

THE MASS SPECTRA OF HETEROAROMATICS. III.¹⁾ MASS-SPECTRAL FRAGMENTATION OF 5-NITRO-2-FUROHYDRAZIDE AND ITS *N'*-ACYL COMPOUNDS

by

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Synopsis

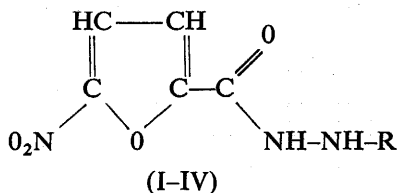
The high-resolution mass spectra of 5-nitro-2-furohydrazide (I) and its *N'*-acetyl (II), *N'*-propionyl (III), and *N'*-butyryl (IV) compounds have been examined. The molecular ion (M^+) of I is prominent and this undergoes three principal modes of cleavage:

- (1) The elimination of N_2H_2 fragment leads to the most prominent $M-30$ ion at m/e 141;
- (2) the loss of $\cdot NO_2$ radical gives the ion with m/e 125, and
- (3) the loss of $\cdot OH$ radical brings about m/e 154 ion.

On the other hand, the *N'*-acyl derivatives, II-IV, gave extremely weak M^+ ion peaks. In the first step of the fission of the M^+ , the elimination of an acyl group occurred with or without the rearrangement of a hydrogen atom. The former process brings about m/e 171 ions, which are consistent with the mass of the M^+ in I, but are differ somewhat from I in their modes of cleavage. While the latter gives rise the most prominent $R-C\equiv O^+$ ion peaks, with the charge-transfer, at m/e 43 (II), 57 (III), and 71 (IV).

Introduction

The mass-spectral fragmentation of simple furans has been established,²⁻⁷⁾ but no systematic investigation concerning more complex nitrofurans has yet been reported. 5-Nitro-2-furohydrazide (I) and its *N'*-acyl derivatives are more complex but ordinary compounds in nitrofurans, while the mass-spectral examination of them has not yet been carried out. In a continuation of a previous paper¹⁾ concerning the mass-spectral fragmentation of 5-nitro-2-furohydrazide imide and its *N*²-acyl derivatives, the mass spectra of I ($R=H$) and its *N'*-acetyl (II, $R=COCH_3$), *N'*-propionyl (III, $R=COC_2H_5$) and *N'*-butyryl (IV, $R=COC_3H_7$) compounds have been examined in order to accumulate the informations on the electron-impact induced reaction and in order to deduce the fragmentation pathways of nitrofurans compounds.



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Experimental

Measurement of the Mass Spectra. The high-resolution mass spectra were obtained with a Hitachi RMU-7M mass spectrometer using the direct-inlet system. The operating conditions were as follows: ionizing energy, 70 eV; total emission current, 250 μ A; accelerating voltage, 7.5 kV; ion multi, 1.5–1.7 kV; ion-source temperature, 200°C; sample-vaporizing temperature, 120–180°C (selected for each sample).

Samples. The samples employed in this examination were prepared by the method previously described.⁸⁾ The mps of the compounds are summarized in Table 1.

Table 1. The melting points of the compounds examined

Compound	Mp (°C)	Solvent for recrystallization
5-Nitro-2-furohydrazide (I)	171–172	Methanol (pale yellow needles)
<i>N'</i> -Acetyl- <i>N</i> -(5-nitro-2-furoyl)hydrazine (II)	194–195	Water (yellow needles)
<i>N'</i> -Propionyl- <i>N</i> -(5-nitro-2-furoyl)hydrazine (III)	185–186	Water (yellow needles)
<i>N'</i> -Butyryl- <i>N</i> -(5-nitro-2-furoyl)hydrazine (IV)	129–130	Water-methanol ^{a)} (yellow powder)

a) Washed with water and then with methanol.

Results and Discussion

The mass-spectral data of the compounds are shown in Table 2, and the major fragmentation paths are postulated in Schema 1 to 3.

Table 2. Mass spectral data of the compounds, I–IV.

