



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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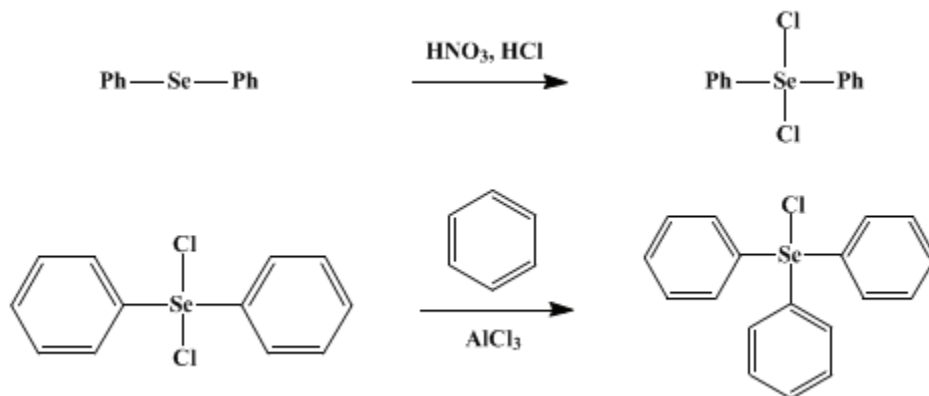
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.240 (1943); Vol. 18, p.30 (1938).

DIPHENYLSELENIUM DICHLORIDE AND TRIPHENYLSELENONIUM CHLORIDE

[Selenium compounds, diphenyl- dichloride]

[Selenonium compounds, triphenyl- chloride]



Submitted by Henry M. Leicester
Checked by W. W. Hartman and R. H. Bullard.

1. Procedure

(A) *Diphenylselenium Dichloride*.—One hundred twenty-five grams (0.53 mole) of *diphenyl selenide* (p. 238) is added in portions to 250 cc. (4 moles) of *nitric acid* (sp. gr. 1.42) in a 1.5-l. beaker. *Hydrochloric acid* (sp. gr. 1.18) is then added until precipitation is complete. About 170 cc. (2 moles) of acid is required. The mixture is then diluted with 500 cc. of water, and the yellow precipitate is separated by filtration and air-dried. The crude product is purified by extracting with 500 cc. of boiling *benzene*. The crystals which separate on cooling are collected on a filter and the filtrate is used for a further extraction. Three such treatments are necessary for a complete crystallization. The yield of yellow needles, decomposing at 187–188°, is 137–141 g. (85–87 per cent of the theoretical amount).

(B) *Triphenylselenonium Chloride*.—To 87 g. (100 cc., 1.1 moles) of *benzene* in a 1-l. three-necked flask provided with a mechanical stirrer, is added 30 g. (0.22 mole) of anhydrous *aluminum chloride*. The suspension is cooled in an ice bath, and to it is added, with stirring, 40 g. (0.13 mole) of *diphenylselenium dichloride* in portions of approximately 1 g. at a time over a period of twenty-five minutes. Before each addition the temperature should be below 10° to prevent the final product from becoming dark. When the addition is complete, the reaction mixture is allowed to stand for three hours at room temperature, and then 200 cc. of water is added cautiously (Note 1). The *benzene* layer is separated and discarded. If the water layer is colored, further extractions with *benzene* will remove most of the color without reducing the yield. The water layer is then extracted three times with 50-cc. portions of *chloroform*. The combined extracts are concentrated to a volume of 40 cc. and treated with 120 cc. of *ether* (Note 2). A yellow oil precipitates and solidifies almost at once to a white powder. The *triphenylselenonium chloride* is collected on a filter and recrystallized from 300 cc. of *methyl ethyl ketone* to which 20 cc. of water has been added (Note 3). The yield of anhydrous product, after drying at 100°, is 30 g. (67 per cent of the theoretical amount) (Note 4).

2. Notes

1. Much heat is evolved during the first part of the hydrolysis.
2. *Triphenylselenonium chloride* may be precipitated from aqueous solution as the zinc chloride double salt.¹

3. Triphenylselenonium chloride is soluble in anhydrous methyl ethyl ketone only to the extent of 2 g. in 300 cc. Using the water-methyl ethyl ketone mixture, the substance crystallizes with two molecules of water. This can be removed by heating for half an hour at 100°, but is again taken up from moist solvents or moist air.
4. This method can also be used for the preparation of *p*-tolyl- or of mixed phenyl-*p*-tolylselenonium salts.

3. Discussion

Diphenylselenium dichloride has been prepared from diphenyl selenide^{2, 3} by the action of chlorine and by treatment first with nitric acid and then hydrochloric acid. Triphenylselenonium chloride has been prepared by fusing together diphenylmercury and diphenylselenium dichloride,⁴ and by the action of diphenylselenium dichloride on benzene in the presence of aluminum chloride.³

References and Notes

1. Crowell and Bradt, J. Am. Chem. Soc. **55**, 1500 (1933).
 2. Foster and Brown, *ibid.* **50**, 1182 (1928).
 3. Leicester and Bergstrom, *ibid.* **51**, 3587 (1929).
 4. Leicester and Bergstrom, *ibid.* **53**, 4428 (1931); Leicester, *ibid.* **57**, 1901 (1935).
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Appendix

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

Selenium compounds, diphenyl- dichloride

Selenonium compounds, triphenyl- chloride

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

chloroform (67-66-3)

nitric acid (7697-37-2)

aluminum chloride (3495-54-3)

chlorine (7782-50-5)

Diphenylmercury (587-85-9)

methyl ethyl ketone (78-93-3)

Diphenyl selenide (1132-39-4)

DIPHENYLSELENIUM DICHLORIDE

Triphenylselenonium chloride (17166-13-1)

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