

**Mass Spectral Fragmentations of
6-Aryl-5,6,7,8-tetrahydro-4H-1,3,2,6-dioxathiazocine 2-Oxides**
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The mass spectral fragmentation of 4-, 5-, and 4,8-disubstituted derivatives of 6-aryl-5,6,7,8-tetrahydro-4H-1,3,2,6-dioxathiazocine 2-oxides is reported.

J. Heterocyclic Chem., **19**, 1223 (1982).

In a previous paper, we reported on the synthesis of 6-aryl-5,6,7,8-tetrahydro-4H-1,3,2,6-dioxathiazocine 2-oxides (I). This time we wish to report the mass spectral fragmentations of 4-, 5-, and 4,8-disubstituted 1,3,2,6-dioxathiazocine 2-oxides. By the use of metastable-ion measurements, the major fragmentation pathways of the four compounds, 6-(*p*-tolyl)-5,6,7,8-tetrahydro-4H-1,3,2,6-dioxathiazocine 2-oxide (I), 4,8-dimethyl-6-(*p*-tolyl)-5,6,7,8-tetrahydro-4H-1,3,2,6-dioxathiazocine 2-oxide (II), 4-methyl-6-(*p*-tolyl)-5,6,7,8-tetrahydro-4H-1,3,2,6-dioxathiazocine 2-oxide (III), and 4,6-diphenyl-5,6,7,8-tetrahydro-4H-1,3,2,6-dioxathiazocine 2-oxide (IV), were deduced.

The mass spectral data of the compounds I and II are shown in Figures 1 and 2. Their major fragmentation pathways are shown in Scheme 1. The molecular ions of these compounds are of low abundance. The base peaks appeared at m/e 119, corresponding to that of $\text{CH}_3\text{-C}_6\text{H}_4\text{-N=CH}_2$ ion (D). The ion (A) can be formed by the α -cleavage of the C-C bond in the heterocyclic ring of the molecular ion and the resulting ion loses an aldehyde to

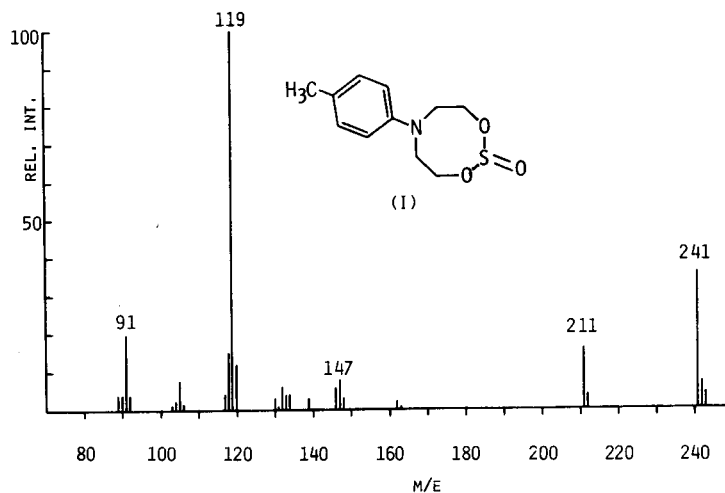
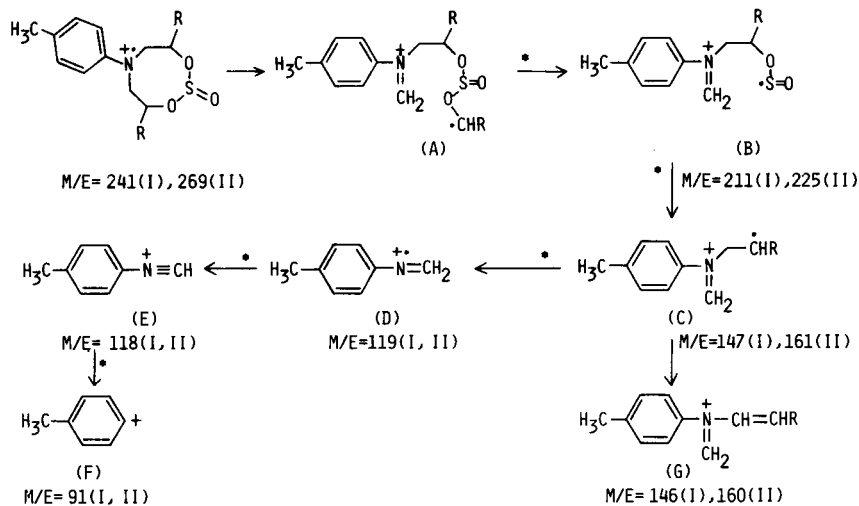


Figure 1 : Mass Spectrum of Compound (I).

give ion (B). Subsequently, the most prominent ion (D) was formed from ion (B) by the loss of a sulfur dioxide and followed by the loss of an olefin from ion (C). The ion (D)

