Fragmentation in Mass Spectrometer of Some Phenylselanylated Azulenes and of the Corresponding Selenoxides and Selenones

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The fragmentation of unsubstituted and substituted 1-phenylselanyl-azulenes, as well as of the corresponding selenoxides and selenones in the electrospray ionization mass spectrometer, was reported and examined. Both their molecular peaks and the fragmentation paths were discussed in function of the azulene substituents and of the selenium oxidation states.

Key words: selenium compounds, azulene, mass spectroscopy, isotopes

The mass spectra of organoselenium compounds are characterized by a peculiar aspect of their molecular ions as well as of the fragments containing selenium atom. They contain the signals including all selenium isotopes in the natural abundance: ^{74}Se (0.87%), ^{76}Se (9.36%), ^{77}Se (7.63%), ^{78}Se (23.78%), ^{80}Se (49.61%), ^{82}Se (8.73%). However, usually were reported only the ions generated by ^{80}Se isotope that is the most abundant.

The fragmentations of diarylselanes, which takes place in the mass spectrometer using electron ionization, have been already reported [1]. They consist in the extrusion of the selenium atom with the formation of the radical cations of biaryls, as well as, in some elimination of an aryl fragment. The ratio between these two major paths is determined by the aryl substituents.

Azulene is a peculiar aromatic system much deeply involved in the extended conjugation of the molecules in comparison with other aromatic systems and more sensible to oxidation. The peculiarity induced in mass spectra of several molecular structures by the presence of azulene moiety was already studied in our research team [2-8]. Therefore, we have considered that it is also interesting to study its influence in the fragmentation of 1-phenylselanyl-azulenes **1** and **2** (scheme 1) in the mass spectrometer. The consequence of the presence of alkyl groups, compounds **2** or other several substituents at azulenyl moiety, compounds **1** (scheme 1), on the molecule splitting was also one target of the research.

The available data in the literature [9] on the fragmentations of the molecular radical cations resulted from several aromatic selenoxide or selenone, suggested us to study the influence of the oxidation of selenium atom as in 1-phenylseleninyl-azulene **3** (selenoxide) and 1-phenylselenonyl-azulene **4** (selenone) [10].

Experimental part

Reagents, instrumentation and methods

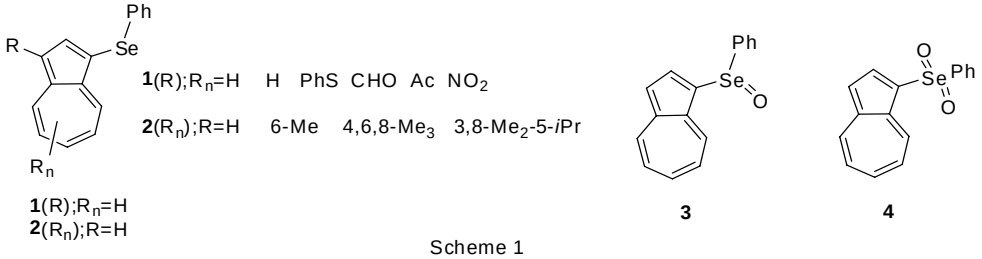
Varian 1200 L/MS/MS triple quadrupole mass spectrometer fitted with an electrospray (ESI) ionization interface was used. The substances were dissolved in methanol to the 1 mmol/L and direct infused into the interface by a Prostar 240 chromatographic pump and the flow was set to 20 μL/min. The used drying gas was air at a pressure of 18 psi and 150 °C and the nebulising gas was nitrogen to 40 psi. The capillary voltage had been established to the potential +5000 V for positive ionization. Thus protonated molecular ion obtained was selected by the first quadrupole. Into the second quadrupole the protonated molecular ion was fragmented by collision with an inert gas (argon) to 1 mtorr pressure. Prior to these experiments it was performed the tuning of mass spectrometer using PPG.

Results and discussions

The mass spectra, which described below, are obtained by electronspray ionization (ESI) using the positive mode, due to its higher importance as compared with the negative mode.

