



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.

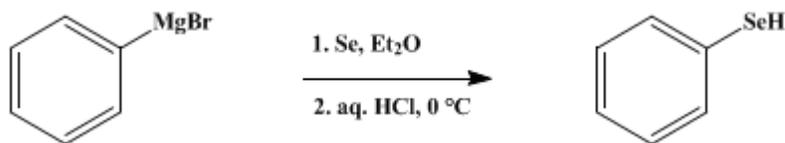
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.771 (1955); Vol. 24, p.89 (1944).

SELENOPHENOL

[Benzeneselenol]



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Checked by C. F. H. Allen and H. W. J. Cressman.

1. Procedure

Most selenium compounds are toxic, and many have a vile odor. It is frequently advisable to work with them on alternate days. All manipulations should be done in a good hood. Rubber gloves should be worn, and it is well to keep the window of the hood down so that the glass is between the apparatus and the face of the operator.

Hydrogen selenide, a possible by-product, is very toxic, being comparable with hydrogen cyanide. Its accidental inhalation in small amounts may produce a sore throat.

A 500-ml. three-necked round-bottomed flask is fitted with an efficient reflux condenser, a glycerol-sealed mechanical stirrer, a dropping funnel, and a gas inlet tube extending nearly to the blades of the stirrer (Note 1). An absorption train,¹ with the addition in *J* of a safety tube which extends nearly to the bottom, is connected to the upper end of the reflux condenser (Note 2). A 2-cm. layer of water in *J* allows it to serve as a bubble counter; *K* is one-third filled with a 50% potassium hydroxide solution. The entire apparatus is set up in subdued light in a hood and swept with dry hydrogen (Note 3) and (Note 4). Phenylmagnesium bromide is prepared in the flask by the usual procedure² from 78.5 g. (0.5 mole) of bromobenzene, 12 g. (0.5 gram atom) of magnesium, and 500 ml. of dry ether. The dropping funnel is then replaced by an addition flask (p. 550) which contains 38 g. (0.48 gram atom) of dry powdered black selenium (Note 5). The solution is warmed sufficiently to bring about gentle refluxing, and the selenium is then added gradually over a period of 30 minutes at such a rate as to maintain gentle refluxing without heating. Stirring is continued for an additional 30 minutes (Note 6).

The contents of the flask are then poured upon 600 g. of cracked ice, and, with hand stirring, 75 ml. of hydrochloric acid (sp. gr. 1.18) is added. The cold mixture is now filtered through glass wool in an ordinary funnel into a 2-l. separatory funnel. The aqueous layer is separated and extracted once with 250 ml. of ether (Note 7). The combined extract and main product are dried over 30 g. of calcium chloride, the ether is removed on a steam bath, and the residue is distilled using a 500-ml. modified Claisen flask. The selenophenol is collected at 57–59°/8 mm. or 84–86°/25 mm.; the yield is 43–54 g. (57–71%) (Note 6) and (Note 9) through (Note 14). The product should be sealed at once in a glass vial (Note 8).

2. Notes

1. Dry hydrogen or dry nitrogen may be used. The gas must be oxygen-free. Hydrogen tends to decrease the amount of oxidation to diselenide.

2. The submitter used a simpler train consisting of two small widemouthed bottles in series closed by stoppers bearing the necessary inlet and outlet tubes constructed of 10-mm. or larger glass tubing. In each flask was a shallow layer of 50% potassium hydroxide solution; the outlet tube of the first bottle extended nearly to the surface of the solution and dipped below the surface of the solution in the second bottle.

3. Most selenium compounds are affected by sunlight, and many by any bright light. It is often essential to use amber glassware or to wrap the flasks in light-proof paper.
4. Selenium compounds which contain an -SeH group are easily oxidizable in the air to diselenides. It is advantageous to replace the air by an inert gas, and to work as rapidly as possible.
5. The selenium is dried overnight in a vacuum desiccator over concentrated sulfuric acid.
6. The higher yields of selenophenol are favored by exclusion of air, rapid stirring, and not too rapid addition of selenium.
7. An alternative procedure is to extract the selenophenol by sodium hydroxide solution, and subsequently to acidify and extract the liberated substance. The yield of selenophenol is not improved by employing such a procedure, but it may be of value with some compounds.
8. The selenophenol is water-white but rapidly turns yellow in contact with the air.
9. The residue in the still (or alkali-insoluble material in the ether layer if Note 6 has been employed) contains diphenyl selenide (b.p. 167°/16 mm.) and diphenyl diselenide (m.p. 63°). It can be separated by a combination of distillation and crystallization from ethanol, but the amounts are small, and, unless the residues from several runs are combined, the procedure is not economical.
10. This is a general reaction. It can be used for preparing other selenophenols whenever the desired Grignard reagent can be obtained. The submitter has made the three selenocresols, *p*-bromophenylselenophenol, and *n*-butylselenol by this procedure. He has also obtained thiophenols by the substitution of sulfur for selenium.
11. The submitter has synthesized nine alkyl phenyl selenides in yields of 85–95% by treating ethanol solutions of the sodium salt (the selenophenol is dissolved in the calculated amount of 50% aqueous sodium hydroxide diluted with ethanol) with the appropriate alkyl halide or sulfate.
12. Many selenophenols are more advantageously prepared by hydrolysis of the aryl selenocyanate.
13. It is well to have a hot sulfuric-nitric acid cleaning bath in the same hood, so that apparatus need not be handled in the open laboratory. The large separatory funnel is conveniently cleaned by pouring into it 50 ml. of concentrated nitric acid. After a few minutes, the acid reacts violently with selenides remaining on the sides. The oxides of nitrogen produced effectively clean the funnel, which can then be rinsed with water.
14. Water-soluble selenium compounds are poured down the sink in the hood and flushed with much water. Rubber stoppers and gloves can be freed from toxic compounds by soaking them for a few minutes in bromine or chlorine water and then in dilute sodium hydroxide solution.

3. Discussion

Selenophenol has been prepared from selenium tetrachloride and benzene in the presence of anhydrous aluminum chloride,³ and by the procedure described,⁴ which is a development of Taboury's.⁵

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 6*, 533

References and Notes

1. *Org. Syntheses Coll. Vol. 1*, 266, Fig. 15 (1941).
 2. *Org. Syntheses Coll. Vol. 1*, 226 (1941).
 3. Chabrie, *Bull. soc. chim. France*, (2) **50**, 133 (1888); *Ann. chim. phys.*, (6) **20**, 229 (1890).
 4. Foster and Brown, *J. Am. Chem. Soc.*, **50**, 1184 (1928).
 5. Taboury, *Bull. soc. chim. France*, (3) **29**, 762 (1903); *Ann. chim. phys.*, (8) **15**, 36, 38 (1908).
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Appendix

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

oxides of nitrogen

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

magnesium (7439-95-4)

nitric acid (7697-37-2)

hydrogen cyanide (74-90-8)

bromine (7726-95-6)

nitrogen (7727-37-9)

sulfur (7704-34-9)

aluminum chloride (3495-54-3)

chlorine (7782-50-5)

potassium hydroxide (1310-58-3)

bromobenzene (108-86-1)

Phenylmagnesium bromide (100-58-3)

Diphenyl selenide (1132-39-4)

selenium

selenium tetrachloride (10026-03-6)

hydrogen selenide (7782-49-2)

Selenophenol

Benzeneselenol (645-96-5)

Diphenyl diselenide (1666-13-3)

p-bromophenylselenophenol

n-butylselenol

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