



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.

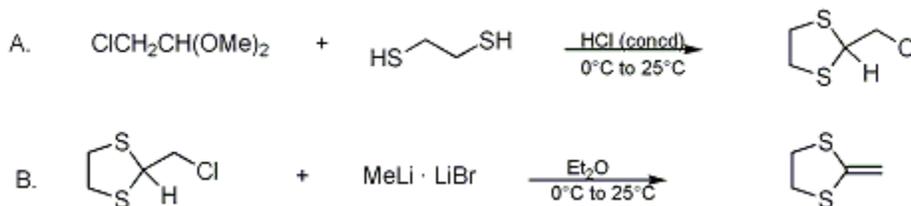
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 9, p.585 (1998); Vol. 71, p.175 (1993).

2-METHYLENE-1,3-DITHIOLANE

[1,3-Dithiolane, 2-methylene-]



Submitted by Karl R. Dahnke and Leo A. Paquette¹.

Checked by M. Amornmarn, A. Focella, and David L. Coffen.

1. Procedure

A. *2-Chloromethyl-1,3-dithiolane*. A 500-mL, three-necked, round-bottomed flask equipped with a dropping funnel and magnetic stirrer is charged with 59.5 mL (0.71 mol) of *1,2-ethanedithiol* (Note 1) and 50 mL of concd *hydrochloric acid*. This mixture is cooled to 0°C and 89 mL (0.78 mol) of *chloroacetaldehyde dimethyl acetal* (Note 2) is added via the dropping funnel over 2 hr (Note 3). After an additional 30 min, the ice bath is removed and the reaction mixture is stirred for 3 hr at room temperature. The resulting two-phase mixture is partitioned between *dichloromethane* (100 mL) and water (100 mL). The organic phase is separated and the aqueous phase is extracted with *dichloromethane* (100 mL). The combined organic layers are washed with water (100 mL), saturated *sodium bicarbonate* solution (100 mL), and brine (100 mL), then dried over *magnesium sulfate*. After removal of the solvent under reduced pressure, the viscous, colored residue (111 g) is subjected to bulb-to-bulb distillation using 500-mL and 250-mL collector bulbs and a 500-mL flask to hold the crude product. The oven temperature is initially 20°C and is gradually increased to 120°C. Pressure is maintained at 0.25 mm. Initially *only* the bulb remote from the oven is cooled, using an acetone/dry ice bath. Solvent and volatile impurities are collected in this bulb. The product is then condensed in the bulb nearest the oven by placing a dry ice/acetone bath under this bulb after the higher boiling material begins to distill. The clear colorless oil thus obtained consists of fairly pure *2-chloromethyl-1,3-dithiolane* (59.3–65.0 g, 54–59%) (Note 4), (Note 5) and (Note 6).

B. *2-Methylene-1,3-dithiolane*. A 1-L, three-necked, round-bottomed flask equipped with a pressure-equalizing dropping funnel, thermometer, magnetic stirrer, and nitrogen inlet is charged with 33.0 g (0.213 mol) of *2-chloromethyl-1,3-dithiolane* and *diethyl ether* (400 mL) (Note 7). After the flask is flushed with *nitrogen*, the solution is cooled to 0°C. *Methylolithium-lithium bromide* complex in *diethyl ether* (156 mL of 1.5 M solution, 0.235 mol) (Note 8) is transferred into the dropping funnel via cannula and added dropwise over 2 hr. After an additional 30 min, the ice bath is removed and the mixture is allowed to warm gradually to room temperature. After 2 hr at room temperature when *methane* evolution has ceased, the mixture is recooled to 0°C and quenched by dropwise addition of 50 mL of saturated *ammonium chloride* solution followed by sufficient water to just dissolve the salts. The organic layer is separated, washed with water (3 × 100 mL), saturated *sodium bicarbonate* solution (100 mL), and brine (100 mL), then dried over *magnesium sulfate*. The solvent is removed under reduced pressure and the residue is distilled through a short-path distillation apparatus (34–40°C at 1.0 mm) (Note 9) to give 20.6–21.6 g (82–86%) of *2-methylene-1,3-dithiolane* as a light yellow oil (Note 10).

2. Notes

- 1,2-Ethanedithiol* was purchased from the Aldrich Chemical Company, Inc., and used without further purification.
- Chloroacetaldehyde dimethyl acetal* was obtained from the Elanco Company and used as received.
- The addition was performed sufficiently slowly to maintain a temperature of 5–10°C.

