

Mass Spectral Fragmentation of 4-Oxo-4*H*-pyrazole 1-Oxides and 1,2-Dioxides

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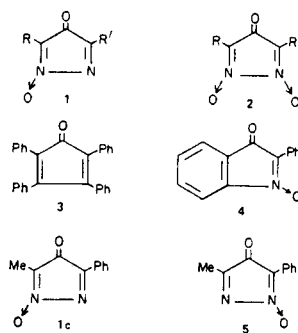
The characteristic fragmentation pattern in the mass spectra of 4-oxo-4*H*-pyrazole 1-oxides and 4-oxo-4*H*-pyrazole 1,2-dioxides involves scission of the ring into two fragments by cleavage of the nitrogen-nitrogen bond and one of the bonds to the carbonyl carbon. Loss of carbon monoxide or oxygen from the molecular ion is not observed.

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Freeman and coworkers have reported the preparation of a number of 4-oxo-4*H*-pyrazole 1-oxides and 1,2-dioxides, **1** and **2** (2). A mass spectral investigation of these compounds was undertaken, first of all, because of a general interest in oxygenated pyrazole derivatives, and secondly, because preliminary evidence suggested that the mass spectral fragmentation pattern might have diagnostic utility in the assignment of particular structural features in certain of the compounds which could only be determined indirectly by other methods.

A consistent fragmentation pattern is observed in the mass spectra of all of the compounds **1** and **2**. In all cases scission of the ring occurs by a process which involves cleavage of the nitrogen-nitrogen bond and one of the bonds to the carbonyl carbon. This produces two fragments, one of which includes one ring carbon and one nitrogen, while the remaining atoms of the ring appear in the other fragment. Either of these fragments may carry the charge. The fragmentation of the pyrazole ring in **1** is shown in Scheme I. The exact structures of the fragments are open to speculation, but the structures shown in the schemes will be used for the purpose of discussion.

The fragmentation pattern shown in Scheme I is general for the 1-oxides studied, and the data for the compounds **1a-1d** are summarized in Table I. The fragments A and B in Scheme I arise from a combination of *N-N* bond cleavage and rupture of the bond between C-4 and C-5 of the ring, while the alternative breaking of the bond between C-3 and C-4 along with the *N-N* bond produces C and D. The



formation of A and C directly from the molecular ion is suggested by the appearance of metastables in the spectra. For example, the spectrum of **1a** includes metastables

Table I

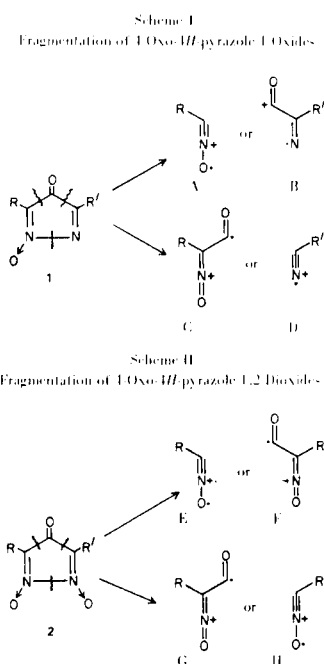
Fragmentation of 4-Oxo-4*H*-pyrazole 1-Oxides

Compound	R	R'	m/e (Relative Abundance)			
			A	B	C	D
1a	Ph	Ph	119(82)	131(<1)	147(5)	103(27)
1b	Me	Me	57(46)	69(1.2)	85(25)	41(100)
1c	Me	Ph	57(100)	131(<1)	85(25)	103(91)
1d	Et	Ph	71(92)	131(1.1)	99(73)	103(100)

Table II
Fragmentation of 4-Oxo-4H-pyrazole 1,2-Dioxides

Compound	R	R'	m/e (Relative Abundance)			
			E	F	G	H
2a	Ph	Ph	119(100)	147(7)	(a)	(a)
2b	Me	Me	57(100)	85(10)	(a)	(a)
2c	Me	Ph	57(62)	147(9)	85(52)	119(100)
2d	Et	Ph	71(40)	147(2)	99(22)	119(57)
2e	Ph	CO ₂ Et	119(100)	143(40)	147(31)	115(4)
2f	CO ₂ Et	CO ₂ Et	115(30)	143(95)	(a)	(a)
2g	CO ₂ Me	CO ₂ Me	101(7)	129(40)	(a)	(a)

(a) For these compounds fragments G and H are the same as fragments F and E, respectively.



at m/e 56.5 and m/e 86.4 which are consistent with the conversion of the molecular ion into A and C, respectively. A metastable at m/e 96.4 in the mass spectrum of **1a** suggests that the loss of CO from C provides a second route to A. The uniformly low abundance of fragment B in all of the spectra may be due to a facile conversion of this fragment to D by loss of CO, however there is no metastable to support this process, and it may simply be that when cleavage occurs to give A and B, the charge resides preferentially with A.