As expected, the signals of charged fragments containing Se, resulted by the splitting in mass spectrometer of the investigated compounds **1** - **4**, are not formed by a single peak as result from figure 1. Normally, the high abundance must be encountered for the generated fragments which contain ^{80}Se followed by that with ^{78}Se, therefore, further, we will take into account for our discussions only the fragments with ^{80}Se.

Following the even-electron rule (EE) in the electrospray mass spectra the protonated molecular ion, $[M+1]^+$, would be expected to be dominant [11]. However, as shown the



Scheme 1

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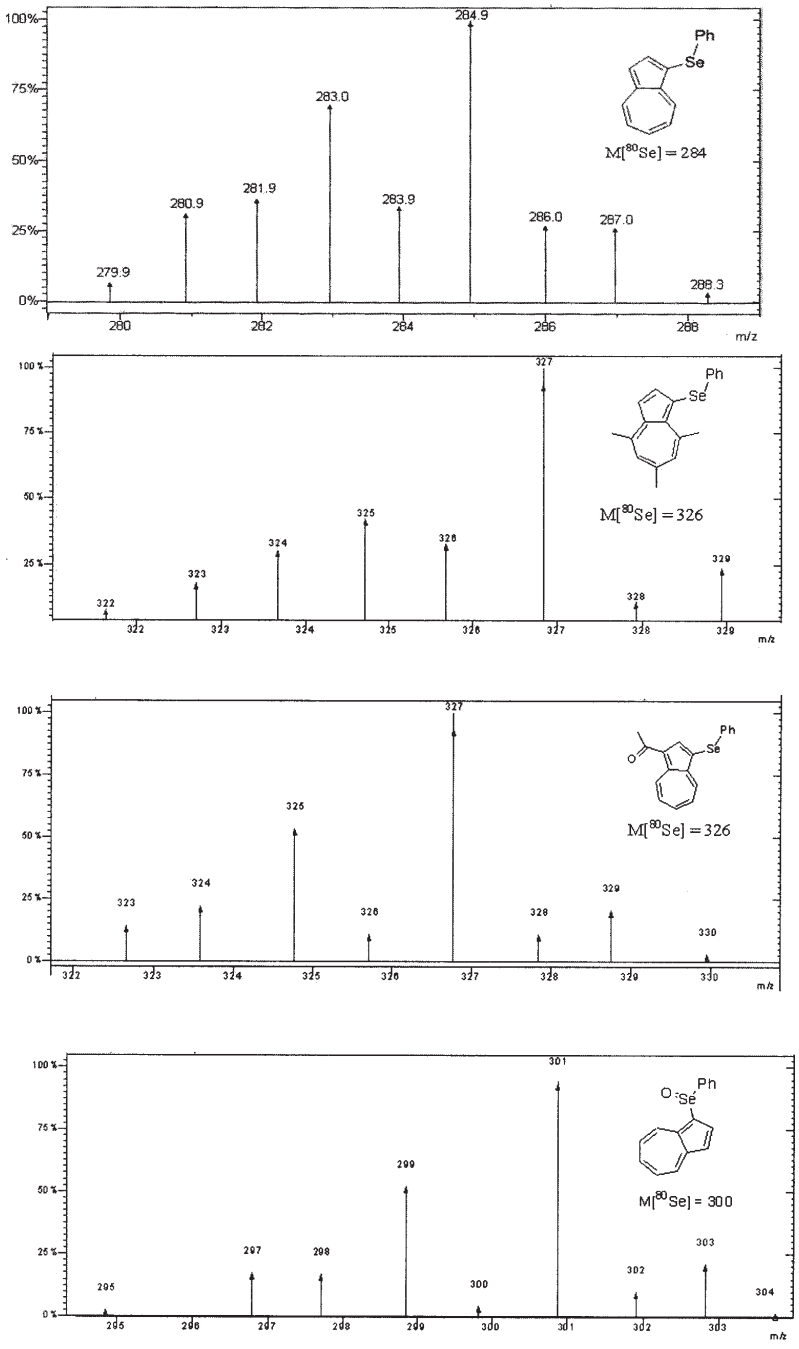


