

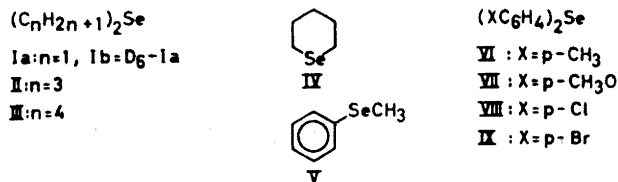
Mass Spectra of Some Aliphatic and Aromatic Selenides

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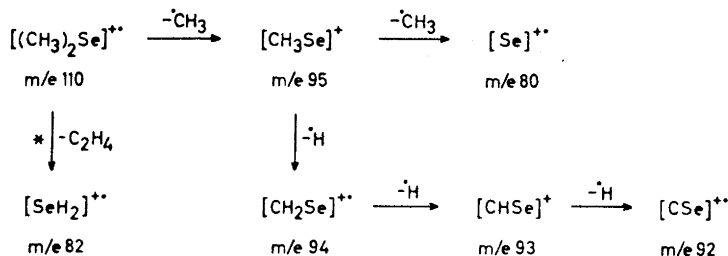
Mass spectra of a number of simple aliphatic and aromatic selenides are given. The spectrum of dimethyl selenide (I) exhibits, in addition to contributions from simple bond fissions, the two-carbon rearrangement-ions $[C_2H_4]^+$ and $[C_2H_5]^+$ and a one-step elimination of C_2H_4 from molecular ion with formation of $[SeH_2]^+$. In the spectra of dipropyl selenide (II) and dibutyl selenide (III) the most abundant selenious fragments are $[RSeH]^+$, but ions derived from C_1-C_2 and C_2-C_3 bond cleavages of one alkyl group also occur. In the spectrum of selenacyclohexane (IV) the dominating process is loss of a SeH radical from the molecular ion, but expulsion of hydrocarbon fragments containing one, two, or three carbon atoms is also observed. The fragmentation pattern of methyl phenyl selenide (V) is similar to that of the corresponding sulphide with elimination of $\cdot CH_3$, CH_2Se , and $\cdot SeH$ from the molecular ion as the main decomposition routes. In the spectra of the substituted aromatic selenides, $(XC_6H_4)_2Se$, $X = p-CH_3$, $p-CH_3O$, $p-Cl$, $p-Br$ (VI-IX) the main degradation process implies elimination of the heteroatom. Alternatively, a stepwise elimination of the substituents followed by loss of the selenium atom is observed.

The selenides, R_2Se , are the largest and most extensively studied class of organic selenium compounds.¹ Their relative availability and stability also make them valuable precursors in the preparation of other types of selenium compounds, *e.g.* selenoxides, R_2SeO , and selenones, R_2SeO_2 . Occasionally, selenides also occur as undesired by-products in syntheses or decompositions of other selenium compounds. For a mass spectrometric investigation on organic selenium-oxygen compounds,² a number of selenides were needed as starting materials in syntheses of selenoxides and selenones. However, with the exception of diethyl selenide,³ dibenzyl selenide,⁴ selenacyclopentane,⁵ and diphenyl selenide,⁶ the mass spectra of the prepared simple selenides seem not to have been reported in the literature but were of interest for comparative purposes during the interpretation of the spectra of their oxidation products. The purpose of the present paper is thus to discuss in some detail the spectra and fragmentation patterns of the selenides I-IX, the ions containing the main isotopes ^{80}Se , ^{35}Cl , and ^{79}Br being taken as representative of the fragment in question.



