

Mass Spectrometric Studies of Selenaanalogues of 1,6,6a λ^4 -Tri-thiapentalenes (1,6,6a λ^4 -Triselenapentalenes and 1,6a λ^4 -Diselena-5,6-diazapentalenes)

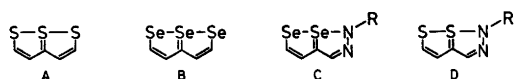
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A number of 1,6,6a λ^4 -triselenapentalenes and 1,6a λ^4 -diselena-5,6-diazapentalenes have together with the corresponding sulfur analogues been subjected to electron impact.

The mass spectra of analogous selenium- and sulfur-containing compounds show great similarities. The main difference results from the more facile loss of selenium compared with sulfur. This gives rise to the formation of abundant hydrocarbon ions corresponding to $[M - Se_nH]^+$ in the spectra of 1,6,6a λ^4 -triselenapentalenes. Corresponding ions are not observed in the spectra of 1,6,6a λ^4 -trithiapentalenes.

The question whether the unusual type of structure and bonding in 1,6,6a λ^4 -trithiapentalenes (A) will also be found in analogous compounds in which the sulfur atoms have been replaced by other heteroatoms has led to the synthesis of 1,6,6a λ^4 -triselenapentalenes (B) and 1,6a λ^4 -diselena-5,6-diazapentalenes (C).¹⁻³ Crystallographic studies^{4,5} suggest a linear selenium arrangement in the triselena compounds which



leads to the assumption that the Se—Se bonds in these compounds may be described as three-center four-electron bonds by analogy with the S—S bonding in trithiapentalenes.⁶ It was therefore of interest to study whether this

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analogy in bonding is also reflected in the electron impact induced fragmentation.

Mass spectra of four 1,6,6a λ^4 -triselenapentalenes have been recorded and compared with those of the sulfur analogues. Three of these (2,4 and 8) have previously been reported,^{7,8} whereas no mass spectrometric data have so far been published on 1,6a λ^4 -dithia-5,6-diazapentalenes (D).

The presence of five relatively abundant selenium isotopes gives rise to rather complex clusters of isotopic peaks for species containing more than one selenium atom, especially pronounced when the mass ranges of two clusters overlap each other. The relative probabilities of occurrence of the various isotopic peaks corresponding to two and three selenium atoms in an ionic species have been calculated and the corresponding isotopic abundance ratios are shown in Fig. 1.

1,6,6a λ^4 -Trithiapentalenes and 1,6,6a λ^4 -triselenapentalenes. The trithia- and triselenapentalenes studied are listed in Table 1. The mass spectra with indication of the predominant modes of fragmentation are shown in Figs. 2 and 3.

A comparison of the spectra of two analogues, *e.g.* 1 and 2 shows closely related behaviour in the two types of compounds upon electron impact. Peaks corresponding to $[M - H]^+$, $[M - CH_3]^+$, $[M - XH]^+$ and $[CH_3CX]^+$ are characteristic features in both spectra.

A remarkable difference is the appearance of two hydrocarbon ion peaks at m/e 78 and 77

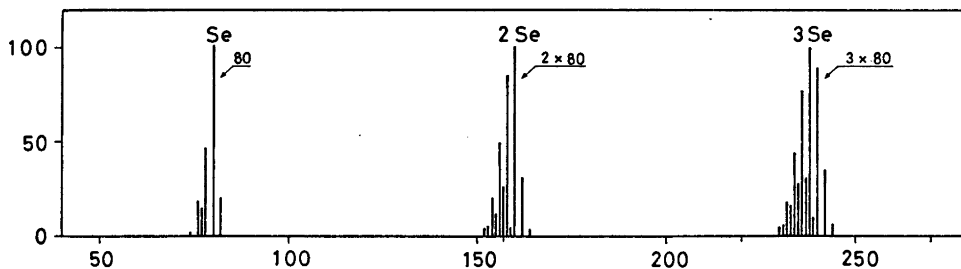


Fig. 1. The isotopic abundance ratios for ions containing 1, 2 and 3 selenium atoms.

