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

CHRISTIAN L. PEDERSEN[a] and JØRGEN MØLLER[b*]

[a]Department of General and Organic Chemistry, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark and [b]Physical Laboratory II, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

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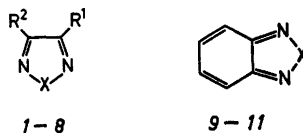
Although the mass spectra of heterocyclic oxygen and sulfur compounds have been intensively investigated (*cf.* Ref. 1), only little attention has been directed towards the study of heterocyclic selenium compounds,[2-14] and only few comparisons have been made with the analogous sulfur and oxygen compounds.[2,6]

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 (*1*,[15] *4*,[16] *6*,[5] *9*,[17] and *11*[3,4]) 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 *1* [18,19] and *3* [20] 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

Table 1. Compounds *1 – 11*.

	R¹	R²	X
1	C_6H_5	C_6H_5	O
2	C_6H_5	C_6H_5	S
3	C_6H_5	C_6H_5	Se
4	H	H	O
5	H	H	S
6	H	H	Se
7	CH_3	CH_3	Se
8	C_6H_5	CH_3	Se
9	–	–	O
10	–	–	S
11	–	–	Se

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 [6] in behaviour of analogous sulfur and selenium compounds, *i.e.* the easier elimination of the selenium atom is demonstrated in the decomposition of the $[M - C_6H_5CN]^+$ 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*

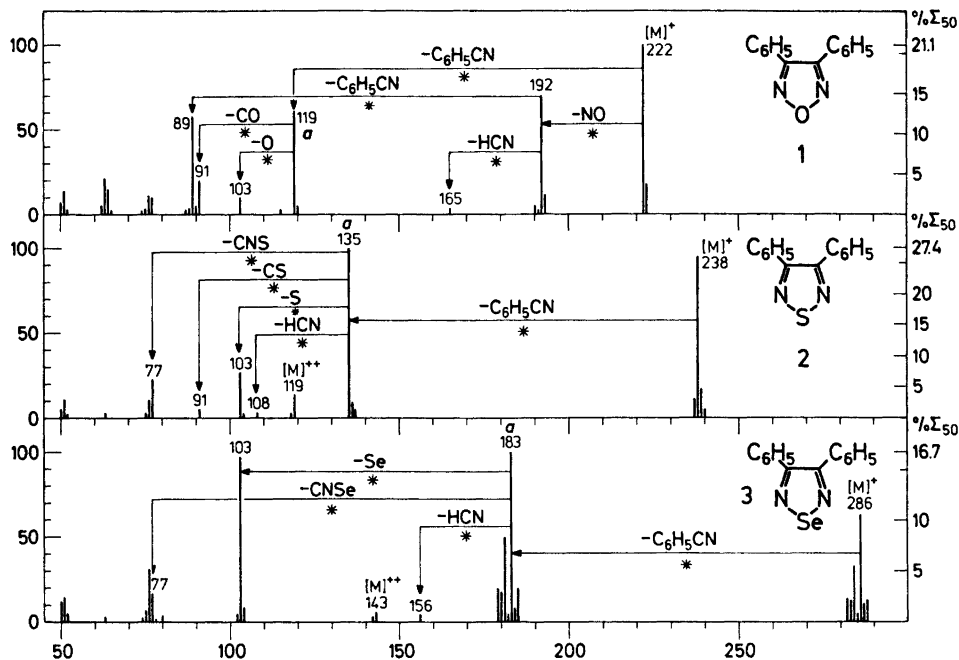* Present address: Department of Chemistry, Odense University, DK-5000 Odense, Denmark.

Acta Chem. Scand. B 29 (1975) No. 4

6

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 $[C_6H_5CNX]^{\ddagger}$ ions (*a*) 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 *a* are clearly different from the fragmentations of C_6H_5XCN (X = O,[21] X = S,[22] and X = Se [23]) similarities are found when comparisons are made with the spectra of C_6H_5NCX (X = O,[21] X = S,[24],* and X = Se*). This suggests that *a* rearranges to some extent to the latter structure (*cf.* the discussion of the phenylthiacylnitrenium ion, $[C_6H_5C(S)N]^{\ddagger}$ [25]). 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 *a* in Fig. 1. (In the spectrum of phenylisoselenocyanate the $[M – Se]^{\ddagger}$ ion is twice as abundant as the molecular ion. Loss of oxygen was not observed in the spectrum of phenylisocyanate [21]).

