BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1152—1153(1971)

The Mass Spectra of 2-Oxo-3-aryl-1,2,3-oxathiazolidines

Fukiko YAMADA, Tomihiro NISHIYAMA, Yasuyoshi FUJIMOTO, and Motokazu KINUGASA
Department of Applied Chemistry, Faculty of Engineering, Kansai University, Senriyama, Suita, Osaka

(Received October 24, 1970)

Various oxathiazolidines are easily prepared by the reactions of *N*-sulfinylanilines with alkene oxides.[1,2] We have prepared 2-oxo-3-phenyl-1,2,3-oxathiazolidine (I) and 2-oxo-3-*p*-tolyl-1,2,3-oxathiazolidine (II) by a reported method[2] and have examined their mass spectra. In this report, we wish to describe the fragmentation schemes of the compounds I and II; the correlation between the fragmentation pathways and the related organic reaction mechanisms will also be discussed.

TABLE 1. MASS SPECTRAL DATA OF COMPOUNDS I AND II[a] (75 eV)

No.	I			II		
	m/e	Ion composition[b]	Rel. Int. (%)	*m/e*	Ion composition	Rel. Int. (%)
1	183	$C_8H_9NO_2S$	55	197	$C_9H_{11}NO_2S$	84
2	119	C_8H_9N	16	133	$C_9H_{11}N$	22
3	118	C_8H_8N	18	132	$C_9H_{10}N$	24
4	105	C_7H_7N	30	119	C_8H_9N	38
5	104	C_7H_6N	100	118	C_8H_8N	100
6	91	C_6H_5N	24	105	C_7H_7N	43
7	77	C_6H_5	78	91	C_7H_7	80

a) The NMR and IR spectra of the compounds were consistent with the assigned structures.[2]

b) 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.

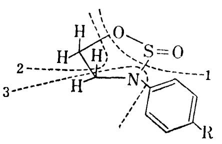
The mass spectral data of I and II are shown in Table 1. The compounds gave distinct molecular ions, as would be predicted from the presence of the aromatic nucleus; the fragment ions were formed by loss of SO_2 from the molecular ions. The base peaks occur from the loss of the SO_2 group, followed by the loss of the methyl radical. The most prominent fragment ions of the masses at 104 and 118 lose HCN to give hydrocarbon ions with masses of 77 II and 91 respectively. There are three steps of cleavage in the oxathiazolidine ring, the eliminations of SO_2 (1), the methyl radical (2), and HCN (3). The path of the fragmentation of the ring in the compounds I and II is indicated

---

[1] V. S. Etlis, A. P. Sineokov. and M. E. Sergeeva, *khim. Geterotsikl. Soedin.*, 682 (1966).

[2] F. Yamada, T. Nishiyama, M. Kinugasa, and M. Nakatani, This Bulletin,**43**, 3611 (1970).

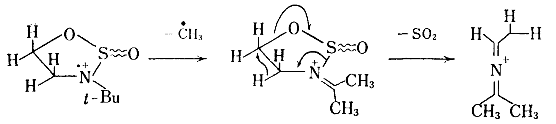
by the dotted lines in the diagram below.



I, R=H II, R=CH_3

These phenomena can be explained in part by the observation that the bond connecting the SO group and the nitrogen atom in the oxathiazolidine ring of I and II has a high probability of fission.

It is interesting to compare this spectrum with the spectra of the other oxathiazolidines reported by Deyrup and Moyer.[3,4] In contrast to the present behavior, the major peak in the fragmentation of 2-oxo-3-*t*-butyl-1,2,3-oxathiazolidine occurs from the loss of the methyl radical, followed by the loss of SO_2, as follows:



2-Oxo-3-aryl-1,2,3-oxathiazolidines, I and II, can be converted to the corresponding *N,N′*-diarylpiperazines by thermal decomposition and can easily be hydrolyzed to the *N*-(2-hydroxyethyl)anilines by water.[2] In the case of the above reactions, we suggest that, after the loss of the SO_2 group, the remaining atoms in the oxathiazolidine ring are rearranged to become an intermediate which has the same composition as the ion 2, as is shown in Table 1. Thus, the intermediate reacts with another one to give *N,N′*-diarylpiperazines or with water to give *N*-(2-hydroxyethyl)anilines. The ions, although few in number, are detected in both the spectra. This is best explained by the formation of the piperazine molecule and of *N*-(2-hydroxyethyl)-aniline.

Moyer[4] attempted the pyrolysis of some 2-oxo-3-*t*-butyl-1,2,3-oxathiazolidines; however, the reaction products have not been determined. Attempts to hydrolyze the above oxathiazolidines under homogeneous basic aqueous conditions failed. These compounds can only be hydrolyzed to the corresponding amino alcohols by dilute acid.

These differences can be explained by the mass spectral data that, in the first step of the fission, the two compounds, I and II, both produce ions corresponding to the loss of the SO_2 group from the molecules, whereas no corresponding ions from the 2-oxo-3-*t*-butyl-1,2,3-oxathiazolidines are observed.

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, about 50μg of a sample was introduced with a marker (PFK), under normal operating conditions (accelerating voltage, 6.4kV). Accurate masses were determined by using a JMC-1A comparator, while the elemental compositions were evaluated by using Lederberg's Table.[5]

---

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

[4] C. L. Moyer, Dissertation on 2-Oxo-1,2,3-oxathiazolidines, Harvard University, (1968).

[5] J. Lederberg, "Computation of Molecular Formulas for Mass Spectrometry," Holden-Day, San Francisco, (1964), p. 12.