



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.

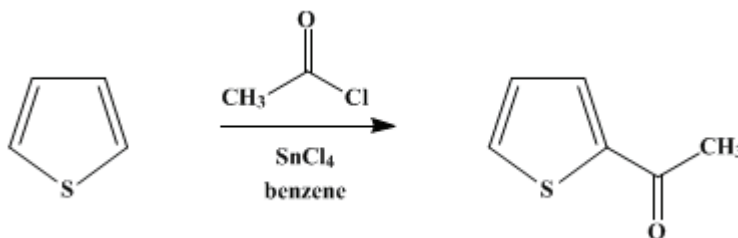
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 2, p.8 (1943); Vol. 18, p.1 (1938).

2-ACETOTHIENONE

[Ketone, methyl 2-thienyl]



Submitted by John R. Johnson and G. E. May.

Checked by Reynold C. Fuson and E. A. Cleveland.

1. Procedure

In a 500-cc. round-bottomed, three-necked flask provided with a thermometer, dropping funnel, a liquid-sealed stirrer, and calcium chloride tube are placed 16.8 g. (0.2 mole) of **thiophene** (p. 578), 15.6 g. (14 cc., 0.2 mole) of **acetyl chloride**, and 200 cc. of dry **benzene**. The solution is cooled to 0°, and 52 g. (23 cc., 0.2 mole) of freshly distilled **stannic chloride** is added dropwise, with efficient stirring, during the course of about forty minutes. The reaction mixture assumes a purple color when the first drops of **stannic chloride** are added, and soon a purple solid precipitates.

After all the **stannic chloride** has been added, the cooling bath is removed and the mixture stirred for one hour longer. The addition product is hydrolyzed by the slow addition of a mixture of 90 cc. of water and 10 cc. of concentrated **hydrochloric acid**. The yellow **benzene** layer is separated, washed with 25 cc. of water, and dried over 5–10 g. of anhydrous **calcium chloride**. **Benzene** and unchanged **thiophene** (Note 1) are distilled through a short fractionating column (using an oil bath), and the residual liquid is distilled under reduced pressure. The yield of **2-acetothiophene**, b.p. 89–91°/9 mm., is 20–21 g. (79–83 per cent of the theoretical amount) (Note 2).

2. Notes

1. By shaking the recovered benzene-thiophene mixture with a solution of 5.5 g. of **mercuric chloride**, 10 g. of **sodium acetate**, and 10 cc. of **alcohol** in 80 cc. of water, the unchanged **thiophene** is converted to the **2-chloromercurithiophene** (containing a small amount of the dimercurichloride); from this the free **thiophene** can be obtained by treatment with **hydrochloric acid**. The recovered **thiophene** amounts to 2–2.5 g.
2. **2-Acetothiophene** has the following physical constants: d_4^{20} 1.168, n_D^{20} 1.566. Its semicarbazone melts at 186–187° (corr.).

3. Discussion

2-Acetothiophene has been prepared by treating **thiophene** with **acetyl chloride** in the presence of **aluminum chloride**¹ or **stannic chloride**,² and by treating **2-chloromercurithiophene** with **acetyl chloride**.³ The present method is essentially that of Stadnikoff and Goldfarb.² **Stannic chloride** is superior to **aluminum chloride** as a catalyst for this reaction as **aluminum chloride** induces polymerization of the **thiophene**.

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 3, 14*

References and Notes

1. Peter, Ber. **17**, 2643 (1884); Biedermann, *ibid.* **19**, 636 (1886).
 2. Stadnikoff and Goldfarb, *ibid.* **61**, 2341 (1928).
 3. Volhard, Ann. **267**, 178 (1892); Steinkopf and Baumeister, *ibid.* **403**, 69 (1914).
-

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

benzene-thiophene

dimercurichloride

alcohol (64-17-5)

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium acetate (127-09-3)

acetyl chloride (75-36-5)

aluminum chloride (3495-54-3)

mercuric chloride (7487-94-7)

Ketone, methyl 2-thienyl (88-15-3)

Thiophene (110-02-1)

stannic chloride (7646-78-8)

2-chloromercurithiophene

2-Acethienone (88-15-3)