

## Mass Spectra of 1,2,3-Triazoles

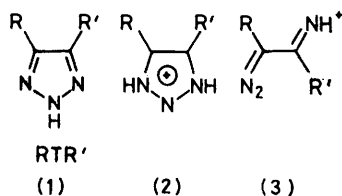
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The mass spectra of substituted 1,2,3-triazoles [RTR', (1)] (R' = H, CO<sub>2</sub>X, COR'', pyrazolyl, or isoxazolyl) are discussed. For a wide variety of structural types, P<sup>+</sup> is always strong and [P + 1]<sup>+</sup> is often of significant intensity. Subsequent breakdown patterns are strongly dependent on the substituents R and R'. The base peak, for example, may be [R''CO]<sup>+</sup> = [R']<sup>+</sup> in some oxotriazoles or [XO]<sup>+</sup> in some esters (R' = CO<sub>2</sub>X). Cleavage of the triazole ring may begin with one or more accessible cyclic (1*H*, 2*H*, or 3*H*) or acyclic (α-diazo-β-imino) parent ions [(1) or (3)] and lead initially to [P - N<sub>2</sub>]<sup>+</sup>, [P - HCN]<sup>+</sup>, [P - RCN]<sup>+</sup>, [P - RCN<sub>2</sub>]<sup>+</sup>, [RCN]<sup>+</sup>, [RCN<sub>2</sub>]<sup>+</sup>, [RC]<sup>+</sup>, and related ions (*m/e* ± 1). These might be regarded as the 'standard' unperturbed possibilities for (1). Thus, examples of the most prominent ions produced by cleavage of the triazole ring (RTR') are: [P - N<sub>2</sub>]<sup>+</sup> (R = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, R' = CO<sub>2</sub>Et), [P - HCN]<sup>+</sup> (R = Ph, R' = H), [RCN<sub>2</sub>]<sup>+</sup> (R = *p*-ClC<sub>6</sub>H<sub>4</sub> or *p*-MeOC<sub>6</sub>H<sub>4</sub>, R' = CO<sub>2</sub>Et), [RCNH]<sup>+</sup> (R, R' = COTR), and [RC]<sup>+</sup> (R = Ph, R = CHO). The mutual effects of ring and substituent are particularly striking in ditiazolyl ketones and in triazolylpyrazoles (5), where skeletal rearrangements of both rings are timed so that the maximum possible number of N<sub>2</sub> are eliminated.

THE elucidation of pyrolytic and photolytic pathways in the decomposition of heterocyclic molecules continues to attract attention.<sup>1</sup> Fragmentations induced by electron impact involve different species (ions) and higher energies so that these are usually more numerous (less selective) processes. Nevertheless, useful parallels can sometimes be drawn among all of these processes. In this paper we examine the mass spectra of the title compounds and essentially provide gross breakdown patterns with which the cleavages produced by the milder techniques may be compared.

### RESULTS AND DISCUSSION

Apart from the parent triazole,<sup>2</sup> 1,2-diphenyltriazole,<sup>3</sup> and benzotriazole,<sup>4</sup> the mass spectra of few 1,2,3-triazoles (T) appear to have been studied in detail. Because N-H tautomerism appears to be ready, even in the gas phase,<sup>2</sup> three structures (1*H*, 2*H*, or 3*H*) are implied by any one of them (1) and may be used as the 'parent'.

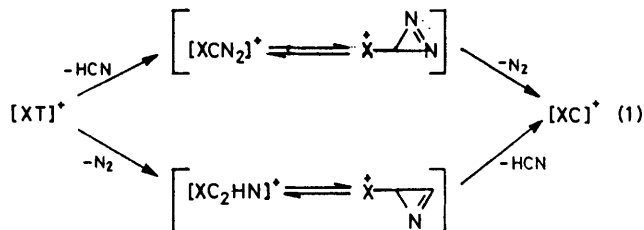


Two early eliminations, of N<sub>2</sub> and/or RCN, dominate the mass spectra when R = R' = H or Ph.<sup>2,3</sup> Here we find these but also establish other fragmentation patterns based on many other members of this family.

The mass-spectral data for our series of 1,2,3-triazoles are given in Table 1. The parent peak P<sup>+</sup> is usually strong and almost half the compounds in the group show a [P + 1]<sup>+</sup> peak (after the isotopic composition of the parent peak has been taken into account). Since such triazoles are weak acids (p*K* 5–9)<sup>5</sup> and the protonated species (2) is symmetrical and aromatic, its presence is perhaps unremarkable. Nevertheless, this is a possible distinctive feature in the mass spectra of the 1,2,3-triazoles.

Although its presence would be difficult to prove, the

acyclic representation (3) of the parent ion from (1) is a useful structure to keep in mind. It would seem that those fragments which formally arise by scission of the middle (single) bond in (3) probably do so in fact.

