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A study of the fragmentation patterns of a variety of substituted 1,2,4-triazine 1- and 2-oxides has been undertaken. It is shown that the fragmentation patterns of the 1- and 2-oxides are extremely similar with the relative peak intensities varying with the type of substituents present.

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Some time ago we described the interpretation of the mass spectra of some 1,2,4-triazine (1) and some of their *N*-oxides (2). This latter analysis had become necessary since the structures of the products obtained from the oxidation of 3-methoxy and 5,6-diphenyl-3-amino-1,2,4-triazine had been incorrectly assigned (3,4). We have recently reported the syntheses of a number of substituted 1,2,4-triazine 1- and 2-oxides (5,6), and now wish to report some interesting mass spectral fragmentation patterns of these compounds.

The mass spectral fragmentation patterns of the 1,2,4-triazine 1-oxides show that the base peak is the parent molecular ion (*cf.* Table I). As had been shown in earlier work, and is reinforced here, the $M^+ - 16$ peak is present in all of those 1-oxides (4, 7, 8, 11-14) which do not bear an alkyl substituent in the 6-position (the latter show an $M^+ - 17$ peak) or which do not possess a more easily lost heavy atom (1, 2, 3, 5, 6, 9, 10).

The loss of 30 mass units results from the loss of an NO fragment and is a major fragmentation in all of the *N*-1 oxides which do not bear a nitrogen containing substituent in the 3-position (1-4, 7, 8). The subsequent loss of an additional 27 mass units arises from the loss of HCN, and is generally less than 20% of the base peak. In those

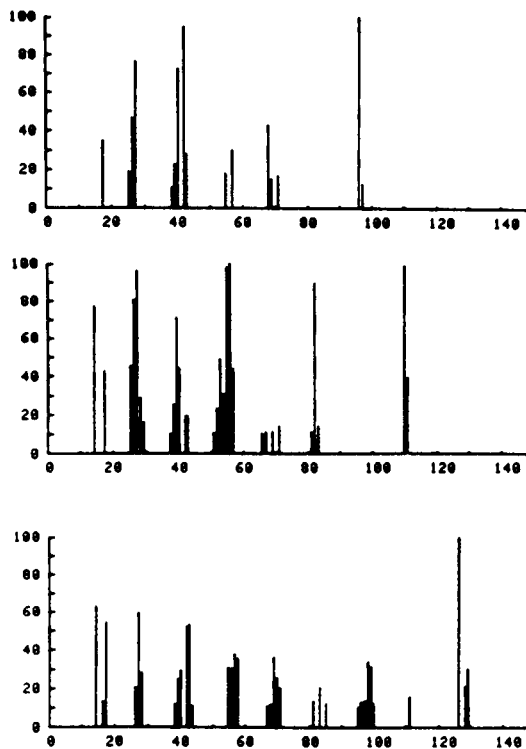


Figure 1. Mass spectra of (a) 3-amino-, (b) 3-monomethylamino-, and (c) 3-methoxy-1,2,4-triazine.

Table I

Mass Spectral Fragments of some 1,2,4-Triazine 1-Oxides



Compound No.	R ₃	R ₅	R ₆	M ⁺	M ⁺¹⁶	M ⁺³⁰	M ⁺⁴⁴	M ⁺⁵⁷	Base Peak m/e
				m/e (Relative Intensity)	m/e (Relative Intensity)	m/e (Relative Intensity)	m/e (Relative Intensity)	m/e (Relative Intensity)	
1	Cl	H	H	131 (100)	115 (5)	101 (20)	87 (5)	74 (20)	131
2	Br	H	H	175 (100)	159 (5)	145 (8)	131 (10)	118 (5)	175
3	Br	H	Br	253 (100)	---	228 (8)	209 (5)	196 (5)	253
4	OCH ₃	H	H	127 (100)	111 (7)	97 (73)	83 (15)	58 (10)	127
5	▷N-	H	H	138 (100)	---	---	96 (15)	---	138
6	N(CH ₃) ₂	H	H	140 (100)	124 (5)	110 (5)	96 (5)	83 (16)	140
7	OCH ₃	CH ₃	H	141 (100)	125 (16)	111 (85)	97 (50)	84 (20)	141
8	OCH ₃	H	Br	205 (100)	189 (9)	175 (20)	161 (6)	---	205
9	NH ₂	H	Br	190 (100)	174 (5)	160 (13)	146 (5)	133 (15)	190
10	NH ₂	H	H	112 (100)	96 (5)	82 (5)	68 (5)	55 (7)	112
11	CH ₃ NH	H	H	126 (100)	110 (10)	---	---	---	126
12	CH ₃ NH	H	Br	204 (100)	188 (5)	---	---	---	204
13	(CH ₃) ₂	H	Br	218 (100)	202 (5)	---	---	---	218
14	(CH ₃) ₂ N	CH ₃	H	154 (100)	138 (12)	---	---	---	154

