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PHOTOLYSIS AND GAS PHASE PYROLYSIS OF 1,2,3-BENZOSELENADIAZOLE - MATRIX-ISOLATION OF BENZOSELENIRENE

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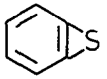
Abstract: Based on comparative studies on 1,2,3-benzothiadiazole benzoselenirene is identified as an intermediate in the low temperature photolysis and gas phase pyrolysis of 1,2,3-benzoselenadiazole by IR spectroscopy.

Low temperature photolysis of 1,2,3-thiadiazoles leads to thiirenes[1]. Accordingly, benzothiirene (1) is formed upon photolysis of 1,2,3-benzothiadiazole (2) in an argon matrix[2]. On the other hand, it is controversially discussed whether 1 is an intermediate of the thermolysis of 2 [3].

Selenirenes are less studied than thiirenes. Unsubstituted selenirene was identified as one of the products of the photodecomposition of matrix-isolated 1,2,3-selenadiazole[4]. Thermal decomposition of 1,2,3-benzoselenadiazole (3) in the gas phase leads to 6-fulveneselone (4)[5]; an intermediate of the reaction was detected whose ionization energies were compatible with benzoselenirene (5)[6].



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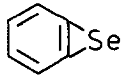

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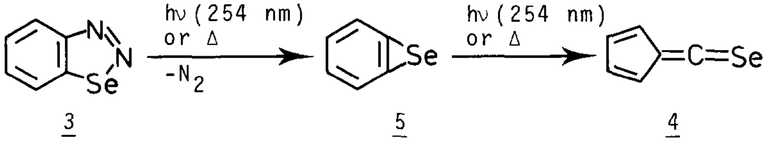
Below we report on the photochemical and thermal generation of benzoselenirene (5) and its IR spectroscopic detection.

Irradiation (254 nm; 4 min) of matrix-isolated 3 produces a reactive intermediate with IR bands at 1672, 1443, 1435, 1156, 1052, 973, 940, 726 and 655 cm^{-1} (cf. the IR spectrum of Fig.1) which on further irradiation rapidly rearranges to 6-fulveneselone (4) with IR bands at 1710, 1685, 1650, 1450, 1360, 1105, 1033, 843, 733 and 590 cm^{-1} (cf. the IR-spectrum of Fig.2). The same intermediate (besides 4) is formed in the gas phase pyrolysis (560°C, ca 10^{-3} mbar) of 3 if the reaction temperature is kept a little lower than required for complete fragmentation of 3. With increasing temperature the amount of the new product steadily decreased and at 700°C its IR bands were at the limit of detection.



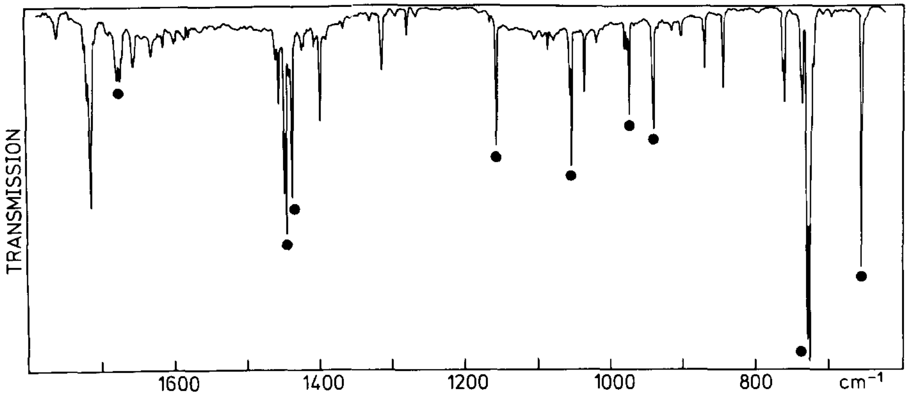
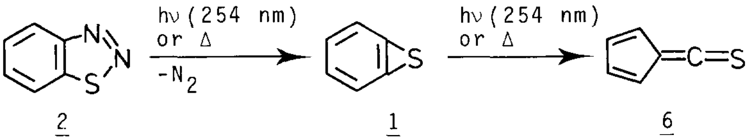


Fig.1. IR-spectrum of argon matrix-isolated photoproducts of 1,2,3-benzoselenadiazole. The bands marked ● are ascribed to benzoselenirene (see text).

In full analogy to these results, the IR-spectrum of the argon matrix-isolated pyrolysis products (500-700°C, ca.10^{-3} mbar) of 2 contains, besides the bands of the main product 6-fulvenethione[7,8], bands at 1685, 1437, 968, 723, 689, 674 cm^{-1} which occurred much more intense in the argon matrix photoproduct (254 nm, 15 min) spectrum of 2 and which were previously ascribed to benzothiirene (1)[2]. Thus, proof of 1 as a product of the gas phase pyrolysis of 2 substantiates the conjecture that the needlelike fine structured region at 8.21 eV in the PE-spectrum of the pyrolysis products of 2 is to be assigned to the $^2B_1(n_s)$ ionization of benzothiirene[6].



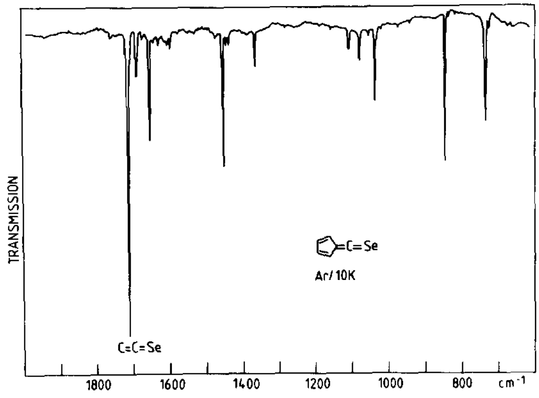


Fig.2. IR-spectrum of the argon matrix-isolated final product (6-fulveneselone) of the thermal decomposition (600^{o}C; ca.10^{-3} mbar) of 1,2,3-benzoselenadiazole. An identical spectrum is obtained upon irradiation of 1,2,3-benzoselenadiazole for a longer period of time (254 nm; ca. 1 h).

As a result of the identical thermal and photochemical behavior of 1,2,3-benzoselena- and thiadiazole described above there is good reason to assign the structure of benzoselenirene to the reactive intermediate occurring in the photo- and thermal decomposition of 3. In particular, this interpretation is supported by the IR spectrum of 5 which is very similar to the one of 1.

Acknowledgement

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