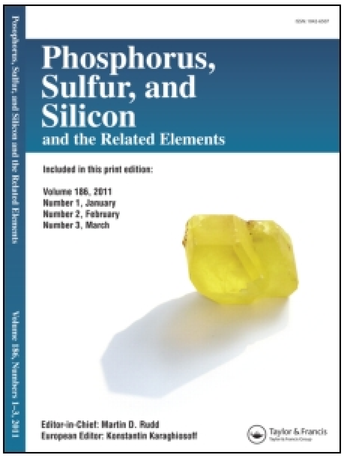

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A MASS SPECTRAL COMPARISON OF STERICALLY HINDERED SELONES AND THIONES

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To cite this Article Guziec Jr., Frank S. and Moustakis, Christine A.(1984) 'A MASS SPECTRAL COMPARISON OF STERICALLY HINDERED SELONES AND THIONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 21: 2, 189 — 195

To link to this Article: DOI: 10.1080/03086648408077656

URL: http://dx.doi.org/10.1080/03086648408077656

Phosphorus and Sulfur, 1984, Vol. 21, pp. 189–195
0308-664X/84/2102-0189/$15.00/0

A MASS SPECTRAL COMPARISON OF STERICALLY HINDERED SELONES AND THIONES

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(*Received March 24, 1984; in final form June 23, 1984*)

The electron impact mass spectra of several sterically hindered aliphatic selones and thiones are compared. The main fragmentation pathways of selones involve loss of selenium or selenium-containing fragments. The corresponding thiones have significantly higher abundances of related sulfur-containing fragments and typically exhibit more intense molecular ions. The detailed fragmentations of a number of thiones and selones are also described.

The use of selenium-containing reagents in organic synthesis has dramatically increased over the past ten years.[1] In addition, the widespread occurrence of selenium-containing compounds in biological systems has only recently been appreciated.[2] Selenocarbonyl compounds, containing a carbon–selenium double bond, have proved to be very important in both of the above areas of interest.[3]

To date mass spectral studies of selenocarbonyl-containing compounds have been quite limited. While the mass spectra of a number of selenoureas,[4] selenothiocarbamic esters,[4] and selenocarboxamides[5] have been reported, no detailed analysis of the mass spectra of selones—selenium analogues of ketones—has appeared. These compounds are especially interesting because they contain a "pure" selenocarbonyl moiety, not stabilized by resonance.

In our continuing studies of the reactivities of selenocarbonyl and thiocarbonyl compounds, we have recently developed a convenient synthesis of sterically hindered selones.[6] We have therefore been able to compare the electron impact mass spectral behavior of α-permethylated selones with that of their better known thiocarbonyl analogues, thiones.[7,8] While the mass spectra of selones and the corresponding thiones are generally similar, there are certain distinct differences between the spectra of the two classes of compounds. This comparison is described below.

RESULTS AND DISCUSSION

The mass spectra of selones and the corresponding thiones examined in this study are listed and compared in Table I. Throughout the study it was assumed that no major isomerization to more thermodynamically stable ions occurred at 70 ev. Running sample spectra at 20 and 50 ev led to no major qualitative differences in fragmentation patterns, indicating that this assumption is reasonable.

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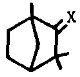
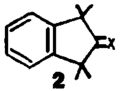
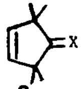
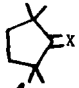
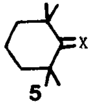
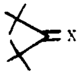
TABLE I

Relative intensities of major fragmentations of selones vs. thiones (M/E)

SELONE or THIONE		$(M)^{+\cdot}$	$(M—X^{\cdot})^+$	$(M—HX^{\cdot})^+$	$(M—a, H^{\cdot})^+$	$(a)^{+\cdot}$	$(b)^+$	$(M—Me^{\cdot})^+$	Base peak (if other)
 1	X = Se	33.7%	12.9	73.4	31.1	10.3	9.3	4.2	93, 100%
	X = S	30.4	3.4	28.0	100	7.3	30.1	10.2	93, 30.1%
 2	X = Se	24.3	67.7	13.0	3.8	0	0	17.1	157, 100% (—Se, —Me)
	X = S	23.6	3.5	17.7	3.2	3.3	3.7	100	157, 8.6%
 3	X = Se	28.6	25.0	90.8	7.5	0	1.8	30.8	91, 100%
	X = S	31.1	2.7	22.1	13.8	0	7.2	100	91, 29.8%
 4	X = Se	14.0	13	100	11.3	2.7	9.0	1.2	—
	X = S	61.6	11	100	45.0	7.6	57.8	24.8	—
 5	X = Se	17.5	12.5	48.8	9.1	8.5	13	0	81, 100%
	X = S	46.0	3.3	27.5	8.3	10.6	32.7	9.6	81, 56.8%
 6	X = Se	5.0	1.0	0	0	0	1.2	0	$t\text{-BuC}{\equiv}\overset{+}{\text{Se}}$, 3.1
	X = S	26.9	0.2	0.2	11.1	0	9.7	1.7	$t\text{-BuC}{\equiv}\overset{+}{\text{S}}$, 100

