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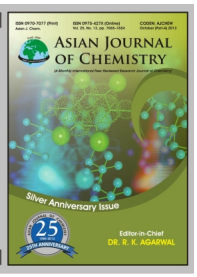

Mass Spectrometry of Substituted 1*H*,6*H*-Pyrano[2,3-*c*]pyrazol-6-ones

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The mass spectra of some *C*- and *N*-alkyl and aryl substituted 1*H*, 6*H*-pyrano[2,3-*c*]pyrazol-6-ones are presented. The fragmentation is initiated by the elimination of CO followed by a loss of hydrogen, rearrangement and then loss of a RCN group. Parallely a disproportionation gives RN_2 which loses N_2 to give the aromatic ion (*m/z* 77 or 91).

Key Words: 1*H*,6*H*-Pyrano[2,3-*c*]pyrazol-6-ones, Fragmentation, Disproportionation.

INTRODUCTION

Pyranopyrazoles are an important class of biologically active heterocycles. They were found to have antimicrobial[1], anticancer[2], potential antiinflammatory[3], insecticidal and molluscicidal activities[4,5]. They are also reported as inhibitors of human Chk1 kinase[6] and have applications as biodegradable agrochemicals[7-10]. Because of its wide applications, many methods[11-14] were reported for their synthesis. A series of pyranopyrazoles of biological interest were synthesized by a three component reaction of pyrazol-5-ones, aldehydes and malononitrile[15] and also by a four component reaction of ethyl acetoacetate, hydrazine hydrate, aldehydes and malononitrile under solvent free condition[16].

Vaid *et al.*[17] had published mass spectral fragmentations of some benzothiazoles containing a pyrano[2,3-*c*]pyrazol-6-one substituent. Herein, we wish to report mass spectral behaviour of a number of pyrano[2,3-*c*]pyrazol-6-ones whose synthesis was published earlier[18].

EXPERIMENTAL

The synthesis of all the 1*H*, 6*H*-pyrano[2,3-*c*]pyrazol-6-ones (**1-13**) has previously been described[18].

The mass spectra were obtained on an AEI MS-902 and VG Micromas LTD-30 instruments normally operating at 70 eV.

RESULTS AND DISCUSSION

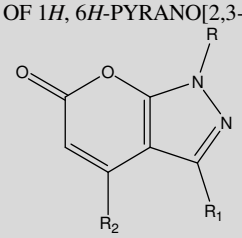
The mass spectral data of various alkyl and aryl derivatives of 1*H*,6*H*-pyrano[2,3-*c*]pyrazol-6-ones is collected in Table-1. Table-2 provides the main fragments of various compounds.

***N*-Arylpyrano[2,3-*c*]pyrazol-6-one (1-8):** The mass spectrum of the first compound in this series *i.e.*, 3,4-dimethyl-1-phenyl-1*H*, 6*H*-pyrano[2,3-*c*]pyrazol-6-one (**1**) was analyzed. The fragmentation pattern of **1** is presented in **Scheme-I**. The base peak was the molecular ion peak and the mass spectrum of **1** resembles somewhat that of 4-methylcoumarins[19]. It fragments by the successive loss of CO, $H^{\bullet}$ and CO to give fragments **c**, **d** and **e**. The metastable peaks for this fragmentation path were present in the spectrum. Further fragmentation probably occurs *via* loss of a molecule of acetonitrile (fragment **f**) also supported by the metastable peak. The loss of $-CH_3^{\bullet}$ from the molecular ion followed by a loss of $-C_2H_2$. These fragmentations by loss of CO, $CH_3^{\bullet}$, C_2H_2 were also observed by Vaid *et al*[17]. The origin of the last two fragments, however, is not known at the present. The molecular ion also loses PhN_2 which in its turn loses N_2 giving rise to the fragment $-C_6H_5$ also appearing in the spectrum from another alternative fragmentation route.

