



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](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.

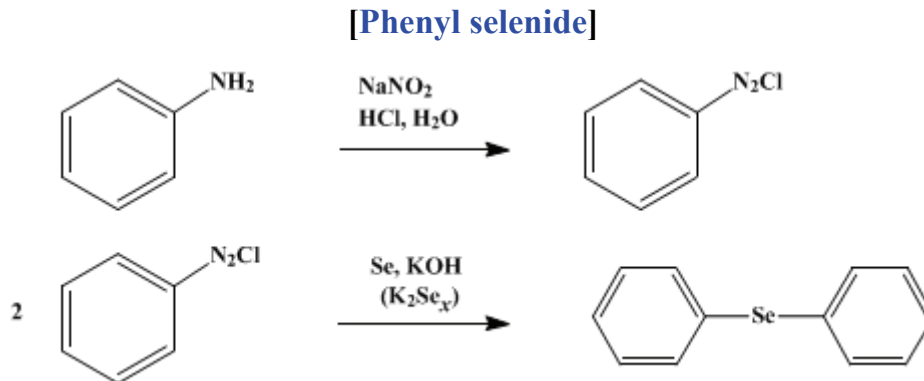
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.238 (1943); Vol. 18, p.27 (1938).*

## DIPHENYL SELENIDE



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### 1. Procedure

In a 500-cc. beaker are placed 360 g. (6.4 moles) of powdered [potassium hydroxide](#) and 240 g. (3 gram atoms) of black powdered [selenium](#) which have been previously ground together in a mortar. This mixture is heated ([Note 1](#)) in an oil bath at 140–150° until a thick, dark red liquid is formed ([Note 2](#)), and then it is added ([Note 3](#)) in small portions to 400 cc. of ice water in a 5-l. flask. The solution is kept in an ice bath until used.

To 375 cc. (4.3 moles) of [hydrochloric acid](#) (sp. gr. 1.18) and 200 g. of ice is added 139.6 g. (1.5 moles) of [aniline](#). The resulting solution is diazotized with a solution of 103.5 g. (1.5 moles) of c.p. [sodium nitrite](#), ice being added to the reaction mixture, as necessary, in order to keep the temperature below 5°. The final volume of the diazotized solution is about 1 l. This solution is added in a slow stream from a dropping funnel to the [potassium selenide](#) solution, which is vigorously stirred with a mechanical stirrer. When all the diazotized solution has been added, the red aqueous solution is decanted from the dark oil which forms and is heated to boiling ([Note 4](#)). It is then poured back on the oil, the mixture is well stirred ([Note 5](#)), 200 cc. of [chloroform](#) is added, and the [selenium](#) is collected on a filter and washed with a little more [chloroform](#) ([Note 6](#)). After the [chloroform](#) layer is separated, the aqueous layer is again extracted with 200 cc. of [chloroform](#). The combined extracts are then distilled, the [diphenyl selenide](#) being collected from 300 to 315°. The yield of yellow oil of rather unpleasant odor is 138–150 g. (79–86 per cent of the theoretical amount) ([Note 7](#)). If a purer product is desired, this material can be distilled under diminished pressure. It boils at 165–167°/12 mm.

### 2. Notes

1. Although no toxic gases are evolved in this reaction, the mixture has a rather unpleasant odor, so that it is best to use a hood throughout.
2. If the [potassium hydroxide](#) and [selenium](#) are absolutely dry, a thick paste is formed. The addition of a few cubic centimeters of water will form the dark red liquid mentioned.
3. If the mass is allowed to cool and solidify, it becomes very hard and is difficult to break up and dissolve.
4. Unless the aqueous layer is heated separately, the beaker containing the viscous oil always cracks, no matter how well the liquid is stirred.
5. This treatment converts the [selenium](#) from the red, colloidal form into the more easily filterable black modification.
6. The amount of [selenium](#) recovered is 101–115 g.
7. When smaller amounts of the selenide are prepared, the yield drops to 70–75 per cent. The method may be applied equally well to the preparation of the selenides from the three toluidines, giving yields

of 50–70 per cent.

### 3. Discussion

The method described here is a modification of that of Schoeller.<sup>1</sup> Diphenyl selenide has also been prepared from diazotized aniline and alkali monoselenides;<sup>2</sup> by the Friedel-Crafts reaction with benzene and selenium tetrachloride<sup>3</sup> or selenium dioxide;<sup>4</sup> from diphenyl sulfone and selenium;<sup>5</sup> from phenylmagnesium bromide and selenium,<sup>6</sup> selenium dichloride,<sup>7</sup> selenium oxychloride,<sup>7</sup> or selenium dibromide;<sup>8</sup> and from sodium selenophenoxide and bromobenzene.<sup>9</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 240](#)

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### References and Notes

1. Schoeller, Ber. **52**, 1517 (1919).
2. Lesser and Weiss, *ibid.* **47**, 2521 (1914).
3. Krafft and Kaschau, *ibid.* **29**, 428 (1896); Bradt and Green, J. Org. Chem. **1**, 540 (1937).
4. Lyons and Bradt, Ber. **60**, 60 (1927).
5. Krafft and Vorster, *ibid.* **26**, 2817 (1893); Krafft and Lyons, *ibid.* **27**, 1761 (1894).
6. Taboury, Ann. chim. (8) **15**, 35 (1908).
7. Strecker and Willing, Ber. **48**, 196 (1915).
8. Pieroni and Balduzzi, Gazz. chim. ital. **45** (II) 106 (1915).
9. Foster and Brown, J. Am. Chem. Soc. **50**, 1182 (1928).

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### Appendix

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

sodium selenophenoxide

[hydrochloric acid \(7647-01-0\)](#)

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

[aniline \(62-53-3\)](#)

[chloroform \(67-66-3\)](#)

[sodium nitrite \(7632-00-0\)](#)

[diphenyl sulfone \(127-63-9\)](#)

[selenium dioxide \(7446-08-4\)](#)

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

[bromobenzene \(108-86-1\)](#)

Phenylmagnesium bromide (100-58-3)

Diphenyl selenide,  
Phenyl selenide (1132-39-4)

selenium

potassium selenide

selenium tetrachloride (10026-03-6)

selenium dichloride (14457-70-6)

selenium oxychloride

selenium dibromide (22987-45-7)