Some general features of the spectra are worth noting. The abundance of the molecular ions in selone spectra is in some cases significantly less than that of the corresponding thione (Table I, entries 4–6). In addition, loss of selenium or the elements of $HSe^{\cdot}$ is generally much more prevalent in selones than loss of sulfur or the elements of $HS^{\cdot}$ in the corresponding thiones. This ready loss of selenium-containing fragments is perhaps the most notable feature of selone spectra. A similar loss of selenium and selenium-containing fragments has been described in a comparison of the mass spectra of selenoureas and thioureas.[4]

In the mass spectra of thiones, formation of an ion of $m/z = 32$, S^+, is generally observed. The intensity of this ion is reported to vary with experimental conditions, but it is often prominent in thione spectra.[10] While our experimental conditions (cutoff $m/z = 40$) did not allow us to make a direct comparison of S^+ versus Se^+ formation, the intensity of ion $m/z = 80$, possibly $^{80}Se^+$, was generally low ($<$ 1–11%). These low abundances and interferences from non-selenium containing fragments in the region $m/z = 76$–82 did not allow for confirmation of Se^+ using predicted intensities derived from the characteristic isotopic intensities of selenium.[9] The relative intensity of the $m/z = 80$ ion however, in the corresponding thione spectra was generally greater than 50% of that from the selone, suggesting that extrusion of X^+ and formation of a carbenoid species is much less likely in the selone than in the case of the thione.

Loss of a methyl radical in a β-fragmentation is a major feature of thione spectra; the related process in the case of the selones is much less prevalent. In selones this fragmentation appears to a reasonable extent only in cases where a resonance stabilized carbocation is formed (Entries 2, 3).

Isopropenyl cation $m/z = 41$ and 2-methylallyl cation $m/z = 55$ are common fragments in all thiones and selones, as would be expected from these highly alkylated compounds. Fragments *a* and *b* also appear prominently in a number of spectra. Loss of *a* plus a hydrogen radical is a major fragmentation in many of the thiones and appears, although with less intensity, in a number of selone spectra. Fragmentations leading to $(a)^{+\cdot}$ and $(b)^+$ are generally more prominent in the thione than in the selone spectra.

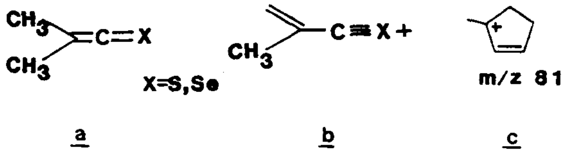
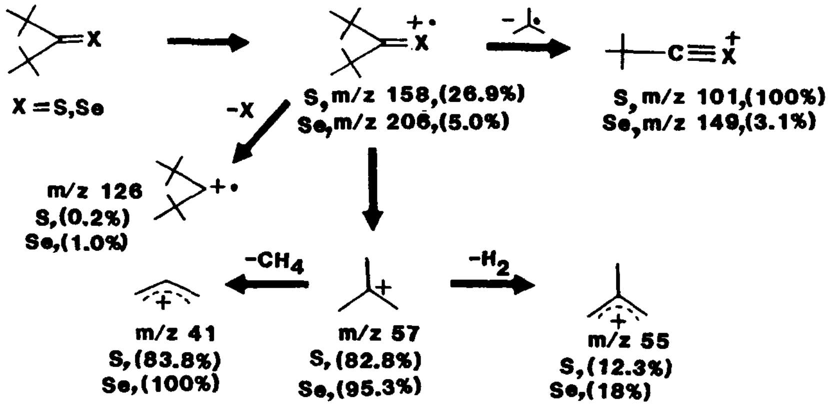


