



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.

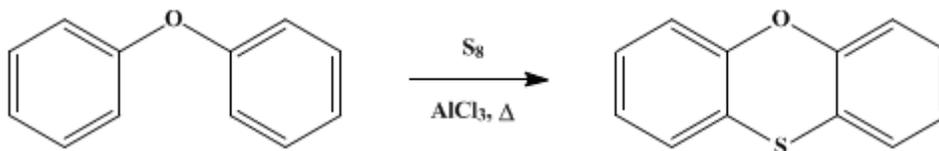
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.485 (1943); Vol. 18, p.64 (1938).

PHENOXTHIN

[Phenoxathiin]



Submitted by C. M. Suter and Charles E. Maxwell.
Checked by Reynold C. Fuson and E. A. Cleveland.

1. Procedure

In a 5-l. flask are placed 1886 g. (11 moles) of [phenyl ether](#) (Note 1), 256 g. (8 gram atoms) of [sulfur](#) (flowers), and 510 g. (3.8 moles) of anhydrous [aluminum chloride](#). The reactants are mixed well by shaking the flask vigorously; the mixture becomes purple. The flask is fitted with a water-cooled reflux condenser (Note 2) and heated on the steam bath in an efficient hood. The evolution of [hydrogen sulfide](#), vigorous at first, becomes slow after one and one-half hours. After the heating has been continued for a total of four hours, with occasional shaking, the reaction mixture is poured slowly, with stirring, into a 4-l. beaker half filled with ice to which 250 cc. of concentrated [hydrochloric acid](#) has been added. More ice is added if necessary. The flask is rinsed with water and the rinsings added to the main product. After the two layers are separated the water layer is discarded and the phenyl ether-phenoxthin layer dried overnight with [calcium chloride](#). This mixture is then distilled at 5 mm. pressure from a 3-l. special Claisen flask having a well-lagged 18-in. column. After removal of the [phenyl ether](#) the fraction boiling at 140–160°/5 mm., practically all of which comes over at 150–152°, is collected as phenoxthin (Note 3). The yield is 700 g. (87 per cent of the theoretical amount). This material, which is somewhat colored and has a strong odor, is purified by crystallization from 1.2–1.5 l. of boiling [methyl alcohol](#); the solution should be chilled rapidly and stirred well to prevent the product from separating as an oil. The loss on crystallization is about 3 per cent and the dried material melts at 56–57° (Note 4). A second crystallization gives a product melting about one degree higher.

2. Notes

1. The commercial "[diphenyl oxide](#)" is satisfactory.
2. The condenser returns to the flask a small amount of [phenyl ether](#), which would otherwise be carried away by the [hydrogen sulfide](#).
3. The fore-run of [phenyl ether](#), b.p. 98–101°/5 mm., may be used in subsequent runs. Other boiling points are: [phenyl ether](#), 134–137°/15 mm., 259–262°/745 mm.; and phenoxthin, 180–183°/15 mm., 311°/745 mm. Fractionation at 15 mm. gives a lower yield with a larger amount of tarry residue remaining in the flask than fractionation at 5 mm.
4. A pure sample melts at 57.5–58°.

3. Discussion

Phenoxthin has been obtained by a series of reactions utilizing [thiocatechol](#) and [3,5-dinitro-4-chlorobenzoic acid](#)¹ as the starting materials, from phenoxtellurin and [sulfur](#),² and by the action of [sulfur](#) and [aluminum chloride](#) upon [phenyl ether](#).³

References and Notes

1. Mauthner, Ber. **39**, 1340 (1906).
2. Drew, J. Chem. Soc. **1928**, 519.

3. Ferrario, Bull. soc. chim. (4) **9**, 536 (1911); Ackermann, Ger. pat. 234,743 [Frđl. **10**, 153 (1910-12)]; Suter, McKenzie, and Maxwell, J. Am. Chem. Soc. **58**, 717 (1936); Bennett, Lesslie, and Turner, J. Chem. Soc. **1937**, 444; Suter and Green, J. Am. Chem. Soc. **59**, 2578 (1937).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

Phenoxthin

phenyl ether-phenoxthin

phenoxtellurin

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

methyl alcohol (67-56-1)

hydrogen sulfide (7783-06-4)

sulfur (7704-34-9)

aluminum chloride (3495-54-3)

phenyl ether,
diphenyl oxide (101-84-8)

Phenoxathiin (262-20-4)

thiocatechol (1121-24-0)

3,5-dinitro-4-chlorobenzoic acid (118-97-8)