

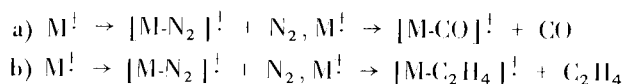
Competitive and Consecutive Eliminations of N₂ and CO (or C₂H₄) from some Heterocyclics Under Electron Impact

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Received March 7, 1974

High resolution mass spectrometry was used to study two types of expected primary competing reactions triggered by two isobaric structural groups in some heterocyclic compounds, I-V, under 70 eV electron impact. The reactions are



In both cases, it was found that the primary loss was exclusively a N₂ molecule which is then followed by the loss of CO or C₂H₄.

Introduction

It has been well established that the ion fragmentation occurring inside a mass spectrometer is a competing consecutive unimolecular ion decomposition (1). For molecules with one functional group, like alcohols, amines, and acids, the major fragmentation routes are known to be triggered by that functional group and the triggering mechanisms have been proposed (2). For molecules with more than one functional group, the reactions triggered by all the functional groups present in the molecules will be competing against each other. The results of the competition will be dependent on the strength of the bond(s) to be broken and the stabilities of ions and neutral species generated. If the competing reactions result in eliminations of different masses, *e.g.* CH₃, HCN, CO, the measurement of the relative importance of the triggering factors will be shown in the mass spectra. If, however, the losses are of the same nominal mass, *e.g.* CO, N₂, C₂H₄, high resolution mass spectrometry is required to differentiate them. Even though the observed results are often empirical, an intuitive understanding of the relative importance of the competing triggering reactions is desirable.

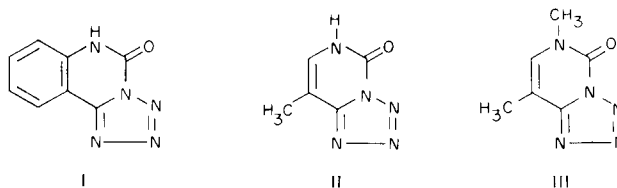
In the recent literature, the primary loss of N₂ from the molecular ions of diazoles (3), triazoles (3,4), and tetrazoles (5) has been reported. The loss of CO from both carbonyl containing compounds like quinones (6) and pyridones (7), and non-carbonyl containing compounds like phenols (8) and diaryl ethers (9) has long been recognized. The elimination of an ethylene molecule from molecular ions has also been studied extensively in the cases of tetraline, 2-methyltetraline, cyclohexenes (10) (Retro-Diels-Alder reaction), and ethyl esters (11).

When any two of the above structural groups are present in a molecule, the ion fragmentations triggered by these two groups compete with each other. S. Meyerson and R. W. Vander Haar (10) reported 74% of the ions arising from the loss of CO and 26% from the loss of C₂H₄ (Retro-Diels-Alder reaction) in the decomposition of molecular ions of tetralone. J. C. Tou, L. A. Shadoff and R. H. Rigterink (12) found that the first loss of 28 mass units was exclusively a nitrogen molecule which is then followed by a CO elimination in the case of benzotriazinone derivatives, when the azo group and the carbonyl group occupied similar positions in the molecules. Recently, C. M. Kerwin and G. A. Nelson (13) reported similar findings of the initial N₂ loss and then a CO elimination in the cases of nickel ketazines (13). In this paper, we studied the competitive losses under 70 eV electron impact of N₂ and CO, and N₂ and C₂H₄ from some heterocyclics containing these groups.

Results and Discussion

A) Competing and Consecutive Losses of N₂ and CO.

The mass spectra of three heterocyclic compounds, I-III, containing -N=N- and >C=O structural groups are shown in Figures 1-3 respectively.



