The Mass Spectra of 3-Aryl-5-chloromethyl-1,2,3-oxathiazolidine-2-oxides

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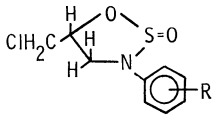
The mass spectra of 3-phenyl- (I), 3-tolyl- (II), 3-chlorophenyl- (III), and 3-trichlorophenyl- (IV), -5-chloromethyl-1,2,3-oxathiazolidine-2-oxides have been obtained. The major path in the electron impact-induced cleavage of all the compounds involves the loss of SO_2 and Cl from each molecular ion (M). The $M-SO_2-Cl$ ions show the loss of $CH=CH_2$, followed by the loss of the hydrogen radical and HCN. On the other hand, in compounds II, III, and IV, the $M-SO_2-Cl$ ions show the loss of the ring-substituted methyl or chloro radical. The above fragmentation pathways associated with metastable transitions or the chlorine isotopic clusters for each ion of III or IV have been outlined and discussed for each group of compounds.

Recently, we have reported the mass spectra of 3-aryl-1,2,3-oxathiazolidine-2-oxides[1] and 3-aryl-5-methyl-1,2,3-oxathiazolidine-2-oxides.[2] This time we wish to report the mass spectral data of new compounds of oxathiazolidines as an extension of our previous work. That is, the 3-aryl-5-chloromethyl-1,2,3-oxathiazolidine-2-oxides have been easily prepared by a previously-reported method,[3] and the mass spectra of the following eight compounds have been determined.



I, R=H (*cis*)
IIa, R=*o*-CH_3 (*cis*)
IIb, R=*m*-CH_3 (*trans*)
IIc, R=*p*-CH_3 (*cis*)
IIIa, R=*o*-Cl (*cis*)
IIIb, R=m-Cl (*trans*)
IIIc, R=*p*-Cl (*cis*)
IV, R=2,4,6-Cl (*trans*)

The present work is concerned with the fragmentation schemes of the above oxathiazolidines.

Experimental

Materials. All the eight oxathiazolidines examined were prepared by the reported method, and the general structures of these compounds were confirmed by means of the NMR spectral data.[3]

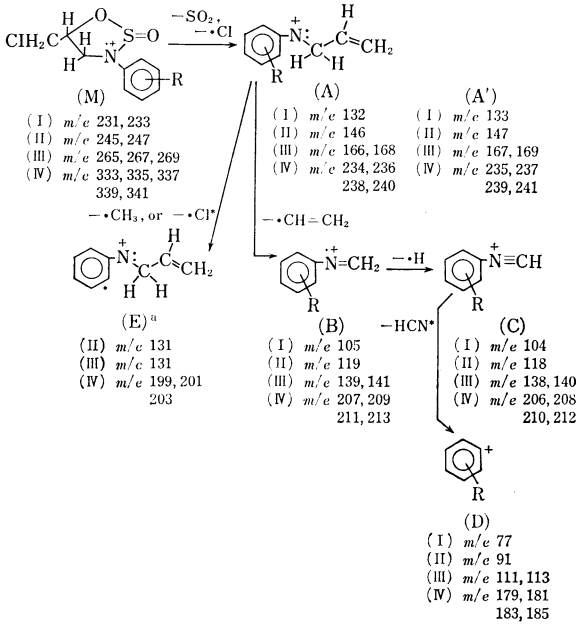
Compound IV: mp 77.5—78.7 °C (uncorrected), elemental analysis, Found: C, 32.31; H, 2.10; N, 4.25; S, 9.51; Cl, 42.10%. Calcd for $C_9H_7NSO_2Cl_4$: C, 32.24; H, 2.09; N, 4.18; S, 9.55; Cl, 42.38%.

Measurement. The high-resolution mass spectra were obtained by means of a Japan Electron Optics Co. Ltd., JMS-O1SG Mattauch-Herzog double-focusing mass spectrometer, at an ionizing voltage of 75 eV, an emission current of 200 μA, an accelerating voltage of 6.4 kV, and a vapor pressure of 1.0×10^{-6} mmHg. The ion-source temperature varied between 100 and 150 °C. The accurate masses and elemental compositions were determined by a previously-reported method.[1]

Results and Discussion

The mass spectral data of compounds I, II, and III, are summarized in Table 1, while their fragmentation pathways are shown in Scheme 1. It has previously been established that the oxathiazolidines exist in the *cis* and *trans* configurations between the S=O group and the chloromethyl group in the 5-position.[3] On the other hand, we have found that the fragmentation patterns of the oxathiazolidines are the same in the *cis* and *trans* configurations.[2] Thus, the fragmentation pattern for each compound will be discussed on the basis of the data obtained in the case of either the *cis* or *trans* isomer.

