small volume before filtering since more concentrated solutions of sulfinyl chloride in ether have less tendency to take up moisture from the atmosphere. The filter is rinsed with a little anhydrous ether.

The checkers used an inverted funnel connected to a source of dry nitrogen to provide an inert atmosphere for the filtration. The filtration was carried out as completely as possible directly beneath the inverted funnel through which a rapid stream of nitrogen flowed.

6. The sulfinyl chloride thus obtained is satisfactory for further preparative work. The checkers found that the average yield of crude material after removal of inorganic salts by filtration was about 81%.

7. On being heated, the sulfinyl chloride undergoes transient color changes (green), and the redistilled material may be darker in color than the pale yellow residue obtained after the removal of the ether.

For distillation the checkers employed a Claisen head with a fraction cutter. Approximately 90% of the product distilled at 93–96°/1.1 mm., $n_D^{23.5}$ 1.6004, and 10% distilled at 98–100°/1.3–1.6 mm., $n_D^{23.5}$ 1.5998. The total yield of distilled material in two runs averaged 74%.

3. Discussion

Arylsulfinyl chlorides have been prepared by treating the corresponding arylsulfinic acids with an excess of thionyl chloride in the absence of solvents, either with gentle heating[3,4,5,6,7,8] or at room temperature.[9] The use of nearly equimolecular proportions of the reactants, and of ether as diluent in this reaction, has been claimed[10,11] to yield a cleaner product. *p*-Toluenesulfinyl chloride may be obtained directly from the hydrated sodium salt of *p*-toluenesulfinic acid by the action of a large excess of thionyl chloride, and the present procedure is based on this variation.[12]

References and Notes

1. University of London, London, England.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sulfonyl chlorides

sulfinyl chloride

calcium chloride (10043-52-4)

hydrogen chloride (7647-01-0)

ether (60-29-7)

thionyl chloride (7719-09-7)

sulfur dioxide (7446-09-5)

nitrogen (7727-37-9)

phosphorus pentoxide (1314-56-3)

Sodium p-toluenesulfinate,
sodium salt of p-toluenesulfinic acid

p-Toluenesulfinyl chloride (10439-23-3)

sodium p-toluenesulfinate dihydrate (7257-26-3)