One distinctive common ion fragmentation mode of the three compounds is the initial loss of 28 mass units, which

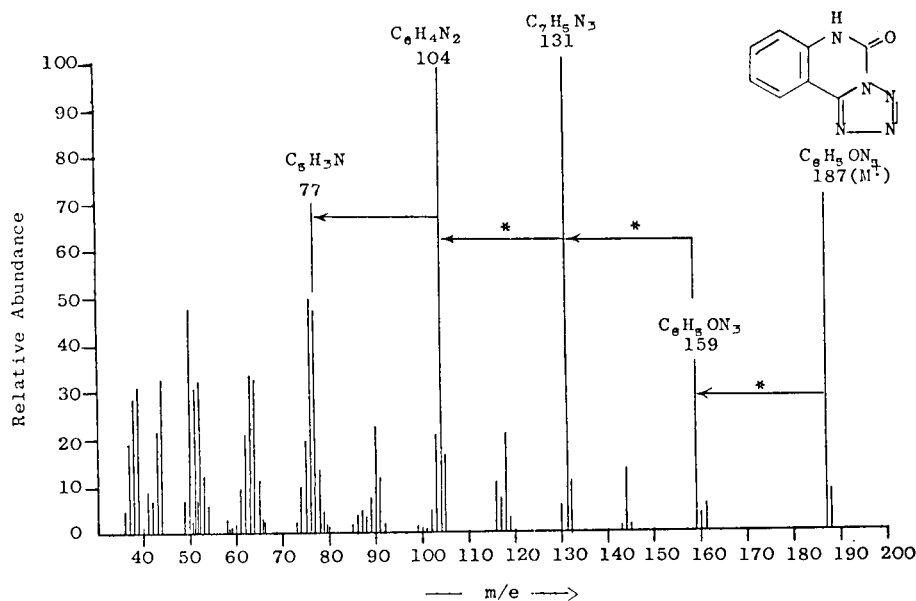


Figure 1. The Mass Spectrum of tetrazolo[1,5-c]quinazolin-5(6H)one.

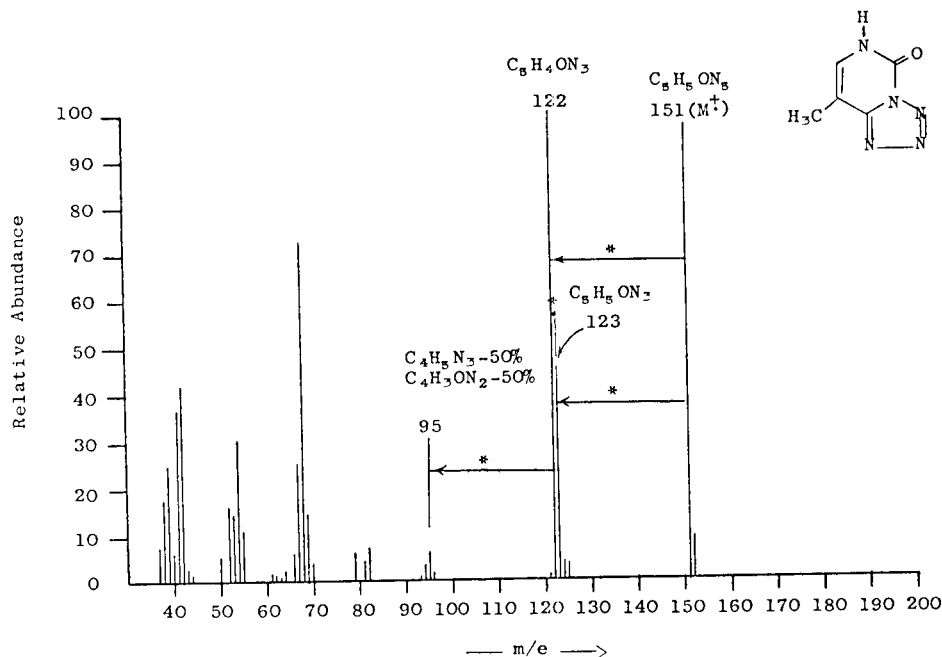


Figure 2. The Mass Spectrum of 8-Methyltetrazolo[1,5-c]pyrimidin-5(6H)one.

