

Mass Spectra of Pyridazines and their *N*-Oxides (1)

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Received January 4, 1971

The mass spectra of pyridazines and their *N*-oxides is reported. Previous electron impact studies on aromatic amine *N*-oxides reported the appearance of M-16 and/or M-17 ion peaks as the usual feature of the fragmentations. In our experiments, the representative fragmentation of the pyridazine *N*-oxides involves formation of a M-30 (M-NO) ion. The fragmentation patterns substantiated by extensive high resolution studies and the analysis of the appropriate metastable ions.

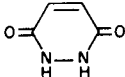
The mass spectra of pyridazines (2,3,4) have been reported, but there is no report on the mass spectra of pyridazine *N*-oxide and derivatives. The present investigation was undertaken to clarify the mass spectral fragmentation of various pyridazines (I-XI) and their *N*-oxides (XII-XXXI) which are shown in Tables I and II. These

compounds were prepared by reported procedures (references are cited in the Tables I and II), and were analytically pure.

Mass spectral studies on quinoline *N*-oxides (5), pyridine *N*-oxides (6), and benzimidazole *N*-oxides (7) have shown that the M-16 (M-O) and M-17 (M-OH) ions were the

TABLE I

Pyridazine Derivatives

	R ₁	R ₂	R ₃	Ref.		R ₁	R ₂	Ref.
I	H	H	H	a	VIII	H	H	i
II	CH ₃	H	H	b,c,d	IX	CH ₃	H	j
III	H	CH ₃	H	e	X	H	CH ₃	b
IV	OCH ₃	H	H	f				
V	C ₆ H ₅	H	H	g				
VI	NH ₂	H	CH ₃	c	XI			k,l
VII	NH ₂	H	Cl	h				

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In the mass spectrum of 3-methoxypyridazine (IV), the ion at m/e 39 is the base peak while the molecular ion and the M-1 ion peaks are of 73 and 29% abundances, respectively (Table III). The parent ion lose N_2 and N_2H to give a m/e 82 and m/e 81 species in relative abundances of 7 and 21%, respectively. A strong peak was observed at m/e 80 (31%) ($M-CH_2O$). This fragmentation appears in the aromatic methoxy derivatives (11).

The fragmentation patterns of 3-amino-6-methyl and of 3-amino-6-chloropyridazines (VI, VII) were also similar to I ($M \xrightarrow{m^*} M-N_2$). In the mass spectra of II and VI, the $M-N_2H$ ion of both compounds are observed in an abundance of 65%, because of the so-called *ortho*-effect (6, 12, 13, 14). On the other hand, the $M-N_2H$ ion was not observed in the mass spectrum of VII.

The mass spectra of 3(2*H*)-pyridazinone (VIII), 4-methyl- and of 6-methyl-3(2*H*)-pyridazinones (IX, X) showed the M-CO ion in preference to that resolvable from the loss of a N_2 molecule. The mass spectra of IX and X exhibited the M-CHO ion, which was observed at m/e 81 in abundances of 36 and 21%, respectively, while in the mass spectrum of VIII, the M-CHO ion was not observed. This result is explained by the influence of the *ortho*-effect (cited above) of the methyl group, in IX and X the same feature observed for 2-methyl-3-indazolone (15). The initial cleavage process of VIII, IX, and X is confirmed by the presence of metastable ions. These M-CO ions were observed at m/e 68, [$C_3H_4N_2$, Calcd. 68.037; Found, 68.037], m/e 82, [$C_4H_6N_2$, Calcd. 82.053; Found, 82.056], and m/e 82, [$C_4H_6N_2$, Calcd. 82.053; Found, 82.055], in abundances of 33, 10, and 21%, respectively.

