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

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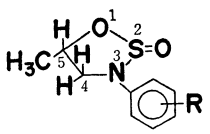
In continuation of our previous reports concerning the formation of 3-aryl-1,2,3-oxathiazolidine-2-oxides[1] and their mass spectra,[2] this report will deal with the fragmentation schemes of 3-aryl-5-methyl-1,2,3-oxathiazolidine-2-oxides.

We have prepared 3-phenyl-5-methyl-1,2,3-oxathiazolidine-2-oxide (I), 3-tolyl-5-methyl-1,2,3-oxathiazolidine-2-oxides (II), and 3-chlorophenyl-1,2,3-oxathiazolidine-2-oxides (III) by the reported method.[3]

The mass spectral data of the compounds are shown in Table 1, while the major fragmentation paths are shown in Scheme 1. The abundances of the molecular



I, R=H
IIa, R=*o*-CH_3
IIb, R=*m*-CH_3
IIc, R=*p*-CH_3
IIIa, R=*o*-Cl
IIIb, R=*m*-Cl
IIIc, R=*p*-Cl

ions of the compounds are quite low. This behavior can be ascribed to the easy cleavage of the oxathiazolidine ring; supporting evidence for this postulate is available from the large peaks (100% abundance) at *m/e* 104, 118, and 138, corresponding to the R-C_6H_4-NCH cation, in the spectra. These peaks occur because of the loss of the SO_2 group from the molecular ion, followed by the loss of both the $CH_2{=}CH_2$ group and the hydrogen radical (Path 1 in Scheme 1). These fragment ions lose the HCN group to give phenyl cations with *m/e* values of 77, 91, and 111 respectively.

The oxathiazolidines, I, II, and III, exist in the *cis*

1) F. Yamada, T. Nishiyama, M. Nakatani, and M. Kinugasa, This Bulletin, **43**, 3611 (1970).
2) F. Yamada, T. Nishiyama, Y. Fujimoto, and M. Kinugasa, *ibid.*, **44**, 1152 (1971).
3) T. Nishiyama and F. Yamada, *ibid.*, **44**, 3073 (1971).

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

Compound I (*trans*)

m/e	Ion composition[a)]	Rel. Int. (%)
197	$C_9H_{11}NO_2S$	17
133	$C_9H_{11}N$	19
132	$C_9H_{10}N$	25
105	C_7H_7N	22
104	C_7H_6N	100
77	C_6H_5	81

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 ±5 millimass units.

Compound II

m/e	Ion composition	Rel. Int. (%) IIa (*trans*)	IIb (*trans*)	IIc (*cis*)
211	$C_{10}H_{13}NO_2S$	11	32	15
147	$C_{10}H_{13}N$	10	19	19
146	$C_{10}H_{12}N$	6	27	16
132	$C_9H_{10}N$	10	15	14
119	C_8H_9N	15	27	27
118	C_8H_8N	100	100	100
105	C_7H_7N	3	11	14
91	C_7H_7	50	81	56

Compound III

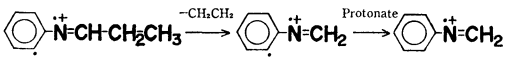
m/e	Ion composition	Rel. Int. (%) IIIa (*cis*)	IIIa (*trans*)	IIIb (*trans*)	IIIc (*trans*)
231	$C_9H_{10}NO_2ClS$	20	18	30	21
167	$C_9H_{10}NCl$	16	14	22	24
166	C_9H_9NCl	14	13	32	23
140	C_7H_5NCl	36	37	36	38
139	C_7H_6NCl	19	19	11	24
138	C_7H_5NCl	100	100	100	100
132	$C_9H_{10}N$	55	53	15	18
113	C_6H_4Cl	13	13	15	16
111	C_6H_4Cl	36	39	53	51

and *trans* configurations between the S=O group and the methyl group in the 5-position, and it is possible to assign the substituent geometry of the isomeric pairs by means of NMR spectroscopy.[3] In the mass spectral data shown in Table 1, the *cis* and *trans* isomers of IIIa show a similar fragmentation pattern. It can be assumed that the fragmentation patterns of the other compounds are the same in the *cis* and *trans* configurations. Thus, the fragmentation pattern for each compound will be discussed by means of the data obtained in the case of either the *cis* or *trans* isomer.

