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Received May 9, 1977

A semi-micro preparation of selenophene is described which offers a convenient technique for the production of milligram quantities of the heterocycle. Selenophene is synthesized from bis(trimethylsilyl)-1,3-butadiyne and sodium hydrogen selenide generated *in situ* from selenium and sodium borohydride in DMF-water.

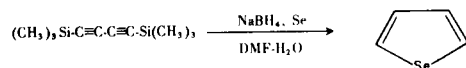
*J. Heterocyclic Chem.*, **14**, 1115 (1977)

Selenophene can be synthesized at elevated temperatures (350-550°) from selenium metal and acetylene (1), from selenium dioxide and butadiene (2), and from hydrogen selenide and furan (3). A detailed description has recently been published (4) of a mole-scale synthesis from elemental selenium and acetylene at 450°. However, no small scale synthesis of selenophene using ordinary laboratory equipment has been published. We have developed a semi-micro synthesis (20-1000 mg.) in order to prepare selenophene derivatives with radioactive labels in the aromatic ring.

Our synthesis is similar to a reported preparation (5) of tellurophene from bis(trimethylsilyl)-1,3-butadiyne and sodium telluride. However, different reaction conditions were necessary, since simple substitution of sodium selenide in place of the sodium telluride did not lead to detectable selenophene. Changing the solvent from methanol-acetone to ethanol and generating the selenide *in situ* by Klayman's method (6) gave a small yield (28%) of selenophene.

Since catalysis by silver(I) and copper(I) ions is known in the synthesis of substituted thiophenes and selenophenes from diynes (7), we investigated silver acetate and silver nitrate as catalysts. An increase in yield was observed when either of the silver ions was included in the reaction mixture; however, similar increases were obtained using 1-2 molar equivalents of water. The catalytic effect of the silver may be real or may be due to traces of water in the commercial samples.

The best yields were obtained when the sodium hydrogen selenide was generated from elemental selenium and two molar equivalents of sodium borohydride in the minimum amount of water-dimethylformamide (1:8) or 95% ethanol-dimethylformamide (1:4):



The selenide solution can be added to the diyne or the diyne can be dissolved in dimethylformamide and added to the selenide solution with little difference in yield (60-80%). A slightly lower yield is obtained if the selenide is generated in the presence of the diyne, but the one-pot procedure is more convenient.

## EXPERIMENTAL

### General.

The dimethylformamide was purified before use by passage through a mixed bed of silica gel and alumina. The selenium metal (99.5%, Bradford Scientific Co., Marblehead, Mass.) and the sodium borohydride (Alfa-Ventron Co., Beverly, Mass.) were used as purchased. Bis(trimethylsilyl)-1,3-butadiyne was prepared from hexachlorobutadiene by the method of Ballard and Gilman (8). Authentic selenophene was a gift from Professor Salo Gronowitz, University of Lund, Sweden. Gas chromatographic analyses were performed on a Pye Unicam 104 with a column of 3% OV17 on Chromasorb W at an oven temperature of 75-80°; chlorobenzene was used as the internal standard. The nmr spectrum was obtained on a Varian T-60 and the mass spectrum on a Nuclide instrument.

### Selenophene.

In a small vial or flask place 1.5 mmoles of selenium metal, an equal weight of sodium borohydride and three times that weight of bis(trimethylsilyl)-1,3-diyne (The mole ratios are 1:2.1:1.2); add a stirring bar and insert a serum stopper. Flush with nitrogen gas, then maintain a small positive pressure of nitrogen. (A bubbler is essential since the volatile product would be lost with a flow through of gas.) Cool in ice and slowly add 2 ml. of water-dimethylformamide (1:8) or 95% ethanol-dimethylformamide (1:4) for each mmole of selenium. There may be an induction period of 1-5 minutes, then hydrogen is evolved vigorously. Stir the mixture for 2 hours at room temperature (longer is not harmful). Work up the reaction by adding water and extracting with ether. The dimethylformamide can be removed by washing the ether layer several times with water or left in if it will not interfere with subsequent reactions. Dry the ether layer over potassium carbonate and remove the solvent through a Vigreux column at atmospheric pressure with the bath temperature less than 60°.

The crude product shows no significant by-products on GC and has been used successfully in a formylation reaction. If higher purity is necessary, the product can be steam distilled.

The nmr and mass spectrum of a sample prepared this way and steam distilled were identical to those of authentic selenophene.

## REFERENCES AND NOTES

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