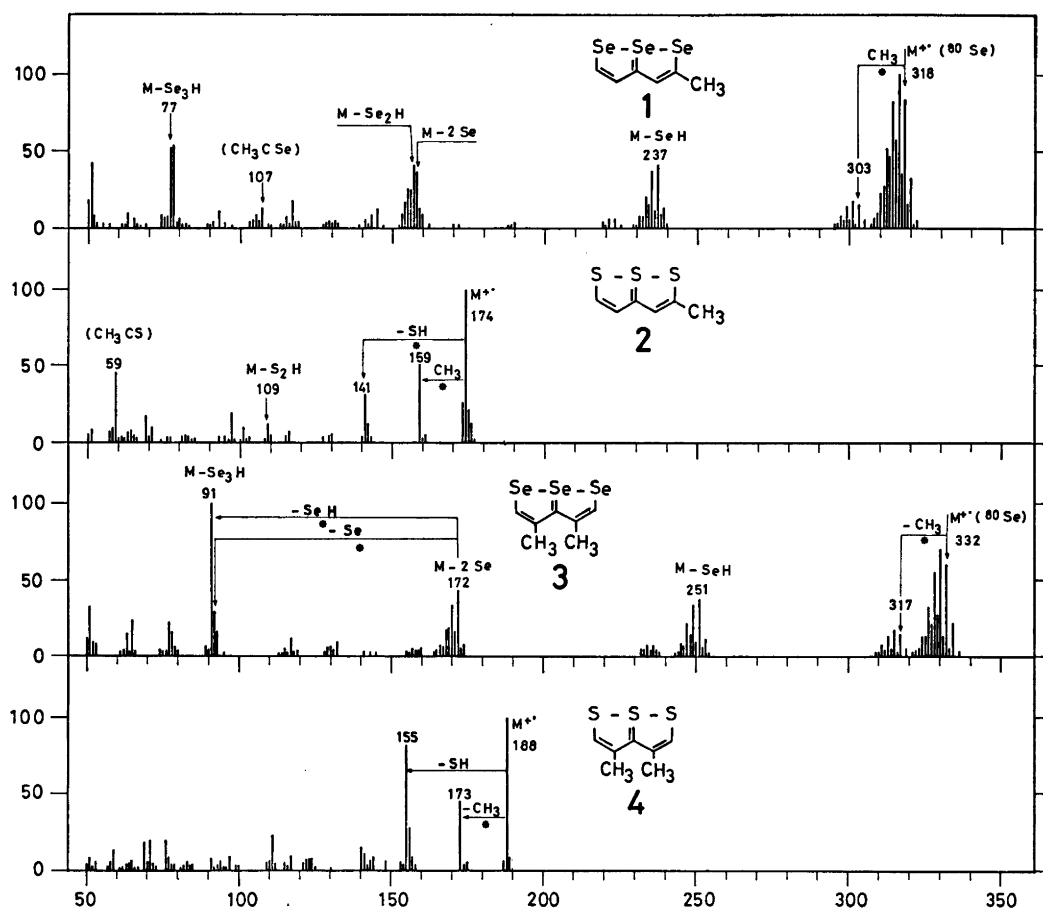


Fig. 2. MS of compounds 1-4.

