



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.

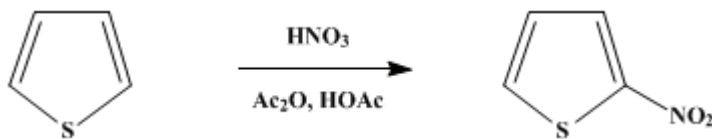
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.466 (1943); Vol. 14, p.76 (1934).

2-NITROTHIOPHENE

[Thiophene, 2-nitro-]



Submitted by V. S. Babasinian

Checked by Roger Adams and A. E. Knauf.

1. Procedure

Eighty-four grams (1 mole) of [thiophene](#) (p. 578) is dissolved in 340 cc. of [acetic anhydride](#), and 80 g. (1.2 moles) of fuming [nitric acid](#) (sp. gr. 1.51) is dissolved in 600 cc. of glacial [acetic acid](#) ([Note 1](#)). Each solution is divided into two equal parts. One-half of the [nitric acid](#) solution is introduced into a 2-l. three-necked, round-bottomed flask, provided with a thermometer, a motor stirrer, and a separatory funnel. The mixture is cooled to 10°. Then with moderate stirring one-half of the [thiophene](#) solution is introduced, drop by drop, and at such a rate as to prevent the heating of the reaction mixture above room temperature. A rapid rise of temperature will occur during the addition of the first fraction of the [thiophene](#) solution. In cool weather the temperature is controlled by dipping the nitrating flask into a bath of cold tap water. Cooling to a very low temperature is not necessary, but it is important to avoid superheating the reaction mixture ([Note 2](#)). After the addition of the first half of the [thiophene](#), the temperature of the reaction mixture is reduced to 10° and the remainder of the [nitric acid](#) solution is rapidly introduced into the flask. Nitration is continued by the gradual addition of [thiophene](#). Throughout the nitration the solution should show a permanent light brown color. The appearance of a pink or dark red color indicates oxidation. The product is allowed to remain at room temperature for two hours. It is then treated with an equal weight of finely crushed ice with rapid shaking. [Mononitrothiophene](#) separates in pale yellow crystals. More crystals form if the mixture is allowed to remain in the ice chest for twenty-four hours or longer. The solid is filtered ([Note 3](#)) on a Büchner funnel or a Jena glass filter plate at a low temperature, washed thoroughly with ice water, pressed, and dried in a brown desiccator or in the absence of light ([Note 4](#)).

The filtrate and the washings contain in solution a small quantity of the product. This is recovered by distillation with steam. The acid distillate consists of snow-white crystals (if it is protected from light) and a solution of the compound. The solid is removed by filtration and washed. The filtrate is made neutral with [sodium carbonate](#) and extracted with [ether](#). Upon drying and evaporating, the ethereal layer yields [mononitrothiophene](#) contaminated with [dinitrothiophene](#) ([Note 5](#)).

The total yield is 90–110 g. (70–85 per cent of the theoretical amount) of a product which melts at 44–45°. If this material is steam-distilled and then repeatedly crystallized from petroleum ether (b.p. 20–40°) it is obtained as colorless crystals melting at 45.5° ([Note 6](#)) and ([Note 7](#)).

2. Notes

1. The two acids should be mixed gradually, the [nitric acid](#) being added to the acetic with shaking. Cooling is often necessary.
2. Success will depend largely upon the proper control of temperature. No trouble may be anticipated if the reaction mixture responds readily to the cooling effect of a cold water bath.
3. [Mononitrothiophene](#) is an active poison.¹ The accidental contact of an ethereal solution with the skin has produced painful blisters. In case of accident the compound should be removed from the exposed surface by washing with alcohol.
4. Earlier workers² have noted that the compound is sensitive toward light.
5. The yellow color of the [nitrothiophene](#) is due to the presence of traces of [dinitrothiophene](#) and other

impurities.

In order to detect the presence of [dinitrothiophene](#), a few crystals of the solid are dissolved in [alcohol](#) and treated with a drop of a weak solution of alcoholic [potassium hydroxide](#). A pink or deep red color will develop at once. An excess of [potassium hydroxide](#) will destroy the color.³

6. Meyer and Stadler² state that [nitrothiophene](#) distils without decomposition at 224–225°.

7. [Mononitrothiophene](#) has been crystallized from [ether](#), alcohol, [benzene](#), and other solvents. As a rule these solvents fail to yield a snow-white product. It has been found in this work that petroleum ether (b.p. 20–40°) possesses decided advantages in that by prolonged refluxing it extracts [mononitrothiophene](#) but does not readily dissolve the impurities. With petroleum ether, snow-white crystals have been obtained in needles 10 to 20 cm. in length.

3. Discussion

[Nitrothiophene](#) has been obtained along with [dinitrothiophene](#) by drawing a vigorous stream of air charged with [thiophene](#) through red fuming [nitric acid](#).² It has also been prepared by nitrating [thiophene](#) between 0° and 5° with a mixture of [acetic anhydride](#) and fuming [nitric acid](#).⁴

References and Notes

1. Meyer, Ber. **18**, 1772 (1885).
 2. Meyer and Stadler, *ibid.* **17**, 2648 (1884).
 3. Meyer and Stadler, *ibid.* **17**, 2780 (1884).
 4. Steinkopf and Lützkendorf, Ann. **403**, 27 (1914); Ger. pat. 255,394 [Frdl. **11**, 144 (1912-14)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

petroleum ether

[alcohol](#) (64-17-5)

[acetic acid](#) (64-19-7)

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

[ether](#) (60-29-7)

[acetic anhydride](#) (108-24-7)

[nitric acid](#) (7697-37-2)

[sodium carbonate](#) (497-19-8)

[potassium hydroxide](#) (1310-58-3)

[Thiophene](#) (110-02-1)

[2-Nitrothiophene](#),
[Thiophene, 2-nitro-](#),

Mononitrothiophene,
nitrothiophene (609-40-5)

dinitrothiophene

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