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Mass-spectral Fragmentation of 3-(5-Nitro-2-furyl)-1,2,4-triazoles[1]

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The mass spectra of 3-(5-nitro-2-furyl)- (I), 5-methyl-3-(5-nitro-2-furyl)- (II), 5-ethyl-3-(5-nitro-2-furyl)- (III), and 5-trideuteriomethyl-3-(5-nitro-2-furyl)-1,2,4-triazole (IV) and their 1-acetyl, 1-trideuterioacetyl, and 1-propionyl derivatives were examined. The mother compounds, I–IV, gave the most prominent molecular ions and showed the same fragmentation pattern. The molecular ions undergo two modes of cleavages; one is the elimination of NO (1) and CO (2), followed by the loss of C_2H_2 (3), thus giving the $M-84$ ions which include the 5-substituents of the triazole ring, while the other is the loss of NO_2-CO, which directly gives rise to the fragment $M-74$ ions. The 1-acyl derivatives gave extremely weak molecular ion peaks. In the first step of the fission of the molecular ions, the elimination of an acyl group occurred, with the rearrangement of a hydrogen atom, thus giving rise to prominent ions. These ions correspond to the molecular ions of the mother compounds, I–IV, and are expected to show a similar fragmentation pathway. The fragmentation of these compounds was also considered to occur in view of the existence of meta-stable ion peaks. The meta-stable peaks appearing at the transition of the loss of NO are flat-topped, releasing kinetic energy of 0.78 ± 0.04 eV.

The mass spectra of simple furans were investigated, and the fragmentation has been established,[2–5] but no systematic mass-spectral investigation concerning more complex nitrofuran derivatives has yet been reported.

3-(5-Nitro-2-furyl)- and 5-alkyl-3-(5-nitro-2-furyl)-1,2,4-triazoles and their 1-acyl derivatives are easily prepared by the reactions of 5-nitro-2-furimidoylhydrazine derivatives with acid anhydrides (or ethyl orthoformate).[6,7] We have prepared nine derivatives of of 3-(5-nitro-2-furyl)-1,2,4-triazole and its seven deuterium-labeled compounds by the reported methods[6,7] and have examined their mass spectra in order to describe the fragmentation schemes of the compounds.

Experimental

Mass-spectral Measurement. The mass spectra were obtained on a Hitachi mass spectrometer, Model RMU-6L, except for two compounds, Ia and Ic, for which a Japan Electron Optics Co., JEOL-O1SG mass spectrometer with a direct inlet was used. The operating conditions were as follows:

	RMU-6L	JEOL-01SG
Ionizing energy (eV)	70	70
Accelerating voltage (kV)	3.20	1.75
Total electron current (μA)	80	80
Temperature of ionization chamber (°C)	220	210
Temperature for vaporization (°C)	110—150	100
Vapor pressure (mmHg)	2.0×10^{-6}	5.0×10^{-7}

Samples. The samples employed in this experiment were prepared by the methods previously reported.[6,7] All the deuterium-labeled compounds except for the 1-deuterated compound (V) were also obtained in a similar manner, by the use of hexadeuterioacetic anhydride. V was obtained by refluxing II or by the hydrolysis of acetyl-II with D_2O for 2—3 hr, and then crystallized from D_2O. The compounds thus obtained were found by mass-spectrometric analysis to be 99% deuterated for Ib-IIIb, IV, IVa, and IVc, and 85% deuterated for V. The mps of the unpublished compounds are shown in Table 1.

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[1] Presented at the 25th Annual Meeting of the Chemical Society of Japan, Tokyo, October, 1971.

[2] a) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957). b) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Amer. Chem. Soc.*, **79**, 842 (1957). c) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

[3] J. Collin, *Bull. Soc. Chim. Belges*, **69**, 449 (1960); **69**, 575 (1960).

[4] R. I. Reed and W. K. Reid, *J. Chem. Soc.*, **1963**, 5933.

[5] G. Spiteller, "Mass Spectrometry of Heterocyclic Compounds," in "Advances in Heterocyclic Chemistry," ed. by A. R. Katritzky, Academic Press, New York and London, (1966), Vol. 7, p. 305.

[6] I. Hirao, Y. Kato, T. Hayakawa, and H. Tateishi, This Bulletin, **44**, 780 (1971).

