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The Mass Spectra of 3-Aryl-1,2,3-oxathiazolidine 2-Oxides

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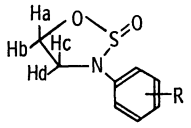
Synopsis. The mass spectra of a series of 3-aryl-1,2,-3-oxathiazolidine 2-oxides were obtained. The fragment ions were chiefly formed by the elimination of SO_2 from the M^+ ion. In this step, both the effects of the ring substituent and the torsion angle of the oxathiazolidine ring on the rate of the elimination were observed.

Recently, the authors reported the mass spectra of a number of 3-aryl-1,2,3-oxathiazolidine 2-oxides and a series of 3-aryl-5-methyl-, or 3-aryl-5-chloromethyl-1,2,3-oxathiazolidine 2-oxides.[1-3] In order to obtain further information about structural influence on the fragmentation pathways, the authors now deal with the correlations of the elimination rates with the substituents of the following 3-aryl-1,2,3-oxathiazolidine 2-oxides (**1**) and with the torsion angles of the oxathiazolidine ring determined from the vicinal coupling constants between the four methylene protons by means of NMR spectroscopy.[4]



1

(2)

I, R=H
IIa, R=*o*-CH_3
IIb, R=*m*-CH_3
IIc, R=*p*-CH_3
IIIa, R=*o*-OCH_3
IIIb, R=*m*-OCH_3
IIIc, R=*p*-OCH_3
IV, R=*p*-Br
Va, R=*o*-Cl
Vb, R=*m*-Cl
Vc, R=*p*-Cl
VI, R=2,4,6-tri-Cl

Experimental

Compounds. A series of **1** was prepared and purified by a previously reported method.[5] The reaction conditions and the physical properties of **1** were reported in a previous paper by the authors.[4]

Measurements. The mass spectra were obtained with a Japan Electron Optics Co., Ltd., JMS-01SG Mattauch-Herzog double-focusing mass spectrometer at an ionizing energy 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

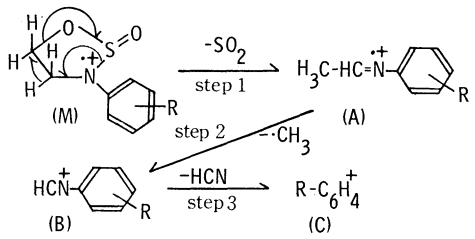
The mass spectral data of I—VI are shown in Table 1, while the main fragmentation pathway is shown in Scheme 1. There are three steps of cleavage in the oxathiazolidine ring, the elimination of SO_2 (step 1), of the methyl radical (step 2), and of HCN (step 3).[1] Examination of the data in Table 1 indicates there is a relation between the rate of elimination and the Hammett σ constant of an *m*- or *p*-substituent.[6] Then, the log Z/Z_0 (relative intensities) in step 1 were plotted against σ, except for the data with *o*- and 2,4,6-tri-substituents, as is shown in Fig. 1. In the case of the I,IIb, IIIb, Vb, and Vc, a reasonably good linear correlation is obtained, and the slope is $\rho=+0.81$. On the contrary, the values for IIc, IIIc, and IV deviated from the line. In the cases of steps 2 and 3, no noticeable substituent effect was found.

In a previous paper by the present authors,[4] it was reported that oxathiazolidines tend to form twist-envelope conformations, that their torsion angles vary with both the position and the nature of the ring substituent,

Table 1. Mass spectral data and torsion angles of the compounds

Compd. No.	Rel. Int. (%) M	A	B	C	Torsion[a] angle (θ°)
I	55	16	100	78	15
IIa	92	13	100	33	−11
IIb	87	23	100	90	12
IIc	84	22	100	80	11
IIIa	100	14	97	22	−5
IIIb	100	37	99	63	14
IIIc	78	26	100	13	4
IV	48	27	100	67	14
Va	69	13	100	36	−11
Vb	50	28	100	65	15
Vc	56	27	100	55	12
VI	14	21	100	21	30

a) These values are taken from Ref. 4.