Table II
Mass Spectral Fragments of some 1,2,4-Triazine 2-Oxides



Compound No.	R ₃	R ₅	R ₆	M ⁺ m/e (Relative Intensity)	M ⁺ -16 m/e (Relative Intensity)	M ⁺ -17 m/e (Relative Intensity)	M ⁺ -30 m/e (Relative Intensity)	M ⁺ -44 m/e (Relative Intensity)	M ⁺ -57 m/e (Relative Intensity)	Base Peak m/e
15	H	H	H	97 (100)	81 (17)	---	67 (72)	---	---	97
16	NH ₂	H	H	112 (100)	96 (10)	95 (55)	---	---	---	112
17	Br	H	H	175 (36)	149 (10)	---	145 (100)	131 (36)	118 (36)	145
18	Cl	H	H	131 (48)	115 (10)	---	101 (100)	83 (10)	74 (54)	101
19	NH ₃	CH ₃	H	126 (100)	110 (10)	109 (60)	---	81 (5)	---	126
20	N(CH ₃) ₂	H	H	140 (32)	124 (28)	123 (100)	170 (10)	96 (10)	83 (10)	123
21	NC ₄ H ₈ O	H	H	182 (19)	166 (12)	165 (100)	---	138 (10)	125 (6)	165
22	NC ₅ H ₁₀	H	H	180 (100)	164 (20)	163 (88)	---	138 (10)	123 (6)	180
23	OCH ₃	H	H	127 (100)	111 (12)	110 (39)	96 (100)	88 (30)	70 (50)	127
24	NHNH ₂	H	H	127 (100)	111 (4)	110 (12)	---	---	---	127
25	NHCH ₃	H	H	126 (89)	110 (20)	109 (100)	---	---	---	109
26	Cl	CH ₃	H	145 (77)	129 (6)	---	96 (28)	82 (55)	69 (39)	88
27	Cl	Ph	H	207 (100)	191 (8)	---	115 (34)	---	88 (100)	207
28	N(CH ₂) ₂	H	H	138 (100)	122 (8)	---	177 (70)	---	150 (80)	138
29	N(CH ₂) ₂	CH ₃	H	152 (100)	136 (20)	135 (8)	108 (28)	94 (9)	81 (96)	152
30	NHCH ₂ CH ₂ Cl	H	H	174 (87)	158 (30)	157 (100)	144 (25)	608 (5)	95 (45)	157
31	NHCH ₂ CH ₂ Cl	Ph	H	250 (68)	234 (15)	233 (100)	220 (16)	---	---	233

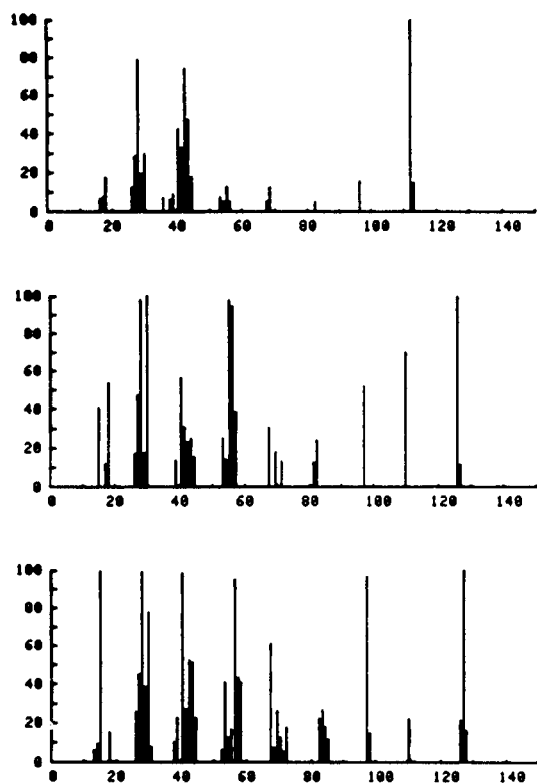


Figure 2. Mass spectra of (a) 3-amino-, (b) 3-monomethyl-amino-, and (c) 3-methoxy-1,2,4-triazine 1-oxides.

