

SHORT
COMMUNICATIONS

Selenophene Synthesis in Thermal Reactions of Dialkyl Selenides with Acetylene in the Presence of Methanol

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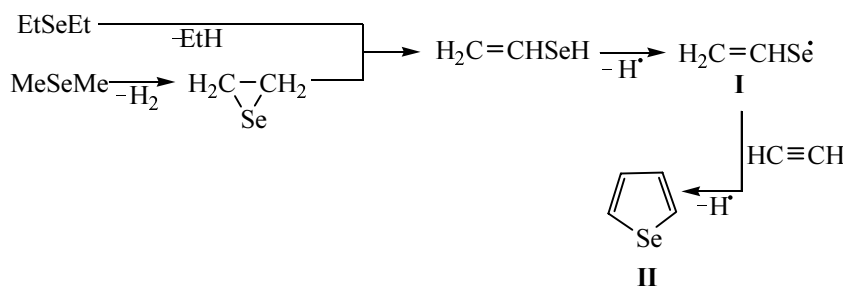
Selenophene derivatives can be used as efficient anti-oxidants, extractants for isolation and partitioning of metals, as polymer materials, and physiologically active substances. However the development of selenophene chemistry is retarded by the lack of convenient procedures for its preparation [1].

We showed formerly that a gas-phase reaction of dimethyl [2] or diethyl [3] selenides with acetylene at 420–470 and 400–600°C respectively furnished selenophene in high yield. However the yields reported in [2, 3] were observed only in the initial period of the reaction. Then the selenophene yield decreased because of accumulation of elemental selenium in the reactor. The elemental selenium formed in the concurrently proceeding decomposition of the organyl selenides. Besides the selenium

promoted condensation of acetylene into aromatic hydrocarbons, and their presence hampered isolation of selenophene in a pure state.

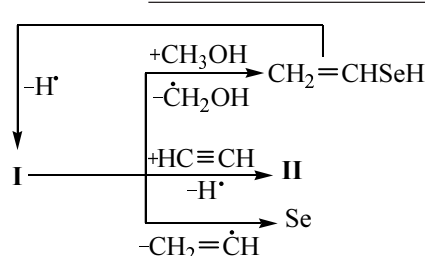
In order to increase the selectivity of selenophene formation from dimethyl or diethyl selenides and acetylene we tried addition of methanol to the reaction system. The addition of 10–50 mol% of methanol with respect to the selenide ensured a stable operation of the system for several hours affording selenophene in 72–93% yield at selenide conversion of 98–100%.

Taking into consideration the data of [2, 3] and also of earlier publications on the thermal reactions of dimethyl sulfide [4] the selenophene synthesis may be represented as going through a stage of vinylselenyl radicals **I** formation that are trapped by acetylene affording **II**.



Apparently, in spite of the acetylene excess in the system, the vinylselenyl radicals partially decompose forming the elemental selenium. Methanol plays the part of hydrogen donor thus converting the vinylselenyl radicals into etheneselenol that like the other unsaturated compounds should be more heat resistant [5] than radicals **I**.

Thus in the presence of methanol the vinylselenyl radicals react along three paths.



At 440 (for Et₂Se) and 490°C (for Me₂Se) reaction (3) becomes negligible, and due to reversibility of reaction (1) the selectivity of selenophene formation along reaction (2) considerably increases compared to the process performed without methanol.

The synthesis was carried out in quartz tubular reactor flushed with nitrogen prior to the experiment. It was heated to the required temperature specified above (heating zone 30×650 mm). Into the heated reactor was charged in an acetylene flow a mixture of Me₂Se (or Et₂Se) with methanol at the molar ratio selenide–acetylene 1:2. At the output of the reactor the products were collected in a cooled trap (–20°C) and were analyzed by GLC on a chromatograph LKhM-80MD at linear programming of oven temperature. The stationary phase used was silicon XE-60, 5% on Chromaton N-AW-HMDS, carrier gas helium, column 2000×3 mm.

Selenophene synthesis from diethyl selenide and acetylene in the presence of 20 mol% of methanol. Into the above described reactor heated to 440°C in a

flow of acetylene (flow rate 3 l/h) was charged a mixture of 14.7 g (107 mmol) of diethyl selenide and 0.63 g (20 mmol) of methanol at a rate 10 ml/h for 77 min. At the output of the reactor was collected 13.76 g of condensate containing according to GLC 13.43 g of selenophene (yield 89.5%).

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