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.

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.

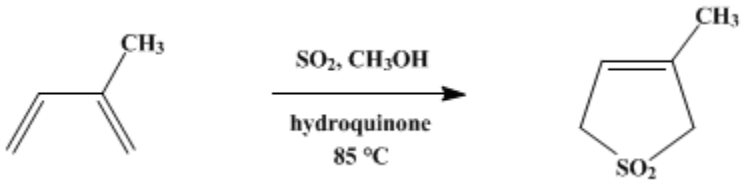
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

DOI:10.15227/orgsyn.029.0059

*Organic Syntheses, Coll. Vol. 3, p.499 (1955); Vol. 29, p.59 (1949).*

# ISOPRENE CYCLIC SULFONE

## [Thiophene, 2,5-dihydro-3-methyl-, 1-dioxide]




Submitted by Robert L. Frank and Raymond P. Seven[1].
Checked by A. E. Barkdoll and R. S. Schreiber.

## 1. Procedure

*Caution! If peroxides are present in the isoprene, they should be destroyed by washing with 10% acidified ferrous ammonium sulfate before distillation.*

A 600-ml. steel reaction vessel (Note 1) is precooled before loading by filling it between one-fourth and one-half full of methanol and Dry Ice. After removal of the methanol and Dry Ice, the autoclave is charged with 120 g. (176 ml., 1.76 moles) of isoprene (Note 2), 113 g. (80 ml., 1.76 moles) of liquid sulfur dioxide, 88 ml. of methanol, and 4 g. of hydroquinone. The vessel is sealed, heated slowly to 85°, and maintained at that temperature for 4 hours. It is then cooled, the sulfone removed, the bomb rinsed with methanol, and the combined product and washings are treated hot with 5 g. of Norite. The filtered solution is concentrated to a volume of 250–300 ml., and the sulfone is allowed to crystallize. The material is filtered and washed with 50 ml. of cold methanol. Recrystallization from methanol (20 ml. per 25 g. of sulfone) yields 140–150 g. of thick, colorless plates. Concentration of the mother liquors raises the total yield to 182–191 g. (78–82%) (Note 3), melting at 63.5–64° (Note 4).

## 2. Notes

1. A steel reaction vessel of the type used for high-pressure catalytic hydrogenations is satisfactory. The pressure generated is less than 200 lb. For smaller quantities a heavy glass tube can also be used with proper precautions.
2. Commercial isoprene, obtained from Phillips Petroleum Company, should be freshly distilled before use, in order to eliminate isoprene dimers and polymers which are likely to accumulate in storage. If peroxides are present, they should be destroyed before distillation of the isoprene by washing with 10% acidified ferrous ammonium sulfate. As an added precaution, the distillation flask should not be permitted to go dry.
3. The yield of the cyclic sulfone depends upon the purity of isoprene. In one experiment, the checkers obtained the sulfone in 86% yield, using freshly distilled isoprene of 99 mole per cent purity, while the yield fell to 77% with commercial isoprene which had been distilled and stored at 5° for 1 week before use.
4. The checkers consistently obtained a slightly higher melting point (uncor.) in the range 64.4–65.4°. The purified cyclic sulfone serves as an ideal intermediate for the preparation of extremely pure isoprene, since isoprene can be regenerated nearly quantitatively at 135–140°[2] Other sulfones that can be prepared by this method and that are useful in the purification of dienes are those of butadiene, m.p. 65.5°,[3] and 2,3-dimethylbutadiene, m.p. 135°[3] The sulfone of piperylene is a liquid.[4]

## 3. Discussion

Isoprene cyclic sulfone has been prepared only from isoprene and sulfur dioxide.[2,3,5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 454

## References and Notes


1. Work done under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.
2. Frank, Adams, Blegen, Deanin, and Smith, *Ind. Eng. Chem.*, **39**, 887 (1947).
3. Staudinger and Ritzenthaler, *Ber.*, **68**, 455 (1935).
4. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943); Frank, Emmick, and Johnson, *J. Am. Chem. Soc.*, 69, 2313 (1947).
5. Eigenberger, *J. prakt. Chem.*, (2) **127**, 307 (1930).


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

Isoprene cyclic sulfone

sulfone of piperylene

methanol (67-56-1)

hydroquinone (123-31-9)

sulfur dioxide (7446-09-5)

Norite (7782-42-5)

butadiene (106-99-0)

ferrous ammonium sulfate (10045-89-3)

2,3-Dimethylbutadiene (513-81-5)

ISOPRENE (78-79-5)

Thiophene, 2,5-dihydro-3-methyl-, 1-dioxide (1193-10-8)