The molecular ions of these compounds are of low abundance. The base peaks of compounds I, IIb and c, and IIIc appeared at the mass numbers of 132, 146, and 166 respectively, corresponding to that of the



* Asterisks denote the processes for which metastable transitions were observed.

a) The radical on the benzene ring exists at *ortho*, *meta*, and *para* position in the corresponding compounds, II and III.

Scheme 1. The major fragmentation pathways of oxathiazolidines, I, II, III, and IV.

1) F. Yamada, T. Nishiyama, Y. Fujimoto, and M. Kinugasa, This Bulletin, **44**, 1152 (1971).
2) T. Nishiyama and F. Yamada *ibid.*, **45**, 928 (1972).
3) T. Nishiyama and F. Yamada *ibid.*, **44**, 3073 (1971).

Table 1. Mass spectral data of compounds I, II, and III (75 eV)

m/e	Compound I	
	Ion composition[a]	Rel. Int. (%)
233	$C_9H_{10}NSO_2Cl$	10
231	$C_9H_{10}NSO_2Cl$	27
133	$C_9H_{11}N$	11
132	$C_9H_{10}N$	100
105	C_7H_7N	30
104	C_7H_6N	91
77	C_6H_5	70

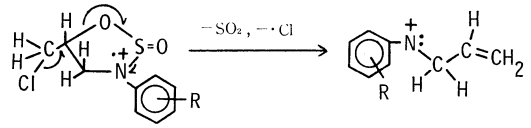
m/e	Compound II			
	Ion composition	Rel. Int. (%)		
		IIa	IIb	IIc
247	$C_{10}H_{12}NSO_2Cl$	9	14	13
245	$C_{10}H_{12}NSO_2Cl$	25	36	35
147	$C_{10}H_{13}N$	8	13	12
146	$C_{10}H_{12}N$	64	100	100
131	C_9H_9N	7	9	9
130	C_9H_8N	6	7	8
119	C_8H_9N	18	28	32
118	C_8H_8N	100	70	82
91	C_7H_7	45	68	71

m/e	Compound III			
	Ion composition	Rel. Int. (%)		
		IIIa	IIIb	IIIc
269	$C_9H_9NSO_2Cl_2$	4	2	5
267	$C_9H_9NSO_2Cl_2$	18	12	26
265	$C_9H_9NSO_2Cl_2$	28	18	37
168	C_9H_9NCl	31	29	32
167	$C_9H_{10}NCl$	11	11	12
166	C_9H_9NCl	81	92	100
141	C_7H_6NCl	8	12	10
140	C_7H_5NCl	33	37	31
139	C_7H_6NCl	27	38	30
138	C_7H_5NCl	100	100	78
131	C_9H_9N	9	13	13
130	C_9H_8N	25	18	15
113	C_6H_4Cl	17	25	14
111	C_6H_4Cl	40	74	46

a) The high-resolution mass spectra of these compounds gave the correct composition of all the ions mentioned in the table within an error of ±5millimass units.

$R\text{-}C_6H_4NC_3H_5$ ion (A). In the case of compounds IIa, IIIa, and IIIb, the $R\text{-}C_6H_4NCH$ cation (C) was the base peak. The ion A was formed from the molecular ion by the loss of the SO_2 group and a chloro radical. In the fragment ion A, the isotope peaks (A') appeared.

Our reports which have appeared in recent years have indicated that in the electron impact-induced cleavage of the 3-aryl-1,2,3-oxathiazolidine-2-oxides[1] and the 3-aryl-5-methyl-1,2,3-oxathiazolidine-2-oxides[2] the major path involves the loss of sulfur dioxide from the molecular ions. In view of these findings, it was interesting to find that the mass spectra of the 3-aryl-5-chloromethyl-1,2,3-oxathiazolidine-2-oxides showed no such $(M-SO_2)^{+\cdot}$ peak at all. Each showed peaks representing the loss of SO_2 and Cl. In none of these spectra were Cl-, SO_2-, or SO_2–Cl-positive ions present. The probable mechanism is indicated by the following diagram.



This decomposition implied that the loss of SO_2 and Cl is either concerted or so nearly so that no substantial amount of the $(M-SO_2)^{+\cdot}$ ion or $(M-Cl)^{+\cdot}$ ion is formed.