[7] I. Hirao, Y. Kato, and H. Tateishi, *ibid.*, **45**, 208 (1972).

TABLE 1. THE MELTING POINTS OF UNPUBLISHED COMPOUNDS

Compound	Mp (°C)	Solvent for recrystallization
1-Acetyl-3-(5-nitro-2-furyl)-1,2,4-triazole (Ia)	167—168	Benzene
1-Trideuterioacetyl- (Ib)	245—246	Benzene
1-Propionyl- (Ic)	167—169	Benzene
5-Methyl-1-trideuterioacetyl- (IIb)	196—197	Ether-ligroin[a]
5-Ethyl-1-trideuterioacetyl- (IIIb)	112—113	Ether-ligroin[a]
5-Methyl-1-deuterio- (V)	251—252	Deuterium oxide
5-Trideuteriomethyl- (IV)	246—247	Water
5-Trideuteriomethyl-1-methyl- (IVa)	201—202	Acetone
5-Trideuteriomethyl-1-propionyl- (IVc)	139—140	Ligroin

a) Washed with ether-ligroin (1 : 3).

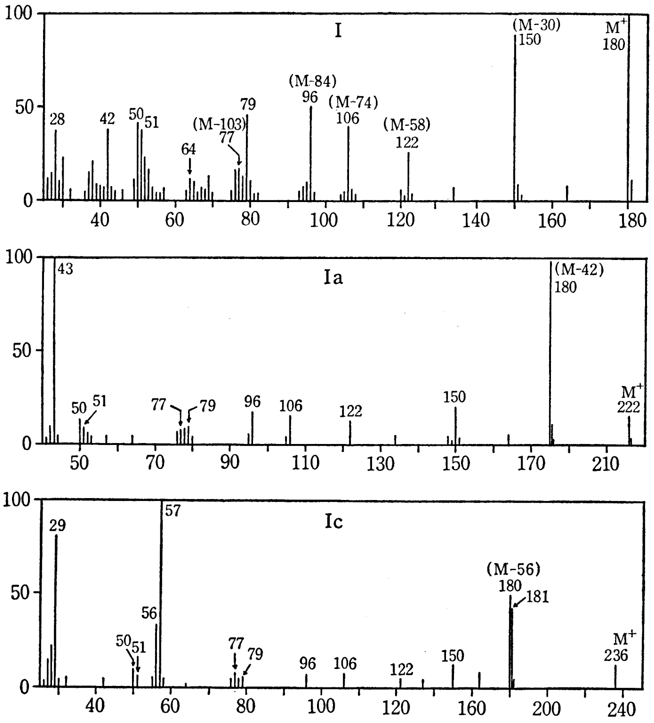
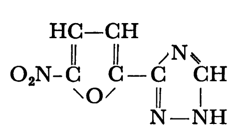
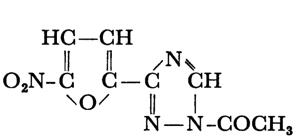
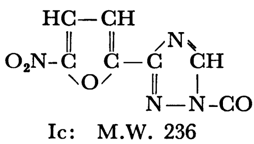


Fig. 1. Mass spectra of I, Ia, and Ic.


I: M.W. 180


Ia: M.W. 222


Ic: M.W. 236

Results and Discussion

3-(5-Nitro-2-furyl)-1,2,4-triazoles. The mass spectra of 3-(5-nitro-2-furyl)- (I), 5-methyl-3-(5-nitro-2-furyl)- (II), and 5-ethyl-3-(5-nitro-2-furyl)-1,2,4-triazole (III) are shown in Fig. 1 and Table 2. The compounds give the most prominent molecular ions (M^+) (the base peaks) with masses of 180, 194, and 208 respectively, as would be predicted from the presence of the stabilized heteroaromatic nucleus. The distinct fragment ions (M—30) of the masses at 150, 164, and 178 are formed by the elimination of NO from the molecular ions; this differs somewhat from nitrobenzene in that the M—46 (NO_2) fragment is weak, and is similar to the behavior of 5-nitro-2-bromofuran.[8] The M—30 ions may lose carbon monoxide[9] to give ion peaks (M—58) with masses of 122, 136, and 150 respectively. The subsequent loss of an acetylene molecule would lead to M—84 ion peaks (*m/e* I: 96, II: 110, and III: 124). There is a three-step process concerned with the fission of the furan ring in the molecular ions. The M—84 ions undergo two modes of cleavage of the triazole ring to give two distinct ions, RCN_2H^+ (*m/e* 42, 56, and 70) and $RCNH^+$ (*m/e* 28, 42, and 56) respectively.

