

Mass Spectra of Some 4- and 5-Substituted Derivatives of Benzoselenadiazoles

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Dedicated to Professor R. Kada in honour of his 65th birthday

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Abstract: Electron impact mass spectra of variety of eight 4-substituted and eight 5-substituted benzoselenadiazoles are presented and their spectral fragmentations are discussed. New mass spectra containing selenium in heterocyclic azole atom containing ring.

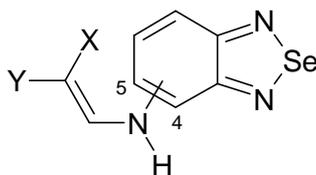
Keywords: Selenium, 2,1,3-benzoselenadiazole, aminoethylenes, aminomethylene compounds, enamine.

Introduction

Although the mass spectra of heterocyclic oxygen and sulphur compounds have been intensively investigated [1], limited data are available in the literature on the mass spectra of benzoselenadiazoles [2, 3]. We have prepared new compounds of some 4- and 5-substituted derivatives of benzoselenadiazoles and in order to prove their structures we used mass spectrometry and ¹H a ¹³C NMR spectroscopy.

Results and Discussion

The structural formulae of the compound studied in the present paper are shown in Table 1.

**Table 1.** 2,1,3-benzoselenadiazol-4-/or 5-ylaminoethylenes.

4-subst.	5-subst.	X	Y
1	9	COCH ₃	COCH ₃
2	10	COOCH ₃	COOCH ₃
3	11	COOC ₂ H ₅	COOC ₂ H ₅
4	12	COOC(CH ₃) ₂ OCO	
5	13	CN	COOCH ₃
6	14	CN	COOC ₂ H ₅
7	15	COCH ₃	COOCH ₃
8	16	COCH ₃	COOC ₂ H ₅

The relative abundances of the mass spectra **1** – **16** are given in Table 2. In the electron impact mass spectra all of the studied compounds are observed the corresponding molecular ions, where the abundance ratio of the isotopes of selenium is characteristic [4].

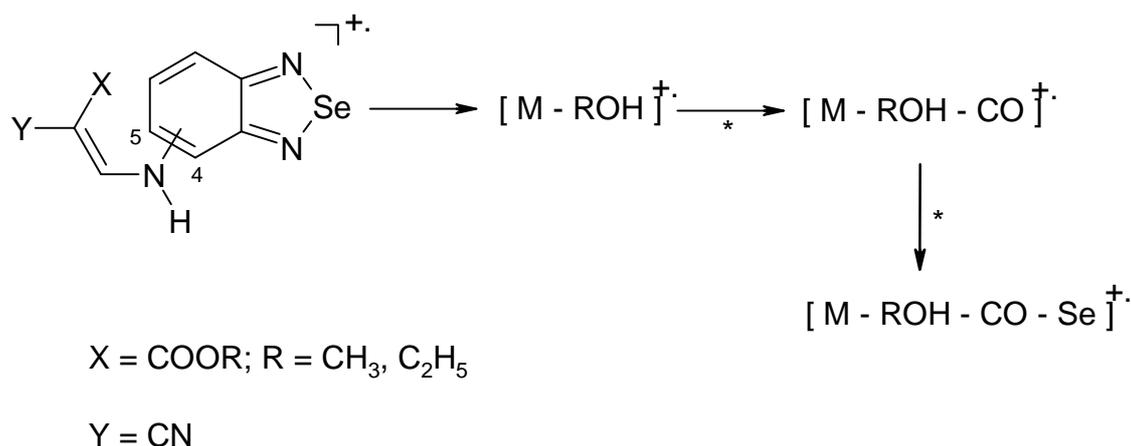
Table 2. EI mass spectra of 4- and 5-substituted derivatives of benzoselenadiazoles^{a,b}.