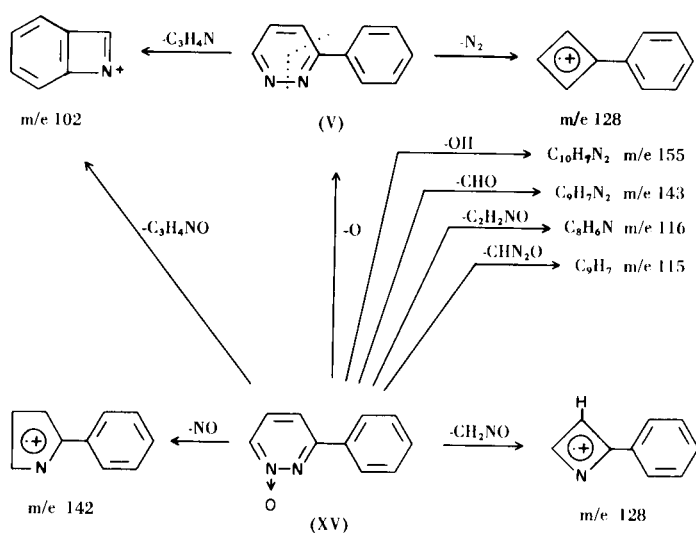


Figure 2

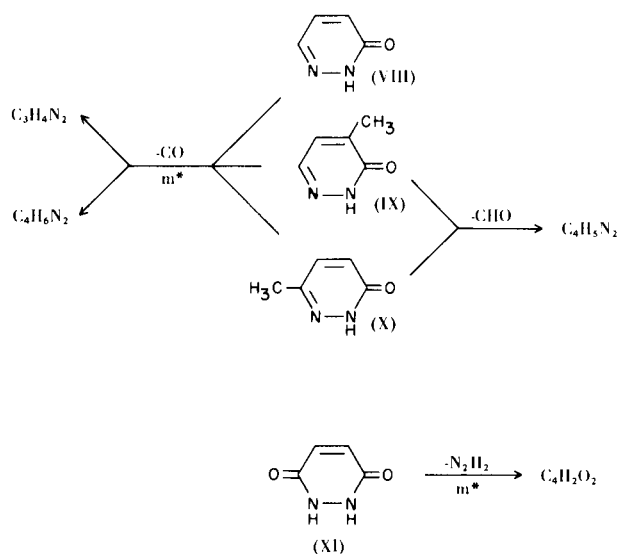


Figure 3

In the mass spectrum of 1,2-dihydro-3,6-pyridazindione (XI), the M-1 ion constitutes the base peak. The initial loss of N_2H_2 from the parent ion formed an ion of m/e 82 (44%) (m/e 112 $\xrightarrow{m^*}$ m/e 82) [$C_4H_2O_2$, Calcd. 82.005; Found, 82.004].

The mass spectra of pyridazine *N*-oxides showed M-16 (M-O), M-17 (M-OH), M-29 (M- N_2H), and M-30 (M-NO) ions, similar to the fragmentations observed in various *as*-triazine *N*-oxides (9). The most abundant fragment ion of pyridazine *N*-oxide (XII) itself appears at M-30, m/e 66 (e, 21%), [C_4H_4N , Calcd. 66.034; Found, 66.034], which showed an initial loss of NO from the parent ion. The M-16 ion was observed in an abundance of only 5% and while the M-17 ion is totally absent. On the other hand, in the mass spectra of 3-phenylpyridazine *N*-oxide (XV), the M-16 and M-17 ions were observed in an abundance of 17 and 12%, respectively (Fig. 2). In the mass spectrum of 6-aminopyridazine *N*-oxide (XXX), the M-16 ion was not observed and the M-30 ion constituted the base peak. The *ortho*-effect was also recognized in 6-methylpyridazine *N*-oxide (XIII), 3-hydroxypyridazine *N*-oxide (XX), but not in 4-hydroxy-6-methylpyridazine *N*-oxide (XXIV).

EXPERIMENTAL

The mass spectra were measured by a Japan Electron Optics JMS-01S high resolution mass spectrometer (Mattauch-Herzog type) with a direct inlet system. Heating temperature of the samples was around 50-250°. The ionizing energy was kept at 75 eV and the ionizing current at 200 μ A.

Experimental data are shown in Tables III and IV.

TABLE III
Mass Spectra of Pyridazines

Compound	(M-N ₂) ⁺	(M-N ₂ H) ⁺	(M-CO) ⁺	(M-CHO) ⁺	base peak	other peak
I	52(23)	51(33)			80(M)	53(5)50(18)39(6)
II	66(24)	65(65)			94(M)	80(2)52(11)51(19)39(50)
III	66(10)	65(43)			94(M)	80(6)52(6)51(14)39(62)
IV	82(7)	81(21)			39	110(73,M)109(29)80(31)67(5)66(5) 56(19)55(13)53(52)52(21)51(13)
V	128(11)	127(5)			102	156(65,M)103(11)77(7)76(14)75(10) 64(10)52(8)51(19)50(10)39(7)
VI	81(47)	80(65)			109(M)	94(6)93(6)65(8)64(13)63(10)55(18)54 (21)53(31)52(21)50(15)41(88)39(23)
VII	101(65)				129(M)	73(23)66(58)52(23)51(19)41(97) 40(28)39(30)
VIII			68(33)		96(M)	52(4)51(4)39(46)
IX			82(10)	81(36)	110(M)	55(12)54(10)53(24)52(9)39(10)
X			82(27)	81(21)	110(M)	55(10)54(34)53(10)39(10)
XI					111(M-1)	112(5,M)82(44)55(16)54(15)