The occurrence of another process of cleavage of the furan ring in the molecular ions is confirmed on the basis of the appearance of the meta-stable ion peaks. The molecular ions lose NO_2 and CO fragments by a one-step process to give M—74 ions at the masses of 106, 120, and 134 respectively. The M—74 ions show four modes of cleavage and give *m/e* 79 (common to all spectra), 65, 64, and M—103 (77, 91, and 105) ions by, respectively, the loss of RCN, (R—H)CN_2H, RCN_2H, and N_2H fragments. The common ion (79) gives two fragment ions at the masses of 51 and 50 from its two modes of cleavage, and the M—103 ions lose RCN to give the *m/e* 50 ion.

To define more precisely the mechanism and ions involved, the 5-trideuteriomethyl compound was synthesized and the hydrogen atom on the triazole nucleus on II was exchanged by equilibration with D_2O. In the mass spectra of 5-trideuteriomethyl-3-(5-nitro-2-furyl)-1,2,4-triazole (IV) and 5-methyl-3-

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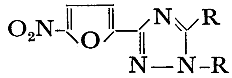
[8] R. Grigg, M. V. Sargent, D. H. Williams, and J. A. Knight, *Tetrahedron*, **21**, 3441 (1965).

[9] The possibility of the loss of N_2 in this pathway was eliminated because the mass spectra of 5-nitro-2-bromofuran (Ref. 8) and 5-nitro-2-furonitrile (measured under the same experimental conditions) showed a fragmentation step which corresponds to the loss of 28 amu. The mass-spectral fragmentation of 5-nitro-2-furonitrile may be shown as follows:

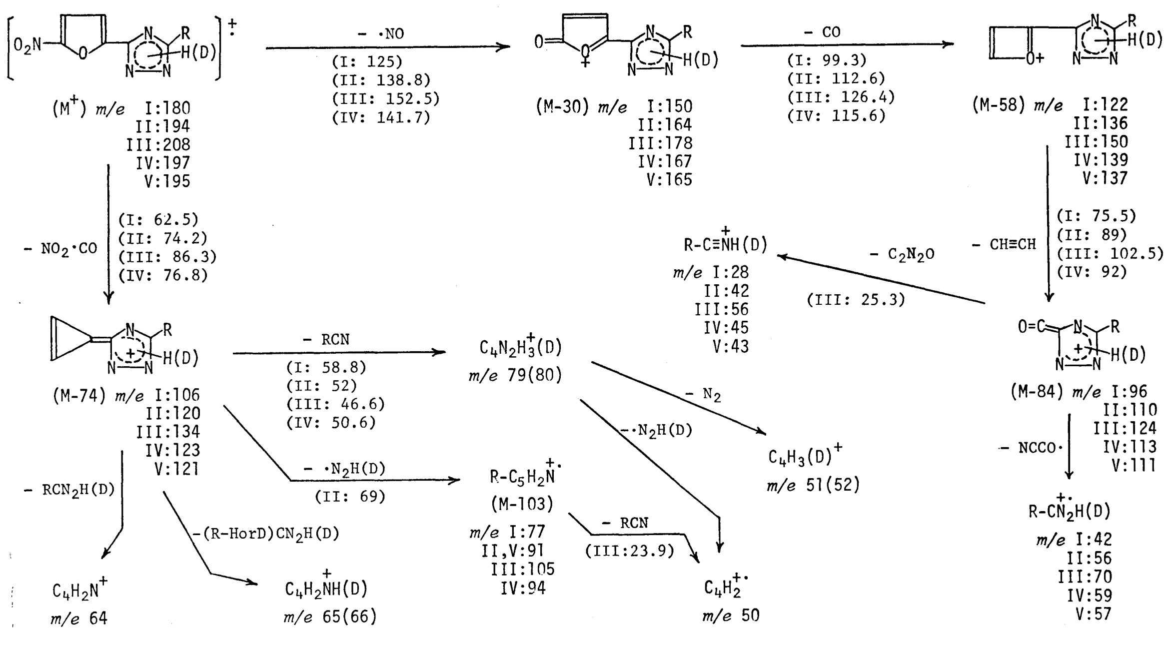
$$\begin{tikzcd} m/e\,138\,(M^+) \arrow[r, "-30", "m^*"'] \arrow[dr, "m^*"', "-(46+28)"] & m/e\,108 \arrow[r, "-28", "m^*"'] & m/e\,80 \arrow[r, "-26", "m^*"'] & m/e\,54 \arrow[r, "-27"] & m/e\,27 \\ & m/e\,64 \arrow[r, "-27"] & m/e\,37 & & \end{tikzcd}$$