Examination of the mass spectra of other *N*-aryl-1*H*, 6*H*-pyrano[2,3-*c*]pyrazol-6-ones (**2-8**, Table-2) revealed that the

molecular ion peak was the base peak for these compounds except for **2, 3** and **7** in which case the base peak appeared due to the N-aryl substituent (*m/z* 77 for **2** and **3** and *m/z* 91 for **7**). Another interesting fragmentation pattern observed for **1**, **4**, **5**, **7** and **8** was the simultaneous formation of two fragments by the loss of RN_2 (fragment **a**) and $R_1R_2C_6HO_2$ (fragment **b**). The fragment **a** in turn loses CO to give fragment **h**. Some of the compounds containing a phenyl substituent at

TABLE-1
MASS SPECTRA OF 1*H*, 6*H*-PYRANO[2,3-*c*]Pyrazol-6-ONES



(ONLY PEAKS WITH AN INTENSITY OF 3% OR MORE RELATIVE TO THE BASE PEAK ARE SHOWN)

Compd. No.	Substituents R, R_1, R_2	Mass spectra *m/z* (relative intensity)
1	Ph, Me, Me	241 (15.2), 240 (100), 225 (5.2), 214 (4.5), 212 (14.5), 211 (8.7), 199 (15.5), 197 (3.9), 183 (4.8), 142 (10.3), 135 (4.8), 131 (10), 119 (10), 118 (7), 107 (10), 105 (18), 91 (12), 77 (4), 69 (42), 51 (28).
2	Ph, H, Me	226 (74), 198 (12), 197 (8), 169 (12), 142 (10), 105 (24), 93 (18), 78 (12), 77 (100), 69 (24), 51 (20).
3	Ph, H, Ph	288 (72), 260 (5), 232 (10), 231 (12), 226 (12), 204 (8), 155 (16), 127 (20), 105 (36), 77 (100), 69 (18), 51(24).
4	Ph, Me, Ph	302 (100), 274 (16), 246 (10), 205 (16), 197 (18), 169 (16), 151 (10), 146 (12), 128 (15), 115 (33), 105 (38), 91 (16), 77 (90), 51 (8).
5	Ph, Ph, Me	303 (27), 302 (100), 301 (27), 274 (8), 264 (9), 246 (5), 236 (38), 197 (12), 169 (14), 142 (12), 115 (20), 105 (16), 103 (11), 91 (18), 77 (55), 51 (13).
6	*o*-$CH_3C_6H_4$, Me, Me	254 (100), 226 (13), 225 (10), 197 (4), 156 (17), 135 (14), 132 (22), 107 (16), 91 (79), 77 (33), 65 (23), 51 (18).
7	*m*- $CH_3C_6H_4$, Me, Me	254 (54), 226 (8), 197 (5), 156 (11), 135 (12), 132 (15), 119 (18), 107 (12), 105 (36), 91 (100), 78 (12), 77 (23), 65 (27), 51 (14).
8	*p*- $CH_3C_6H_4$, Me, Me	254 (100), 226 (12), 225 (10), 212 (8), 211 (10), 184 (5), 156 (16), 135 (12), 132 (27), 119 (22), 107 (14), 91 (96), 77 (52), 68 (28), 65 (22), 51 (18).
9	Me, Me, Me	178 (100), 150 (31), 149 (30), 135 (23), 123 (10), 108 (8), 107 (33), 80 (33), 79 (30), 77 (38), 66 (15), 51 (24).
10	Me, Me, Ph	240 (100), 239 (20), 213 (20), 212 (40), 211 (13), 197 (35), 183 (12), 169 (33), 143 (30), 142 (18), 139 (15), 115 (38), 105 (8), 102 (8), 77 (10), 66 (12), 63 (10), 51 (10).
11	Me, Ph, Me	241 (20), 240 (100), 239 (25), 212 (16), 211 (14), 197 (10), 183 (6), 169 (28), 141 (21), 139 (6), 115 (28), 92 (12), 80 (12), 77 (10), 51 (12).
12	H, Me, Me	164 (100), 149 (9), 136 (39), 135 (50), 121 (12), 53 (17), 51 (18).
13	H, Ph, Me	227 (21), 226 (100), 225 (32), 198 (25), 197 (14), 169 (11), 160 (12), 129 (18), 115 (18), 102 (18), 85 (9), 83 (14), 77 (12), 67 (10), 51 (10).

