



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.

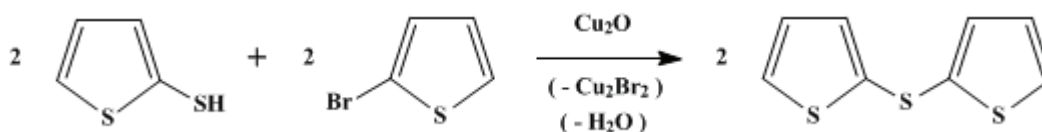
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.558 (1988); Vol. 50, p.75 (1970).

2,2'-DITHIENYL SULFIDE

[Thiophene, 2,2'-thiobis-]



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1. Procedure

Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

A three necked, 250-ml. flask fitted with a reflux condenser stirrer and a thermometer pocket with a nitrogen inlet is charged with 100 ml. of *N,N*-dimethylformamide, 5.6 g. (0.10 mole) of potassium hydroxide (Note 1), and 7.15 g. (0.0500 mole) of freshly precipitated copper(I) oxide² (Note 2). 2-Bromothiophene (16.4 g., 0.101 mole) (Note 3) is added, and the apparatus is flushed with nitrogen (Note 4). 2-Thiophenethiol³ [11.6 g., 0.100 mole; *Org. Synth., Coll. Vol. 6*, 979 (1988)] is then added slowly through the condenser; an exothermic reaction begins, and the temperature may rise to 50–60°. The flask is heated in an oil bath at 130–140° for 16 hours (Note 5). The mixture is cooled to room temperature before the contents of the flask are poured into 100 ml. of 6 *N* hydrochloric acid in ice. The mixture is stirred vigorously for 2 hours (Note 6); the oily black paste obtained is removed by filtration and thoroughly extracted in a Soxhlet extractor with benzene until a colorless extract is obtained. The filtrate is also extracted with two 100-ml. portions of benzene. These extracts are combined, washed with water until neutral, and dried over anhydrous sodium sulfate. Removal of the solvent gives a yellow-colored oil which, on vacuum distillation, yields 11.5–12.5 g. (58–63%) of 2,2'-dithienyl sulfide as a pale yellow oil, b.p. 75–78° (0.06 mm.) n_D^{25} 1.6643.

2. Notes

1. The presence of an equivalent of potassium or sodium hydroxide is necessary to promote the substitution reaction of the 2-bromothiophene with copper(I) oxide.
2. Freshly precipitated copper(I) oxide was dried at 110° before use. Commercial grades were found to give lower yields (*ca.* 35–40%) of the desired sulfide. The checkers dried copper(I) oxide in a vacuum oven at 100° for 6 hours.
3. 2-Bromothiophene was supplied by Columbia Organic Chemicals, Inc. 2-Chloro- or 2-iodothiophenes may be used; however, the former gives poorer yields of the sulfide.
4. Nitrogen is passed through the system to provide an inert atmosphere, preventing possible oxidation of the 2-thiophenethiol to the corresponding disulfide.
5. Reaction is sluggish at temperatures below 130°.
6. Vigorous stirring helps to break up the thick sludge formed on addition of the reaction mixture to the acid and also removes soluble inorganic salts.

3. Discussion

The submitters have also prepared 2,2'-dithienyl sulfide in 34% yield by condensation of 2-thiophenethiol with 2-bromothiophene in the presence of copper(I) oxide in a quinoline-pyridine mixture.⁴ Challenger and Harrison⁵ have obtained 2,2'-dithienyl sulfide in 50–55% yield by treatment of 2-thienylmagnesium bromide with excess sulfur. This sulfide may also be obtained in 20% yield by

condensation of [thiophene](#) with [sulfur monochloride](#), followed by pyrolysis of the resultant disulfide.⁶

This synthetic process offers a route to the preparation of the isomeric dithienyl sulfides⁷ (2,3- and 3,3-) which cannot be prepared readily by any of the standard methods. Thus, condensation of [2-thiophenethiol](#) with [3-bromothiophene](#) or [3-thiophenethiol](#) with [2-bromothiophene](#) gives 2,3'-dithienyl sulfide in 63.0 and 73.5% yields, respectively. Similarly, 3,3'-dithienyl sulfide is obtained in 48% yield. The method has also been extended to the synthesis of the isomeric *bis*-(thienylthio)thiophenes in 40–50% yield.⁴

This method may also be used for the preparation in high yields of other aromatic sulfides.⁸

References and Notes

1. Work done at the former Arthur D. Little Research Institute, Inveresk, Midlothian, Scotland.
 2. A. King, "Inorganic Preparations," rev. ed., Geo. Allen and Unwin, London, 1950, p. 40.
 3. W. H. Houff and R. D. Schuetz, *J. Am. Chem. Soc.*, **75**, 6316 (1953).
 4. E. Jones and I. M. Moodie, unpublished observations.
 5. F. Challenger and J. B. Harrison, *J. Inst. Pet.*, **21**, 135 (1935).
 6. E. Koft, U.S. Pat. 2,571,370 (1951).
 7. E. Jones and I. M. Moodie, *Tetrahedron*, **21**, 2413 (1965).
 8. R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1108 (1964).
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Appendix

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

2,2'-DITHIENYL SULFIDE

potassium or sodium hydroxide

2-Chloro- or 2-iodothiophenes

quinoline-pyridine

2,3'-dithienyl sulfide

3,3'-dithienyl sulfide

[hydrochloric acid](#) (7647-01-0)

[Benzene](#) (71-43-2)

[sodium sulfate](#) (7757-82-6)

[nitrogen](#) (7727-37-9)

[sulfur](#) (7704-34-9)

[copper\(I\) oxide](#)

potassium hydroxide (1310-58-3)

sulfur monochloride

Thiophene (110-02-1)

N,N-dimethylformamide (68-12-2)

2-thiophenethiol (7774-74-5)

2-Bromothiophene (1003-09-4)

2-thienylmagnesium bromide

3-Bromothiophene (872-31-1)

3-thiophenethiol

Thiophene, 2,2'-thiobis- (3988-99-6)