was found to be a one step transition as supported by an observed corresponding metastable ion. It is very difficult to predict *a priori* which are of the structural groups $-N=N-$ and $>C=O$ in the molecules was involved in the above transition. However, high resolution mass spectrometry established that the primary loss of the 28 mass units was exclusively a $N\equiv N$ group. This is similar to the cases of benzotriazinones (12) and nickel ketazines (13) reported

previously. Following the elimination of a N_2 molecule from the molecular ion of compound 1, the fragment ion formed at $m/e = 159$, exhibited a loss of a CO group in the generation of an intense ion peak, $m/e = 131$. Both the high resolution mass measurement and the detection of the metastable ion showed successive losses of two HCN molecules from the ion observed at $m/e = 131$, which yielded peaks at $m/e = 104$ and 77 in the spectrum. Severe skeletal

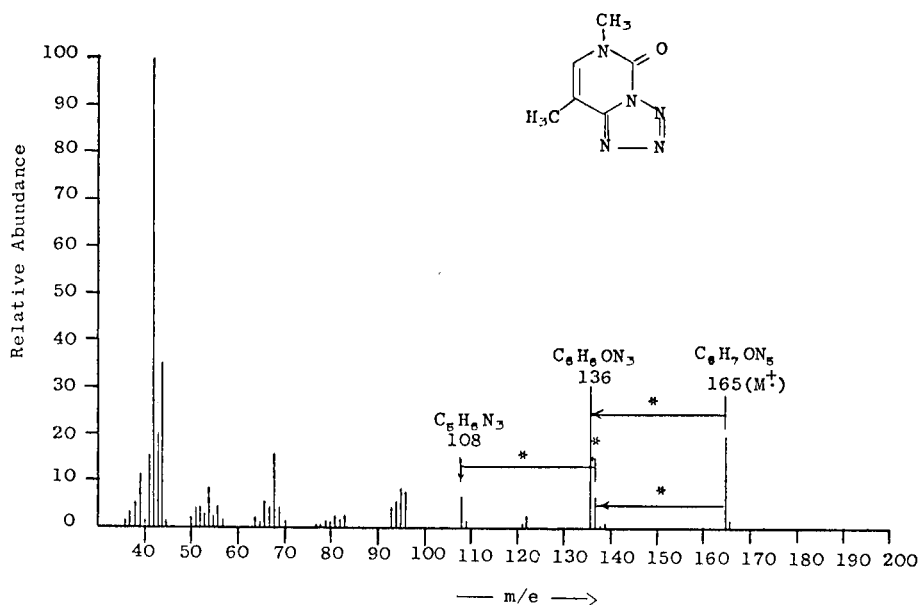


Figure 3. The Mass Spectrum of 6,8-Dimethyltetrazalo[1,5-c]pyrimidin-5(6H)one.