FIGURE 1

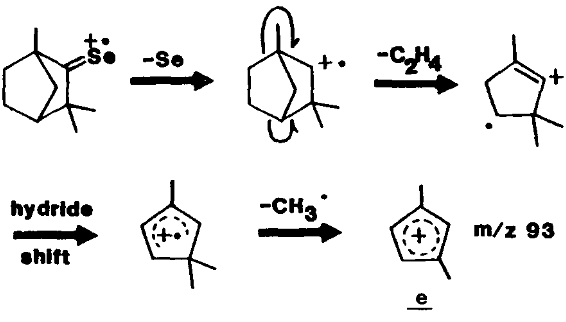
A comparison of the mass spectral behavior of di-*tert*-butyl selone and the corresponding thione is especially noteworthy (Scheme 1). This selone is, for synthetic reasons, the only acyclic compound investigated. As previously described, the molecular ion from the selone is much less prominent (5%) than that from the thione (26.9%). While the base peak in the thione spectrum ($m/z = 101$) corresponds to the thioacylium ion, the corresponding fragment ($m/z = 149$), selenoacylium ion, in the selone spectrum has a relatively low abundance (3.1%). The major fragments observed from the selone correspond to formation of tertiary-butyl carbocation (m/z = 57) (95.3%) and isopropenyl carbocation (m/z = 41) (100%).



SCHEME 1

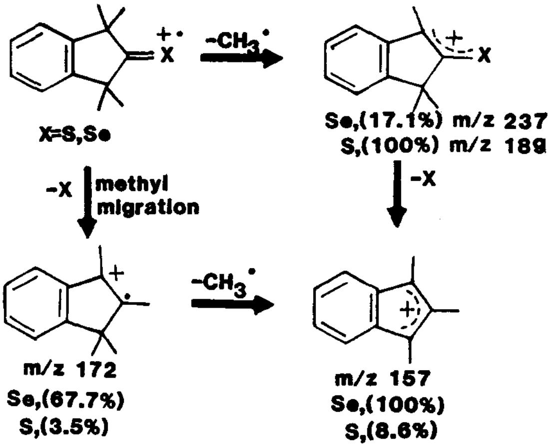
The mass spectrum of thiofenchone (Entry 1) has been previously reported.[10] Our results were in general agreement with this study, except that we observed a base peak of m/z = 81, corresponding to structure (*c*), via loss of the elements of (*a*) and a hydrogen radical. The reported major fragmentation m/z = 85 which corresponds to loss of (*b*)˙ was much less prominent (30.1%) in our spectrum.

Selenofenchone (Entry 1a) gave a base peak m/z = 93 which was also present to a lesser extent (30%) in the thione spectrum. A contribution to this observed mass fragment could correspond to a structure (*d*) ($HCSe^+$). The characteristic isotopic pattern of selenium[9] would lead to a prediction of m/z = 89 (18%), 90 (15%), 91 (47%) if (*d*) were in fact a major contributor to ion m/z = 93. The observed abundances: m/z = 89 (4%), 90 (< 1%), 91 (74%) are not consistent with this assignment. The fact that m/z = 93 also appears in the thione spectrum, and also that it is not a major fragmentation in other selone spectra leads us to suggest an alternate non-selenium containing structure (*e*) for this fragment (Scheme 3). Similar structures have been postulated for major fragmentations of bicyclic ketones.[11] Further loss of hydrogen from (*e*) could explain the presence of peaks at m/z = 92 (30.1%) and 91 (74.4%) (Scheme 2).



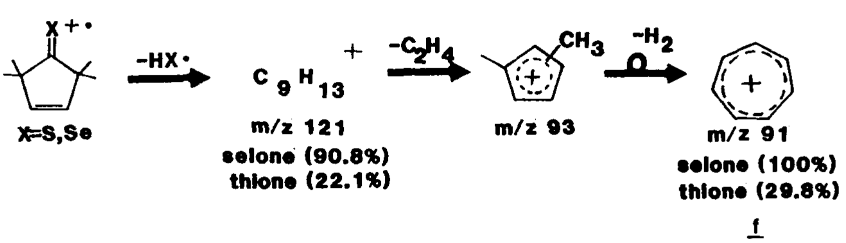
SCHEME 2

The tetramethylindanone derivatives (Entry 2) differ significantly in their behavior. The base peak of the thione corresponds to loss of methyl radical; on the other hand this is a relatively minor fragment in the selone (17.1%). The base peak in the selone corresponds to loss of elemental selenium and a methyl radical. This is not unexpected since another major fragmentation of the selone involves initial loss of selenium (67.7%), where the thione is much less likely to lose sulfur (3.5%) (Scheme 3).