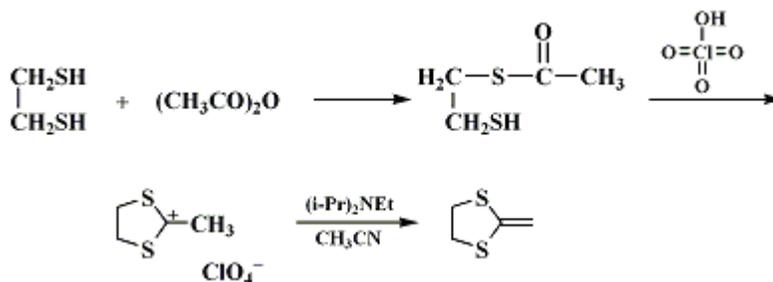
- During the thioketalization and distillation, thermal extrusion of HCl and isomerization to [2,3-dihydro-1,4-dithiin](#) is observed² and the product of Step A typically contains ca. 10% of this impurity.
- Storage of this material in a freezer is recommended.
- Spectral characteristics are as follows: IR (CHCl₃) cm⁻¹: 3000, 2910, 1430, 1260; ¹H NMR (300 MHz, CDCl₃) δ: 3.22 (s, 4 H), 3.61 (d, 2 H, J = 7.2), 4.63 (t, 1 H, J = 7.2); ¹³C NMR (CDCl₃) δ: 38.36, 49.64, 54.23. Peaks arising from the 1,4-dithiin impurity appear at 3.18 and 6.08 ppm in the ¹H NMR.
- [Ether](#) was distilled from sodium-benzophenone ketyl before use.
- [Methylithium-lithium bromide](#) complex was purchased from the Aldrich Chemical Company, Inc., and was titrated prior to use.
- The receiver was cooled to -78°C and a small amount of [triethylamine](#) was added to the cold solution to stabilize the product against acid-catalyzed polymerization. As an added precaution, all glassware was base-washed prior to use.
- Spectral characteristics are as follows: IR (CHCl₃) cm⁻¹: 3000, 2930, 1675, 1575, 1525, 1425, 1285; ¹H NMR (300 MHz, CDCl₃) δ: 3.37 (s, 4 H), 5.13 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ: 38.47, 99.60, 144.50. Peaks attributable to the 1,4-dithiin impurity carried through from Step A also appear in the ¹H NMR spectrum.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

Despite the latent reactivity of ketene thioacetals,^{3,4} some members of this class such as the title compound have been little studied, perhaps because of preparative inaccessibility. The only previously reported route to [2-methylene-1,3-dithiolane](#) involves monoacetylation of [1,2-ethanedithiol](#), cyclization to [2-methyl-1,3-dithiolan-2-yl perchlorate](#), and exposure of this salt to [diisopropylethylamine](#) in [acetonitrile](#):⁵



The process requires vast amounts of solvent, proceeds in low yield, and is plagued by the need to isolate and handle a potentially explosive intermediate.

Herein is described a much simpler dehydrohalogenation alternative that had been earlier applied successfully to the preparation of ketene acetals^{6,7} and 2-alkylidene-1,3-dithianes.⁸ This route appears not to have been examined for preparing the title compound because of an early report that 2-lithio-1,3-dithiolanes undergo ready fragmentative elimination to form [ethylene](#) and [dithiocarbonate](#) unlike their stable [1,3-dithiane](#) homologues.⁸ In point of fact, the loss of chloride ion from lithiated [2-chloromethyl-1,3-dithiolane](#) is the kinetically-favored elimination reaction. Use of the present two-step procedure makes possible the safe, direct acquisition of [2-methylene-1,3-dithiolane](#) in unlimited quantities.

One of the uses of this reactive intermediate is illustrated on [page 396](#).⁹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 9, 396](#)

References and Notes

1. Department of Chemistry, The Ohio State University, Columbus, OH 43210.
 2. Russell, G. A.; Law, W. C.; Zaleta, M. *J. Am. Chem. Soc.* **1985**, *107*, 4175.
 3. Kolb M. In "The Chemistry of Ketenes, Allenes, and Related Compounds", Part 2, Patai, S., Ed.; John Wiley and Sons: New York, 1980; Chapter 16.
 4. Gröbel, B.-T.; Seebach, D. *Synthesis* **1977**, 357.
 5. Okuyama, T. *Tetrahedron Lett.* **1982**, *23*, 2665; Okuyama, T.; Fujiwara, W.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 453.
 6. Taskinen, E.; Pentikäinen, M.-L. *Tetrahedron* **1978**, *34*, 2365.
 7. Aben, R. W. M.; Scheeren, J. W. *Tetrahedron Lett.* **1988**, *29*, 3597; Aben, R. W. M.; Scheeren, J. *W. Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 399.
 8. Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231.
 9. Dahnke, K. R.; Paquette, L. A. *Org. Synth., Coll. Vol. IX* **1998**, 396.
-

Appendix

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

brine

sodium-benzophenone ketyl

2-lithio-1,3-dithiolanes

hydrochloric acid (7647-01-0)

ether,
diethyl ether (60-29-7)

ammonium chloride (12125-02-9)

acetonitrile (75-05-8)

sodium bicarbonate (144-55-8)

nitrogen (7727-37-9)

methane (7782-42-5)

ethylene (9002-88-4)

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

triethylamine (121-44-8)

1,2-ethanedithiol (540-63-6)

1,3-Dithiane (505-23-7)

diisopropylethylamine (7087-68-5)

Methylithium-lithium bromide (332360-06-2)

2-Methylene-1,3-dithiolane,
1,3-Dithiolane, 2-methylene- (26728-22-3)

2-Chloromethyl-1,3-dithiolane (86147-22-0)

chloroacetaldehyde dimethyl acetal (97-97-2)

2,3-dihydro-1,4-dithiin

2-methyl-1,3-dithiolan-2-yl perchlorate

dithiocarbonate