A significant difference in the mass spectral pattern on the position in the ring-substituted group in the III compounds can be observed at *m/e* 132, which is of 55% abundance for the *ortho* isomer, 15% for the *meta*, and 18% for the *para*. On the other hand, in the compounds of II, the abundance of the peak at *m/e* 132 is 10% for the *ortho* isomer, 15% for the *meta*, and 14% for the *para*. This ion at *m/e* 132, corresponding to $C_6H_5NC_3H_5$, can be produced by the loss of the SO_2 group from the molecular ion, followed by the loss of the ring substituent, methyl, or chloro group (Path 2 in Scheme 1). The above findings suggest that the abnudance of IIIa at *m/e* 132 may be caused by the substituent at the *ortho*-position.

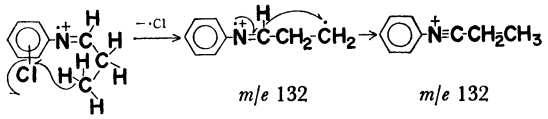
In constrast to the present behavior, the above fragment ion was not observed in the spectra of either 3-phenyl-1,2,3-oxathiazolidine-2-oxide or 3-*p*-tolyl-1,2,3-oxathiazolidine-2-oxide bearing no 5-methyl group.

In the compounds of II, peaks at *m/e* 104 and 105, corresponding to the $C_6H_4NCH_2$ and $C_6H_5NCH_2$ cations respectively, were observed. On the contrary to this fact, these peaks were so small as to be negligible in the spectra of III. These differences can be explained by the following fragmentation mechanisms. It is thought that, in the compounds of II, the fragment ion at *m/e* 132 eliminates the $CH_2=CH_2$ group to give the ion at *m/e* 104, and that then a proton adducts to the benzene ring to give the ion at *m/e* 105, as follows:



m/e 132 *m/e* 104 *m/e* 105

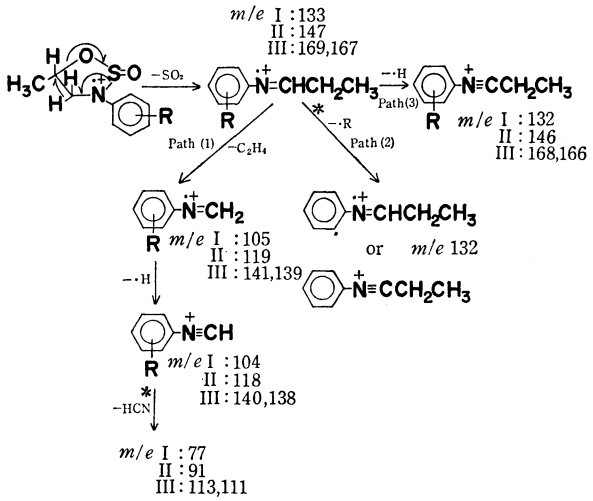
On the other hand, in the compounds of III, we supposed that the ion at *m/e* 132 can be formed by the elimination of the chloro substituent, followed by the migration of the hydrogen radical from the 5-methyl group to the position on the benzene ring, as follows:



m/e 132 *m/e* 132

m/e 169, 167

As has been described above, there are three principal paths of the fragmentation of the ion corresponding to R-C_6H_4N=$CHCH_2CH_3$ as a result of the loss of the SO_2 group from the molecular ion:



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

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

(1) the elimination of the $CH_2=CH_2$ group
(2) the loss of the ring substituent (radical)
(3) the loss of the hydrogen radical.

Experimental

The mass spectra were obtained with a Japan Electron Optics Co., Ltd., JMS-O1SG Mattauch-Herzog double-focusing mass spectrometer. In the photographic-plate measurements, a sample was introduced with a marker (PFK), under normal operating conditions (accelerating voltage, 6.4 kV). Accurate masses were determined by the previously-reported method.[2)]