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The mass spectra of a series of 6-phenyl-5,6,7,8-tetrahydro-4*H*-1,3,6-dioxazocin-2-ones have been examined.

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Mass spectral fragmentations of 1,3-dioxolan-2-ones have been discussed in a number of recent papers [1,2]. For example, Djerassi [1] reported that the base peak in the fragmentation of 1,3-dioxolan-2-ones occurs from initial loss of the carbon dioxide with a hydrogen rearrangement, followed by loss of the methyl radical. On the other hand, two major decomposition pathways of 1,3,2-dioxathiolane 2-oxides have been reported [1]. The decompositions are initiated (i) by α -cleavage of the C-C bond in the ring and (ii) by cyclic elimination of sulfur dioxide or sulfenic acid radical with concurrent hydrogen migration.

In this paper, we wish to report the mass spectral fragmentations of 6-phenyl-5,6,7,8-tetrahydro-4*H*-1,3,6-dioxazocin-2-ones, which have a structure similar to that of 1,3-dioxolan-2-one skeleton. By the use of metastable-ion measurements, the major fragmentation pathways of the three compounds, 4,8-dimethyl-6-(*p*-tolyl)-5,6,7,8-tetrahydro-4*H*-1,3,6-dioxazocin-2-one (**1**), 6-(*p*-tolyl)-5,6,7,8-tetrahydro-4*H*-1,3,6-dioxazocin-2-one (**2**) and 4-methyl-6-(*p*-tolyl)-5,6,7,8-tetrahydro-4*H*-1,3,6-dioxazocin-2-one (**3**) were deduced.

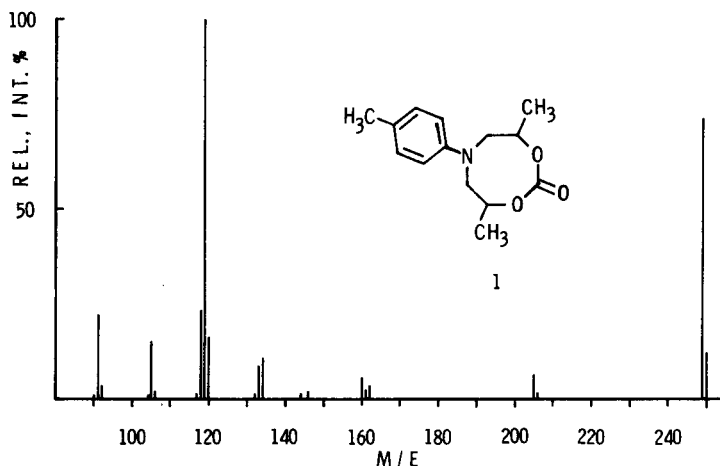
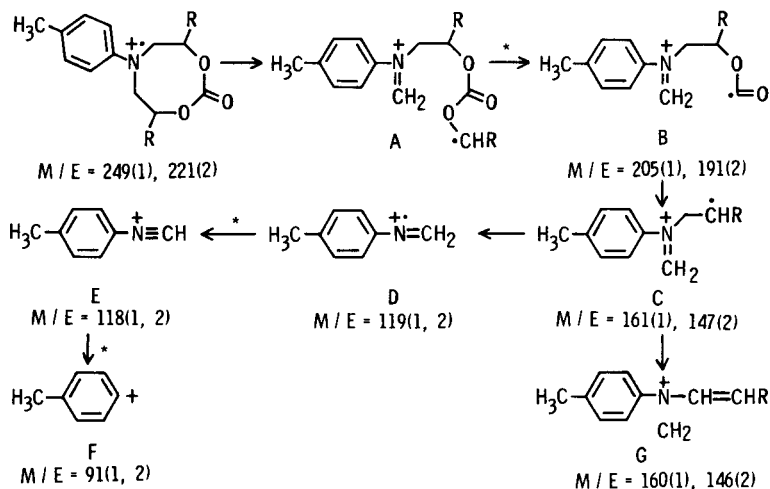


Figure 1. Mass Spectrum of Compound 1.