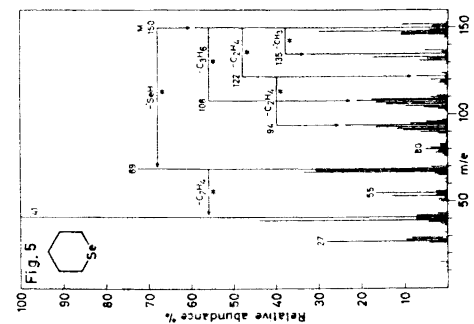
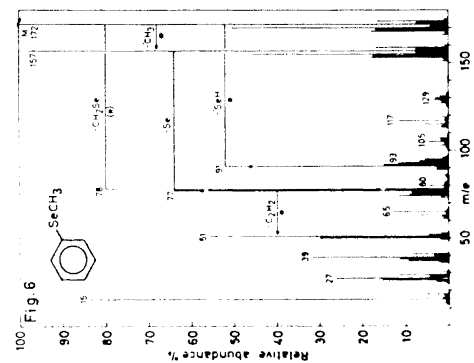
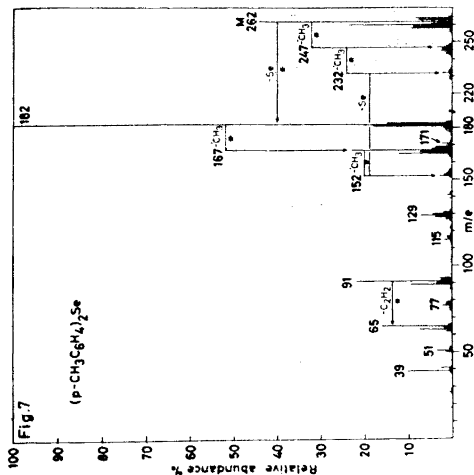
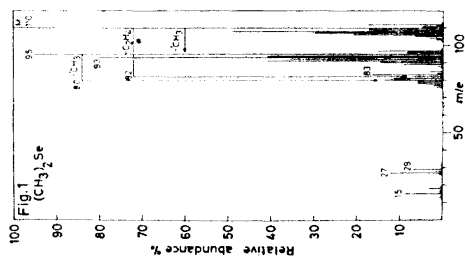
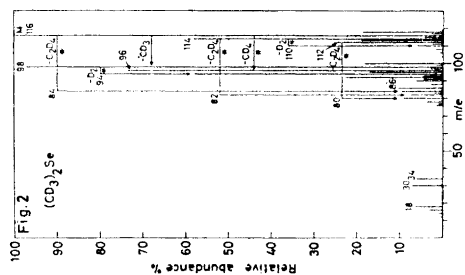
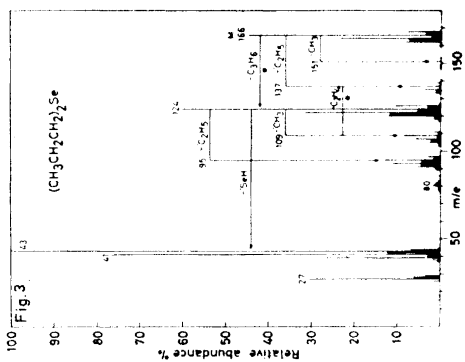
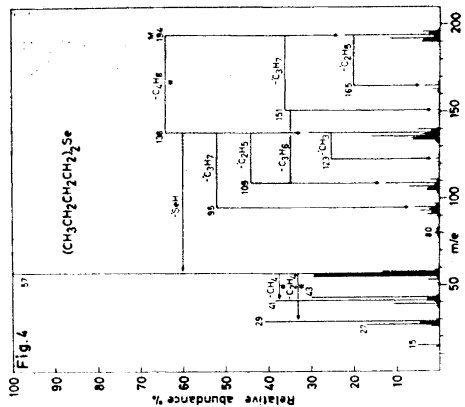
The mass spectrum of Ia, Fig. 1, is characterized by abundant selenious ions, the molecular ion at m/e 110 constituting the base peak. Investigation of the spectrum provides evidence for the fragmentation pattern proposed in Scheme 1.