Fig. 1. Selenium isotopic contribution on the $[M+1]^+$ and $[M]^{\cdot+}$ pecks of several representative 1-phenylselanyl-azulenes or selenoxide

figure 1, this ion resulted together with molecular radical cation $[M]^{\cdot+}$ and this is a general rule also for the other compounds containing selenium in the molecule investigated in this paper. This fact can be explained by the peculiarity of azulenyl system to easily generate radical-cations at the oxidation. Moreover, similar behaviour is also observed in the case of other easily oxidizable polyaromatic system, such as pyrene or antracene, which instead of the protonated molecular peak, generate the radical cation of the molecular ion [12]. The abundance of the ion $[M+1]^+$ increases for the alkylated derivatives **2** and it is predominant for the compounds substituted in 3-position of 1-phenylselanyl-azulene with groups possessing -E and -I effect, as carbonyl or nitro, **1**(Ac), **1**(CHO) or **1**(NO_2) as well as for selenoxide **3**.

As expected, the individual fragmentations at 5 eV of the two ions occurred on different routes, as can be seen in the figure 2. Whereas the ion $[M+1]^+$ produced the azulenyl radical cation, the ion $[M]^{\cdot+}$ eliminated the selenium atom. The selenium extrusion is also observed to many other selenium derivatives [1] however when electron ionization was used.

The splitting mechanism for the ions $[M+1]^+$ and $[M]^{\cdot+}$ was suggested in scheme 2, route a and b, respectively.

At higher collisions energies (30 eV) the fragmentation becomes not selective, involving more profound changes, as results from figure 3 for the compound **1**(H). Thus, the mass spectrum, which contains the protonated as well as the ionized molecular peaks, reflects both decomposition paths (a and b). However, together with the azulene radical cation and the product of selenium elimination, the presence of the fragments with $[M]^+$ = 203 or 202 were also observed. These fragments could be assigned to the intramolecular cyclization of the 1-phenylazulenyl radical cation (Step (b1).

It is notable that whereas the azulenyl-selenium cation, $[M]^+$ = 207, is present in the mass spectrum, even if in low abundance, the selenium atom by no means leaves molecular ions bounded to phenyl group in a charged fragment as results from the absence of the peak with $[M]^+$=157.

Interestingly, the presence of methyl groups in the neighborhood of the PhSe group as in **2**(4,6,8-Me_3) or **2**(3,8-