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 phenylisoselenocyanate 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 %). Phenylisoselenocyanate, m/e 183 (M+(^{80}Se), 48 %), m/e 156 (M+ – HCN, 3 %), m/e 103 (M+ – Se, 96 %) and m/e 77 (M+ – NCSe, 100 %).
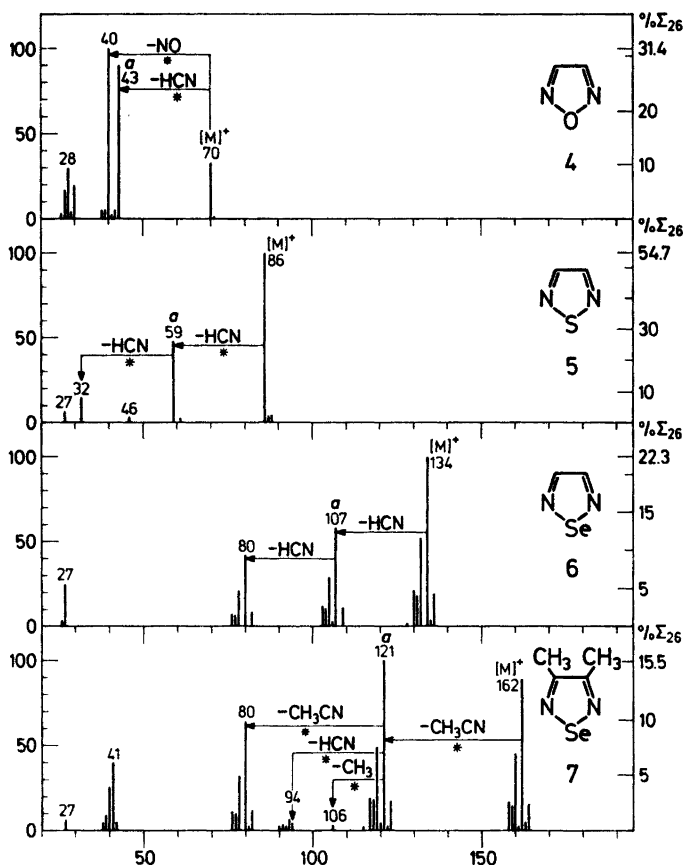
Fig. 2. MS of compounds *4 − 7*.

The loss of HCN from the molecular ions is a parallel to the loss of C_6H_5CN in the spectra of *1 − 3*. However, the further fragmentation of the [M − RCN]$^+$ 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/e* 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
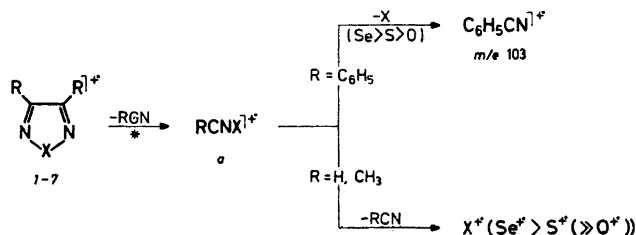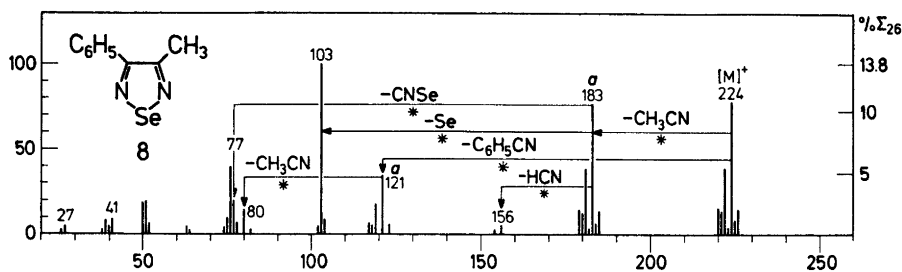

Scheme 1.