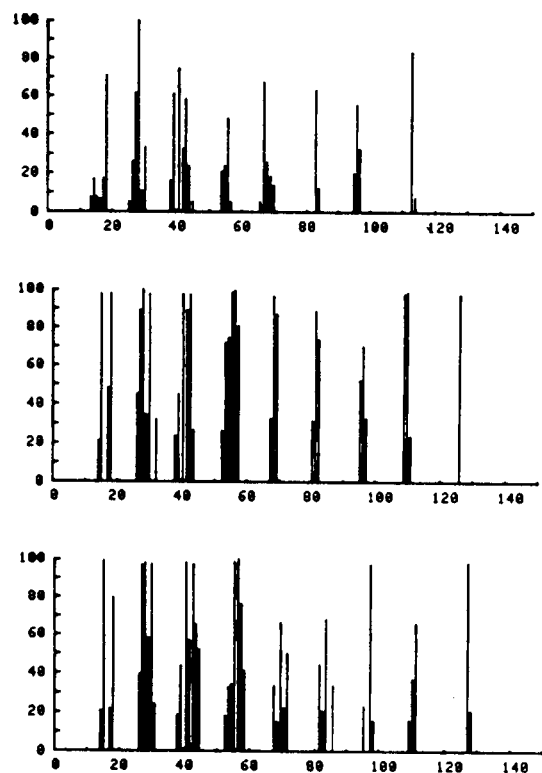


Figure 3. Mass spectra of (a) 3-amino-, (b) 3-monomethyl-amino-, and (c) 3-methoxy-1,2,4-triazine 2-oxides.

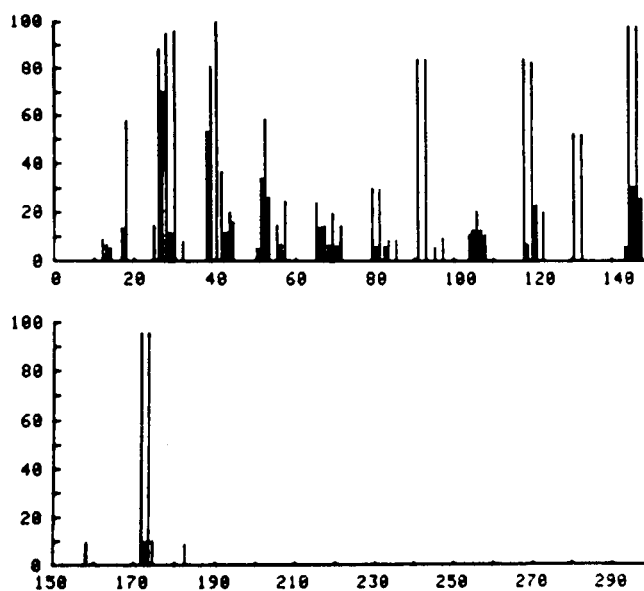
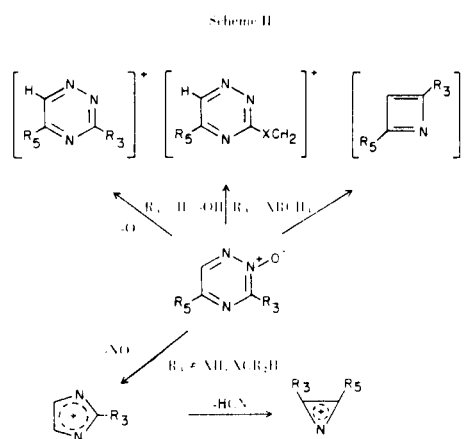
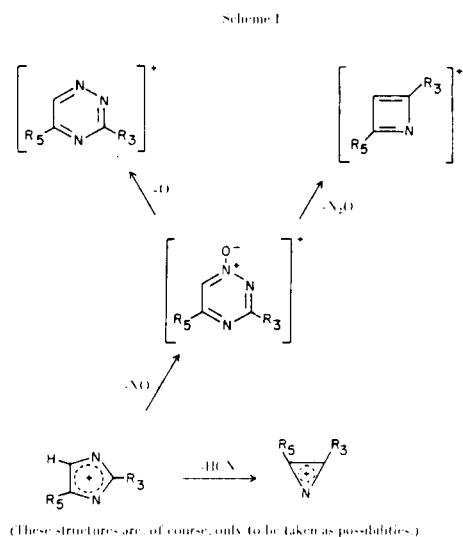


