



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.

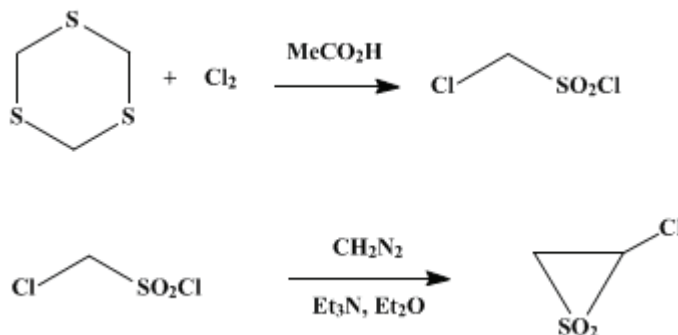
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.231 (1973); Vol. 49, p.18 (1969).

2-CHLOROTHIIRANE 1,1-DIOXIDE

[Thiirane, 2-chloro-, 1,1-dioxide]



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1. Procedure

Caution! Because of the toxic nature of chlorine and diazomethane and the lachrymatory properties of chloromethanesulfonyl chloride, both steps of this preparation should be carried out in a well-ventilated hood. Diazomethane is also explosive; follow the directions for its handling given in earlier volumes.^{2,3}

A. *Chloromethanesulfonyl chloride*. A slurry of 210 g. (1.52 moles) of *s*-trithiane (Note 1) in a mixture of 1 l. of glacial acetic acid and 210 ml. of water is prepared in a 2-l., three-necked, round-bottomed flask equipped with an efficient mechanical stirrer, a thermometer, a coarsely fritted gas inlet tube (Note 2), and an exit tube by which excess fumes are carried to the rear of the hood. The flask is immersed in an ice bath, and the stirrer is started. A stream of chlorine is introduced at such a rate (Note 3) that the temperature of the mixture is maintained between 40° and 50° by the mildly exothermic reaction. After 1–2 hours a yellow solution results. To this solution is added 300 ml. of water, at which point the temperature rises to *ca.* 60°.

Chlorine is again introduced, and the stirred reaction mixture is cooled to maintain the temperature initially in the vicinity of 40°. During 3 hours the temperature slowly returns to that of the surroundings, and the stream of chlorine is stopped. The yellow solution is allowed to stand overnight at room temperature and is then transferred to a 4-l. Erlenmeyer flask and diluted with 1.5 l. of ice water. The flask is stoppered and placed in a refrigerator for 2–3 hours. The aqueous phase is decanted from the denser, organic layer that has separated (Note 4) and is extracted with four 300-ml. portions of methylene chloride. The methylene chloride extracts are combined with the original organic layer, dried over anhydrous magnesium sulfate, filtered, and evaporated on a rotary evaporator at 20–30°. The material that remains is distilled through a 15-cm. Vigreux column. Chloromethanesulfonyl chloride is collected as a colorless, lachrymatory liquid, b.p. 80–81° (25 mm.), *n*²⁰_D 1.4840–1.4850; yield 135–220 g. (20–32%) (Note 5).

B. *2-Chlorothiirane 1,1-dioxide*. In a 500-ml., three-necked, round-bottomed flask fitted with an efficient mechanical stirrer, a thermometer, and two pressure-equalizing addition funnels is placed an ethereal solution of 4.6 g. (0.11 mole) of diazomethane (Note 6). The system is blanketed with nitrogen, the stirrer is started, and the solution is cooled to –10° with an ice-methanol bath. A solution of 14.9 g. (0.100 mole) of chloromethanesulfonyl chloride in 40 ml. of ether and a solution of 10.0 g. (0.099 mole) of triethylamine in 40 ml. of ether are simultaneously added dropwise from the two addition funnels. The addition requires about 45 minutes. The insoluble triethylamine hydrochloride is separated by

filtration and washed with 25 ml. of cold ether. The combined filtrate and washings are evaporated at reduced pressure below 25° to give white crystalline 2-chlorothiirane 1,1-dioxide, m.p. 49–51° (Note 7); yield 10.0–10.5 g. (80–84%). The product may be further purified by recrystallization from ether-hexane at –70°; m.p. 53–54° (8.9 g. after two recrystallizations) (Note 8) and (Note 9).