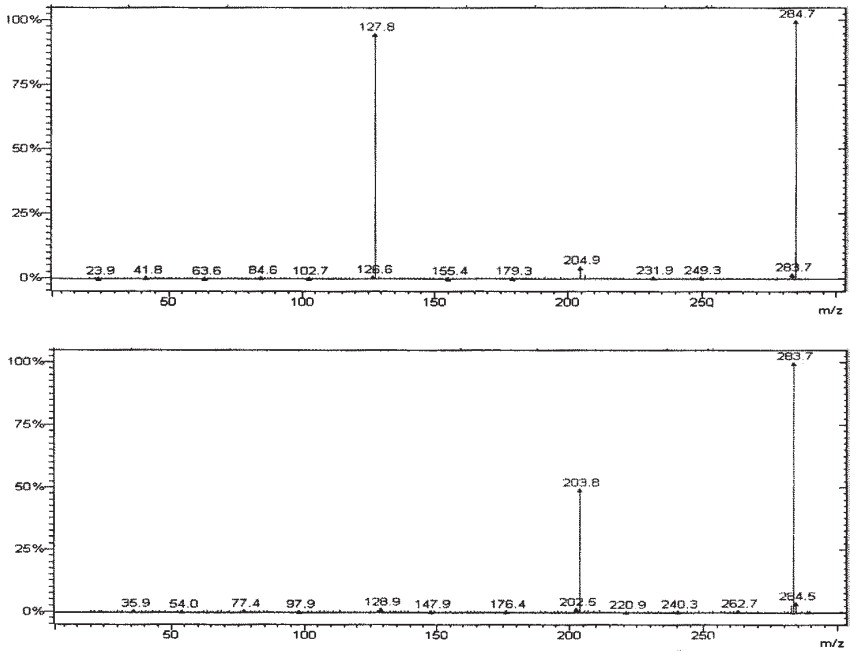
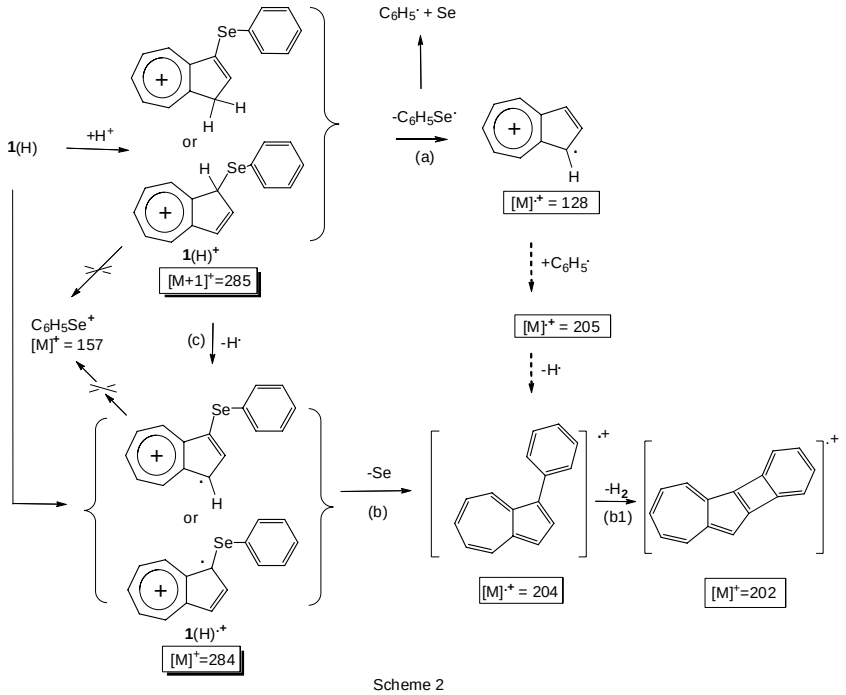


Fig. 2. Fragmentations of the ions $[M+1]^+$ and $[M]^{\cdot+}$ resulted from the compound **1**(H)



Scheme 2

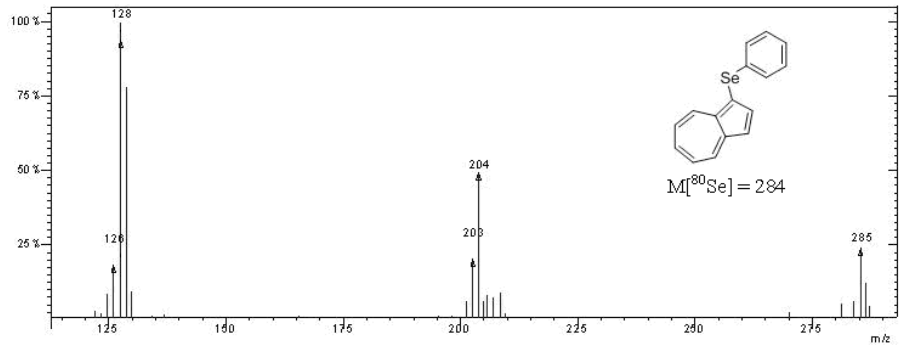


Fig. 3. The fragmentation of the protonated molecular ion of 1-phenylselanylazulene, **1**(H)

Me_2-5-*i*Pr) decreases significantly the abundance of the 1-phenylazulene radical cation obtained by the recombination of the phenyl and the azulenyl moieties due to the steric hindrance exerted by the azulenyl methyl groups. At higher splitting energies (30 eV) the fragments with a low mass become more abundant in the mass spectra.

The presence of phenyl-selenium together with phenyl-sulfur moieties in 1,3-positions of azulene **1**(PhS) allows the comparison between the influence of the two chalcogen atoms on the splitting in mass spectrometer. From the figure 4 resulted a lower abundance of protonated molecular ions $[M+1]^+ = 393$ than that of the molecular radical cation $[M]^{\cdot+} = 392$.

