Mass Spectra of 1,2,5-Selenadiazoles and their Oxygen and Sulfur Analogues

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The mass spectra of a series of 1,2,5-selenadiazoles and some of their oxygen and sulfur analogues are reported and discussed. Their main fragmentation modes, inferred from results of metastable defocusing and high resolution mass measurements, are compared. A close analogy to thermal and photochemical reactions was found.

Although the mass spectra of heterocyclic oxygen and sulfur compounds have been intensively investigated (cf. Ref. 1), only little attention has been directed towards the study of heterocyclic selenium compounds,2–14 and only few comparisons have been made with the analogous sulfur and oxygen compounds.5,6

The present paper is concerned with the study of the mass spectra of compounds 1–11 (Table 1). Although the spectra of some of these compounds have been reported earlier (I15,16 16, 9,17 and 11,18) no detailed investigation of the fragmentations was made.

RESULTS AND DISCUSSION

Compounds 1–3. The major fragmentation modes for compounds 1–3 are shown in Fig. 1. In order to minimize thermal decompositions prior to ionization (compounds 115,16 and 316 are known to decompose to benzonitrile upon heating) the spectra were recorded at the lowest possible ion source temperatures with direct sample insertion into the ion source. At higher ion source temperatures the relative abundances of the benzonitrile ion (m/e 103) were observed to increase drastically. In all cases reproducible mass spectra were obtained.

Direct loss of the heteroatom X (O, S, Se) from the molecular ions was not observed in any case. However, the reported difference in behaviour of analogous sulfur and selenium compounds, i.e. the easier elimination of the selenium atom is demonstrated in the decomposition of the [M–C6H5CN]1+ ion, a. Application of the metastable defocusing technique revealed that elimination of O, S and Se takes place from ion a with formation of m/e 103.
Fig. 1. MS of compounds 1–3.

103. Since this process appears to be the predominant mode for formation of this ion (a metastable transition of very low intensity for direct formation of m/e 103 from the molecular ions was also detected by metastable defocusing) the abundance of m/e 103 in the three spectra may reflect the ease of elimination of X (Se > S > O).

However, these observations may not be due only to a different ability of initially formed \([C_4H_5CNX]^+\) ions (α) to perform a simple N–X bond cleavage. Other fragmentation processes observed for these ions (loss of CX and HCN) indicate that they undergo rearrangement involving a migration of the heteroatom X. A possible structure for the rearranged ion may correspond to the molecular ions of \(C_6H_5XCN\) or \(C_6H_5NCX\). While the fragmentations of α are clearly different from the fragmentations of \(C_6H_5XCN\) (X = O, \(\alpha_1\), X = S, \(\alpha_2\), and X = Se \(\alpha_3\)) similarities are found when comparisons are made with the spectra of \(C_6H_5NCX\) (X = O, \(\alpha_1\), X = S, \(\alpha_4\), and X = Se \(\alpha_5\)). This suggests that α rearranges to some extent to the latter structure (cf. the discussion of the phenylthiacynitrenium ion, \([C_6H_5C(S)N]^+\)). However, the internal energy distribution may be quite different for a molecular ion and a fragment ion of the same structure and the abundances of their decomposition products may as well be quite different. Thus it is not possible to determine to what extent the rearrangement may depend on the nature of X and to what extent the elimination of X takes place from the two structures in question, \(C_6H_5CNX\) and \(C_6H_5NCX\). However, the difference in ability to eliminate X (Se > S > O) is much more pronounced in the spectra of \(C_6H_5NCX\) than observed for α in Fig. 1. (In the spectrum of phenylisolelenocyanate the \([M-Se]^+\) ion is twice as abundant as the molecular ion. Loss of oxygen was not observed in the spectrum of phenylisocyanate \(\alpha_7\).)

Compounds 4–8. The mass spectra of the parent compounds 4–6 are shown in Fig. 2.