No	m/z (%)
1	309 M ⁺ (27), 307 (14), 268 (12), 266 (62), 264 (31), 263 (12), 262 (11), 224 (12), 112 (11), 43 (100).
2	341 M ⁺ (35), 309 (80), 307 (40), 282 (70), 250 (35), 249 (46), 143 (53), 103 (36), 59 (57), 53 (100).
3	369 M ⁺ (50), 323 (92), 321 (48), 296 (100), 294 (49), 249 (32), 223 (58), 221 (28), 143 (93), 53 (51).
4	353 M ⁺ (8), 295 (29), 225 (18), 223 (94), 221 (47), 143 (100), 116 (15), 103 (17), 53 (52), 43 (76).
5	308 M ⁺ (82), 306 (42), 276 (36), 249 (61), 248 (100), 246 (55), 168 (57), 103 (50), 76 (45), 52 (54).
6	322 M ⁺ (64), 320 (32), 276 (31), 249 (62), 248 (100), 247 (31), 246 (47), 168 (31), 103 (28), 52 (35).
7	325 M ⁺ (20), 293 (16), 282 (62), 280 (31), 250 (34), 248 (18), 223 (17), 143 (46), 53 (35), 43 (100).
8	339 M ⁺ (41), 296 (100), 294 (59), 293 (54), 265 (44), 250 (71), 248 (37), 223 (32), 143 (80), 53 (53).
9	309 M ⁺ (77), 307 (36), 266 (28), 252 (42), 250 (28), 224 (27), 172 (20), 143 (27), 112 (100), 70 (26).
10	341 M ⁺ (78), 339 (39), 309 (100), 307 (50), 250 (51), 157 (50), 143 (32), 103 (36), 59 (66).
11	369 M ⁺ (71), 367 (35), 323 (100), 321 (49), 267 (42), 250 (50), 223 (44), 170 (28), 143 (68), 103 (28).
12	353 M ⁺ (11), 295 (36), 251 (27), 250 (59), 248 (32), 223 (33), 143 (100), 76 (23), 53 (50), 43 (99).
13	308 M ⁺ (95), 306 (46), 276 (54), 249 (71), 248 (42), 169 (69), 168 (100), 103 (76), 76 (65), 52 (63).
14	322 M ⁺ (93), 320 (45), 276 (66), 249 (95), 247 (49), 169 (100), 168 (95), 103 (72), 76 (65), 52 (92).
15	325 M ⁺ (51), 323 (26), 293 (35), 291 (18), 265 (69), 263 (34), 250 (35), 248 (19), 143 (33), 43 (100).
16	339 M ⁺ (44), 337 (21), 293 (36), 291 (17), 265 (71), 263 (35), 250 (35), 248 (17), 143 (32), 43 (100).

^aTen the most abundant ions in the mass spectra are presented.

^bM⁺ for the most abundant isotope ⁸⁰Se.

The most abundant isotopes are ^{80}Se (49,7 %) and ^{78}Se (23,6 %). The main fragmentation pathways depend on the presence of substituents X and Y. The fragmentation of M^+ with $\text{Y} = \text{COOCH}_3$ or COOC_2H_5 substituents include the elimination of CH_3OH or $\text{C}_2\text{H}_5\text{OH}$ to produce $[\text{M} - \text{CH}_3\text{OH}]^+$ or $[\text{M} - \text{C}_2\text{H}_5\text{OH}]^+$ species, which further lose CO , and if $\text{X} = \text{CN}$, then the subsequent decomposition is the elimination of Se (Scheme 1). The elimination of the radicals $\cdot\text{COOCH}_3$ and $\cdot\text{COOC}_2\text{H}_5$ from M^+ show a rise in abundant fragment ions in most cases, too. There are some differences between 4- and 5-substituted isomers as, for example, the fragment ion $[\text{M} - \text{COOC}_2\text{H}_5]^+$, m/z 296 is 100 % in **6**, unlike in **11**, it is only 5 %.



Scheme 1.

The presence of $\text{X} = \text{COCH}_3$ group in the molecules show a rise in fragment ions $[\text{M} - \cdot\text{COCH}_3]^+$ with different relative abundance. If the second substituent $\text{Y} = \text{COOCH}_3$ or COOC_2H_5 , then the subsequent decomposition of the ion $[\text{M} - \text{COCH}_3]^+$ is the elimination of the molecule methanol or ethanol respectively. In **1** and **7**, the fragment $[\text{COCH}_3]^+$, m/z 43 itself represents the base peak. If both $\text{X} = \text{Y} = \text{COCH}_3$, the peak at m/z 112 represents the fragment ion with a probable structure $[(\text{CH}_3\text{CO})_2\text{C} = \text{CH}_2]^+$. This species is formed by β -cleavage to the aromatic ring with the hydrogen rearrangement, as it was described previously [5]. Fragment ion at m/z 112 represents the base peak in **9** (5-substituted) while in **1** (4-substituted) it is only 11 %.

Conclusion

We decided to publish the mass spectra of the new prepared selenium containing compounds as well as their fragmentation behaviour under electron impact.

Experimental

The EI mass spectra (low resolution) were recorded on a MS 902 S (A.E.I. – Kratos, Manchester) mass spectrometer using a direct probe heated to suitable temperature. The ionizing energy was maintained at 70 eV and the electron current was 100 μA . The temperature of the ion source was kept at 200°C. The metastable transitions were recorded in the second field free region.

The compounds studied in the present paper were synthesised at the Department of Organic Chemistry and the publication is under preparation (6).

References and Notes

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Sample Availability: Available from the authors.