I (R=H)			I (R=COCH ₃)			III (R=COC ₂ H ₅)			IV (R=COC ₃ H ₇)		
<i>m/e</i>	Ion composition ^{a)}	Rel. int. %	<i>m/e</i>	Ion composition	Rel. int. %	<i>m/e</i>	Ion composition	Rel. int. %	<i>m/e</i>	Ion composition	Rel. int. %
			213	C ₇ H ₇ N ₃ O ₅	2.3	227	C ₈ H ₉ N ₃ O ₅	2.9	241	C ₉ H ₁₁ N ₃ O ₅	2.7
171	C ₅ H ₅ N ₃ O ₄	45.1	171	C ₅ H ₅ N ₃ O ₄	34.7	171	C ₅ H ₅ N ₃ O ₄	12.6	171	C ₅ H ₅ N ₃ O ₄	8.5
154	C ₅ H ₄ N ₃ O ₃	0.8									
141	C ₅ H ₃ NO ₄	100.0	141	C ₅ H ₃ NO ₄	9.1	141	C ₅ H ₃ NO ₄	4.5	141	C ₅ H ₃ NO ₄	4.2
				C ₅ H ₃ N ₂ O ₃	0.5						
140	C ₅ H ₂ NO ₄	42.9	140	C ₅ H ₄ N ₂ O ₃	9.6	140	C ₅ H ₄ N ₂ O ₃	4.9	140	C ₅ H ₄ N ₂ O ₃	5.0
125	C ₅ H ₃ NO ₃	0.8	125	C ₅ H ₃ NO ₃	0.6				125	C ₅ H ₃ NO ₃	0.6
	C ₅ H ₃ N ₂ O ₂	2.3									
124	C ₅ H ₂ NO ₃	12.3	124	C ₅ H ₂ NO ₃	3.5	124	C ₅ H ₂ NO ₃	0.9			
	C ₅ H ₄ N ₂ O ₂	0.7							124	C ₅ H ₄ N ₂ O ₂	0.8
111	C ₅ H ₃ O ₃	1.3	97	C ₄ H ₃ NO ₂	0.4						
96	C ₄ H ₂ NO ₂	14.5	96	C ₄ H ₂ NO ₂	1.6	96	C ₄ H ₂ NO ₂	1.0	96	C ₄ H ₂ NO ₂	0.6
	C ₄ H ₄ N ₂ O	0.8		C ₄ H ₄ N ₂ O	0.5					C ₄ H ₄ N ₂ O	0.4
95	C ₄ H ₃ N ₂ O	3.0	43	C ₂ H ₃ O	100.0	57	C ₃ H ₃ O	100.0	71	C ₄ H ₇ O	100.0
94	C ₅ H ₂ O ₂	16.1	15	CH ₃	9.2	29	C ₂ H ₅	59.4	43	C ₂ H ₃ O	18.4
82	C ₄ H ₂ O ₂	11.0								C ₃ H ₇	73.6

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.

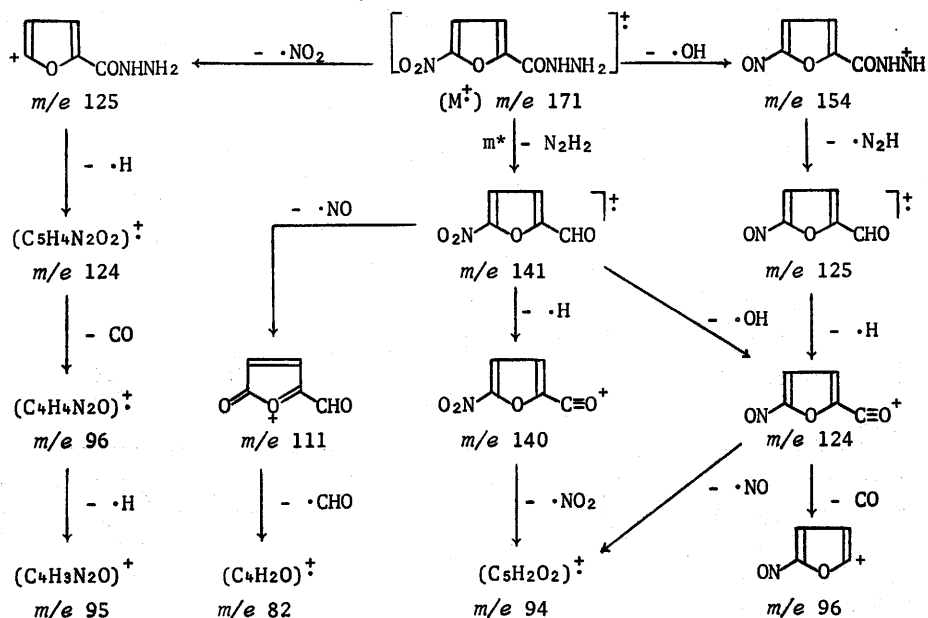
5-Nitro-2-furohydrazide (I). Compound I gave the distinct molecular ion (M^+), with an m/e value of 171, reflecting its stability caused by the resonance between the furan ring and its side chain at the 2-position; this differs somewhat from 5-nitro-2-furohydrazide imide¹⁾ in that the molecular ion is most prominent (the base peak). The most prominent $M-30$ ion (the base peak) at m/e 141 is formed by the elimination of the N_2H_2 molecule from the M^+ . This ion shows three modes of cleavage and may give ions at m/e 140, m/e 124 (Ion composition $C_5H_2NO_3$) and m/e 111 by respectively, the loss of $\cdot H$, $\cdot OH$, and $\cdot NO$ radicals. The subsequent loss of $\cdot NO_2$ from the m/e 140 ion gives distinct ion at m/e 94; this can be formed from the m/e 124 ion by the loss of $\cdot NO$ radical. The m/e 111 ion undergoes the elimination of a $\cdot CHO$ radical giving the m/e 82 ion.

