



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.

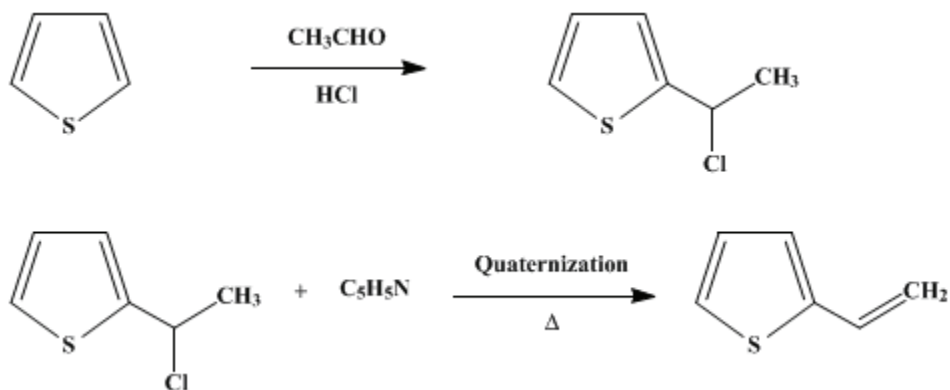
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.980 (1963); Vol. 38, p.86 (1958).

2-VINYLTHIOPHENE

[Thiophene, 2-vinyl-]



Submitted by W. S. Emerson and T. M. Patrick, Jr.¹
 Checked by Max Tishler, P. Tishler, and F. W. Bollinger.

1. Procedure

A 2-l. three-necked flask is fitted with a thermometer, a stirrer, a gas inlet tube which will reach beneath the surface of the liquid, and a vent. The flask is placed in a bath of acetone to which Dry Ice can be added. To the flask are charged 336 g. (318 ml., 4.0 moles) of thiophene (Note 1), 176 g. (177 ml., 1.33 moles) of paraldehyde, and 300 ml. of concentrated hydrochloric acid. While this mixture is stirred and maintained at 10–13° (Note 2) by means of Dry Ice, gaseous hydrogen chloride is bubbled in. At the end of 25 minutes the solution is saturated (Note 3).

The contents of the flask are poured onto 300 g. of ice, the layers are separated, and the organic portion is washed three times with 200-ml. portions of ice water (Note 4). The organic layer is added, with some cooling (Note 5), to 316 g. (322 ml., 4.0 moles) of pyridine and 2.0 g. of α -nitroso- β -naphthol in a 1-l. distilling flask. The aqueous layer is extracted with two 100-ml. portions of ether, and the combined ethereal extract is used to wash each aqueous wash in turn (Note 6). The ethereal layer is concentrated on the steam bath under a stream of nitrogen and combined with the organic mixture in the distilling flask. The mixture is allowed to stand for 1.5 hours before distillation. The distillation is performed under reduced nitrogen pressure. The distillate is collected over 1.0 g. of α -nitroso- β -naphthol in an ice-cooled receiver at successively lower pressures ending at 125°/50 mm. (Note 7). The distillate is poured onto a mixture of 400 g. of ice and 400 ml. of concentrated hydrochloric acid. The layers are separated, and the organic portion is washed successively with 100-ml. portions of 1% hydrochloric acid, water, and 2% ammonia.

The organic layer is filtered through 1 cm. of anhydrous magnesium sulfate on a sintered-glass funnel into a 500-ml. distilling flask. The aqueous layer is extracted with two 100-ml. portions of ether which are combined and used to extract the aqueous washes. The ethereal layer is washed with 50 ml. of saturated salt solution and filtered through the same funnel into a fresh suction flask. The funnel is finally washed with two 50-ml. portions of ether. The ethereal washes are concentrated on a steam bath under nitrogen (Note 8) and combined with the filtrate in the distilling flask. The filtrate is fractionally distilled under nitrogen through a 2-cm. column, 35 cm. high, packed with 6-mm. glass helices (Note 9). The column is jacketed and provided with a heater inside the jacket to minimize heat losses during distillation. The receiver is cooled in an ice bath, and the distillate is collected in three fractions, thiophene 45.6–27.9 g., b.p. 36°/150 mm.–35°/100 mm. (Note 10), intermediate 11.8–4.8 g., b.p. 35°/100 mm.–80°/98 mm., and 2-vinylthiophene (Note 11) and (Note 12) 191.3–224.0 g., b.p. 65–67°/50 mm., n_D^{25} 1.5701, lit.² b.p. 65.5–66.5°/48 mm., lit.³ n_D^{25} 1.4698. The yield is 50–55% of the theoretical amount based on the thiophene consumed. The undistilled residue amounts to about 27 g.