Furthermore, evidence for some additional transitions is obtained from the spectrum of the deuterated analogue Ib (Fig. 2). Thus the fragments and the metastable transitions observed in these spectra indicate that, in addition to the main decompositions routes involving simple carbon-selenium and carbon-hydrogen bond fissions, skeletal rearrangements implying carbon-carbon bond formation occur. One such process, supported by the appearance of an appropriate metastable peak (m/e 61.2 in Ia, m/e 61.0 in Ib),

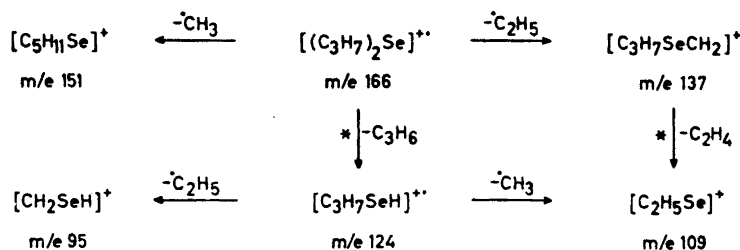


Scheme 1.

involves the elimination of the two-carbon fragment C_2H_4 from the molecular ion with formation of $[SeH_2]^+$ at m/e 82 and m/e 84 in Ib. This transition may proceed *via* an initial isomerization of the molecular ion and involve a hydrogen shift to selenium with a simultaneous methyl group migration forming the ion $[C_2H_5SeH]^+$. Loss of C_2H_4 , in analogy with the m/e 110 \rightarrow m/e 82 process in the spectrum of diethyl selenide,³ or simple carbon-selenium bond fission with formation of $[C_2H_5]^+$ at m/e 29 and m/e 34 in Ib, may then be obtained. However, elimination of C_2D_4 is also found, as indicated by metastable peaks at m/e 59.0 and m/e 57.2, from the $[M-D]^+$, m/e 114 and $[M-D_2]^+$, m/e 112, fragments of Ib (Fig. 2) with the formation of $[SeD]^+$ and $[Se]^+$, respectively. These processes might suggest the occurrence of a common selenacyclopropane intermediate in the eliminations of two-carbon fragments in the mass spectrum of dimethyl selenide. An alternative possibility for the generation of, for example, the $[SeH_2]^+$ fragment, implying the expulsion of two methylene units from the molecular ion, is very unlikely.⁸ Similar skeletal



rearrangements with carbon-carbon bond formation are also observed in the mass spectra of dimethyl sulphide⁹ and dimethyl phosphine.¹⁰ Moreover, in the spectrum of Ib a somewhat unexpected elimination of CD₄ from the molecular ion

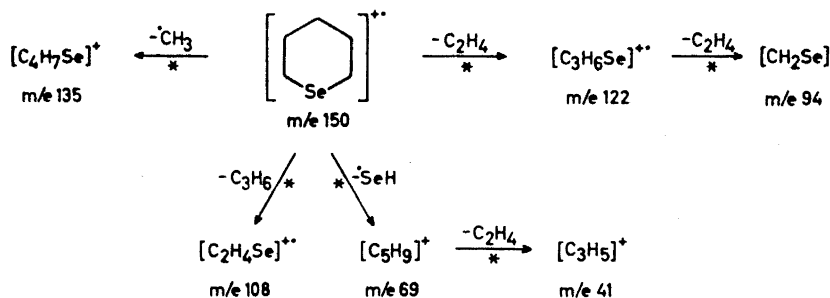


Scheme 2.

is observed, a transition which is supported by an appropriate metastable peak at m/e 79.5.

The mass spectra of II (Fig. 3) and III (Fig. 4) are characterized by abundant hydrocarbon ions, the selenious fragments giving peaks of lower intensity, particularly in the case of III. A detailed investigation of the spectra gives evidence for analogous fragmentation patterns as visualized for II in Scheme 2. The most abundant selenious fragments arise from cleavage of one carbon-selenium bond in the molecular ion with a simultaneous hydrogen migration to selenium from the expelled hydrocarbon fragment and the generation of the ions $[\text{C}_n\text{H}_{2n+1}\text{SeH}]^+$ at m/e 124, $n=3$ and m/e 138, $n=4$ in II and III, respectively. This process is analogous to that found for diethyl selenide³ and the corresponding sulphides.⁹

