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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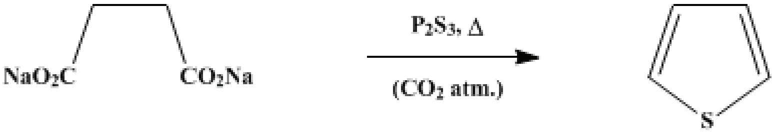
THIOPHENE



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1. Procedure

In a 3-l. round-bottomed flask is placed an intimate mixture of 486 g. (3 moles) of finely powdered anhydrous sodium succinate (Note 1) and 648 g. (4.1 moles) of finely ground phosphorus trisulfide (Note 2). The flask is fitted to a 100-cm. (40-in.) condenser set for distillation (Note 3), and a tube for introduction of carbon dioxide is extended through the stopper to the center of the flask. The condenser is connected to a 2-l. flask cooled in an ice-salt mixture. The uncondensed gases are bubbled through two 2-l. flasks connected in series with the receiving flask; each flask is cooled by an ice-salt mixture and contains 1 kg. of cracked ice and 200 cc. of 40 per cent sodium hydroxide solution.

The reaction flask is thoroughly swept out with carbon dioxide (Note 4) while the flask is rotated to remove any air that is trapped by the solid. The flask is then connected to the condenser, and a slow stream of carbon dioxide is passed through the system while the mixture is heated moderately for thirty minutes with a low Bunsen flame (Note 5), and then with the full force of the Bunsen burner until no more yellow vapors are produced (about thirty minutes). Carbon dioxide is passed through more rapidly during the latter heating period to ensure complete removal of the thiophene (Note 6). The contents of the receiver and the two absorption flasks are combined and steam-distilled from a 5-l. flask until no more oily drops are formed in the distillate. The thiophene layer in the distillate is separated, dried successively over solid sodium hydroxide and sodium, and fractionated. The yield of product boiling at 83–86° is 63–75 g. (25–30 per cent of the theoretical amount) (Note 7) and (Note 8).

2. Notes

1. The sodium succinate, prepared from succinic acid, was dried in shallow pans on a water bath for several days.
2. If phosphorus trisulfide is not obtainable, it may be prepared by the following method developed by A. M. Griswold: An intimate mixture of the calculated amounts of finely powdered sulfur and red phosphorus is placed in an earthenware flower pot, sealed at the bottom with a cork. The pot is imbedded in a bucket of sand, and a heavily weighted cover is held in readiness over the top. A lighted match is dropped into the mixture, the lid is quickly put in place, and the crevices are sealed with sand. The reaction should be carried on out-of-doors as it is extremely vigorous and often gives an excellent display of fireworks. When thoroughly cool, the flower pot is broken and the contents are removed and kept in a tightly stoppered bottle. It is desirable to keep this material for some time before grinding, as the freshly prepared product is not completely crystallized and is difficult to grind.
3. Because of the rapid evolution of a large volume of gas, the tube connecting the flask to the condenser should be about 2 cm. in diameter and all stoppers should fit tightly.
4. If the air is not completely removed before heating the flask, the reaction may take place with explosive violence.
5. The checkers found that continual heating was necessary during this part of the preparation.
6. The stopper should not be removed from the reaction flask until the flask is quite cool, in order to prevent ignition of the excess phosphorus trisulfide on contact with the air. The hard mass remaining may be softened by treatment with hot water, after which it may be broken up and shaken out.
7. The freshly prepared product often deposits a small amount of a brown precipitate on standing for some time. If this is removed by filtration, no further precipitate is formed.
8. Larger runs have been made successfully, but there is greater danger of a violent reaction.

3. Discussion

Thiophene is found in small amounts in coal gas and benzene.[1] It has been prepared by passing ethylene or acetylene into boiling sulfur;[2] by passing ethyl sulfide through a hot tube;[3] by passing ethylene or illuminating gas over hot pyrites;[4] by heating succinic anhydride with phosphorus pentasulfide;[5] by treatment of erythritol with phosphorus pentasulfide;[6] by treatment of succinic aldehyde with phosphorus trisulfide;[7] by passing acetylene over pyrites at 300°;[8] by treatment of sodium succinate with phosphorus trisulfide;[9] by passing acetylene and hydrogen sulfide over bauxite at 320°, or over nickel hydroxide at 300°;[10] and by passing furan and hydrogen sulfide over heated alumina.[11]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 8
- Org. Syn. Coll. Vol. 2, 357
- Org. Syn. Coll. Vol. 2, 466
- Org. Syn. Coll. Vol. 2, 520
- Org. Syn. Coll. Vol. 4, 671

References and Notes

1. Meyer, Ber. **16**, 1471 (1883); **17**, 2642 (1884).
2. Meyer and Sandmeyer, ibid. **16**, 2176 (1883).
3. Kekulé, ibid. **18**, 217 (1885).
4. Nahnsen, ibid. **18**, 217 (1885).
5. Volhard and Erdmann, ibid. **18**, 454 (1885).
6. Paal and Tafel, ibid. **18**, 689 (1885).
7. Harris, ibid. **34**, 1496 (1901).
8. Steinkopf and Kirchoff, Ann. **403**, 5 (1914); Ger. pat. 252,375 [C. A. **7**, 538 (1913)]; Steinkopf, Chem. Ztg. **35**, 1098 (1911).
9. Volhard and Erdmann, Ber. **18**, 454 (1885); Friedburg, J. Am. Chem. Soc. **12**, 85 (1890).
10. Stuer and Grob, U. S. pat. 1,421,743 [C. A. **16**, 3093 (1922)].
11. Yur'ev, Ber. **69**, 440 (1936).

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

red phosphorus

alumina

phosphorus trisulfide

bauxite

acetylene (74-86-2)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

hydrogen sulfide (7783-06-4)

sulfur (7704-34-9)

carbon dioxide (124-38-9)

Succinic acid (110-15-6)

sodium (13966-32-0)

ethylene (9002-88-4)

Furan (110-00-9)

Thiophene (110-02-1)

Succinic anhydride (108-30-5)

sodium succinate (150-90-3)

phosphorus pentasulfide

ethyl sulfide (352-93-2)

erythritol

succinic aldehyde (638-87-9)

nickel hydroxide (12054-48-7)