The ion B is formed from the ion A by the loss of the $CH{=}CH_2$ radical, and the resulting ion loses a hydrogen radical to give the ion C. In compound I, the peak at mass 77 due to the hydrocarbon ion (D), $C_6H_5^+$, is about 70% of the base peak intensity and was produced by the loss of the HCN group from the ion C. Similar methyl- or chloro-substituted hydrocarbon ions, $R-C_6H_4^+$, can also be observed in the spectra of compounds II, III, and IV and are abundant. This fragmentation pathway, (C)→(D), is verified by the metastable peaks at *m/e* 57.0, 70.2, and 89.3 respectively. On the other hand, no metastable peak was observed in Compound IV. Moreover, there have been many reports concerning the fragmentation pathway of $R\text{-}C_6H_4N^+{\equiv}CH \longrightarrow R\text{-}C_6H_4^+ + HCN$.[1,2,4,5]

In the spectra of II, the ion at *m/e* 131, which is of a 7% abundance for the *ortho* isomer, 9% for the *meta*, and 9% for the *para*, is present. This ion, corresponding to the C_9H_9N cation (E), is formed from the ion A. On the other hand, in the oxathiazolidines having the ring-substituted chloro atom, such as IIIa, IIIb, and IIIc, the ion at *m/e* 131, which is of a 9% abundance for the *ortho*, 13% for the *meta*, and 13% for the *para* isomer, is observed. In this case, the metastable peaks at *m/e* 103.3 are also observed. In the case of IV, the $C_9H_7NCl_2$ ion (*m/e* 199, 201, and

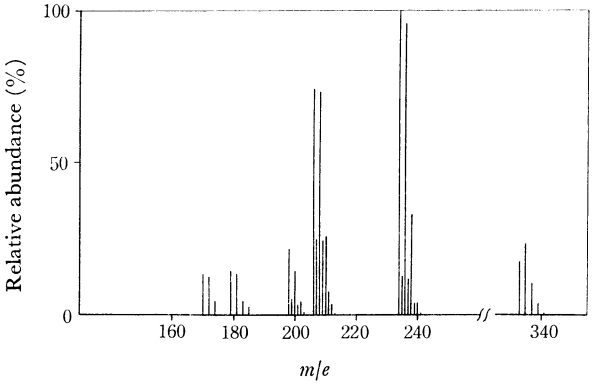
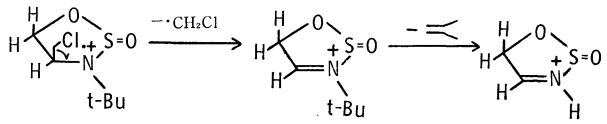


Fig. 1. Relative abundance of the fragment ions of the compound IV (75 eV).
The peaks below *m/e* 160 are omitted here.

4) F. Yamada, Y. Fujimoto, and T. Nishiyama, *ibid.*, **45**, 280 (1972).
5) D. J. Elias and R. G. Gillis, *Aust. J. Chem.*, **19**, 251 (1966).

203), with two ring-substituted chloro atoms, is present (E in Scheme 1). The above results suggest that these ions are produced by the loss of the methyl- or chloro-radical from the ion A.

It is interesting to compare these spectra with the spectra of the other oxathiazolidines reported by Deyrup and Moyer.[6,7] They reported that the mass spectrum of 2-oxo-3-*t*-butyl-4-chloromethyl-1,2,3-oxathiazolidines showed the $M-CH_3$ and $M-CH_3-SO_2$ peaks. The molecular ion is obviously of low abundance, and there are intense peaks at *m/e* 162 and *m/e* 106 as a result of the loss of the chloromethyl radical, followed by the loss of the isobutylene.



m/e 162 *m/e* 106 (Base peak)

On the contrary, in the cases of compounds I, II, III, and IV, the $M-CH_2Cl$ peaks are extremely small (4—5% of the base peak). These differences can be explained by the substituted groups on the oxathiazolidine ring. The fragmentations are influenced by the presence of the *N*-substituted aromatic nucleus and the position of the chloromethyl group (4- or 5-position).

The present fragmentation pathways are further illustrated by those of the 2,4,6-trichlorophenyl-5-chloromethyl-1,2,3-oxathiazolidine-2-oxide (IV). The mass-spectral data of IV are shown in Fig. 1, and the major fragmentation pathways are shown in Scheme 1.

6) J. A. Deyrup and C. L. Moyer, *J. Org. Chem.*, **34**, 175 (1969).

7) C. L. Moyer, 2-Oxo-1,2,3-oxathiazolidines, Dissertations, II, Harvard University (1968), (Avail. Univ. Microfilms, Ann, Arbor, Mich., Order No. 68–16878), p. 134; *Chem. Abstr.*, **70**, 77677d (1969).