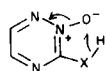
Figure 4. Mass spectrum of 3-bromo-1,2,4-triazine-2-oxide.

compounds which have a NRCCH_3 group at position 3 (11, 12, 13), the loss of 29 units (NCH_3) becomes a major fragmentation path.

Finally, the loss of 44 mass units occurs in those N-1 oxides which do not bear a nitrogen containing substituent in position 3. This peak probably arises from the loss of an N_2O fragment from the parent molecular ion. Thus, the 1,2,4-triazine 1-oxides not substituted at the 6-position with an alkyl group fragment in some unique ways (Scheme I). Examples of the actual spectra are shown in Figure 2.

The mass spectral fragmentation patterns of the 1,2,4-triazine 2-oxides (cf. Table II, Scheme II) are, as expected, in many ways similar to those of the 1-oxides. Examples of the actual spectra are given in Figure 3. The one glaring exception is again seen in those compounds which bear a nitrogen containing substituent at the 3-position. The parent molecular ion is again the base peak, except in those cases where easily lost heavy atoms (see Figure 4) allow other facile fragmentations (17, 18, 19).

The M^+-16 and M^+-17 losses depend upon the substituents in the 3-position which do not contain a hydrogen (15, 17, 18, 26-28), the M^+-16 peak, though small, is present. However, if the 3-substituent contains a hydrogen (16, 19-25, 29-31), the M^+-17 peak, which results from a McLafferty type rearrangement is large (55-100% relative intensity).



Another interesting observation is the dependence of this rearrangement on the ring size of the 3-substituent of compounds 21, 22, 29, 30. The 2-oxides 21 and 22 both

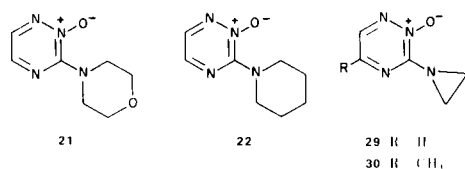
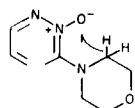


exhibit an M^+-17 peak of relative intensity greater than 85%. This fragment arises from the loss of a hydrogen on the carbon α to the nitrogen, again *via* a McLafferty type rearrangement. The 3-aziridino-1,2,4-triazine 2-oxide,



however, does not show this loss, and in fact shows the presence of an M^+-16 fragment of relative intensity approximately equal to 20%.

Fragmentation resulting in the loss of 30 mass units [N_2O], occurs in most cases with the relative intensities of these fragments varying between 20 and 100%. Further loss of an HCN fragment produces a peak at M^+-57 mass units, as in the case for the 1-oxides.

The mass spectral fragmentation patterns of the 1,2,4-triazine 1- and 2-oxides give valuable information for the elucidation of their structures. Substituents on the carbon α to the N-oxide function generally control the M^+-16 , M^+-17 fragmentations. The remaining fragmentations of both the 1- and 2-oxides are quite similar.

EXPERIMENTAL

Mass spectra were measured with a Hitachi-Perkin-Elmer RMU-6M mass spectrometer. Maximum peak heights were obtained at an ionizing voltage of about 70 eV on all spectra reported in this paper. All samples were introduced through the solid sample direct introduction system at approximately 100° . The mass range utilized was 1000 with a slit width of 1 mm. Mass spectra shown in Figures 1-4 were obtained with a Columbia Scientific Industries CSI260 in conjunction with a Bell 620 Gaussmeter and a Tektronix 4021 computer equipped with a Model 4631 hard copier.

For the CSI260 the following settings were used: Normalizer (10%), minimum peak widths (100 msec), maximum peak widths (1k msec), minimum peak height (500), and peak sensitivity (2). The computer program is available to any reader by request.

All compounds were checked for purity by tlc and nmr (using a Varian HA-100).

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