



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.

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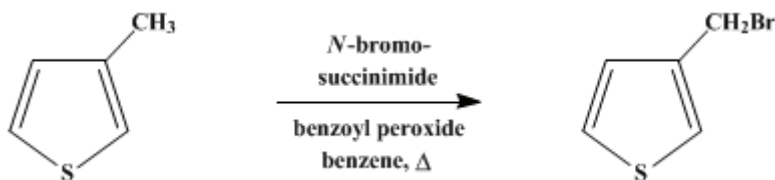
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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3-THENYL BROMIDE

[Thiophene, 3-bromomethyl-]



Submitted by E. Campaigne and B. F. Tullar¹.

Checked by Charles C. Price and E. A. Dudley.

1. Procedure

Caution! This preparation should be run in a well-ventilated hood.

A 5-l. three-necked flask (Note 1) is fitted with a stirrer, an efficient reflux condenser, and a wide-mouthed funnel with a 15-cm. water-cooled stem (Note 2). A solution of 220 g. (2.24 moles) of 3-methylthiophene (Note 3) and 4 g. of benzoyl peroxide in 700 ml. of dry benzene is brought to vigorous reflux in this flask, and a mixture of 356 g. (2 moles) of N-bromosuccinimide (Note 4) and 4 g. of benzoyl peroxide is added portionwise through the wide-mouthed funnel. The dry powder is added as rapidly as the violent foaming will permit (Note 5) and is worked down through the stem of the funnel with a stirring rod. Refluxing benzene washes the lower part of the funnel continuously. The total addition requires about 20 minutes. As soon as the foaming from the last addition of N-bromosuccinimide has subsided, the flask is cooled, first with a water bath and then an ice bath. The succinimide is filtered off and washed once with dry benzene.

The filtrate is immediately transferred to a distilling flask, and the benzene is removed at reduced pressure (Note 6). The residue is distilled at 1 mm., and the fraction boiling between 75° and 78° is collected (Note 7). The major portion boils at 76° and has n_D^{25} 1.6030. This procedure yields 250–280 g. (71–79%) of a water-white product, which remains colorless for several days when stored over calcium carbonate in a refrigerator (Note 8).

2. Notes

1. The large volume of the flask is desirable to control foaming.
2. The checkers used a short, large-bore condenser.
3. Commercial 3-methylthiophene, formerly available from Socony-Vacuum Oil Company, was used. 3-Methylthiophene is now available from Winthrop-Stearns, Inc., Special Chemicals Division, New York 18, N. Y.
4. N-Bromosuccinimide can be prepared in an active state by two slight modifications of the Ziegler procedure.² A slight molar excess of sodium hydroxide is used, and the reaction mixture is stirred vigorously while the bromine, dissolved in an equal volume of carbon tetrachloride, is added rapidly. This produces a finely crystalline white product which is ready for use as soon as it is filtered from the water and carbon tetrachloride and thoroughly dried. The yields are generally improved by this procedure, and the N-bromosuccinimide is ready to use sooner than the product described by Ziegler et al.² Acetic acid is an excellent solvent for crystallization of crude N-bromosuccinimide.
5. Unless the reaction mixture is maintained at strong reflux during this addition, considerable nuclear bromination occurs with a corresponding decrease in 3-thenyl bromide yield.
6. If necessary to interrupt the procedure, the benzene solution of 3-thenyl bromide may be stored over calcium carbonate and distilled directly from the carbonate later. The addition of a little calcium carbonate before distillation avoids the formation of a difficultly removable tarry residue.

7. *Caution! This distillation should be carried out behind a safety shield.* Thenyl bromide is a powerful lachrymator, and some individuals may develop extensive irritation of the skin upon exposure to its vapors. The checkers observed boiling points of 78–82°/2 mm. and 80–85°/3 mm.

8. The product contains a trace of 2-bromo-3-methylthiophene, but no 2-bromo-3-thenyl bromide, and is sufficiently pure for most purposes. Samples of 3-thenyl bromide have sometimes exploded without warning, leaving deposits of black resinous material. However, storage over calcium carbonate slows this acid-catalyzed reaction. The addition of a small amount of a tertiary amine likewise increases the stability.

3. Discussion

The only method of preparative interest is that described by Campaigne and LeSuer,³ upon which the present method is based. This method has been applied by Dittmer and others.⁴

References and Notes

1. Indiana University, Bloomington, Indiana.
 2. Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Ann.*, **551**, 80 (1942).
 3. Campaigne and LeSuer, *J. Am. Chem. Soc.*, **70**, 1555 (1948); Campaigne and LeSuer (to Indiana University Foundation), U. S. pat. 2,543,544 [*C. A.*, **45**, 7601 (1951)].
 4. Dittmer, Martin, Herz, and Cristol, *J. Am. Chem. Soc.*, **71**, 1201 (1949); Shapira, Shapira, and Dittmer, *J. Am. Chem. Soc.*, **75**, 3655 (1953).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

acetic acid (64-19-7)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

calcium carbonate (471-34-1)

benzoyl peroxide (94-36-0)

N-bromosuccinimide (128-08-5)

3-Methylthiophene (616-44-4)

3-Thenyl bromide

Thiophene, 3-bromomethyl- (34846-44-1)

Thenyl bromide

2-bromo-3-methylthiophene (14282-76-9)

2-bromo-3-thenyl bromide

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