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The Mass Spectra of Heteroaromatics. II.[1] Mass-spectral Fragmentation of 5-Nitro-2-furohydrazide Imide and Its N^2-Acyl Compounds[2]

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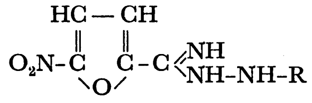
Synopsis. The high-resolution mass spectra of 5-nitro-2-furohydrazide imide and its N^2-acetyl, N^2-propionyl, and N^2-butyryl compounds have been examined. The major fragmentation pathways of the compounds were thus deduced.

It has been reported that the N^2-acyl derivatives of 5-nitro-2-furohydrazide imide (I) are cyclized to 5-alkyl-3-(5-nitro-2-furyl)-1,2,4-triazoles, with the release of a molecule of water, when heated at their melting points in a nitrogen stream.[3] In a continuation of a previous paper[1] concerning the mass-spectral fragmentation of the 1,2,4-triazoles, the mass spectra of I (R=H) and its N^2-acetyl (II, R=$COCH_3$), N^2-propionyl (III, R=COC_2H_5), and N^2-butyryl (IV, R=COC_3H_7) compounds have been examined in order to obtain information on the electron-impact reaction and in order to deduce the fragmentation pathways of the compounds.



(I—IV)

Experimental

Measurement of the Mass Spectra. The high-resolution mass spectra were obtained with a Japan Electron Optics Laboratory Co., Ltd., JMS-01SG-2 mass spectrometer, using the direct-inlet system. The operating conditions were as follows: ionizing energy, 75 eV; total emission current, 250 μA; accelerating voltage, 8 kV; ion multi., 1.5 kV (I and III) and 1.7 kV (II and IV); ion-source temperature, 200 °C; sample-vaporizing temperature, 100—120 °C (selected for each sample).

Samples. The samples used in this experiment were prepared by methods previously described.[4,5] IV; orange-yellow needles (recrystallized from methanol); mp 197—199 °C (decomp.).

Results and Discussion

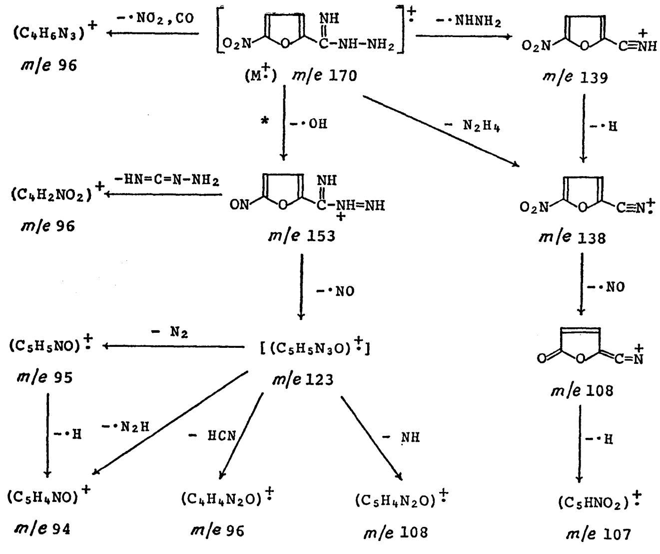
The mass-spectral data of the compounds are shown in Table 1, while the major fragmentation paths are postulated in Schema 1 and 2.

5-*Nitro-2-furohydrazide Imide (I).* Compound I gave the most prominent molecular ion (M^+) (the base peak), with an *m/e* value of 170, reflecting its stability, caused by the resonance between the furan ring and its side chain at the 2 position. The distinct M–17 ion at *m/e* 153 is formed by the elimination of the ·OH radical from the M^+. This ion shows two modes of cleavage and may give ions at *m/e* 123 (Rel. int. 5%)[6] and *m/e* 96 (Ion composition, $C_4H_2NO_2$) by respectively, the loss of ·NO and HN=C=N-NH_2 fragments. The subsequent loss of HN, HCN, N_2, or ·N_2H from the *m/e* 123 ion would lead to the $(C_5H_4N_2O)^+$, $(C_4H_4N_2O)^+$, $(C_5H_5NO)^+$, and $(C_5H_4NO)^+$ ions at *m/e* 108, 96, 95, and 94. It may also be possible that the *m/e* 95 ion gives the *m/e* 94 ion by the loss of a ·H radical. On the other hand, the elmination of the

TABLE 1. MASS SPECTRAL DATA OF THE COMPOUNDS, I—IV.