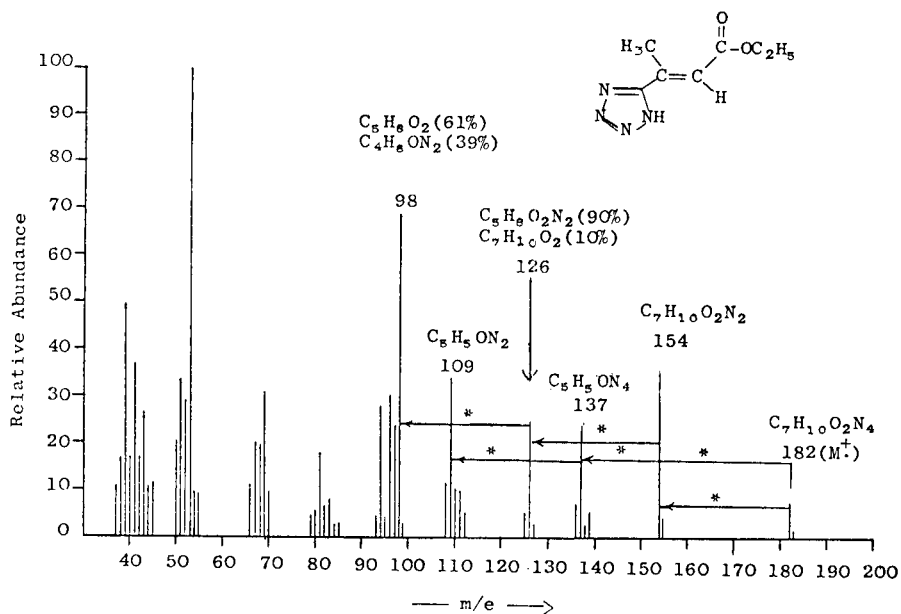


Figure 4. The Mass Spectrum of Ethyl *trans*-3-Methyltetrazole-5-acrylate.

rearrangements involving hydrogen atom migration and possibly ring expansion must be implicated in the ion fragmentation.

Both the molecular ions of compounds II and III after eliminating a N_2 molecule, show a relatively strong loss of a hydrogen radical in the generations of fragment ions at $m/e = 122$ and 136 respectively. The hydrogen atom splitting off could be from the methyl group attached to the six membered ring. Both the high resolution mass

measurement and the meta-stable transition show the loss of a CO molecule from the ($M^+ - N_2$) fragment ions of compounds II and III in the generation of ions at $m/e = 95$ and 108 respectively as shown in Figures 2 and 3. However, the ion peak at $m/e = 95$ was found to be a doublet due to ions of compositions $C_4H_5N_3$ and $C_4H_3ON_2$ with approximately equal contributions and the ion peak at $m/e = 108$ a singlet due to ions of composition $C_5H_6N_3$. The ion, $C_4H_3ON_2$, could be generated from the ion observed at

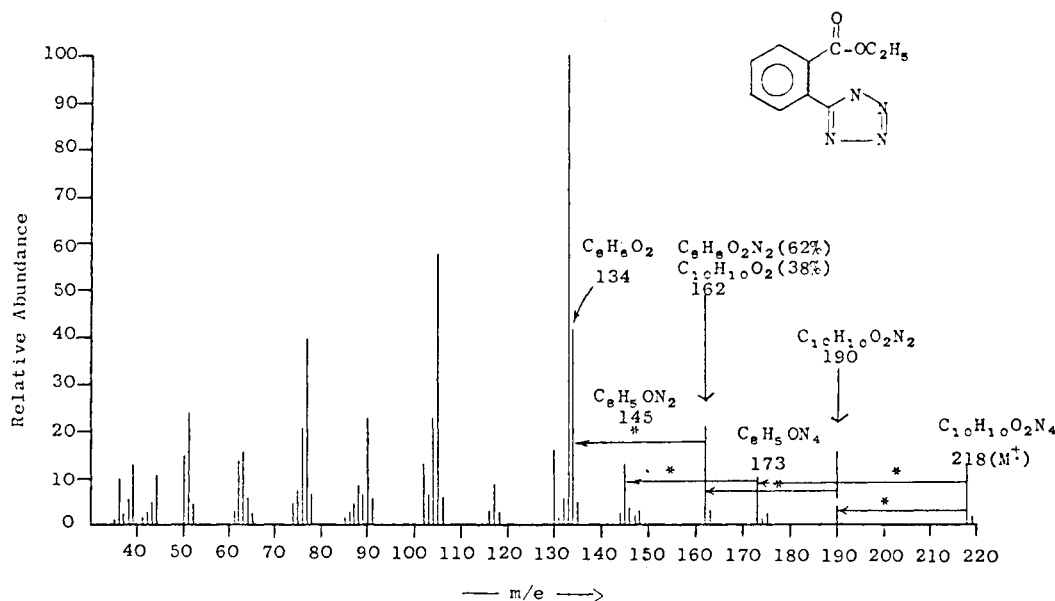
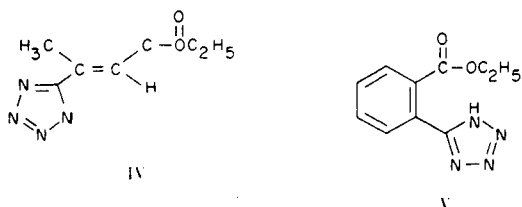


Figure 5. The Mass Spectrum of Ethyl O-(5-Tetrazolyl)benzoate.