Scheme 1. The main fragmentation pathway of the **1** compounds.

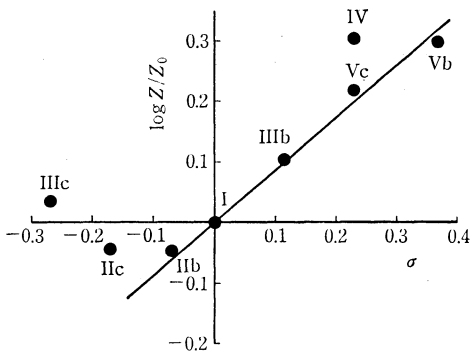
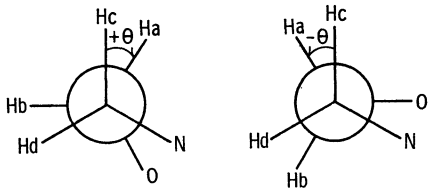


Fig. 1. Correlation of the intensities of the A ion in the 75 eV mass spectra of the **1** compounds. Slope=0.81.

and that the distortions of the oxathiazolidine ring of the compounds with *m*- and *p*-substituents are in the direction of the projection **2**, while those with an *o*-substituent cause a distortion toward the projection **3**, as can be seen in the diagram. The values of the torsion angles are listed in Table 1.



2 **3**

θ; Torsion angle

Regarding the greater deviation from the Hammett correlation in the case of IIIc (Fig. 1), it was considered that there is another energy factor for the elimination of SO_2 because of the small torsion angle for IIIc given in Table 1. The torsion angles of the compounds showed in Fig. 1 are in the range of 11—15 °C except for IIIc.

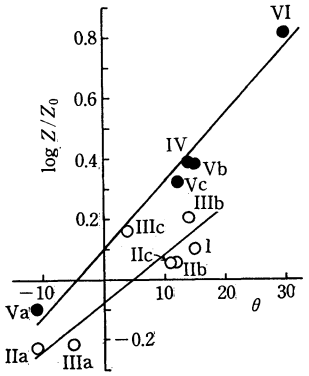


Fig. 2. The plot of the *Z*-values of the initial fragmentation of the **1** compounds against torsion angles (θ).
Z_0-value is obtained from the curve plotted of θ *vs.* A/M and is 23% at $\theta=0°$.
$Z=[R\text{-}C_6H_4\text{-}\overset{+}{N}\text{-}CHCH_3]/[M^+]$
●: Electron-withdrawing group, ○: electron-donating group.

Therefore, an attempt was made to plot the *z*-values of all the compounds against their torsion angles (Fig. 2). As can be seen in Fig. 2, two kinds of linear correlation are obtained. The upper line due to the data of the compounds with an electron-withdrawing group and the lower line due to those with an electron-donating group.

As is indicated in Scheme 1, the transfer of a hydrogen atom from the C-4 to the C-5 position and the ring cleavage of the molecular ion afford the elimination of the SO_2 group. In the molecular ion, the positive charge is distributed over the nitrogen atom and the aromatic ring. Figure 1 indicates that an electron-withdrawing substituent strongly enhances the formation of the elimination product and the value of approximately +0.81 is relatively large compared with any previously reported values for the rate of an electron-impact collision.[7] Thus, it appears that the reaction is enhanced by an increased positive charge at the reaction site. Figure 2 indicates that, in general, an electron-withdrawing group enhances the rate of elimination, and an electron-donating group supresses it. Moreover, the magnitude of the distortion of the oxathiazolidine ring may markedly affect the rate of elimination. The above two factors, the magnitude of the positive charge at the reaction site and the torsion angle of the oxathiazolidine ring, should make an important contribution to the driving force for an electron-impact collision.

References

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