TABLE IV
Mass Spectra of Pyridazine N-oxides

Compound	M ⁺	(M-O) ⁺	(M-HO) ⁺	(M-NO) ⁺	(M-CHO) ⁺	base peak	other peak
XII	96(46)	80(5)		66(21)	67(2)	39	52(10)51(14)40(20)
XIII	110(100)	94(9)	93(4)	80(45)	81(6)	110	66(6)65(16)54(9)53(63)52(16) 51(16)39(29)
XIV	110(73)	94(6)		80(9)	81(4)	53	66(3)65(6)54(9)52(12)51(22) 39(25)
XV	172(100)	156(17)	155(12)	142(5)	143(14)	172	128(7)127(7)103(12)102(45) 101(23)93(12)89(17)77(42) 76(19)75(12)65(12)52(12) 51(31)50(14)39(38)
XVI	126(100)	110(6)	109(6)	96(1)	97(2)	126	83(9)81(6)80(6)69(14)55(11) 54(9)53(9)52(8)41(8)40(8) 39(23)
XVII	126(100)	110(8)		96(4)		126	84(6)83(3)81(3)80(3)69(12) 68(9)56(6)54(10)53(5)52(4) 41(3)40(5)39(7)
XVIII	126(100)	110(8)		96(2)		126	69(9)68(7)56(5)54(6)53(5) 52(5)41(4)40(5)39(11)
XIX	140(100)	124(18)	123(14)	110(4)	111(4)	140	97(9)96(4)95(12)94(8)93(11) 83(15)78(7)69(15)78(7)67(19) 66(8)55(18)54(21)53(42)52 (21)51(21)42(29)41(66)40(16) 39(30)
XX	112(100)	96(12)		82(7)	83(7)	112	68(11)67(13)55(27)54(7)41 (27)40(13)39(41)

XXI	112(100)	96(14)		82(13)	83(2)	112	69(9)68(7)67(4)55(5)41(11) 40(17)39(5)
XXII	112(100)	96(14)	95(4)	82(4)		112	69(7)68(16)67(6)55(33)54(8) 53(10)41(14)40(19)39(10)
XXIII	112(52)	96(5)	95(8)	82(93)	83(6)	39	67(6)55(8)54(6)
XXIV	126(100)	110(15)		96(78)	97(10)	126	83(11)82(23)69(8)68(20)67(11) 55(11)54(19)53(11)52(7) 41(25)40(11)39(37)
XXV	126(100)	110(15)	109(9)	96(15)	97(2)	126	85(26)84(6)81(6)69(13)68(24) 67(11)66(11)57(24)56(9)55 (13)54(15)41(20)40(32)39(13)
XXVI	126(60)	110(7)		96(100)	97(9)	96	78(15)68(7)54(6)53(60)52(9) 51(11)41(15)40(5)39(11)
XXVII	126(100)	110(26)	109(24)	96(31)	97(7)	126	83(12)82(21)81(12)69(10) 68(16)67(10)55(16)54(12)53 (52)52(26)51(23)41(21)39(19)
XXVIII	126(100)	110(28)	109(2)	96(6)	97(6)	126	82(6)81(25)69(10)68(5)55(10) 54(14)53(33)52(10)51(25) 41(21)40(8)39(21)
XXIX	126(100)	110(20)		96(1)	97(5)	126	82(9)81(17)69(17)68(5)55(14) 54(17)53(72)52(17)51(17) 41(46)40(9)39(42)
XXX	111(33)			81(100)	82(13)	81	66(27)65(22)64(16)53(13) 52(80)51(17)50(13)40(24) 39(43)
XXXI	145(80)	129(23)	128(9)	115(95)	116(14)	73	104(9)103(9)101(38)100(28) 99(33)95(14)90(19)88(62) 78(19)77(23)76(9)75(48)74 (19)66(28)65(19)64(48)63 (14)56(19)55(19)53(96)52 (76)51(38)50(19)41(38)40 (14)39(28)

Acknowledgment.

We thank Dr. K. Takagi and Mrs. A. Hatano for the mass spectra measurements.

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