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.

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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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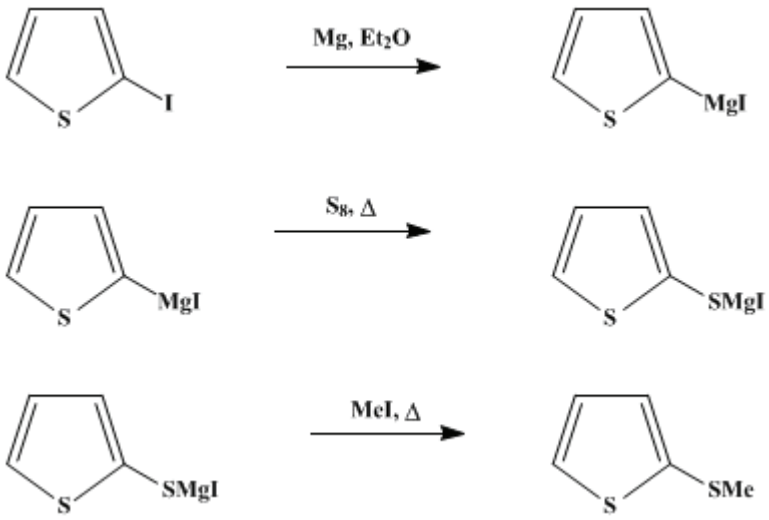
METHYL 2-THIENYL SULFIDE

[Thiophene, 2-(methylthio)-]



Submitted by J. Cymerman-Craig and J. W. Loder[1].
Checked by Charles C. Price and E. A. Dudley.

1. Procedure

In a 1-l. three-necked flask fitted with a liquid-sealed mechanical stirrer, a reflux condenser, and a dropping funnel are placed 8 g. (0.33 g. atom) of magnesium turnings and 600 ml. of absolute ether. There is placed in the dropping funnel 70 g. (0.33 mole) of 2-iodothiophene (p.545), the stirrer is started, and about 10 ml. of the iodothiophene is added. The reaction generally begins within a few minutes (Note 1), and the iodothiophene is then added dropwise at such a rate that moderate refluxing occurs. When the addition is complete, the mixture is refluxed gently until only a small residue of unreacted magnesium remains. The solution is then cooled in an ice bath, the dropping funnel is removed, and 10.7 g. (0.33 g. atom) of finely powdered sulfur (Note 2) is added (Note 3), the funnel is replaced, and the mixture is refluxed (Note 4) for 45 minutes. The solution is again cooled in an ice bath, and 22.6 ml. (0.36 mole) of methyl iodide is added dropwise from the funnel, and the stirring is then discontinued (Note 5). The reaction mixture is refluxed 10 hours. It is then cooled, and an aqueous solution of ammonium chloride is run in with vigorous stirring (Note 6). The liquid is transferred to a separatory funnel, the lower aqueous layer is run off, and the ethereal solution is washed three times with a 2% solution of potassium hydroxide, then with water, and finally is dried over anhydrous sodium sulfate. The ether is removed by distillation at ordinary pressure, and the residual dark liquid is distilled under reduced pressure. The yield of colorless methyl 2-thienyl sulfide is 23–26 g. (53–60%), b.p. 82–86°/22 mm., n_D^{25} 1.5978 (Note 7) and (Note 8).

2. Notes

1. If the reaction does not start, it may be assisted by the addition of a small amount of methylmagnesium iodide in ethereal solution.
2. The sulfur was distilled and then ground in a mortar before use.
3. The mechanical stirring is continued. The sulfur dissolves during the refluxing period to give a clear yellow solution. A sludge which adheres to the bottom of the flask may form, but the yield is unaltered.
4. On reheating, a vigorous reaction with the sulfur occurs. A means of cooling the reaction flask should be at hand to ensure control of the reaction.
5. The solution may be left overnight at this stage, sealed under nitrogen.
6. The decomposition of the unreacted Grignard reagent is best carried out in a hood to remove the

strong odor of thiols.
7. Considerable decomposition occurs if distillation is attempted at atmospheric pressure. The product is sometimes pale yellow, and darkens slightly on standing.
8. A dark oil remains which decomposes at this pressure when strongly heated.

3. Discussion

Methyl 2-thienyl sulfide has been prepared by the action of phosphorus trisulfide on dimethyl succinate[2] and by the action of methyl iodide on the sodium salt of 2-thiophenethiol,[3] both of which methods are of little preparative value. The procedure described above is that of Cymerman-Craig and Loder.[4] 2-Bromothiophene has been used in the latter method in place of the iodine derivative.[5]

References and Notes

1. University of Sydney, Sydney, Australia.
2. Steinkopf and Leonhardt, *Ann.*, **495**, 166 (1932).
3. Meyer and Neure, *Ber.*, **20**, 1756 (1887).
4. Cymerman-Craig and Loder, *J. Chem. Soc.*, **1954**, 237.
5. Gol'dfarb, Kalik, and Kirmalova, *Zhur. Obshchei Khim.*, **29**, 2034 (1959) [*C. A.*, **54**, 8775 (1960)].

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

phosphorus trisulfide

ether (60-29-7)

ammonium chloride (12125-02-9)

magnesium,
magnesium turnings (7439-95-4)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

sulfur (7704-34-9)

iodine (7553-56-2)

potassium hydroxide (1310-58-3)

Methyl iodide (74-88-4)

methylmagnesium iodide (917-64-6)

2-IODOTHIOPHENE,
iodothiophene (3437-95-4)

Methyl 2-thienyl sulfide,
Thiophene, 2-(methylthio)- (5780-36-9)

dimethyl succinate (106-65-0)

2-Bromothiophene (1003-09-4)

sodium salt of 2-thiophenethiol