Scheme 1



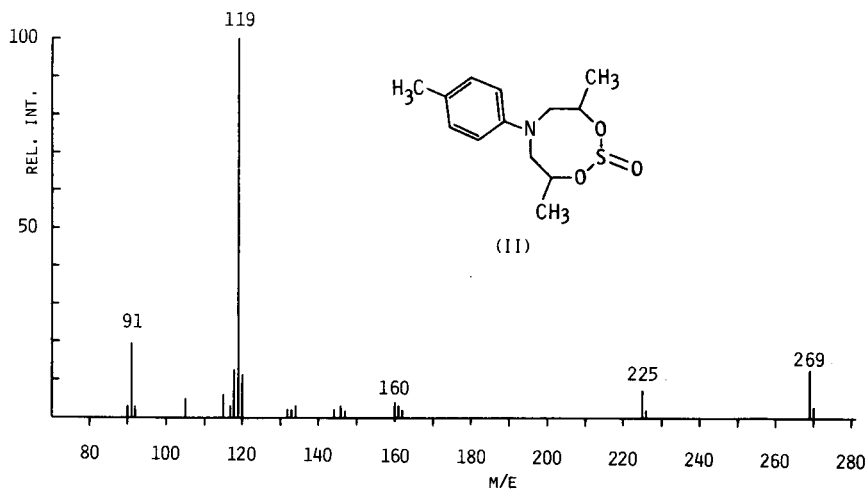


Figure 2 : Mass Spectrum of Compound (II).

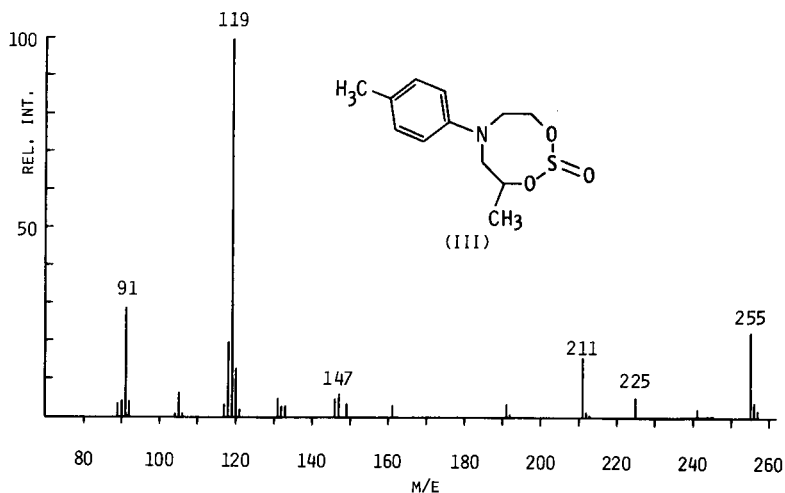


Figure 3 : Mass Spectrum of Compound (III).

loses a hydrogen radical and then a hydrogen cyanide to give a hydrocarbon ion (F). Moreover, there have been many reports concerning the pathway of (E) \rightarrow (F) (2,3). As can be seen in Scheme 1, I and II exhibit a simple fragmentation pattern and the pathway from (A) to (F) is supported by the corresponding metastable transition in each process which is depicted by an asterisk in the scheme.

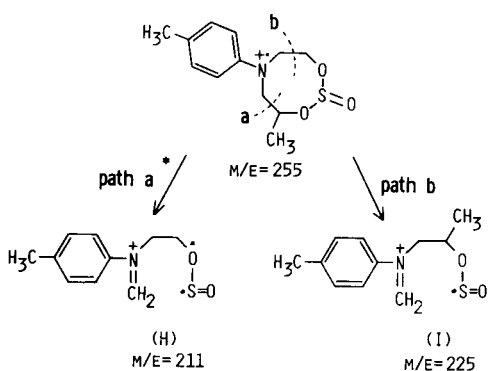
The peaks of low intensity appear at m/e 146 or 160 (G), but the corresponding metastable peak was not found in the process by the loss of SO_2H radical from ion (B) or by the loss of hydrogen radical from ion (C). Djerassi, *et al.* have reported the process from m/e 57 to m/e 56 in the mass fragmentation of piperidine ring, which has a fragmentation similar to that of the pathway from (C) to (G). The occurrence of this process was supported by recognition of a metastable ion (4). We have, therefore, considered that the ion (G) may be produced by the loss of a hydrogen radical from ion (C).

It is interesting to compare these spectra with those of the 1,3,2-dioxathiolane 2-oxides (5,6). There are three steps of cleavage in the 1,3,2-dioxathiolane ring, (i) elimination of an aldehyde by α -cleavage of the C-C bond in the ring, (ii) elimination of a sulfur dioxide, and (iii) loss of SO_2H radical with concurrent hydrogen migration. In contrast to 1,3,2-dioxathiolane 2-oxides, the mass spectra of compounds I and II did not occur the loss of a sulfur dioxide or SO_2H radical from the molecular ion.

In order to know the stability of the molecular ion for the loss of sulfur dioxide, we attempted the hydrolysis of I at 100°. However, the starting material was quantitatively recovered, and these results support that the loss of sulfur dioxide from the molecular ion did not occur in the mass fragmentation of I and II.