(m^*: meta-stable ion observed)

Table 2. Mass-spectral data of 5-alkyl-3-(5-nitro-2-furyl)-1,2,4-triazoles



II R=CH_3, R′=H		V R=CH_3, R′=D		IV R=CD_3, R′=H		III R=C_2H_5, R′=H	
m/e	Rel. Int. (%)	m/e	Rel. Int. (%)	m/e	Rel. Int. (%)	m/e	Rel. Int. (%)
194	100	195	100	197	100	208	100
164	53	165	51	167	50	178	36
136	16	137	15	139	16	150	15
120	44	121	30	123	44	134	31
110	46	111	43	113	45	124	33
91	16	91	11	94	16	105	11
80	14	81	12	80	12	80	13
79	67	80	84	79	70	79	57
65	26	65	11	66	20	70	28
64	29	64	15	64	19	65	18
56	73	57	62	59	66	64	27
53	19	54	14	53	18	56	53
52	31	53	17	52	25	55	18
51	54	52	50	51	49	52	27
50	46	51	16	50	48	51	46
42	84	43	68	45	76	50	34



I: R=H, II=V: R=CH_3, III: R=C_2H_5, IV: R=CD_3

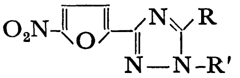
Scheme 1. Fragmentation of I, II, III, IV, and V.

(5-nitro-2-furyl)-1-deuterio-1,2,4-triazole (V) (Table 2), *m/e* 194, 164, 136, 110, 56, and 42 are shifted completely to *m/e* 197, 167, 139, 113, 59, and 45, and to *m/e* 195, 165, 137, 111, 57, and 43, respectively. Moreover, the two peaks at *m/e* 79 and 51 in the spectrum of II are shifted to, respectively, *m/e* 80 and 52 in that of V, while *m/e* 91 and 64 remain without being shifted. We may conclude, therefore, that the fragmentation pathways in the foregoing occur for I, II, III, and IV.

The major fragmentation, common to I–V, is postulated in Scheme 1. Some of the pathways of the fragmentation were confirmed by the presence of meta-stable ion pekas.

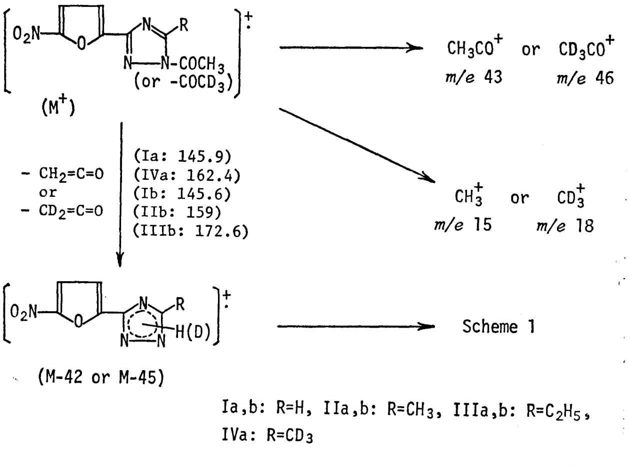
1-Acetyl and 1-Trideuterioacetyl Derivatives of I, II, and III. The mass-spectral data of 1-acetyl- (Ia), 1-trideuterioacetyl- (Ib), 5-methyl-1-acetyl- (IIa), 5-methyl-1-trideuterioacetyl- (IIb), 5-ethyl-1-acetyl- (IIIa), 5-ethyl-1-trideuterioacetyl- (IIIb), and 5-trideuteriomethyl-1-acetyl-3-(5-nitro-2-furyl)-

Table 3. Mass-spectral data of 1-acetyl- and 1-trideuterioacetyl-3-(5-nitro-2-furyl)-1,2,4-triazoles