I (R=H)			II (R=$COCH_3$)			III (R=COC_2H_5)			IV (R=COC_3H_7)		
m/e	Ion composition[a]	Rel. int. %	*m/e*	Ion composition	Rel. int. %	*m/e*	Ion composition	Rel. int. %	*m/e*	Ion composition	Rel. int. %
170	$C_5H_6N_4O_3$	100	212	$C_7H_8N_4O_4$	98	226	$C_8H_{10}N_4O_4$	48	240	$C_9H_{12}N_4O_4$	55
153	$C_5H_5N_4O_2$	77	195	$C_7H_7N_4O_3$	25	209	$C_8H_9N_4O_3$	13	223	$C_9H_{11}N_4O_3$	16
139	$C_5H_3N_2O_3$	13	194	$C_7H_6N_4O_3$	25	208	$C_8H_8N_4O_3$	13	212	$C_7H_8N_4O_4$	13
138	$C_5H_2N_2O_3$	4	171	$C_6H_7N_2O_4$	25	197	$C_6H_5N_4O_4$	23	197	$C_6H_5N_4O_4$	20
108	$C_5H_4N_2O$	4	170	$C_5H_6N_4O_3$	100	180	$C_8H_{10}N_3O_2$	10	194	$C_7H_6N_4O_3$	21
	$C_5H_2NO_2$	4	154	$C_5H_6N_4O_2$	18	170	$C_5H_6N_4O_3$	100	170	$C_5H_6N_4O_3$	100
107	$CH_5N_3O_3$	9	153	$C_5H_5N_4O_2$	52	169	$C_5H_5N_4O_3$	6	153	$C_5H_5N_4O_2$	53
	C_5HNO_2	7		$C_5H_3N_3O_3$	36	153	$C_5H_5N_4O_2$	52	149	$C_6H_3N_3O_2$	16
96	$C_4H_2NO_2$	4	139	$C_5H_3N_2O_3$	29	149	$C_6H_3N_3O_2$	6			
	$C_4H_4N_2O$	3									
	$C_4H_6N_3$	5									
95	C_5H_5NO	5									
94	C_5H_4NO	18									

a) The high-resolution mass spectra of the compounds gave correct composition of all ions mentioned in the table, within the error of ±5 millimass units.



*; meta-stable ion observed

Scheme 1. Fragmentation of the compound, I.

$\cdot N_2H_3$ radical or N_2H_4 molecule from the M^{+} gives distinct ions at m/e 139 and 138; the latter can be formed from the former by the loss of a ·H radical. The m/e 138 ion undergoes the elimination of an ·NO radical, followed by the loss of a ·H radical, thus giving the m/e 107 ion, which is consistent with the composition of C_5HNO_2.

Much as in the case of 3-(5-nitro-2-furyl)-1,2,4-triazoles,[1] the M^{+} loses NO_2 and CO fragments by a one-step process to give an ion with the composition of $C_4H_6N_3$ at m/e 96.

N^2-*Acyl Compounds (II, III, and IV).* In the spectra of II-IV, M^{+} were also observed as intense peaks. In the first step of the fission of the M^{+}, as is shown in Scheme 2, there are four principal modes of elimination of the acyl groups:

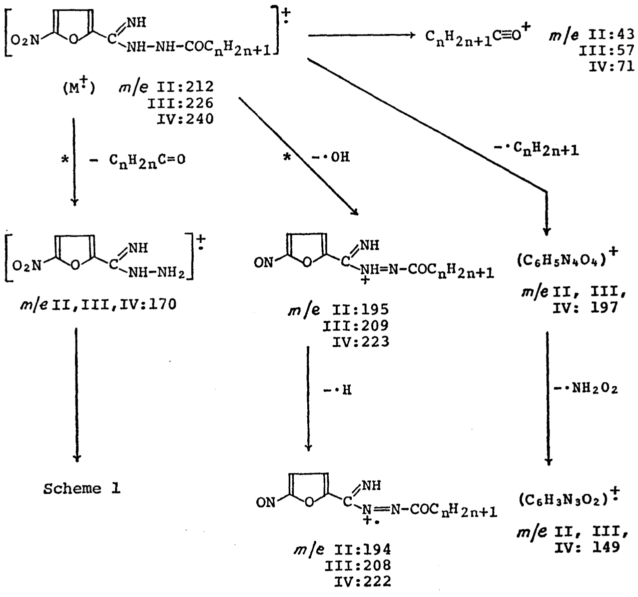
(1) With the rearrangement of a hydrogen atom, the base peaks at m/e 170, which are consistent with the mass of the M^{+} in I, result from the elimination of C_nH_{2n}-C=O (n=1, 2, and 3 respectively);

(2) the loss of an alkyl radical leads to the ion with m/e 197;

(3) the loss of an ·OH radical gives m/e 195 (II), m/e 209 (III), and m/e 223 (IV) ions respectively, and

(4) the elimination of an acyl group with the charge-transfer brings about m/e 43, 57, and 71 ions with 99, 50, and 43% intensities respectively, although the ion compositions have not been determined.

The ion at m/e 170 may be expected to show the same fragmentation as that of I, as is indicated in Scheme 1.



*; meta-stable ions observed

Scheme 2. Fragmentation of the compounds, II, III, and IV.

In addition to the four principal modes of fragmentation discussed above, there may exist some other fragmentation paths. Only in the case of Compound II, the ion at m/e 153 with the composition of $C_5H_3N_3O_3$ can be formed by the expulsion of the CH_3CONH_2 molecule from the M^{+}. In III, the NO_2 fragment is eliminated from the M^{+}, thus affording an ion at m/e 180, while in IV, the butyryl group of the M^{+} is cleaved in the course of the McLafferty rearrangement to give the m/e 212 ion.

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References

1) Part I of this series: Y. Kato and I. Hirao, This Bulletin, **45**, 1876 (1972).

2) Presented at the 27th Annual Meeting of the Chemical Society of Japan, Nagoya, October 13, 1972.

3) The 25th Annual Meeting of the Chemical Society of Japan, Tokyo, October, 1971. Preprint, p. 511.

4) Y. Kato and I. Hirao, *Bull. Kyushu Inst. Technol.*, **No 15**, 57 (1965).

5) I. Hirao, Y. Kato, and H. Tateishi, This Bulletin, **45**, 208 (1972).

6) The composition of the m/e 123 ion was not determined.