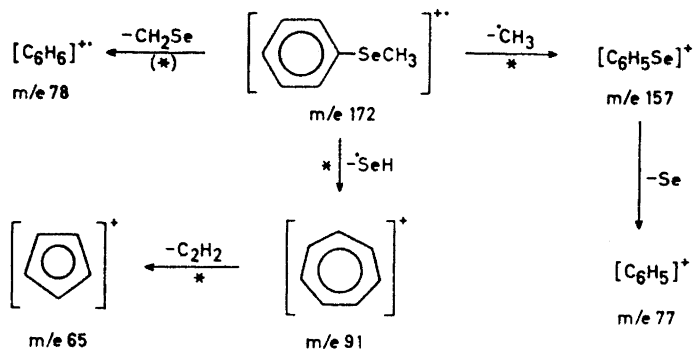
Other selenious ions observed in the spectra of these selenides are derived from fragmentation processes in the alkyl groups. Thus, peaks due to C₁-C₂ and C₂-C₃ bond cleavages in one alkyl group of the molecular ion are found at m/e 137 and m/e 151 in II (Fig. 2) and at m/e 151 and m/e 165 in III (Fig. 3). Analogous degradation steps of the remaining alkyl group in the $[\text{C}_n\text{H}_{2n+1}\text{SeH}]^+$ ions are also observed, as indicated in Figs. 3-4. Part of the ions at m/e 109 $[\text{C}_2\text{H}_5\text{Se}]^+$ are also formed from the $[\text{RSe}=\text{CH}_2]^+$ fragments, a transition supported by an appropriate metastable peak in the case of II (m/e 86.7), probably by a McLafferty type of hydrogen migration with simultaneous cleavage of the C₁-C₂ bond and elimination of an alkene molecule. Thus the general mass spectrometric behaviour of these selenides resembles that of the corresponding sulphides and ethers.^{9,11} However, pronounced differences also occur. The spectra of II and III do not exhibit to any considerable extent ions analogous to the $[\text{RS}]^+$ and $[\text{RSH}_2]^+$ fragments observed in the spectra of the corresponding sulphides, which are also much more strongly characterized by ions derived from C₁-C₂ bond cleavages.⁹



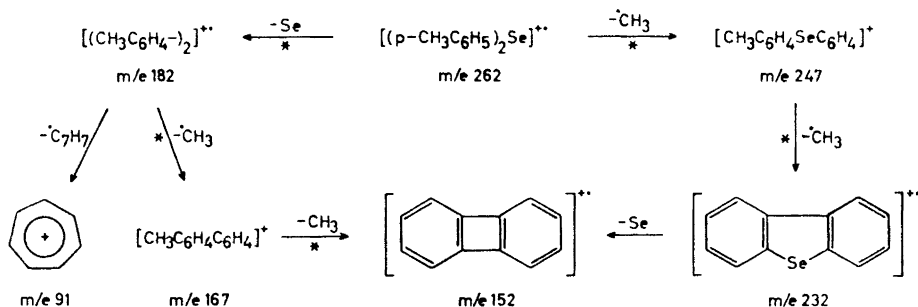
Scheme 3.

The spectrum of IV (Fig. 5) contains evidence for the fragmentation pattern given in Scheme 3. The dominating process is elimination of the heteroatom as a SeH radical, a process, which is also encountered in the spectrum of selenacyclopentane⁵ but which seems to have no counterpart in the spectrum of the corresponding sulphide.¹² Other fragmentation modes of the molecular ion of IV, substantiated by appropriate metastable peaks, m/e 121.5, m/e 99.2, and m/e 77.8 involve elimination of hydrocarbon fragments containing one, two, and three carbon atoms and lead to the ions at m/e 135, 122 and m/e 108, respectively. The group of peaks around m/e 108 also contains selenious fragments at m/e 109 and 107, indicating the elimination of the fragments $\cdot C_3H_5$ and $\cdot C_3H_7$, respectively, from the molecular ion. Furthermore, at least part of the ions at m/e 94 $[CH_2Se]^+$ are generated by the two-step process $M - C_2H_4 - C_2H_4$, although a concerted process with simultaneous loss of two molecules of ethylene may also be visualized. Remaining selenious ions in IV are observed at m/e 93 $[CHSe]^+$, m/e 81 $[SeH]^+$, and m/e 80 $[Se]^+$. These ions are often found in the spectra of aliphatic selenium compounds.¹²