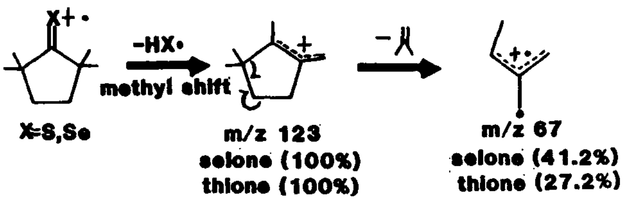
SCHEME 3

The tetramethylcyclopentenone derivatives (Entry 3) show a similar behavior. Loss of methyl leads to the base peak for the thione, but is less prominent in the case of the selone (30.8%). The base peak of the selone m/z = 91 could arise from the loss of ethylene or its equivalent from m/z = 121, (90.8%), followed by loss of hydrogen and rearrangement presumably to give tropylium ion (*f*). The fragment at m/z = 91 also appears in the thione spectrum (29.8%) and could conceivably arise in a similar manner (Scheme 4).



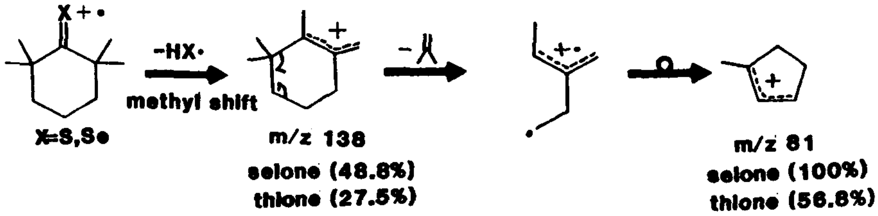
SCHEME 4

In only one case did a selone and its corresponding thione show the same base peak. 2,2,5,5-Tetramethylcyclopentaneselone and -thione (Entry 4) both lose the elements of HX to give a fragment m/z = 123, presumably (*g*) (Scheme 5). A similar fragmentation occurs in the 2,2,6,6-tetramethylcyclohexaneselone and thione (Entry 5) affording fragment (*h*) m/z = 137; loss of isobutylene from (*h*) would afford the major fragment (*i*) m/z = 81 (Scheme 6). Thiones and selones (4) and (5)



g

SCHEME 5

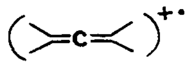


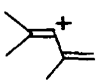
h i

SCHEME 6

both give peaks m/z = 95, 96, presumably structures (*j*) and (*k*). Fragment (*k*) also appeared with lowered intensity in the spectra of the tetramethylcyclopenteneselone (5%) and thione (17%) (Entry 3).

While the similarities in the spectra are obvious, the differences—especially the scarcity of selenium-containing fragments—must be adequately explained. A previously described comparison of the mass spectra of a series of thiones with the corresponding ketones showed that thione fragments were likely to contain sulfur, while hydrocarbon fragments tended to predominate in the mass spectra of ketones.[10] Molecular ions of thiones were also substantially stronger than those of the corresponding ketones. It was suggested that this was due to a greater ability of sulfur versus oxygen to stabilize radical cations. If these effects were simply due to polarizability, presumably selenium would be even more effective in stabilization of the radical cation. This is in sharp contrast to the results observed.





	m/z 96 j	m/z 95 k
selone 4	(1.7%)	(15.2%)
thione 4	(2.1%)	(11.9%)
selone 5	(79.1%)	(81.0%)
thione 5	(29.0%)	(38.3%)

FIGURE 2

To understand the selone fragmentation behavior as compared to that of the corresponding thione π bonding in these molecules must also be considered. The 2p–4p π bond of the selone is expected to be much less stable than the 2p–3p π bond of thiones due to less favorable overlap characteristics of the atomic orbitals.[3] Indeed, selones prove to be far more reactive than thiones in reactions where the π overlap is destroyed.[12,13] Presumably any fragment containing a multiply bonded selenium would be much less stable than the corresponding multiply bonded sulfur fragment. It is therefore likely that the ability of selenium to stabilize a positive charge is more than counterbalanced by the instability of a multiply bonded selenium-containing cation, leading to the observed reactions where selenium-containing fragments are lost.

EXPERIMENTAL

Mass spectra were obtained with a Hewlett-Packard 5995A gas chromatograph-mass spectrometer with an HP 9885M flexible disk drive and electron impact source at 70 ev. Samples were introduced via temperature-programmed gas chromatography. Comparison spectra at 20 and 50 ev were obtained on a Hitachi Perkin Elmer RMU-6E mass spectrometer. Molecular ions were based on ^{80}Se, the most abundant isotope of selenium (49.82%);[9] a mass cutoff as $m/z = 40$ was used throughout. Selones and thiones were prepared as previously described.[6,8]

ACKNOWLEDGEMENTS

We thank the New Mexico State University Arts and Sciences Research Center for partial financial support of this research (Grant 1-3-43673). We also than Professor Paul Vouros for helpful comments, and Dr. N. Soundararajan for running low energy mass spectra.

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