Table 1. Trithia- and triselenapentalenes studied.

| X | R ¹ | R ² | R ³ | |
|---|----------------|-------------------------------|--|-----------------|
| 1 | Se | CH ₃ | H | H |
| 2 | S | CH ₃ | H | H |
| 3 | Se | H | CH ₃ | CH ₃ |
| 4 | S | H | CH ₃ | CH ₃ |
| 5 | Se | H | -CH ₂ -CH ₂ -CH ₂ - | |
| 6 | S | H | -CH ₂ -CH ₂ -CH ₂ - | |
| 7 | Se | C ₆ H ₅ | H | H |
| 8 | S | C ₆ H ₅ | H | H |

in the spectrum of compound 1 only. The peak of m/e 78 formally corresponds to the loss of all three selenium atoms from the molecular ion. Metastable peaks indicate that a stepwise formation *via* the $[M - \text{Se}_2]^+$ ion is possible. The m/e 77 ion is formed from the $[M - \text{SeH}]^+$ ion by additional losses of two selenium atoms.

Direct loss of Se from the molecular ion appears to be less favourable than the loss of Se₂. The integrated abundances of the two corresponding ions are 5 and 17 %, respectively, of that of the molecular ions. In the sulfur analogues the corresponding $[M - \text{S}]^+$ and $[M - 2\text{S}]^+$ ions are practically absent.

Similar differences appear when comparisons are made between the other pairs of compounds.

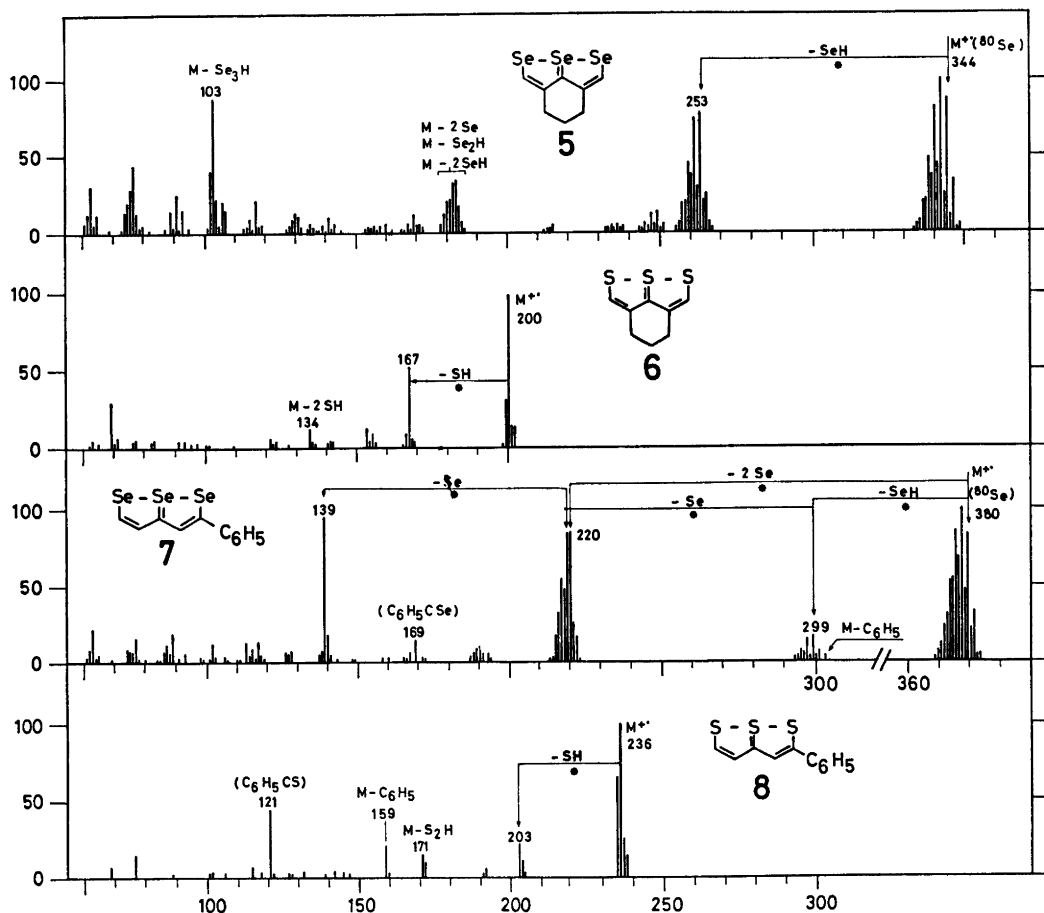


Fig. 3. MS of compounds 5-8.