The fragmentation of **2** follows the same pattern seen for **1**. Scheme II illustrates the ring cleavage pattern for **2**, while the data for the compounds in this series are summarized in Table II.

The mass spectra of **2** also contain important fragments corresponding to (E - 16) and (H - 16), indicating the

subsequent loss of oxygen from these ions.

Although the loss of carbon monoxide and of oxygen plays a role in the decomposition of the ions produced by ring cleavage, the notable absence of (M - 28) and (M - 16) fragments of appreciable abundance in the spectra of **1** and **2** indicates that loss of CO or oxygen directly from the molecular ion is not involved to any significant extent. The absence of such fragments is somewhat surprising, since the loss of carbon monoxide is important in the mass spectra of the structurally analogous compounds, tetraphenylcyclopentadieneone **3** (3) and phenylisatogen **4** (4). Similarly, the loss of oxygen from the molecular ion is fairly common for *N*-oxides, being observed for **4** as well as for nitrones (5,6) and other *N*-oxides (7).

The very characteristic ring cleavage pattern makes mass spectral analysis useful in the structural elucidation of 4-oxo-4H-pyrazole 1-oxides and 1,2-dioxides. It has particular utility in assigning the structures of those 1-oxides such as **1c** and **1d** for which R and R' are not identical. The method used by Freeman for the preparation of **1c**, for example, provides no *a priori* evidence eliminating the assignment of the isomeric structure **5**, although subsequent studies have indirectly provided unequivocal evidence for the assignment of structure **1c** (8). A direct assignment is possible from mass spectral analysis, since the appearance of fragments of m/e 85 and m/e 57 is uniquely consistent with **1c**, in which the methyl group is located on the ring position adjacent to the *N*-oxide. No fragments are seen at m/e 147 or m/e 119 which would be expected for the isomer **5**, in which the phenyl substituent is adjacent to the *N*-oxide. Using similar reasoning, the assignment of the structure of **1d** follows from the appearance of fragments in its mass spectrum at m/e 99 and m/e 71.

EXPERIMENTAL

Mass spectra were obtained using an AEI Model MS 902 mass spectrometer with an ionizing potential of 70 ev. Sample intro-

duction was by direct insertion, with the source block operating at 130°. Samples were prepared by the methods of Freeman (2), and were purified by silica gel chromatography and recrystallization.

The principal ions, m/e (relative abundance) are recorded below.

1a: 251(19), 250(100), 119(82), 103(27), 89(52), 63(16).

1b: 126(24), 85(25), 57(46), 44(36), 41(100), 40(59), 39(19).

1c: 188(49), 104(17), 103(91), 85(71), 77(15), 76(38), 75(10), 57(100), 51(13), 50(17), 44(13), 41(19), 39(11).

1d: 202(30), 104(15), 103(100), 99(73), 76(32), 71(92), 54(20), 41(49), 39(20).

2a: 266(20), 147(10), 119(100), 117(11), 105(15), 104(10), 103(34), 91(11), 89(43), 77(24), 76(13), 64(11), 63(18), 51(14), 39(11).

2b: 142(4), 57(100), 43(35), 42(10), 41(30), 40(20), 39(19).

2c: 205(10), 204(88), 119(100), 104(11), 103(50), 91(23), 89(62), 85(52), 77(17), 76(13), 64(15), 63(26), 57(62), 51(15), 43(15), 39(17).

2d: 218(34), 119(57), 103(100), 99(22), 89(20), 77(12), 76(18), 71(40), 54(11), 41(10).

2e: 262(14), 147(31), 143(40), 120(14), 119(100), 117(12), 106(10), 105(21), 104(37), 103(61), 92(21), 89(55), 77(40), 76(22), 75(15), 74(11), 71(23), 70(22), 64(19), 63(24), 54(14), 51(38), 50(19), 44(44), 43(14), 41(22), 39(23).

2f: 258(<1), 143(95), 115(30), 72(40), 71(61), 70(100), 68(21), 55(21), 54(92), 45(21), 44(35), 43(70), 42(27), 41(52).

2g: 228(2), 143(31), 129(40), 86(18), 84(14), 71(12), 70(12), 59(38), 54(40), 45(17), 44(100), 43(15), 41(17).

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