and the distillate in the Dry Ice-acetone trap to about 4 g.

2. Notes

1. Specific gravities at 25° were used to determine the volumes of reagents. Eastman Kodak Company [thiophene](#), b.p. 83–85°, n_D^{25} 1.5252, and U.S.P. [paraldehyde](#) were used.
2. The submitters used an ice-salt bath, but the checkers found a Dry Ice-acetone bath more convenient and almost indispensable. Temperature control is important. Small deviations from the prescribed range result in a lower yield.
3. When the solution is saturated, copious fumes of [hydrogen chloride](#) are evolved from the vent. The reaction should not be continued beyond this point. With an ice-salt bath the time required for addition of [hydrogen chloride](#) was 35 minutes.
4. The yield will be much lower if the washing process is not carried out quickly.
5. If the mixture is too cold, the quaternization reaction will be delayed. On the other hand, if no cooling is provided, the reaction mixture may boil over spontaneously because of the exothermic nature of the reaction. Heat cracks the quaternary compound to [2-vinylthiophene](#) which, if not removed by distillation, may undergo thermal polymerization.
6. Omission of this ethereal extraction will reduce the quoted yield by about 2 per cent.
7. At this temperature and pressure volatilization of [pyridine hydrochloride](#) occurs. Passage of vapors during the distillation through a Dry Ice-acetone trap yields 8.8 g. of [thiophene](#) contaminated with its original odoriferous impurities and 2.2 g. of an aqueous layer, both of which were discarded.
8. Omission of this ethereal extraction will reduce the quoted yield by about 6 per cent.
9. A packed column is essential to achieve the degree of fractionation required.
10. The distillation is conducted so as to keep the pot temperature below 90° until about 90% of the product has been distilled. This is done to minimize thermal polymerization of the product.
11. If the intermediate and product fractions are not to be used immediately, [α-nitroso-β-naphthol](#) is added as a stabilizer.
12. [5-Chloro-2-vinylthiophene](#) and [5-bromo-2-vinylthiophene](#) have been prepared in 47% and 35% yields, respectively, by essentially the same procedure.

3. Discussion

[2-Vinylthiophene](#) has been prepared by the dehydration of [α-\(2-thienyl\)ethanol](#)^{3,4,5,6,7} or [β-\(2-thienyl\)ethanol](#);⁸ by the condensation of [vinyl chloride](#) with [2-thienylmagnesium bromide](#) in the presence of [cobaltous chloride](#);⁹ by the dehydrochlorination of [α-\(2-thienyl\)ethyl chloride](#);¹⁰ and by the dehydrogenation of [2-ethylthiophene](#).¹¹

References and Notes

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Appendix

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

hydrogen chloride,
hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

nitrogen (7727-37-9)

acetone (67-64-1)

pyridine (110-86-1)

α -nitroso- β -naphthol (131-91-9)

Thiophene (110-02-1)

magnesium sulfate (7487-88-9)

pyridine hydrochloride (628-13-7)

vinyl chloride (9002-86-2)

cobaltous chloride

2-thienylmagnesium bromide

2-Vinylthiophene,
Thiophene, 2-vinyl- (1918-82-7)

5-Chloro-2-vinylthiophene

5-bromo-2-vinylthiophene

α -(2-thienyl)ethanol

β -(2-thienyl)ethanol (5402-55-1)

α -(2-thienyl)ethyl chloride

2-ethylthiophene (872-55-9)

paraldehyde (123-53-7)