The fragmentation of **1**(PhS) in mass spectrometer, showed in figure 4, highlights the higher abundance of the

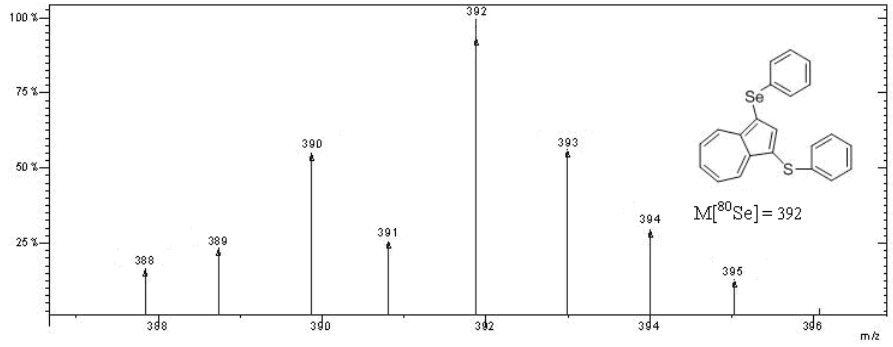


Fig. 4. Isotopic composition of the molecular ion of 1-phenylselanyl-3-phenylthioazulene, **1**(PhS)

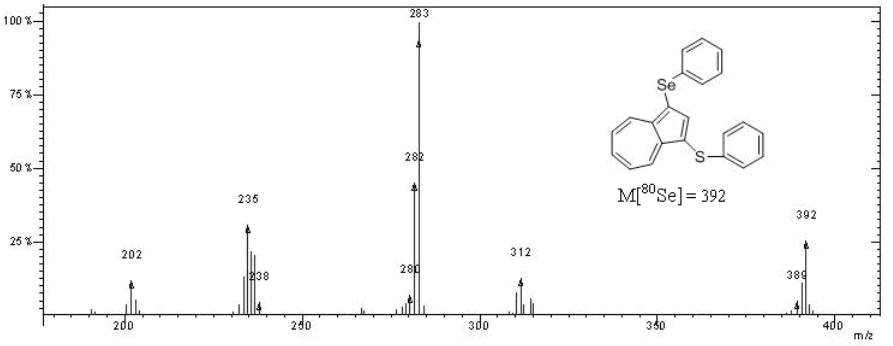


Fig. 5. The fragmentation of the protonated molecular ions of 1-phenylselanyl-3-phenylthioazulene, **1**(PhS)

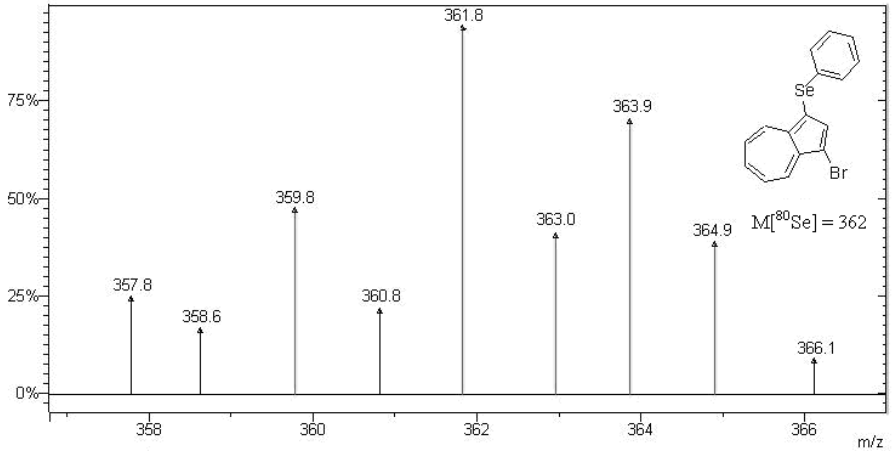


Fig. 6. Isotopic composition of the molecular ion of 1-phenylselanyl-3-bromoazulene, **1**(Br)

fragments that have lost the phenyl-sulfur and mainly the phenyl-selenium radicals. Interestingly, the presence of the peak with M = 312 corroborated with the absence of that with M = 360 relieves the fact that the splitting similar to route (b) in scheme 2 occurs only with the extrusion of the selenium atom and not of sulfur one. The fragment with M = 202 could be obtained on the route (b1) shown in scheme 1.