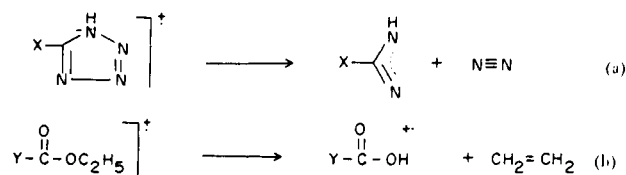
$m/e = 122$ with a loss of HCN molecule. The nitrogen atom in the HCN molecule split off is suggested to be from the secondary amine group on the sixth position. This is consistent with the fact that the ion peak at $m/e = 108$ was found to be singlet in the spectrum of compound III, where the nitrogen on the sixth position is methyl group substituted.

B) Competing and Consecutive Losses of N_2 and C_2H_4 .

Two heterocyclic compounds, IV and V, both containing an ethyl ester group, are studied. Their mass spectra are shown in Figures 4 and 5 respectively. As expected, both



molecular ions exhibit a loss of ethoxy group due to the rupture of a bond α to the carbonyl group which is then followed by a N_2 elimination. Competing with this path of consecutive fragmentations was found to be a one step loss of a group with 28 mass units. Two structural groups with 28 mass units are possible to split off. One is a nitrogen molecule splitting off by simple bond breaking and one



is an ethylene group splitting off possibly involving scrambling of the ethoxy hydrogens (11), i.e. where X and Y represent the remaining parts of molecules IV and V. High resolution mass measurements proved that the primary 28 mass unit loss was exclusively a nitrogen molecule (Scheme a). Following the initial elimination of a nitrogen molecule from the molecular ions, the competing and consecutive losses of an ethylene molecule and a second nitrogen molecule in the generation of final product ions at $m/e = 98$ and 134 in the spectra of compounds IV and V, respectively, were found. The ion at $m/e = 98$ in the spectrum of compound V was found to be a doublet due to ions of compositions $C_5H_6O_2$ (61%) and $C_4H_6ON_2$ (39%). The origin of the generation of ion $C_4H_6ON_2^+$ is not known. As shown in Figures 4 and 5 all the fragmentation mechanisms discussed above are supported by both the ion empirical formula assigned from the high resolution accurate mass measurement and the metastable ion transitions observed using the defocusing techniques.

Conclusions.

High resolution mass spectrometry has been used to study two types of primary competing reactions triggered by two isobaric structural groups in the molecules under 70 eV electron impact. One is the case of the molecules containing a carbonyl group and an azo group, where the competing losses of CO and N_2 are expected. One is in the case of molecules containing an azo group and an ethyl ester group, where the competing losses of N_2 and C_2H_4 are anticipated. In both types of competing reactions, it was found that the primary loss of 28 mass units was exclusively a nitrogen molecule which was then followed by the loss of CO or C_2H_4 .

EXPERIMENTAL

The compounds were synthesized (14) by Dr. Eugene R. Wagner of Chemical Biology Research, The Dow Chemical Co. The mass spectra were recorded with three types of mass spectrometers, Varian MAT CH4B (I, III, V, source temperature 250°), CEC 21-491 (II, source temperature 200°) and CEC 21-110B (IV, source temperature 80°). The direct probe technique was employed in every case. The energy of the ionizing electrons was maintained at 70 eV. The accurated mass measurements were made with a Nier peak matching unit attached to a CEC 21-110B double focusing mass spectrometer. The accuracy of the measurement is within 10 ppm. The beam defocusing technique for obtaining the metastable ion transitions has been described elsewhere (15).

Acknowledgement.

The author would like to extend his appreciation to Dr. Eugene R. Wagner for many valuable discussions and to Mr. J. Storey and Mr. R. Beckrow for their help in obtaining mass spectrometric data.

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