Compound III exhibits two major fragmentation pathways from the molecular ion. The two pathways from the molecular ion are indicated by the dotted lines a and b in Scheme 2. The peak at m/e 211 (H) due to the loss of an

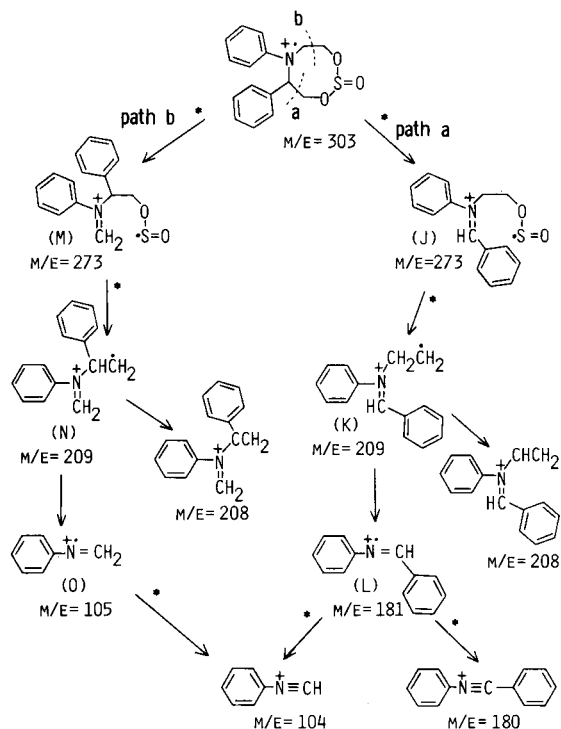
Scheme 2



acetaldehyde from the molecular ion is three times greater in abundance compared to the ion at m/e 225 (I). The following fragmentations of ions (H) and (I) are undertaken by the similar mechanism to that of I and II, respectively.

The mass spectrum of compound IV is shown in Figure 4 and Scheme 3. This compound exhibits two major fragmentation pathways a and b. In the path a, the molecular ion eliminates a formaldehyde to give ion (J). Then (J) produced by the loss of sulfur dioxide to give ion (K). After this fragmentation, ion (K) loses an ethylene group to give ion (L), which is the base peak in this spectrum. In the path b, the ion (M) forms from the molecular ion by the loss of a formaldehyde, and the resulting ion loses a sulfur dioxide to give ion (N), followed by the loss of the phenyl ethylene. The ion (L) is three times greater in abundance

Scheme 3



compared to the ion (O). This indicates that the α -cleavage of C_4-C_5 in the molecular ion is more easily accomplished than that of C_7-C_8 because of a bulky substituent at $C-5$.

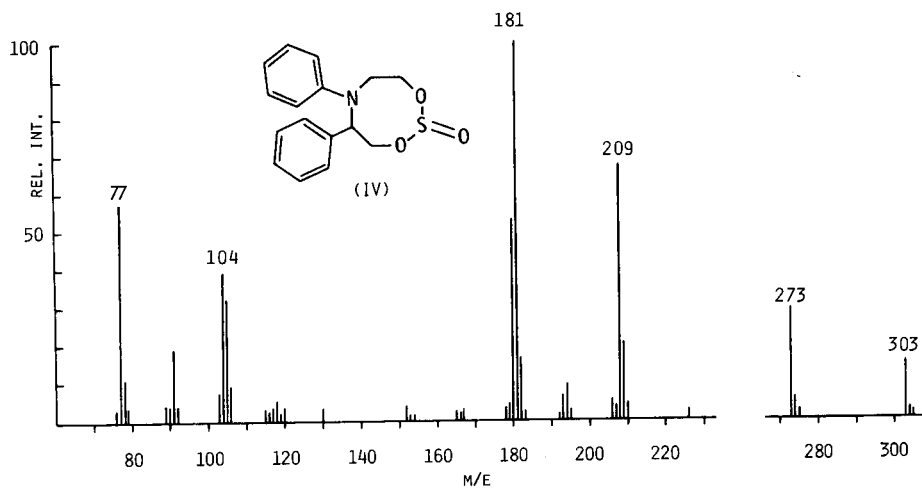


Figure 4 : Mass Spectrum of Compound (IV).

EXPERIMENTAL

The preparations and the physical properties of I and II have been reported in our previous paper (1). The compounds III and IV were obtained in a similar manner to the preparation of I and II and their structures are supported by analytical and spectral data.

Compound III had mp 78.3-79.5°.

Anal. Calcd. for $C_{12}H_{17}NSO_3$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.38; H, 6.76; N, 5.53.

Compound IV had a mp of 118.2-119.1°.

Anal. Calcd. for $C_{16}H_{17}NSO_3$: C, 63.35; H, 5.65; N, 4.62. Found: C, 62.82; H, 5.52; N, 4.55.

The spectra were determined with a Japan Electron Optics Co., Ltd.,

JMS-01SG double-focusing mass spectrometer. The samples in all cases were analysed by use of a direct probe with an ion energy of 75 eV.

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