Fig. 3. MS of compound 8.

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_6H_5CN 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
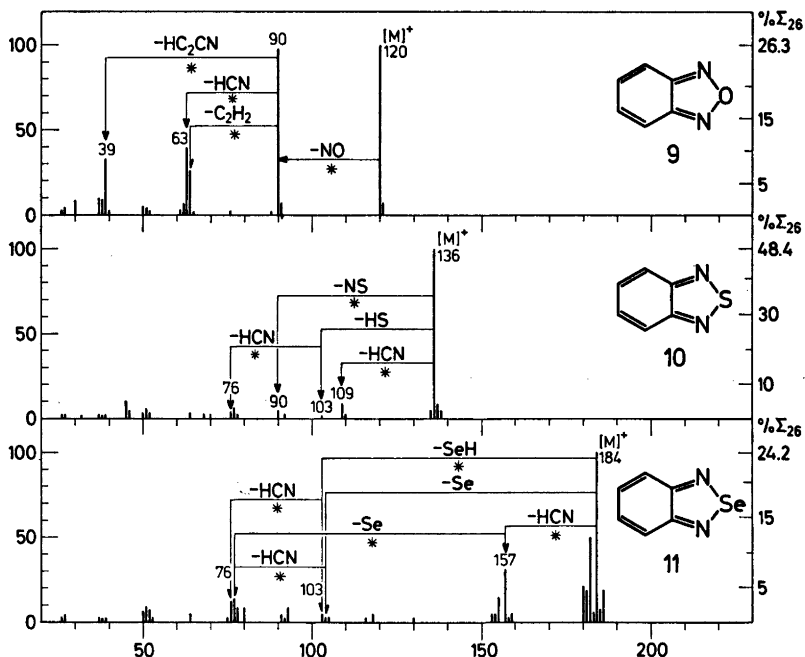

Fig. 4. MS of compounds 9−11.

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 benzoselenadiazole (*11*) has previously been suggested[3] 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 C_5H_2N. Similarly, the composition of m/e 77 and 78 was found to be C_5H_3N and C_5H_4N, 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 C_6H_5CN and C_6H_5CNX (with charge retention preferably on the latter moiety) show a close analogy to their thermal and photochemical behaviour. Thermolysis of diphenylfurazan (*1*) was reported[18,19] 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 benzonitrile N-oxide. Similarly, it has been found that the primary products in the photolysis of *1* are benzonitrile and its N-oxide.[15,26]

Thermolysis of *3* and photolysis at room temperature of *2* and *3* give benzonitrile.[20] However, low temperature photolysis (85 K) of compound *3* gives, besides benzonitrile, an intermediate assigned as benzonitrile N-selenide. This intermediate is converted to benzonitrile upon irradiation or by raising the temperature above 110 K.[20]

Irradiation of benzofurazan (*9*) was reported to give 4-cyanobutadiene-1-carbonitrile N-oxide as the primary product.[17,27] This double cleavage reaction is analogous to the photochemistry of diphenylfurazan (*1*).[15,26]

EXPERIMENTAL

Materials. All compounds were prepared by previously described methods (*1*,[18] *2*,[28] *3*, *6* and *7*,[29] *4*,[16] *5*,[30] *8* by a procedure analogous to that given for compound *3* in Ref. 29, *9*,[31] *10*,[32] and *11*[33]).

The mass spectra were recorded on an AEI MS-902 mass spectrometer operating at 70 eV.

Compounds *4* – *7*, *9* – *11*, phenylisothiocyanate, and phenylisoselenocyanate were introduced through the all-glass heated inlet system (temperatures 25 – 80 °C). The remaining compounds were introduced through the direct insertion lock, and the temperature of the water-cooled source was kept as low as possible. Typical sample temperatures were 50 °C for *1*, 60 °C for *2*, and 90 °C for *3*. When necessary, the elemental composition of an ion was determined by high resolution mass measurements ($\pm$ 5 ppm). Peaks of relative abundance lower than 2 % are omitted in the spectra.