As can be seen in figure 6, the mass spectrum of molecular ion(s) of compound **1**(Br) is more complicate due to the presence of the two stable bromine isotopes, ^{79}Br and ^{81}Br in equal amounts.

The compounds in which 1-phenylselanyl-azulene is substituted in position 3 with groups containing the function carbonyl or nitro, **1**(CHO), **1**(Ac), or **1**(NO_2), respectively, can be easily protonated at the rich electrons substituents therefore the protonated molecular ions is good represented (figs. 7 and 8).

Both protonated molecular ions of, **1**(CHO), **1**(Ac), eliminate the phenyl-selenium group before other fragmentations (fig. 7 and scheme 3). This behaviour can be explained by the stability of the remaining fragment provided by the conjugation of protonated acyl substituent with the azulene moiety as showed in scheme 3.

The higher abundance for both fragmentations is represented by the cation with M = 155. For the fragmentation of **1**(CHO) this fragment could be obtained after the intramolecular cyclization of the radical cation with M = 156 on the routes represented in the scheme 3. However, starting from **1**(Ac) the fragment with M = 170 in the mass spectrum loses the methyl radical for the generation of cation with M = 155. This crowded cation lost the very stable carbon monooxide molecule and gains a hydrogen atom affording the azulene radical cation. Although the splitting of phenylselenium fragment was favorite, the small fragment with $[M]^{\cdot+}$ = 204 could be obtained on the route (b) showed in scheme 2. The azulene radical cation can be also generated either by the elimination of carbon monooxide molecule from the radical cation of azulenyl-carbaldehyde or by loss of ketene from the acetyl-azulene radical cation.

Whereas in all cases discussed above, the first splitting occurs between selenium and azulenyl, or with Se loss, for 3-nitro-1-phenylselanyl-azulene, **1**(NO_2) an oxygen atom was first removed giving the cation with M=313 followed by NO elimination M=283. The obtained fragment with 1-phenylselanyl-azulene structure adopts the same splitting route as it has already been described.

1-Phenylseleninylazulene (selenoxyde) **3** also looses an oxygen atom (fig. 9) to form the 1-phenylselanylazulene fragment (M=284) whose splitting has already been described. A small amount of the pattern structure can undergo a transposition to 1-phenylselanyloxyazulene [9] that, finally, generates 1-hydroxiazulene radical cation