The mass spectral data of compound **1** is shown in Figure 1, while their fragmentation pathways are shown in Scheme 1. The base peak appeared at m/e 119, corres-



Scheme 1

ponding to that of $\text{CH}_3\text{-C}_6\text{H}_4\text{-N}=\text{CH}_2$ 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 acetaldehyde (M-44) give ion **B**. The possibility that M-44 ion resulted from loss of carbon dioxide (MW, 44) in a similar to 1,3-dioxolan-2-ones was disproved by running the spectrum of compound **2** shown in Figure 2. That is, no M-44 ion is observed in the cleavage of compound **2**; M-30 ion is observed by loss of formaldehyde

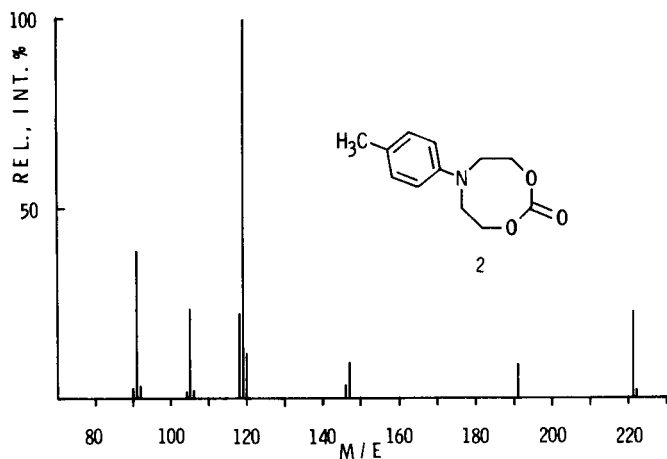


Figure 2. Mass Spectrum of Compound **2**.

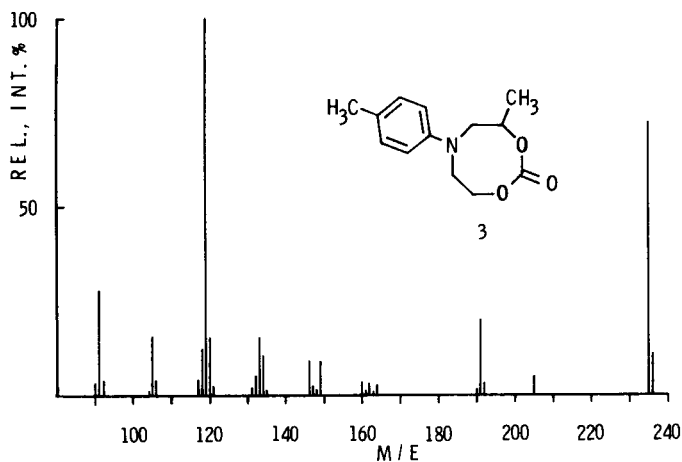
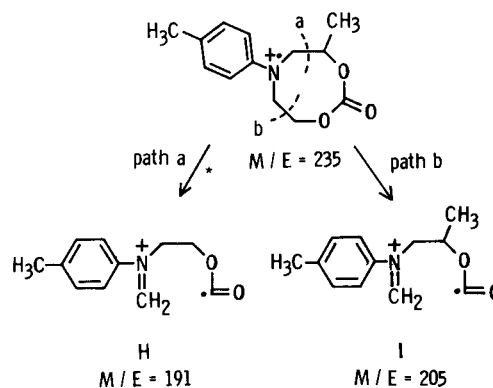


Figure 3. Mass Spectrum of Compound **3**.

from the molecular ion. Therefore, the initial fragmentation from the molecular ions of 5,6,7,8-tetrahydro-4H-1,3,6-dioxazocin-2-ones involves the loss of aldehydes.

The most prominent ion **D** was formed from ion **B** by the loss of a carbon dioxide and followed by the loss of an olefin from ion **C**. There are no detectable metastable peaks in the pathways from ion **C** to **D** or **G**. A fragmentation similar to that of the pathways from ion **C** to **D** or **G** has been reported by several workers. For examples, Djerassi, *et al.* [3,4] have reported that in the electron impact cleavage of the pyrrolidines and piperidines the ma-

ior pathway involves the loss of the neutral ethylene from the molecular ions, and the resulting ions lose a hydrogen radical. The ion (**D**) loses a hydrogen radical and then a hydrogen cyanide to give a hydrocarbon ion (**F**). Moreover, there have been many reports concerning the pathways from ion (**E**) to (**F**) [5,6].



Scheme 2

Compound **3** undergoes the expected 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 191 (**H**) due to the loss of an acetaldehyde from the molecular ion is four times greater in abundance compared to the ion at m/e 205 (**I**) since secondary radical formed from pathway a is stable than primary radical formed from pathway b.

EXPERIMENTAL

The preparations and the physical properties of compounds **1** and **2** have been reported in our previous paper [7]. Compound **3** was obtained in a similar manner to the preparations of **1** or **2**, and this structure was supported by the analytical and the spectral data.

Compound **3** had mp 93.2-94.0°.

Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.33; H, 7.26; N, 5.86.

The mass spectra were obtained by means of a Japan Electron Optics Co. Ltd., JMS-01SG Mattauch-Herzog double-focusing mass spectrometer, at an ionizing voltage of 75 eV, an emission current of 200 μA , an accelerating voltage of 7.8 kV.

REFERENCES AND NOTES

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