TABLE-2
MASS SPECTRAL FRAGMENTS OF 1*H*,6*H*-PYRANO[2,3-*c*]PYRAZOL-6-ONES
m/z (RELATIVE INTENSITIES)

Fragments*	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
M	240 (100)	226 (74)	288 (72)	302 (100)	302 (100)	254 (100)	254 (50)	254 (100)	178 (100)	240 (100)	240 (100)	164 (100)	226 (100)
a	135 (20)	-	-	197 (18)	197 (12)	135 (20)	135 (12)	135 (12)	135 (23)	197 (35)	197 (35)	135 (50)	197 (14)
b	105 (18)	105 (24)	105 (36)	105 (38)	105 (16)	-	119 (18)	119 (22)	-	-	-	-	-
c	212 (14)	198 (12)	260 (5)	274 (16)	274 (8)	226 (13)	226 (8)	226 (12)	150 (31)	212 (40)	212 (16)	136 (39)	198 (25)
d	211 (8.7)	197 (8)	-	-	-	225 (10)	-	225 (10)	149 (30)	211 (13)	211 (14)	135 (50)	197 (14)
e	183 (4.8)	169 (12)	-	-	-	197 (4)	197 (5)	-	-	183 (12)	183 (6)	-	169 (11)
f	142 (10.3)	142 (10)	-	-	-	156 (17)	156 (11)	-	-	142 (18)	80 (12)	-	-
g	77 (4)	77 (100)	77 (100)	77 (90)	77 (55)	-	91 (100)	91 (96)	-	-	-	-	-
h	-	-	-	169 (10)	160 (14)	107 (16)	107 (12)	107 (14)	107 (33)	169 (33)	169 (28)	-	-