Ib $R=H$, $R'=COCD_3$		IIa $R=CH_3$, $R'=COCH_3$		IIb $R=CH_3$, $R'=CO_3CD_3$		IVa $R=CD_3$, $R'=COCH_3$		IIIa $R=C_2H_5$, $R'=COCH_3$		IIIb $R=C_2H_5$, $R'=COCD_3$	
m/e	Rel. Int. (%)	*m/e*	Rel. Int. (%)	*m/e*	Rel. Int. (%)	*m/e*	Rel. Int. (%)	*m/e*	Rel. Int. (%)	*m/e*	Rel. Int. (%)
225	6	236	14	239	5	239	12	250	10	253	5
181	43	194	100	195	47	197	100	208	100	209	63
151	10	164	17	165	13	167	24	178	24	179	14
123	5	136	11	137	6	139	12	150	10	151	4
107	8	120	12	121	8	123	13	134	13	135	7
97	10	110	12	111	7	113	12	124	11	125	6
80	6	91	8	91	7	94	9	105	9	105	4
77	5	79	10	80	8	79	13	79	14	80	9
64	3	65	8	65	8	66	8	70	7	71	4
52	7	64	7	64	6	64	4	65	10	65	7
50	11	56	9	57	6	59	9	64	10	64	8
46	100	51	7	52	9	51	7	56	11	57	7
43	6	50	8	50	10	50	10	51	10	52	8
30	6	43	53	46	100	45	11	50	9	50	6
29	4	42	11	43	8	43	89	43	83	46	100
18	9	15	16	18	8	15	10	15	14	18	11

1,2,4-triazole (IVa) are summerized in Table 3 (Ia, in Fig. 1). The 1-acetyl compounds, Ia–IVa, give weak molecular-ion peaks (10—15% of the base peak). The elimination of an acetyl group from the molecular ion occurs in the following processes. One process, by the rearrangement of a hydrogen atom, produces base peaks at M—42, which are consistent with the masses of the molecular ion of I, II, III, or IV, by the loss of a ketene ($CH_2=C=O$). The other process, without any rearrangement, produces a strong peak with a mass of 43 due to $CH_3C\equiv O^+$ and a distinct peak of the CH_3^+ ion at mass 15. The M—42 ions of the masses at 180, 194, and 208 may undergo the same fragmentation as the corresponding mother compound (I, II, III, or IV), as has been described above. On the other hand, in the mass spectra of 1-trideuterioacetyl compounds, Ib–IIIb, the molecular ions are extremely weak (5—6% of the base peak). The peaks corresponding to M—42 in Ia-IIIa are shifted completely to one atomic mass unit (amu); those corresponding to *m/e* 43 and 15 are consistent with a mass shift of 3 amu. This suggests that a similar mode of the cleavage of the trideuterioacetyl group also occurs, with or without the rearrangement of a deuterium atom, giving the prominent peaks (M—44) by the loss of $CD_2=C=O$, the base peak at mass 46 ($CD_3C\equiv O^+$), and a fragment ion peak with mass 18 (CD_3^+) by N^1-CO and α-bond cleavages (Scheme 2). It might, therefore, be expected that a mode of fragmentation similar to that of V would occur for the M—44 ions with the masses of 181, 195, and 209.



Scheme 2. Fragmentation of 1-acetyl (Ia-IVa) and 1-trideuterioacetyl (Ib-IIIb) compounds.