Analogous to the case of 5-nitro-2-furohydrazide imide, the processes to eliminate $\cdot NO_2$ and $\cdot OH$ radicals from the M^+ could also be observed, however, the resulting m/e 125 (Ion composition $C_5H_5N_2O_2$) and m/e 154 ion peaks were extremely weak. In the former process, the loss of NO_2 and CO fragments by a one-step process did not occur, which was observed in the fragmentations of 5-nitro-2-furohydrazide¹⁾ and 3-(5-nitro-2-furyl)-1, 2, 4-triazoles.⁹⁾ In further cleavage of the m/e 125 ion, the loss of $\cdot H$ radical preferentially occurred, followed by the loss of CO , thus giving the $(C_5H_4N_2O_2)^+$ ion at m/e 124 and the $(C_4H_4N_2O)^+$ ion at m/e 96. On the other hand, the m/e 154 ion gives the $(C_5H_3NO_3)^+$, $(C_5H_2NO_3)^+$, and $(C_4H_2NO_2)^+$ ions at m/e 125, 124, and 96 by the subsequent loss of $\cdot N_2H$, $\cdot H$, and CO fragments.

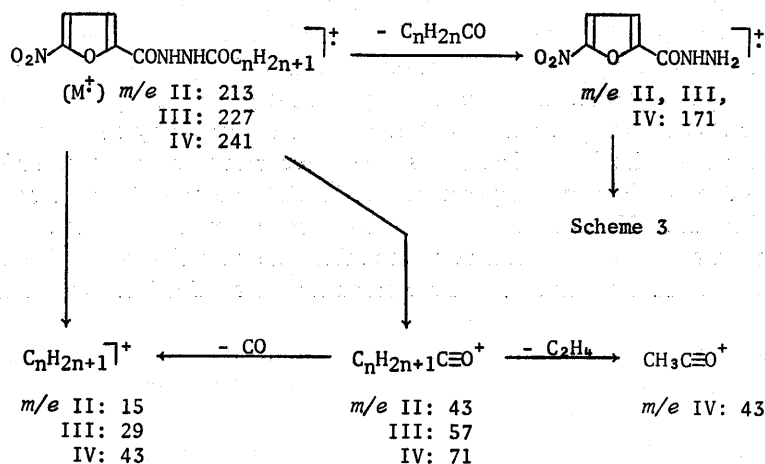
N'-Acyl Compounds (II, III, and IV). The acyl compounds, II-IV, give weak molecular ion (M^+) peaks (2.3-2.9% of the base peak). In the first step of the fission of the molecular ions, as is shown in Scheme 2, there are three principal modes of elimination of the acyl groups:

(1) With the rearrangement of a hydrogen atom, the prominent ion peaks at m/e 171, which are consistent with the mass of the M^+ in compound I, result from the elimination of $C_nH_{2n}C=O$ ($n=1, 2,$ and 3 respectively);