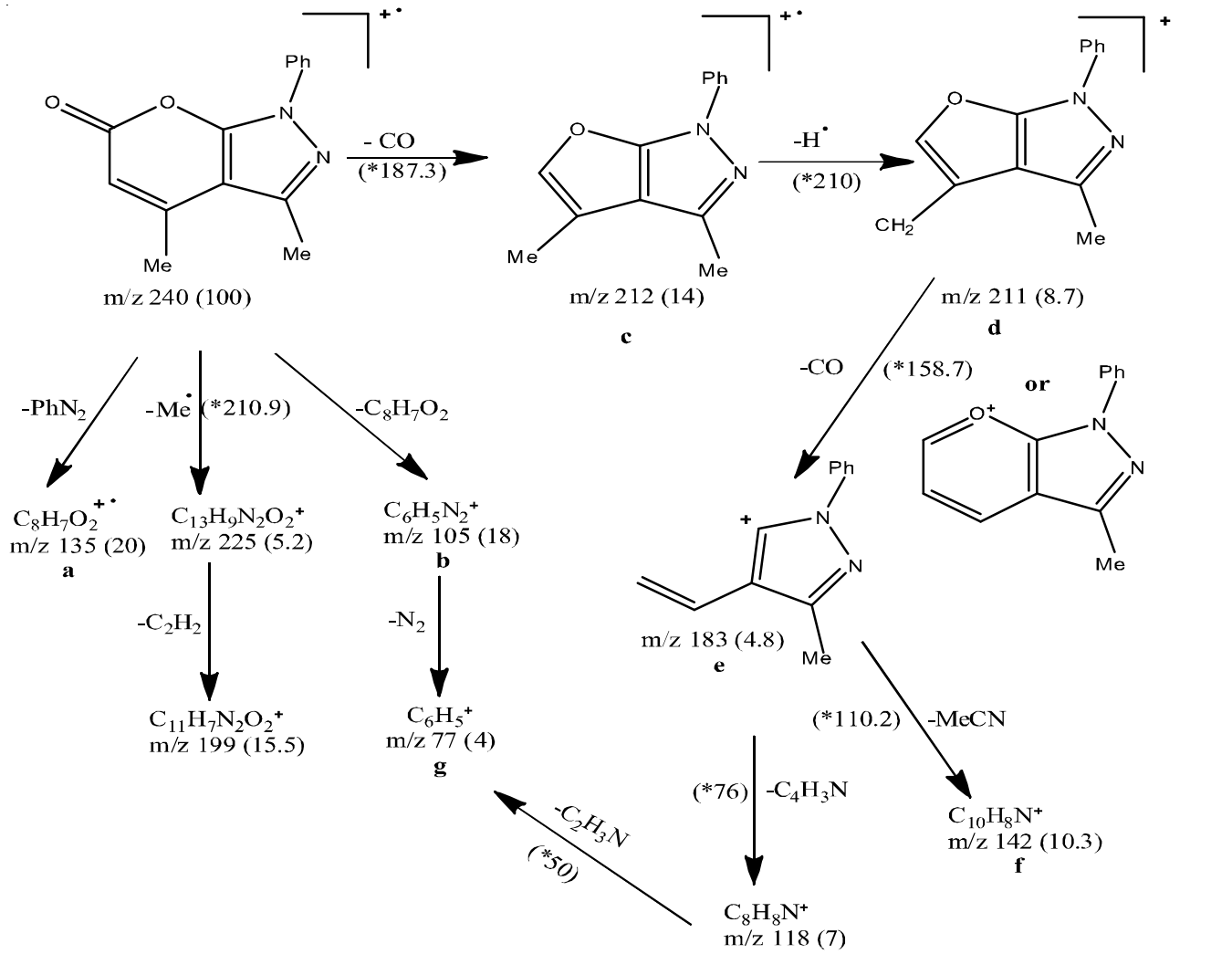
Fragments*	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
[$M^{+\bullet}$-$Me^{\bullet}$]	225 (5.2)	-	-	-	-	-	-	-	-	-	-	149 (9)	-
[$M^{+\bullet}$-CO-H-CO-C_4H_3N]	118 (7)	-	-	-	-	132 (22)	132 (15)	-	-	-	-	-	-
[$M^{+\bullet}$-CO-$H^{\bullet}$-CO-C_4H_3N-C_2H_3N]	77 (4)	-	-	-	-	91 (79)	91 (100)	-	-	-	-	-	-
[$M^{+\bullet}$-$Me^{\bullet}$-C_2H_2]	199 (15.5)	-	-	-	-	-	-	-	-	-	-	-	-
[$M^{+\bullet}$-CO-RN_2]	-	93 (18)	155 (16)	169 (10)	-	-	-	-	-	-	-	-	-
[$M^{+\bullet}$-CO-RN_2-CO]	-	-	127 (20)	-	-	-	-	-	-	-	-	-	-
[$M^{+\bullet}$-CO-CO]	-	-	232 (10)	246 (10)	246 (5)	-	-	-	-	-	-	-	-
[$M^{+\bullet}$-CO-CO-RN_2]	-	-	127 (20)	-	-	-	-	-	-	-	-	-	-
[$M^{+\bullet}$-CO-CO-R_1CN]	-	-	-	205 (16)	-	-	-	-	-	-	-	-	-
[$M^{+\bullet}$-$H^{\bullet}$]	-	-	-	-	301 (27)	-	-	-	-	239 (20)	-	-	225 (32)
[$M^{+\bullet}$-$H^{\bullet}$-CO]	-	-	-	-	-	-	-	-	-	-	-	-	197 (14)
[$M^{+\bullet}$-$C_8H_7NO_2$]	-	-	-	-	-	-	105 (36)	-	-	-	-	-	
[$M^{+\bullet}$-CO-$H^{\bullet}$-CH_2]	-	-	-	-	-	-	-	211 (8)	135 (23)	-	-	-	
[$M^{+\bullet}$-CO-CH_2-$H^{\bullet}$-CO]	-	-	-	-	-	-	-	184 (5)	-	-	-	-	
[$M^{+\bullet}$-CO-CH_2-$H^{\bullet}$-CO-C_2H_4]	-	-	-	-	-	-	-	156 (16)	-	-	-	-	
[$M^{+\bullet}$-CO-$H^{\bullet}$-R_1CN]	-	-	-	-	-	-	-	-	108 (8)	-	-	-	
[$M^{+\bullet}$-CO-$H^{\bullet}$-R_1CN-CO]	-	-	-	-	-	-	-	-	80 (33)	-	-	-	
[$M^{+\bullet}$-CO-$H^{\bullet}$-CO-CH_2]	-	-	-	-	-	-	-	-	-	169 (33)	-	-	
[$M^{+\bullet}$-RN_2-CO-C_2H_2]	-	-	-	-	-	-	-	-	-	143 (30)	-	-	
[$M^{+\bullet}$-RN_2-CO-C_2H_2-Ph]	-	-	-	-	-	-	-	-	-	66 (12)	-	-	
[$M^{+\bullet}$-RN_2-CO-CO]	-	-	-	-	-	-	-	-	-	-	141 (21)	-	
[$M^{+\bullet}$-RN_2-CO-CO-C_2H_2]	-	-	-	-	-	-	-	-	-	-	115 (28)	-	
[$M^{+\bullet}$-RN_2-CO-Ph]	-	-	-	-	-	-	-	-	-	-	92 (12)	-	
[$M^{+\bullet}$-$Me^{\bullet}$-CO]	-	-	-	-	-	-	-	-	-	-	-	121 (12)	
[$M^{+\bullet}$-$Me^{\bullet}$-CO-$C_3H_4N_2$]	-	-	-	-	-	-	-	-	-	-	-	53 (17)	