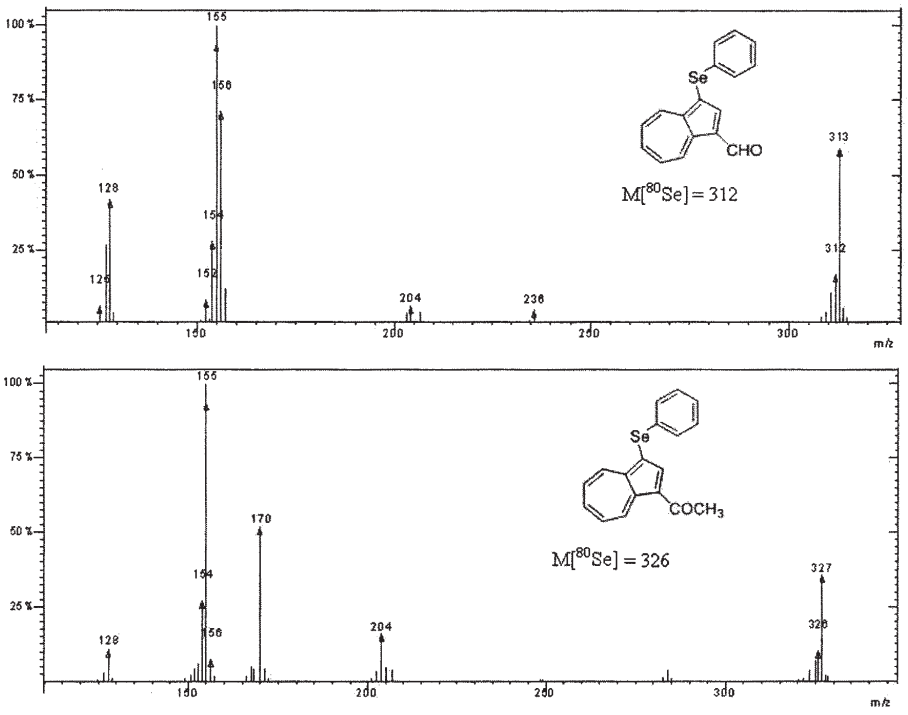
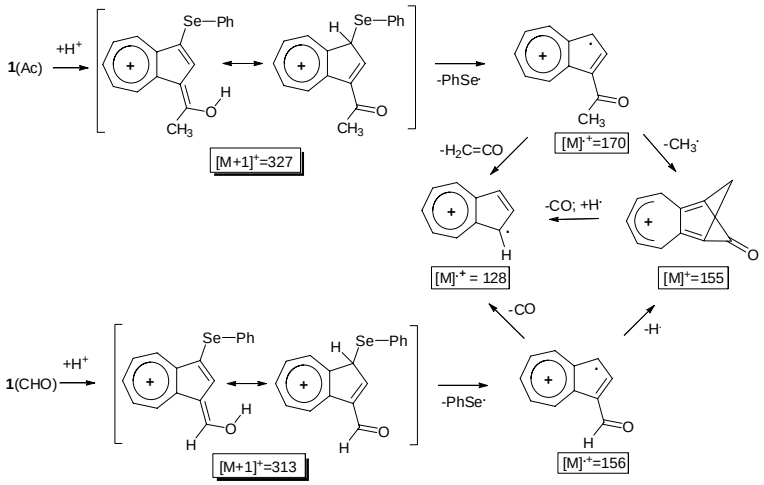


Fig. 7. The fragmentation of the protonated molecular ion of 3-phenylselanyl-1-azulenecarbaldehyde, **1**(CHO) and 3-acetyl-1-phenylselanylazulene, **1**(Ac)



Scheme 3

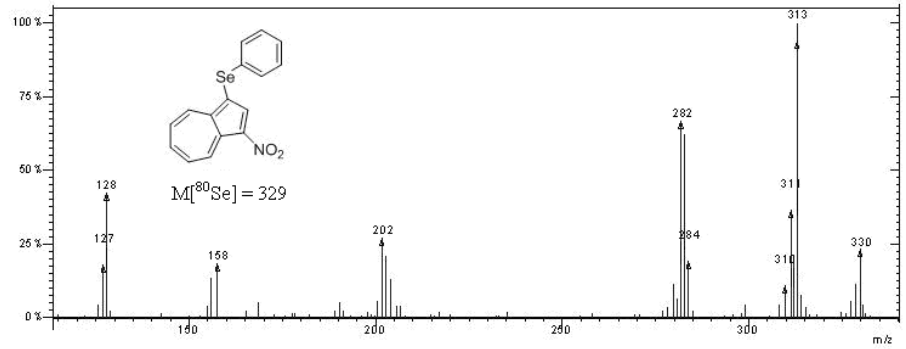


Fig. 8. The fragmentation of the protonated molecular ion of 3-nitro-1-phenylselanylazulene, **1**(NO_2)

(M=144 in scheme 4). The signal belonging to azulene radical cation is also present in mass spectrum. It is also interesting the ability of compound **3** to form the ion $[2M+1]^+$ = 601 in consistent abundance.

The mass spectrum of 1-phenylselenonyl-azulene, **4** (fig. 10), shows also the generation of the products of the intramolecular migration. However, for this compound, as it is reported in scheme 4, two transposition routes were adopted. The migration of phenyl (route (a) in scheme 4) followed by radical PhO elimination which produces the fragment with $[M]^+$ = 223 stabilized as radical cation. The migration of azulenyl moiety (route (b) in scheme 4) leads to azulenyl-ketone cation, which eliminates the carbon monooxide molecule [6]. In the mass spectrum of the compound **4** can be also signaled the fragments with M=207, M = 204 and M = 128 corresponding to the cation azulenyl-selenium, 1-phenylazulene radical cation and to azulene radical cation, respectively.

