

## On the Synthesis of Selenophene

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A convenient method for the preparation of selenophene on a semi-large scale is described.

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Selenophene has been known for almost fifty years, but still no report seems to exist about a detailed synthesis of this heterocycle on a larger scale. We report here a semi-large scale synthesis of selenophene, which gives about 150-200 g. (~ 58% yield) of selenophene per day.

The first reliable preparation of selenophene was reported by Mazza and Solazzo (1) and by Briscoe, *et al.*, (2,3), who heated selenium in a Pyrex tube in a current of acetylene (400°). The yield was later reported to be 30-40% based on selenium (4,5). Yur'ev, *et al.*, (6) prepared selenophene by heating selenium dioxide in a current of butane, butenes, or butadiene in the presence of chromic oxide on alumina at 450-500°. The yields were rather low (3-13%) and therefore we repeated the synthesis with acetylene and selenium and analysed the crude product by glc. It appeared that it consisted mainly of benzene and toluene with a small amount of selenophene (5%), which has almost the same boiling point as toluene (110°). Several higher boiling compounds (10%) were also formed (2,3,5,7). Obviously, the formation of toluene was a serious problem, which had not been noticed earlier.

Mixing the selenium with alumina (8) solved this problem, since selenophene now became the main product; benzene and toluene amounted to only about 2-3%. The higher boiling compounds have previously been identified to some extent (7,9), and a more detailed investigation is in progress (10). The isolated yield of selenophene (mean value of the 11 last runs according to Figure 1) with this latter method is 58% (based on selenium).

Since substantial amounts of selenophene are needed in these laboratories, a tube oven, containing 10 tubes, was constructed, which delivered 150-200 g. of selenophene (once distilled) per day. In the first 5-6 runs, the yield of selenophene was increasing from about 5% to about 50% (Figure 1). This tendency was also observed by Briscoe, *et al.*, (2,3) and others (4,5), and was attributed to the formation of a carbonaceous residue that promotes the

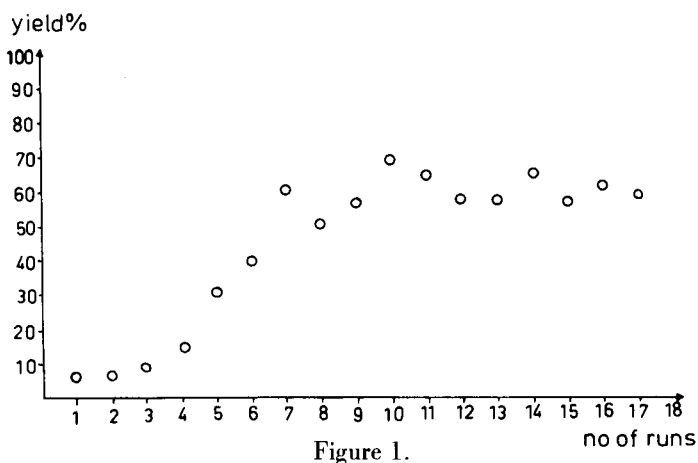
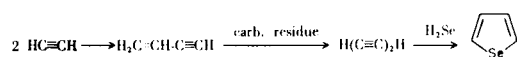


Figure 1.

reaction (even without alumina). We think that the alumina has mainly an area-increasing effect since the alumina pellets became completely covered with the mentioned tarry material, which seems to be the necessary substance to give good yields.

If the reaction temperature is kept below 340°, the formation of selenophene is very slow, and above 550° the formation of benzene and toluene starts to become a serious drawback (even with alumina). We found that the reaction gives the best yields of selenophene at 450°. Note that the fresh alumina and the residue from the synthesis must be protected from contact with acids (14).

A detailed investigation of the pyrolysis of acetylene at temperatures ranging from 500 to 1000° has been made by Cullis and Franklin (11). They found that 1-buten-3-yne was the sole initial reaction product, which was subsequently dehydrogenated by carbonaceous reaction products to give 1,3-butadiyne. Briscoe and Peel (2) found that hydrogen selenide was formed in the reaction between selenium and acetylene, which makes it reasonable to anticipate that selenophene originates from the addition of hydrogen selenide to diacetylene:



This parallels the way in which some thiophene derivatives have been prepared (12) and, formally, their assumed biogenesis (13).

#### EXPERIMENTAL

##### Selenophene.

Ten Pyrex tubes (25 x 600 mm) were each filled with 20.0 g. (0.253 mole) of selenium and 100 g. of alumina pellets (Fluka 1-3 mm). The tubes had been cleaned with hot concentrated nitric acid, water and finally preheated empty but with a slow stream of nitrogen in the tube oven at 450° for 2 hours. The filled tubes were subsequently placed in the oven, and a slow stream of nitrogen was passed through the tubes until the temperature was 450°. Then the nitrogen was replaced by acetylene and after some minutes a flashing occurred, which deposited a carbonaceous material in the tubes. If flashing does not occur spontaneously, the introduction of some air into the tubes will help. This is done by removing the gas inlet joints at each tube (one at a time) for one second. A brown crude oil begins to form, and after 7-8 hours the formation of the oil subsides and it is not worthwhile to continue the reaction. The crude product is collected from several runs and distilled.

After cooling, the tubes are emptied of alumina pellets, which are used again together with a new portion of 200 g. of selenium. The reaction becomes more efficient after 5-6 runs, and the same catalyst (alumina covered with a black material formed in the reaction) could be used 25 times without any significant drop in yield.

The crude product is distilled, b.p. 105-120°, to give 95% pure selenophene, which is sufficiently pure for most synthetic purposes.

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- (14) We found that the catalyst became very inefficient when stored in a hood in which a cleaning bath with concentrated nitric acid was placed. Similarly, the outlet gas stream from the reaction tubes, which certainly contains hydrogen selenide, deactivates the catalyst at ordinary temperatures. The yield of selenophene dropped to less than 5% when the catalyst was stored in the same hood as the tube oven.