*__a__- $M^{+\bullet}$-RN_2 ; __b__- $M^{+\bullet}$-$R_1R_2C_6HO_2$; __c__- $M^{+\bullet}$-CO ; d- $M^{+\bullet}$-CO-$H^{\bullet}$; __e__- $M^{+\bullet}$-CO-$H^{\bullet}$-CO ; __f__- $M^{+\bullet}$-CO-$H^{\bullet}$-CO-R_1CN ; __g__- $M^{+\bullet}$-$R_1R_2C_6HO_2$-N_2 ; __h__- $M^{+\bullet}$-RN_2-CO

the 3 or 4 position (**3**, **4** and **5**) fragmented by way of the loss of two CO molecules. Another alternate fragment path which is noted in all the compounds except for **12** is the first loss of a CO molecule followed by the loss of a RN_2 fragment.

***N*-Methylpyrano[2,3-*c*]pyrazol-6-ones (9-11):** The *N*-methyl compounds (**10** and **11**) also showed molecular ions as the base peaks and fragmentation by the loss of CO which was followed by the successive loss of $H^{\bullet}$, CO and RCN (**c**, **d**, **e**, **f**). However, in the case of **9** the loss of a CO molecule was followed by a loss of $H^{\bullet}$ and the fragment formed there from now lost a CH_3CN and a CO (**c-d**, **-H**, **-CH_3CN**). Fragmentation also occurs through the loss of a molecule of CH_3N_2 (**a**). Compounds **10** and **11** also lose an $H^{\bullet}$ and this probably occurs with the rearrangement of the pyrazole molecule into a pyridazine or a pyrimidine ring a phenomenon often observed in the mass spectra of *N*-methypyrazoles[20].

***N*-Unsubstituted pyrano[2,3-*c*]pyrazol-6-ones (12 and 13):** Only two compounds in this series were studied and their mass spectra were very simple. These displayed fragments **a**, **c** and **d** formed by the loss of HN_2 and by the successive loss of CO and $H^{\bullet}$ from the molecular ion which was the base peak in their spectra. Other fragments $M^{+\bullet}$-CH_3 and $M^{+\bullet}$-CH_3-CO (for **12**) and $M^{+\bullet}$-$H^{\bullet}$ and $M^{+\bullet}$-$H^{\bullet}$-CO (for **13**) were also observed in the mass spectra.



Scheme-I

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