The unsymmetrical selenide V, Fig. 6, exhibits an abundant molecular ion, the stability of which is reflected by the presence of doubly charged ions at m/e 86.¹³ The dominating process is elimination of a methyl radical, Scheme 4, to form the ion at m/e 157, which in a second step gives rise to a phenyl ion at m/e 77 by loss of a selenium atom. No metastable peak has been detected to support the elimination of a CSe fragment from $[C_6H_5Se]^+$, although loss of CX is well-known from the corresponding sulphur and oxygen fragments.¹⁴ A rearrangement of the molecular ion of V making the expulsion of a SeH radical possible, leads to the abundant ion at m/e 91, usually described as a tropylium ion. Another characteristic process in the spectrum of V involves a hydrogen migration to the aromatic ring with a simultaneous elimination of CH_2Se from the molecular ion and leads to the benzene ion at m/e 78. Both these rearrangements are also observed in the spectrum of the corresponding sulphide.¹⁵ Finally, in the spectrum of V, there are the characteristic series of selenious fragments in low abundance at m/e 93 $[CHSe]^+$, m/e 105 $[C_2HSe]^+$, m/e 117 $[C_3HSe]^+$, and m/e 129 $[C_4HSe]^+$. These are frequently observed in the mass spectra of



Scheme 4.



Scheme 5.

aromatic selenium compounds and apparently originate from fragmentation processes in the aromatic ring of the ion at m/e 157 $[C_6H_5-Se]^+$.⁴

Mass spectra of only a few aromatic selenides have been published.⁷ The spectrum of diphenyl selenide has been recorded although the complete spectrum was not published.⁶ The spectra of VI–IX, Figs. 7–10 are characterized by ions from fragmentations predominantly occurring around the selenium atom, but also by ions arising from loss of the substituents. The main fragmentation routes are formulated for VI in Scheme 5. In the spectrum of VI the dominating process is the $ABC^{+*} \rightarrow AC^{+*} + B$ type elimination of the selenium atom from the molecular ion leading to the ion at m/e 182, represented as a substituted biphenyl ion, Scheme 5.⁴ This is also the principal process in the case of VII, Fig. 8, and VIII, Fig. 9, while in the spectrum of IX, Fig. 10, the alternative loss of a substituent gives rise to a peak of about equal intensity at m/e 311.¹⁶ Cleavage of carbon-selenium bonds in the molecular ion occurs only to a minor extent to m/e 171 $[CH_3C_6H_4Se]^+$ in VI, with the analogous ions at m/e 187, m/e 191, and m/e 235 in the spectra of VII–IX, respectively.

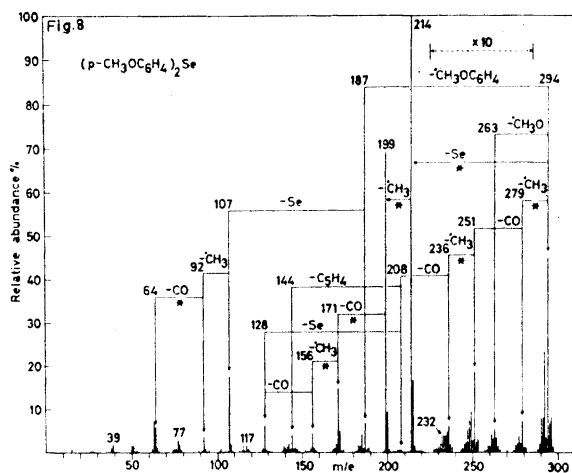


Fig. 8.