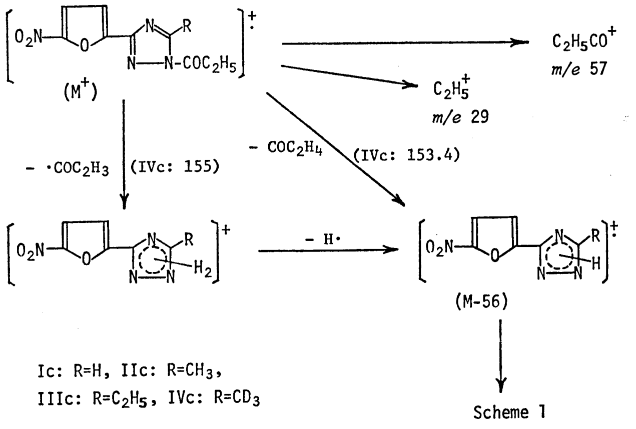
1-Propionyl Derivatives of I, II, III, and IV. The mass-spectral data of 1-propionyl- (Ic), 5-methyl-1-propionyl- (IIc), 5-ethyl-1-propionyl- (IIIc), and 5-trideuteriomethyl-1-propionyl-3-(5-nitro-2-furyl)-1,2,4-triazole (IVc) are shown in Table 4. The molecular ions here are also weak (10—15% of the base peak). In the first step of the fission of the molecular ions, as is shown in Scheme 3, there are four modes of the elimination of the propionyl group. With the rearrangement of one or two atoms of hydrogen, strong peaks (the base peak of IIIc) at M—56 result from the eliminations of (1) the $CH_3CH=C=O$ (or $CH_2=CHCHO$) molecule and (2) the $CH_2=CHC=O$ radical, successively a hydrogen atom. On the other hand, cleavage occurs without any rearrangment, giving (3) the base peaks (except for IIIc) at the mass 57 ($C_2H_5C\equiv O^+$) and (4) a prominent ion ($C_2H_5^+$) at mass 29, which also might come somewhat from the cleavage of the ion *m/e* 57. The M—56 ions correspond to the molecular ions of I—IV and may be expected to show the same fragmentation as that of the corresponding compounds, as is indicated in Shceme 1.

TABLE 4. MASS-SPECTRAL DATA OF 1-PROPIONYL-3-(5-NITRO-2-FURYL)-1,2,4-TRIAZOLES.

IIc, R=CH_3		IVc, R=CD_3		IIIc, R_2H_5	
m/e	Rel. Int. (%)	m/e	Rel. Int. (%)	m/e	Rel. Int. (%)
250	15	253	10	264	12
195	57	198	43	209	52
194	81	197	66	208	100
164	25	167	22	178	25
136	8	139	6	150	6
120	9	123	8	134	8
110	8	113	7	124	6
91	13	94	10	105	7
79	9	79	7	79	8
65	10	66	8	70	5
64	7	64	4	65	8
57	100	59	4	64	7
56	23	57	100	57	95
51	7	56	18	56	22
50	9	51	6	51	7
42	12	50	8	50	8
41	6	45	10	41	9
29	82	29	85	29	76
28	24	28	8	28	16
27	19	27	14	27	16

The molecular ions in the spectra of I–IV and the ions of $[M-(R'CO-H \text{ or } D)]^+$ in the spectra of the acyl compounds decompose to yield meta-stable ion peaks corresponding to the following transitions:

$$M^+ \rightarrow (M\text{-}30)^+ + NO$$



Scheme 3. Fragmentation of 1-propionyl compounds (Ic-IVc).

$$[M-(R'CO-H \text{ or } D)]^+ \rightarrow$$
$$[M-(R'CO-H \text{ or } D)-30]^+ + NO$$

The meta-stable peaks in these transitions are flat-topped, indicating a formation with a release of kinetic energy.[10] As is shown in Table 5, the energy values found for these compounds correspond approximately to that of *o*-nitrophenol[10a] and are 2.5 times that of 5-nitro-2-furonitrile.

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TABLE 5. THE KINETIC ENERGY RELEASED IN THE FLAT-TOPPED META-STABLE TRANSITION

Compound	Molecular weight	Precursor ion	Transition	Kinetic energy (eV)
I	180	M^+	180→150	0.81
II	194	M^+	194→164	0.77
III	208	M^+	208→178	0.75
IV	197	M^+	197→167	0.79
Ib	225	$(M\text{-}COCD_2)^+$	181→151	0.77
IIb	239	$(M\text{-}COCD_2)^+$	195→165	0.77
IIIb	253	$(M\text{-}COCD_2)^+$	209→179	0.77
IVa	239	$(M\text{-}COCH_2)^+$	197→167	0.79
IVc	253	$(M\text{-}COC_2H_4)^+$	197→167	0.78
o-Nitrophenol[11a]	139	M^+	139→109	0.75
5-Nitro-2-furonitrile	138	M^+	138→108	0.29

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[10] a) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, **20A**, 180 (1965). b) T. W. Shannon, F. W. McLafferty, and C. R. McKinney, *Chem. Comm.*, **1966**, 478. Many applications of meta-stable peak study were attempted by F. W. McLafferty *et al.*, *cf.*, for example, *J. Amer. Chem. Soc.*, **88**, 5021 (1966), and related papers.