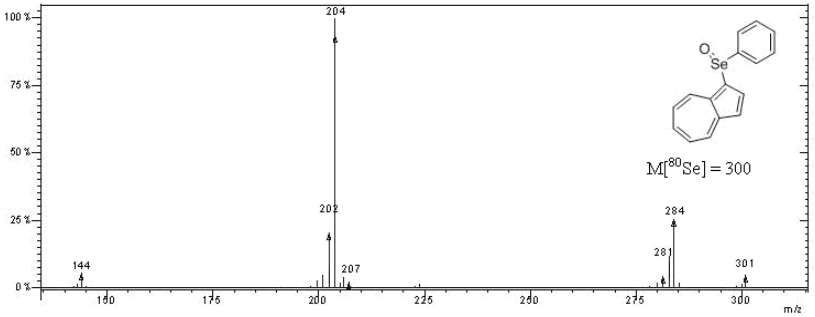


Fig. 9. The fragmentation of the protonated molecular ion of 1-phenylseleninylazulene, **3**

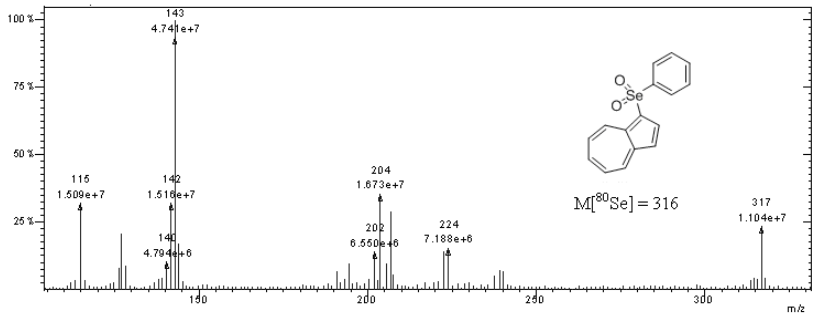
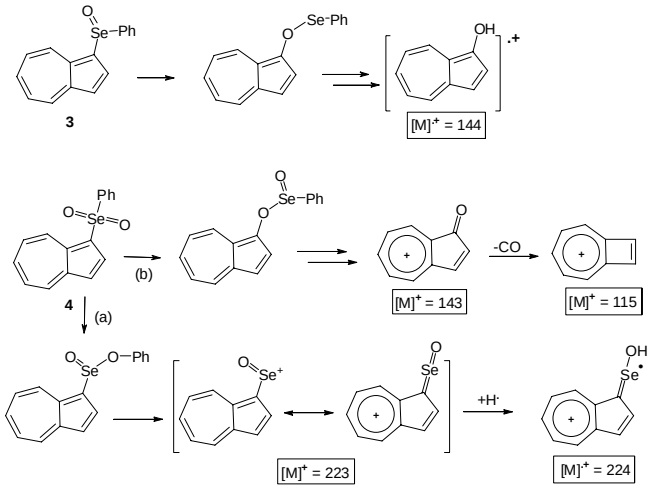


Fig. 10. The fragmentation of the protonated molecular ion of 1-phenylselenonyl-azulene, **4**



Scheme 4

Conclusions

The protonated 1-phenylselanyl-azulenes are stable in the mass spectrometer and can be analyzed using electrospray method in a positive mode. However, in all recorded mass spectra the molecular ion, $[M]^{\cdot +}$ was also observed in the more or less abundance. The facts that seem to infringe the well-known EE-rule encountered at the fragmentation using electrospray method can be explained by the high azulene oxidizability. The subsequent decay differs depending on the substituents at the azulenyl moiety. Nevertheless, the phenyl-selenium radical splitting with generation of azulene radical cation seems to be the first fragmentation route for the most of the investigated compounds. It is interesting that, whereas the bond breaking between selenium and phenyl affords the cation azulenyl-selenium, the cation phenyl-selenium appears only at the compounds 3-subsituted with acyl. The compounds containing oxygen attached to the selenium atom eliminate the oxygen atom and decay as selanides. Other splitting route of these last compounds consists first in a transposition of azulene from selenium to oxygen atom, followed by the elimination of radical PhSe.

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