Hydrocarbon ions corresponding to $[M-S_3]^+$ and $[M-S_3H]^+$ are not found whereas $[M-Se_3H]^+$ ions are important in all selenium compounds. (The abundance of the odd electron $[M-Se_3]^+$ ion varies considerably.)

These differences in behaviour of analogous sulfur and selenium compounds, *i.e.* the easier elimination of the selenium, may be ascribed to general differences in influence of sulfur and selenium on the behaviour of such compounds upon electron impact.^{9,10}

Apart from differences mentioned above the fragmentation behaviour of a trithiapentalene shows great similarities with that of the corresponding seleno analogue. This supports the assumption that the bonding in the Se-Se-Se sequence in 1,6,6aλ⁴-triselenapentalenes is much like that in the S-S-S sequence of 1,6,6aλ⁴-trithiapentalenes.

1,6aλ⁴-Diselena-5,6-diazapentalenes and 1,6aλ⁴-dithia-5,6-diazapentalenes. Since only few examples of these types of compounds are available so far, it has not been possible to draw general conclusions concerning their behaviour upon electron impact. The compounds listed in Table 2 are studied.

Table 2. Dithia- and diselena-5,6-diazapentalenes studied.

| | X | R ¹ | R ² | R ³ |
|----|----|-----------------|-----------------|-----------------|
| 9 | S | CH ₃ | CH ₃ | H |
| 10 | Se | CH ₃ | CH ₃ | H |
| 11 | Se | H | H | CH ₃ |

The mass spectrum of 9 exhibits an abundant molecular ion. The fragmentation pattern is to a great extent characterized by the -N-N-C₆H₅ function. The predominant process is cleavage of the nitrogen-phenyl bond with charge retention almost exclusively on the phenyl moiety. Also important is the direct elimination of C₆H₅N₂ yielding *m/e* 143 and of C₆H₅NH giving rise to the peak *m/e* 156. Loss of CH₃ and SH is much less important than for the corresponding methyl substituted trithiapentalene 4.