2. Notes

1. *s*-Trithiane obtained from Eastman Organic Chemicals was used without further purification.
2. The gas inlet tube must be sufficiently long to allow the chlorine to enter near the bottom of the flask, and sufficiently coarse to prevent the pores from becoming clogged by the suspended *s*-trithiane. A 6-mm. glass tube with a slightly constricted orifice has been found to be equally satisfactory.
3. The rate of addition of chlorine appears to be important. With rates adequate to maintain the temperature between 40° and 50°, addition times of 1–2 hours are required.
4. This separation is most conveniently achieved by first decanting as much water as possible from the 4-l. Erlenmeyer flask. The remaining mixture is then placed in a 4-l. separatory funnel, and the lower layer is collected. The separatory funnel is then used in the ensuing extractions.
5. The yield is based on the assumption that 3 molecules of chloromethanesulfonyl chloride arise from each molecule of *s*-trithiane. The checkers obtained a yellow product which had to be redistilled to provide material with the reported refractive index.
6. The ethereal diazomethane is prepared by the method of Arndt.⁴ The checkers employed undistilled material as described in (Note 3) of the preparation cited.
7. Use of undistilled diazomethane solution gives a less pure product, m.p. 38–42°, which can be recrystallized as described.
8. The characteristic infrared maxima of 2-chlorothiirane 1,1-dioxide (Nujol) occur at 3.24, 7.53, and 8.56 μ . Its n.m.r. spectrum (CDCl₃) shows a doublet of doublets at δ 3.17 ($J = 9.5$ and 5.5 Hz), a triplet at δ 3.75 ($J = 9.5$ Hz), and a doublet of doublets at δ 4.85 ($J = 9.5$ and 5.5 Hz).
9. A characteristic property of thiirane 1,1-dioxides is the ease with which such molecules fragment into sulfur dioxide and the related olefin on standing for several hours at room temperature. The title compound is no exception; however, the rate of decomposition may be reduced substantially by storage under an inert atmosphere in a freezing compartment (*ca.* –5°). Under such conditions the product may be kept for many months.

3. Discussion

2-Halothiirane 1,1-dioxides are known to be intermediates in the Ramberg-Bäcklund rearrangement of α,α -dihalo sulfones.^{5,6,7,8} These three-membered cyclic sulfones are not isolable from such reactions, however, because they are not stable under the conditions of the rearrangement and they undergo further transformations. The present procedure represents the only means presently available for the preparation of halogen-substituted thiirane dioxides.^{5,6,9} The addition of halosulfenes to diazoalkanes is a convenient and general synthesis which may be extended to the preparation of a variety of thiirane 1,1-dioxides with relative ease.¹⁰

References and Notes

1. Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.
2. T. J. de Boer and H. J. Backer, *Org. Syntheses*, Coll. Vol. 4, 250 (1963).
3. J. A. Moore and D. W. Reed, *this volume*, p. 351.
4. F. Arndt, *Org. Syntheses*, Coll. Vol. 2, 165 (1943).
5. L. A. Paquette and L. S. Wittenbrook, *Chem. Commun.*, 471 (1966).
6. L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *J. Am. Chem. Soc.*, **89**, 4487 (1967).
7. L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4089 (1964).
8. L. A. Carpino and L. V. McAdams, III, *J. Am. Chem. Soc.*, **87**, 5804 (1965).
9. L. A. Carpino and R. H. Rynbrandt, *J. Am. Chem. Soc.*, **88**, 5682 (1966).
10. G. Opitz and K. Fischer, *Z. Naturforsch.*, **186**, 775 (1963); *Angew. Chem.*, **77**, 41 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 70 (1965); N. Fischer and G. Opitz, *Org. Syntheses*, **48**, 106 (1968).

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

acetic acid (64-19-7)

ether (60-29-7)

sulfur dioxide (7446-09-5)

nitrogen (7727-37-9)

chlorine (7782-50-5)

Triethylamine hydrochloride (554-68-7)

methylene chloride (75-09-2)

magnesium sulfate (7487-88-9)

Diazomethane (334-88-3)

hexane (110-54-3)

triethylamine (121-44-8)

2-Chlorothiirane 1,1-dioxide,
Thiirane, 2-chloro-, 1,1-dioxide (10038-13-8)

chloromethanesulfonyl chloride (3518-65-8)

s-trithiane (291-21-4)