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.

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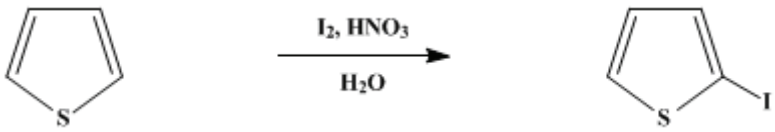
Organic Syntheses, Coll. Vol. 4, p.545 (1963); Vol. 30, p.53 (1950).

2-IODOTHIOPHENE

[Thiophene, 2-iodo-]



Submitted by Henry Y. Lew and C. R. Noller[1].
Checked by Cliff S. Hamilton and Frank A. Bower.

1. Procedure

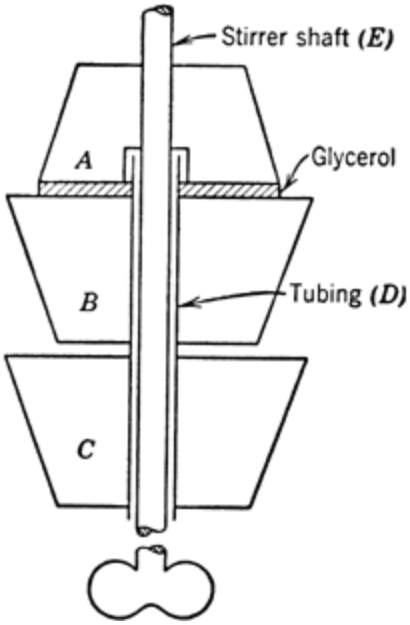
In a 200-ml. three-necked flask fitted with a mechanical stirrer (Note 1), a reflux condenser, and a separatory funnel, and set up in a hood, are placed 38 g. (0.15 mole) of iodine and 42 g. (39 ml., 0.50 mole) of thiophene (Note 2). A solution of 28 ml. (0.44 mole) of nitric acid (sp. gr. 1.42) diluted with an equal volume of water is placed in the separatory funnel, from which approximately one-fourth of the nitric acid is added slowly and with vigorous stirring. Slight heating may be necessary to start the reaction, but once initiated it proceeds vigorously with the evolution of brown oxides of nitrogen. Cooling with an ice bath may be necessary to control the reaction. After the evolution of gases has subsided, the remaining nitric acid is added dropwise, and the reaction proceeds smoothly at room temperature with continual evolution of oxides of nitrogen. After all the nitric acid has been added, the solution is heated under reflux on a water bath for 30 minutes.

The reaction mixture is allowed to stand, and the red organic layer is separated, mixed with 40 ml. of 10% sodium hydroxide solution, and steam-distilled (Note 3). The yellow oil is separated, dried over anhydrous calcium chloride, and distilled at reduced pressure from a modified Claisen flask. The yield is 43–45 g. (68–72%); b.p. 89–93°/36 mm.; n_D^{25} 1.6465.

2. Notes

1. The seal for the mechanical stirrer used (Fig. 10) is made from two one-hole rubber stoppers and a piece of glass tubing with glycerin as a seal and lubricant. According to the submitters, it is better than a mercury seal, not only for reactions where halogens, halogen acids, or compounds that react with mercury are present, but also for practically any other reaction since the handling of mercury always requires a considerable amount of care.
The glass tubing *D*, about 10 cm. in length, is just large enough in diameter to permit the stirrer *E* to rotate freely. The smaller of the two one-hole rubber stoppers, *A*, is bored to a depth of about 7 mm. with a cork-borer whose diameter is approximately 3 mm. larger than that of tubing *D*, and then this section is cut out with a pair of scissors. Rubber stopper *B* is 10–15 mm. larger in diameter than *A*. When assembled, tubing *D* fits tightly in rubber stopper *B*, and protrudes out at the top about 4 mm., and rubber stopper *A* fits tightly about stirrer *E* and rests on top of rubber stopper *B*. Glycerol is used as a seal and as a lubricant between the contact surfaces of rubber stoppers *A* and *B*, and the portion of tubing *D* protruding out of rubber stopper *B* acts as a wall in preventing glycerol from flowing down inside the tubing. When the stirrer motor is on, rubber stopper *A* rotates with stirrer *E*. Rubber stopper *C* fits tightly over tubing *D* and in the mouth of the reaction flask.

Fig. 10. Seal for a mechanical stirrer made from rubber stoppers and glass tubing using glycerol as a seal and lubricant.



2. When the preparation is carried out in larger quantities, evolution of heat accompanies the mixing of iodine and thiophene, and unless the mixture is stirred well, it will solidify into a hard mass. By keeping the quantities reasonably small, this tendency to solidify is reduced to a minimum.
3. Toward the end of the distillation a small amount (0.5–2.0 g.) of 2-iodo-5-nitrothiophene is collected in the condenser and the receiver. The amount formed increases with increase in the temperature of the reaction mixture.

3. Discussion

2-Iodothiophene has been prepared by the action of iodine and mercuric oxide on thiophene.[2] The present method has been published.[3]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 427
- Org. Syn. Coll. Vol. 4, 667

References and Notes

1. Stanford University, Stanford, California.
2. Meyer and Kreis, *Ber.*, **17**, 1558 (1884); Thyssen, *J. prakt. Chem.*, [2] **65**, 5 (1902); *Org. Syntheses Coll. Vol.* **2**, 357 (1943).
3. Lew and Noller, *J. Am. Chem. Soc.*, **72**, 5715 (1950).

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

calcium chloride (10043-52-4)

sodium hydroxide (1310-73-2)

glycerol,
glycerin (56-81-5)

nitric acid (7697-37-2)

nitrogen (7727-37-9)

mercury (7439-97-6)

mercuric oxide (21908-53-2)

iodine (7553-56-2)

Thiophene (110-02-1)

2-IODOTHIOPHENE,
Thiophene, 2-iodo- (3437-95-4)

2-iodo-5-nitrothiophene