* The most important features in the spectra of phenylisothiocyanate and phenylisolelenocyanate are the following: Phenylisothiocyanate, m/e 135 (M+, 100%), m/e 108 (M+–HCN, 3%), m/e 103 (M+–S, 4%), m/e 91 (M+–CS, 4%), and m/e 77 (M+–NCS, 58%). Phenylisolelenocyanate, m/e 183 (M+–(Se), 48%), m/e 156 (M+–HCN, 3%), m/e 103 (M+–Se, 96%) and m/e 77 (M+–NCS, 100%).
The loss of HCN from the molecular ions is a parallel to the loss of C₆H₄CN in the spectra of 1 – 3. However, the further fragmentation of the [M – R-CN]⁺ ion is clearly affected by the nature of R as demonstrated by a comparison between the mass spectra (Figs. 1 and 2) of the selenadiazoles 3 and 6. In 3 the elimination of selenium takes place with charge retention preferentially on the phenyl containing moieties leading to very low abundances of the selenium ions (m/z 80: 4 %). In the case of 6 reversed charge retention leads to the formation of abundant Se⁺ ions and elimination of HCN. The total abundance of the selenium ions is approximately three times as high as that of [HCN]⁺.

Corresponding differences are found in the spectra of the thiadiazoles 2 and 5. However, the sulfur ion is less abundant in 5 than the

\[ \text{Scheme 1.} \]

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selenium ions in 6 and in the spectrum of 1,2,5-oxadiazole (4) m/e 16 is negligible.

3,4-Dimethyl-1,2,5-selenadiazole (7) exhibits similar fragmentation modes as 1,2,5-selenadiazole (6). The selenium ions and the [RCN]+ ion are formed in approximately the same mutual ratio in both spectra.

Except for the loss of NO the more important differences in the fragmentation modes of compounds 1 to 7 are summarized in Scheme 1.

Both fragmentation routes are observed in the spectrum (Fig. 3) of 4-methyl-3-phenyl-1,2,5-selenadiazole (8). One is initiated by the loss of CH_3CN from the molecular ion, yielding the m/e 183 ion, the further decomposition of which is identical to that observed for a in the spectrum of 3. The other involves the initial elimination of C_H_3CN with generation of m/e 121 which then decomposes as ion a in the spectrum of 7. The former route, giving rise to a sequence of ions involving the phenyl group, is more pronounced than the latter (cf. Fig. 3).

Compounds 9–11. The spectra and the predominant fragmentation modes of compounds 9–11 are shown in Fig. 4. The stability of NO versus NS and NSe shows a marked influence on the fragmentation of these compounds. Thus, the only major fragmentation of the molecular

Fig. 3. MS of compound 8.

Fig. 4. MS of compounds 9–11.
ions of 9 is elimination of NO. The corresponding NS-loss is much less important in 10 and NSe-loss does not occur in 11.

The m/e 76 ion in the spectrum of benzo-selenadiazole (11) has previously been suggested to be the benzyne ion. However, the metastable defocusing technique showed that m/e 103 (M⁺ – XH) in the spectra of 10 and 11 was the progenitor for m/e 76 and exact mass measurements established its elemental composition as C₄H₄N. Similarly, the composition of m/e 77 and 78 was found to be C₅H₅N and C₆H₄N, respectively.

Comparison with thermal and photochemical reactions. With the exception of the fragmentation mode initiated by loss of NO from the molecular ion of 1, the primary electron impact induced cleavages of compounds 1, 2, and 3 into C₅H₅CN and C₄H₄CNX (with charge retention preferably on the latter moiety) show a close analogy to their thermal and photochemical behaviour. Thermolysis of diphenylfurazan (1) was reported to give a mixture of benzonitrile, phenylisocyanate and diphenyl-1,2,4-oxadiazole. These findings strongly suggest that the primary reaction is cleavage to benzonitrile and benzonitriile N-oxide. Similarly, it has been found that the primary products in the photolysis of 1 are benzonitrile and its N-oxide.

Thermolysis of 3 and photolysis at room temperature of 2 and 3 give benzonitrile. However, low temperature photolysis (85 K) of compound 3 gives, besides benzonitrile, an intermediate assigned as benzonitriile N-selenide. This intermediate is converted to benzonitrile upon irradiation or by raising the temperature above 110 K.

Irradiation of benzofurazan (9) was reported to give 4-cyanobutadiene-1-carbonitriile N-oxide as the primary product. This double cleavage reaction is analogous to the photochemistry of diphenylfurazan (1).

EXPERIMENTAL

Materials. All compounds were prepared by previously described methods (1, 2, 3, 6 and 7, 8, 9, 10, 11). The mass spectra were recorded on an AEI MS-902 mass spectrometer operating at 70 eV.

REFERENCES


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