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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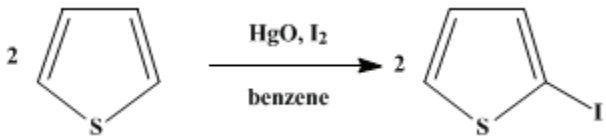
Organic Syntheses, Coll. Vol. 2, p.357 (1943); Vol. 12, p.44 (1932).

2-IODOTHIOPHENE

[Thiophene, 2-iodo-]



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1. Procedure

In a glass-stoppered, wide-mouthed bottle cooled by ice water are placed 35 g. (0.42 mole) of thiophene (p. 578) and 50 cc. of benzene (Note 1). With constant shaking (Note 2), and cooling when necessary, 75 g. (0.35 mole) of yellow mercuric oxide and 109 g. (0.43 mole) of iodine are added alternately in small amounts during a period of fifteen to twenty minutes. The yellow mercuric oxide changes to crimson mercuric iodide. The mixture is filtered, and the residue is washed with three 25-cc. portions of ether. The ether-benzene filtrate is shaken with a dilute solution of sodium thiosulfate to remove excess iodine and then dried over 5 g. of calcium chloride and filtered. The ether and benzene are removed by distillation on a steam bath (Note 3), and the residue is fractionally distilled under reduced pressure. 2-Iodothiophene distils at 73°/15 mm.; 80–81°/20 mm.; 90–94°/34–38 mm. (Note 4). The yield is 63–66 g. (72–75 per cent of the theoretical amount) (Note 5). If the iodothiophene is still colored by traces of iodine, the color may be removed by shaking with a small amount of mercuric oxide.

2. Notes

1. Ligroin (b.p. 100–120°) may be substituted for benzene.
2. Better yields are obtained when the mixture is vigorously shaken by hand than when mechanical stirring is used. The ordinary stirrer will not keep the mercuric oxide in suspension.
3. Unreacted thiophene can be recovered from the ether-benzene distillate by treating the latter with mercuric oxide and dilute acetic acid, collecting the white precipitate [$C_4H_2S(HgOCOCH_3)HgOH$] on a Büchner funnel, and decomposing it with concentrated hydrochloric acid.[1] In checking this preparation there was not enough unreacted thiophene to be recovered.
4. A small amount of 2,5-diiodothiophene is formed in the reaction. About 4 g. of crystalline diiodothiophene, m.p. 40–41°, can be isolated from the residue remaining after distillation of the 2-iodothiophene (b.p. 65.5–66.5°/9 mm.). (O. Ivan Lee, private communication.)
5. 2-Iodothiophene reacts with magnesium to form a Grignard reagent and is hence useful in the preparation of other thiophene derivatives.

3. Discussion

2-Iodothiophene has been prepared only by the action of iodine and mercuric oxide on thiophene.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 545

References and Notes

1. Dimroth, Ber. **32**, 759 (1899).

2. Meyer and Kreis, ibid. **17**, 1558 (1884); Thyssen, J. prakt. Chem. (2) **65**, 5 (1902).

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

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

magnesium (7439-95-4)

sodium thiosulfate (7772-98-7)

mercuric oxide (21908-53-2)

iodine (7553-56-2)

mercuric iodide (7774-29-0)

Thiophene (110-02-1)

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

2,5-diiodothiophene (625-88-7)

diiodothiophene