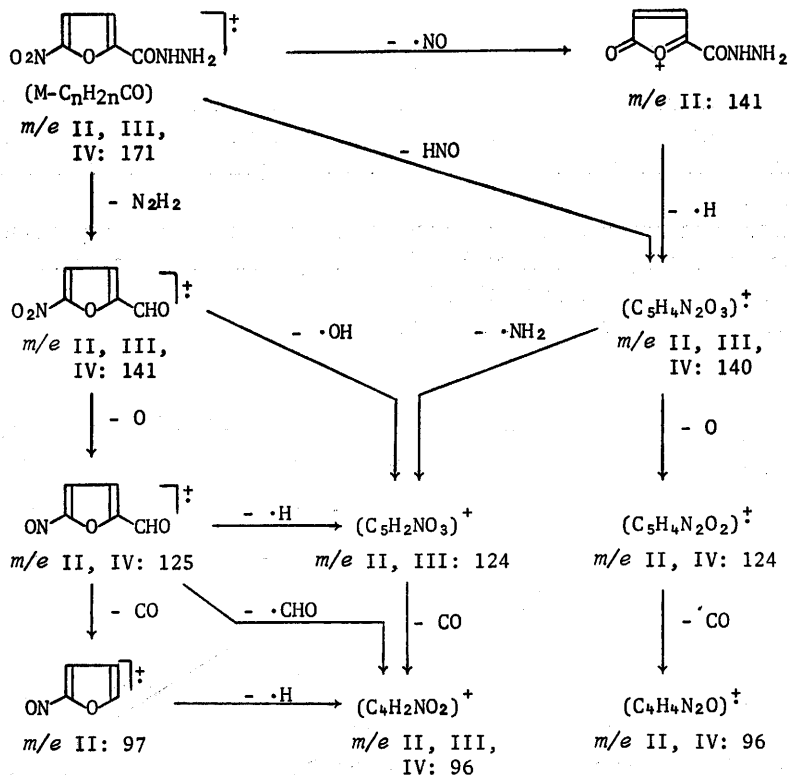
(2) the elimination of an acyl group with the charge-transfer brings about the most



Scheme 1 Fragmentation of the compound, I.



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



Scheme 3 Further cleavage of the $(\text{M}-\text{C}_n\text{H}_{2n}\text{CO})$ ion generated from II, III, and IV.

prominent $\text{C}_n\text{H}_{2n+1}\text{CO}^+$ ions (the base peak) at *m/e* 43, 57, and 71, and

(3) also with the charge-transfer, the cleavage of an alkyl group occur, giving rise the *m/e* 15, 29, and 43 ions with 9.2, 59.4, and 73.6% intensities respectively, although these ions may be possible to form from the above $\text{C}_n\text{H}_{2n+1}\text{CO}^+$ ions by the loss of CO.

In comparison of the fragmentation paths, as is shown in Scheme 1 and 3, there is apparent difference between the $\text{M}-\text{C}_n\text{H}_{2n}\text{CO}$ ion (*m/e* 171) and the M^+ of I in their modes

of cleavage, however, they show the same ion composition of $C_5H_5N_3O_4$. This may be due to the difference in the atomic configuration or in the ionic structure between them. Two processes to eliminate $\cdot NO_2$ and $\cdot OH$ radicals (Scheme 1) can not be observed in the fragmentations of II-IV (Scheme 3), while the cleavages of N_2H_2 and HNO fragments from the $M-C_nH_{2n}CO$ ion preferentially occur, giving the ion with nitrofurfural-like structure at m/e 141 and the ion at m/e 140, respectively.

In further cleavage of these m/e 141 and 140 ions, the compounds, II-IV, show considerably different behavior to one another. The elimination of $\cdot OH$ and $\cdot NH_2$ radicals, respectively from the m/e 141 and 140 ions, are commonly observed in II and III; these two processes produce the same ion (Ion composition $C_5H_2NO_3$) at m/e 124. On the other hand, the loss of an oxygen atom also occur, common to II and IV, thus giving the m/e 125 ion and m/e 124 ion (Ion composition $C_5H_4N_2O_2$).

In addition to these major fragmentations discussed above, there may exist some other fragmentation paths. Only in the case of II, the $M-C_nH_{2n}CO$ ion undergoes the elimination of an $\cdot NO$ radical to give the $(C_5H_5N_2O_3)^+$ ion at m/e 141; this ion successively loses $\cdot H$ radical to afford the m/e 140 ion. The ion at m/e 97 can be formed by the elimination of CO molecule from the m/e 125 ion. In IV, the C_2H_4 molecule is eliminated from the m/e 71 ion ($C_3H_7CO^+$), thus affording the CH_3CO^+ ion at m/e 43.

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