REFERENCES

1. a. Budzikiewicz, H., Djerassi, C. and Williams, D. H. *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco 1967; b. Porter, Q. N. and Baldas, J. *Mass Spectrometry of Heterocyclic Compounds*, Wiley-Interscience, New York 1971.
2. Duffield, A. M., Budzikiewicz, H. and Djerassi, C. *J. Amer. Chem. Soc.* 89 (1965) 2920.
3. Buu-Hoï, N. P., Jacquignon, P. and Mangane, M. *Chem. Commun.* (1965) 624.
4. Buu-Hoï, N. P., Jacquignon, P., Roussel-Périn, O., Périn, F. and Mangane, M. *J. Heterocycl. Chem.* 4 (1967) 415.
5. Weinstock, L. M., Davis, P., Mulvey, D. M. and Schaeffer J. C. *Angew. Chem.* 79 (1967) 315.
6. Buu-Hoï, N. P., Mangane, M., Renson, M. and Christiaens, L. *J. Chem. Soc. B* (1969) 971.
7. Buu-Hoï, N. P., Mangane, M., Périn-Roussel, O., Renson, M., Ruwet, A. and Maréchal, M. *J. Heterocycl. Chem.* 6 (1969) 825.
8. Elmaleh, D., Patai, S. and Rappoport, Z. *J. Chem. Soc. C* (1970) 939.
9. Kendall, R. V. and Olofson, R. A. *J. Org. Chem.* 35 (1970) 806.
10. Harts, G. H., De Roos, K. B. and Salemink, C. A. *Rec. Trav. Chim. Pays-Bas* 89 (1970) 5.
11. Buu-Hoï, N. P., Dufour, M., Jacquignon, P., Renson, M., Maréchal, G. and Ruwet, A. *J. Chem. Soc. C* (1971) 2308.
12. Ajello, E. *J. Heterocycl. Chem.* 9 (1972) 1427.
13. Fitjer, L. and Lüttke, W. *Chem. Ber.* 105 (1972) 919.
14. Meier, H. and Voigt, E. *Tetrahedron* 28 (1972) 187.
15. Mukai, T., Oine, T. and Matsubara, A. *Bull. Chem. Soc. Jap.* 42 (1969) 581.
16. Olofson, R. A. and Michelman, J. S. *J. Org. Chem.* 30 (1965) 1854.
17. Georgarakis, M., Rosenkranz, H. J. and Schmid, H. *Helv. Chim. Acta* 54 (1971) 819.
18. Dodge, F. D. *Justus Liebigs Ann. Chem.* 264 (1891) 178.
19. Auwers, K. and Meyer, V. *Ber. Deut. Chem. Ges.* 21 (1888) 784.

20. Pedersen, C. L. and Harrit, N. *Unpublished results.*
21. Jensen, K. A., Holm, A., Wentrup, C. and Møller, J. *Acta Chem. Scand. 20* (1966) 2107.
22. Agenäs, L.-B. *Ark. Kemi 30* (1969) 465.
23. Agenäs, L.-B. *Acta Chem. Scand. 22* (1968) 1763.
24. Kjær, A. Ohashi, M., Wilson, J. M. and Djerassi, C. *Acta Chem. Scand. 17* (1963) 2143.
25. Jensen, K. A., Treppendahl, S., Christophersen, C. and Schroll, G. *Acta Chem. Scand. B 28* (1974) 97.
26. Cantrell, T. S. and Haller, W. S. *Chem. Commun.* (1968) 977.
27. Mukai, T. and Nitta, M. *Chem. Commun.* (1970) 1192.
28. Pilgram, K. *J. Org. Chem. 35* (1970) 1165.
29. Bertini, V. *Gazz. Chim. Ital. 97* (1967) 1870.
30. Weinstock, L. M., Davis, P., Handelsman, B. and Tull, R. *J. Org. Chem. 32* (1967) 2823.
31. Zincke, T. and Schwarz, P. *Justus Liebigs Ann. Chem. 307* (1899) 28.
32. Beecken, H. *Chem. Ber. 100* (1967) 2164.
33. Parker, C. A. and Harvey, L. G. *Analyst London 87* (1962) 558.