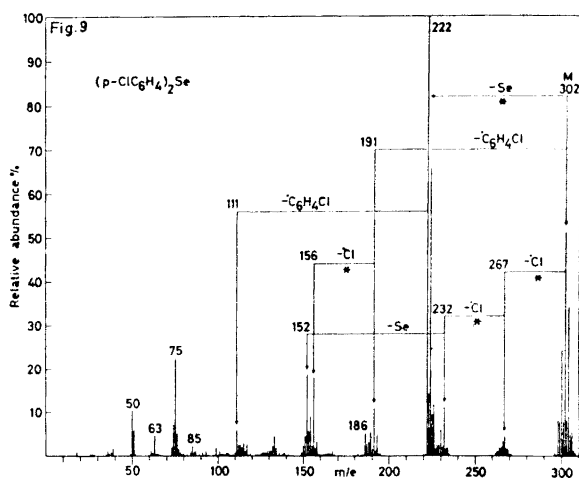


Fig. 9.

An alternative fragmentation route of the aromatic selenides VI–IX involves the stepwise elimination of the substituents from the molecular ion. This transition is shown for VI in Scheme 5 and leads to the ion at m/e 232. This fragment is rather abundant and associated with a doubly charged ion at m/e 116 in case of IX but is of very low abundance in the spectrum of VIII owing to alternative fragmentations as indicated in Fig. 8 around the ether function analogous to the degradation processes observed for anisole.¹⁷ Finally,

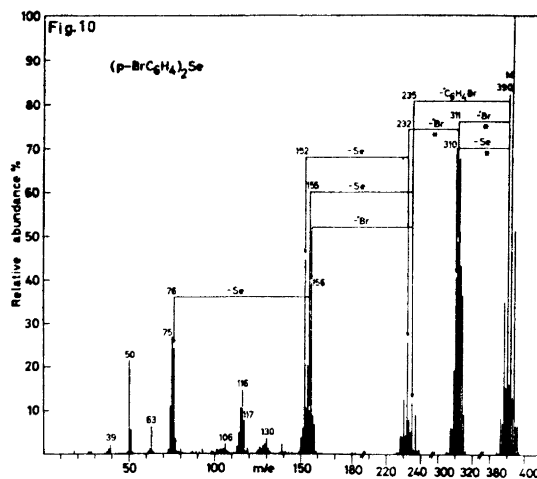


Fig. 10.

the fragment at m/e 232, described as a dibenzo[b,d]selenophene ion, Scheme 5, eliminates the selenium atom forming the biphenylene ion at m/e 152.¹³ The remaining selenious fragments at lower masses in VI–IX are analogous to those usually found in the spectra of aromatic selenium compounds⁴ and are not discussed further here. Finally, a number of low molecular hydrocarbon fragments are observed common to the mass spectra of aromatic compounds.¹⁸

EXPERIMENTAL

The mass spectra were recorded on an LKB model 9000 A gas chromatograph-mass spectrometer, operating at 70 eV. The spectra were recorded using the heated inlet system in case of I–IV, 50–100°, and the direct inlet system at 60–70°C for the selenides VI–IX. The purity of the selenides was checked by microanalysis for selenium and by TLC.

The aliphatic selenides I–IV were prepared from the corresponding alkyl halides and sodium selenide solution.¹⁹ They were purified by redistillation and the fractions with boiling points in accordance with values in the literature were used. B.p. (°C) Ia: 53–54,²⁰ Ib: 52–54, II: 156–158,²¹ III: 83.5–84/14, IV: 157–158.²²

Methyl phenyl selenide, V, was prepared from selenophenol and dimethyl sulphate.²³ B.p. 89–91°/15.

The aromatic selenides VI–IX were obtained by treating the diazotized anilines with a potassium polyselenide solution as for the preparation of diphenyl selenide described in Organic Syntheses.²⁴ The selenides were purified by repeated recrystallizations from ethanol or methanol. VI and VII were distilled before recrystallization. M.p. (°C) VI: 68–69,²⁵ VII: 53–54,²⁵ VIII: 95.5–96.5,²⁶ IX: 114–115.²⁷

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