



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.

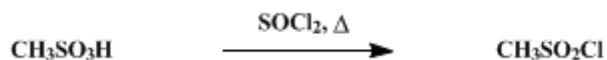
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

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METHANESULFONYL CHLORIDE



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1. Procedure

In a 1-l. three-necked flask fitted with a mechanical stirrer, a reflux condenser, a thermometer, and a separatory funnel (Note 1), and set up in a hood, is placed 152 g. (105 ml., 1.5 moles) of methanesulfonic acid (Note 2). The acid is heated to 95° on a steam bath, and 238 g. (146 ml., 2.0 moles) of thionyl chloride (Note 3) is added over a period of 4 hours. The temperature is kept at 95° throughout the addition and for 3.5 hours after it is completed.

The product is transferred to a modified Claisen flask (Note 4) and distilled under reduced pressure, heat being supplied by an oil bath (Note 5). Most of the thionyl chloride distils at room temperature. The yield of almost colorless product distilling at 64–66°/20 mm. (Note 6) is 122–143 g. (71–83%); n_D^{23} 1.451.

2. Notes

1. The checkers recommend the use of silicone grease on all glass joints.
2. The methanesulfonic acid is a commercial product supplied by the Standard Oil Company of Indiana and reported to be 95% pure and to contain 2% water.
3. Eastman Kodak Company thionyl chloride (b.p. 75–76°) was used without further purification.
4. The checkers used a Claisen head with an attached 10-cm. Vigreux column.
5. A free flame should be avoided, because local superheating causes charring and decomposition. The fumes from the decomposition cause the product (which normally is colorless) to darken. The bath temperature should not exceed 115° at the end of the distillation.
6. The checkers observed a boiling point of 61–62°/18 mm.

3. Discussion

Methanesulfonyl chloride has been prepared by the chlorination of methyl thiocyanate,² S-methylthiourethan,³ sodium methylthiosulfate,⁴ S-methylisothiuronium sulfate⁵ or S-methylisothiuronium *p*-toluenesulfonate,⁶ and dimethyl disulfide in the presence of water;⁷ from sodium methanesulfonate by the action of phosphorus pentachloride,^{8,9} phosphorus oxychloride,⁹ or benzotrichloride;¹⁰ from methanesulfonic acid by the action of phosphorus pentachloride¹¹ or thionyl chloride;¹² or by the reaction of methylmagnesium iodide with sulfuryl chloride.¹³

References and Notes

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6. Klamann and Drahowzal, *Monatsh.*, **83**, 463 (1952).
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 13. Cherbuliez and Schnauder, *Helv. Chim. Acta*, **6**, 256 (1923).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

S-methylisothiuronium sulfate

S-methylisothiuronium p-toluenesulfonate

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

Phosphorus Oxychloride (21295-50-1)

sulfuryl chloride (7791-25-5)

benzotrichloride (98-07-7)

methylmagnesium iodide (917-64-6)

methyl thiocyanate (556-64-9)

Methanesulfonyl chloride (124-63-0)

methanesulfonic acid (75-75-2)

S-methylthiourethan

sodium methylthiosulfate

dimethyl disulfide (624-92-0)

sodium methanesulfonate (2386-57-4)