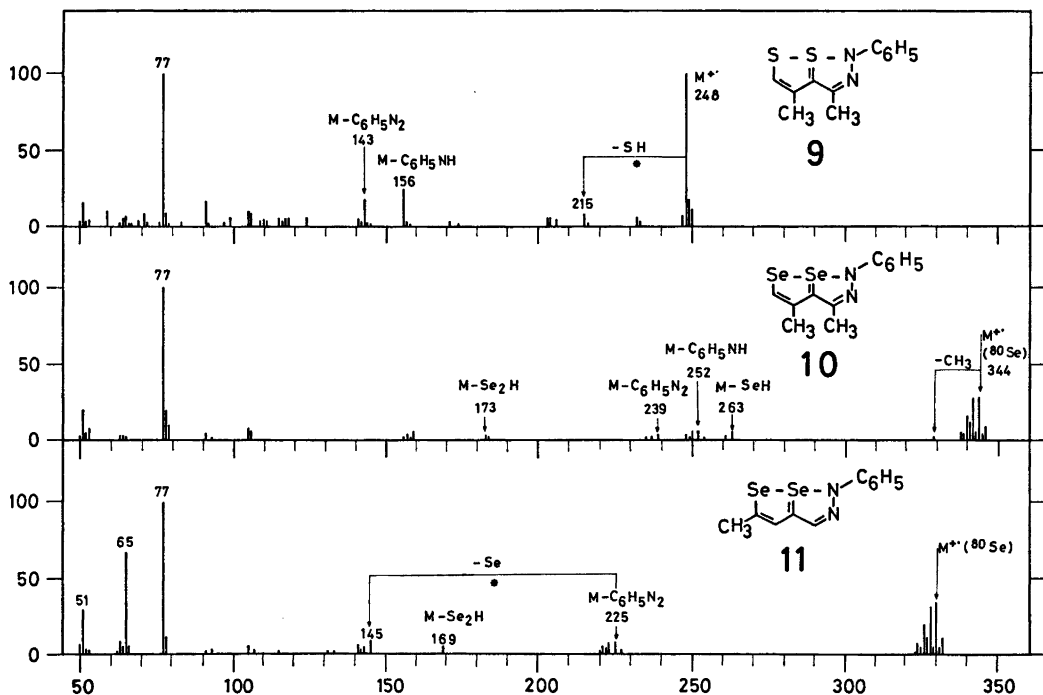


Fig. 4. MS of compounds 9-11.

The mass spectrum of 10 (Fig. 4) is very similar to that of the sulfur analogue 9. The m/e 77 peak appears with approximately the same intensity as the normalized molecular ion peak corresponding to a 100 % content of the ^{80}Se isotope.*

Elimination of two selenium atoms from the molecular ions of 10 and 11 is not a likely process, as it was in the case of the triselenapentalenes, and peaks corresponding to $[\text{M}-\text{Se}_2\text{H}]^+$ appear with relatively low abundance. However, in the corresponding sulfur analogues no $[\text{M}-\text{S}_2]^+$ and $[\text{M}-\text{S}_2\text{H}]^+$ ions are formed at all, demonstrating the easier elimination of selenium as compared with sulfur.

Peaks corresponding to losses of $\text{C}_6\text{H}_5\text{NH}$ and $\text{C}_6\text{H}_5\text{N}_2$ are exhibited in the spectrum of 10 in accordance with the behaviour of the sulfur analogue, whereas no $[\text{M}-\text{C}_6\text{H}_5\text{NH}]^+$ ion is generated in the fragmentation of 11. Also the $[\text{M}-\text{SeH}]^+$ ion is practically absent in this case. The hydrogen atoms involved in these elimination processes are probably not accessible in the case of 11.

The abundant hydrocarbon ion m/e 65 in 11 has no counterpart in the spectrum of 10. It may be generated from the $[\text{M}-\text{C}_6\text{H}_5\text{N}_2]^+$ ion by loss of two selenium atoms (*cf.* the abundant hydrocarbon ions in the spectra of the triselenapentalenes). The abundance of the m/e 39 ion is 44 % in the spectrum of 11 and only 8 % in that of 10.

EXPERIMENTAL

Mass spectra were obtained with an MS 902 mass spectrometer using the direct sample insertion system with the lowest feasible ion source temperature (70–120 °C). 70eV Electrons were used. Peaks corresponding to doubly charged ions appearing at half mass numbers as well as peaks of abundance lower than 2 % were omitted in the spectra shown.

1,6,6a λ^4 -Triselenapentalenes and 1,6a λ^4 -diselena-5,6-diazapentalenes were prepared according to Refs. 1–3.

2-Methyl-1,6,6a λ^4 -trithiapentalene (2).¹¹

3,4-Dimethyl-1,6,6a λ^4 -trithiapentalene (4).¹²

3,4-Trimethylene-1,6,6a λ^4 -trithiapentalene (6).¹³

2-Phenyl-1,6,6a λ^4 -trithiapentalene (8).¹¹

* A reduced spectrum is easily obtained by increasing the intensities of the ions containing one, two and three ^{80}Se atoms by a factor of 2.0, 3.4 and 4.6, respectively, and removing peaks corresponding to other selenium isotopes.

Acknowledgement. The authors are indebted to Mrs. E. Wolff-Jensen, The H. C. Ørsted Institute, University of Copenhagen, for recording the mass spectra and to The Danish Science Research Council for support of studies of dithiol derivatives.

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Received November 28, 1975.