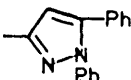


4-Substituted Triazoles(RTH).—Maquestiau *et al.*, have reported that unsubstituted triazole loses HCN three to four times more readily than N<sub>2</sub> under electron impact.<sup>2</sup> Our six monosubstituted triazoles (1; R' = H, R = aryl or formyl) are only roughly similar. Diversity in the patterns arises because formation of [P - N<sub>2</sub>]<sup>+</sup>, [P - HCN]<sup>+</sup>, and [P - HCN - N<sub>2</sub>]<sup>+</sup> are sometimes preceded by, or are less prominent than, fragments attributable to the substituents. This is apparent in the fragmentations of 4-formyltriazole or in the 4-aryltriazoles, especially those containing *p*-Cl, *p*-OMe or *p*-NO<sub>2</sub>. But whenever they do occur, the eliminations of N<sub>2</sub> and HCN usually succeed one another so that the pattern has the standard segment shown in equation (1) [the cyclic diazirine and azirine intermediates in equation (1) have been postulated by previous workers<sup>2,3</sup>]. In the 4-aryltriazoles the early elimination of [ArCN]<sup>+</sup> is usually of minor importance. But, depending on the substituent, there are indications that deep-seated skeletal rearrangements become significant. The peak due to [C<sub>7</sub>H<sub>5</sub>]<sup>+</sup> at *m/e* 89, for example, is often intense and derives *formally* from the loss of CN<sub>3</sub>XH, probably with rearrangement of the original 4-XC<sub>6</sub>H<sub>4</sub>TH. From metastable transitions it would seem that *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C<sub>2</sub>N<sub>3</sub>H and *p*-MeOC<sub>6</sub>H<sub>4</sub>C<sub>2</sub>N<sub>3</sub>H give the same ion at *m/e* 160 ([P - NO]<sup>+</sup> or [P - Me]<sup>+</sup>); but the ion at *m/e* 132 can form by the further loss of 28 or by the loss of 43 from the parent (*m*<sup>\*</sup> 109) in the methoxy-compound. In

TABLE 1  
Mass spectra of 1,2,3-triazoles (1) RC<sub>2</sub>N<sub>3</sub>HR' (RTR')

R	R'	Formula	Molecular weight	Probe temperature (°C)	<i>m/e</i> (relative intensity)
CHO	H	C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> O	97	20	98(6), 97(90), 96(100), 69(27), 68(10), 42(25), 41(12), 49(25), (29)(12)
Ph	H	C <sub>8</sub> H <sub>7</sub> N <sub>3</sub>	145	25	146(13), 145(100), 118(21), 116(7), 104(5), 103(5), 96 * ± 2(145→118), 91(16), 90(12), 89(18), 77(12), 70 *(118→91), 64(6), 63(13), 51(8), 42(6), 40(5), 39(7)
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	H	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub>	159	20	160(13), 159(100), 158(16), 132(6), 131(10), 130(17), 117(6), 116(6), 104(9), 103(15), 102(5), 91(8), 90(4), 89(5), 78(8), 77(14), 65(4), 51(4)
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	H	C <sub>8</sub> H <sub>6</sub> N <sub>3</sub> Cl	179	40	180(13), 179(100), 152(20), 151(5), 150(5), 137(6), 125(21), 124(14), 123(10), 117(5), 116(18), 111(8), 102(7), 90(12), 89(41), 75(9), 63(12), 42(9), 40(6), 39(6)
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	H	C <sub>8</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>	190	60	191(13), 190(100), 160(29), 144(11), 135 * ± 1(190→160), 132(17), 109 * ± 1.5(160→132), 90(12), 89(51), 88(7), 77(6), 76(5), 63(19), 62(8), 51(7), 40(8), 39(7)
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	H	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> O	175	20	176(15), 175(100), 160(21), 146.2 *(175→160), 133(13), 119(4), 132(32), 109 *(160→132), 105(6), 104(4), 99.4 *(177→132), 90(5), 77(10), 89(4), 76(5), 51(6)
MeO <sub>2</sub> C	CO <sub>2</sub> Me	C <sub>6</sub> H <sub>7</sub> N <sub>3</sub> O <sub>4</sub>	185	25	186(3), 185(18), 156(9), 155(100), 154(100), 150* ± 1(185→155), 127(37), 126(23), 125(8), 124(83), 104 *(155→127), 100* ± 1(155→124), 154→124, 99(5), 98(7), 97(14), 95(5), 82(5), 69(13), 68(16), 67(15), 59(32), 58(7), 44(5), 42(10), 40(8,5), 29(6), 15(13)
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CO <sub>2</sub> Et	C <sub>10</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub>	211	130	212(17), 211(61), 210(9), 183(14), 182(60), 169(17), 168(92), 167(11), 166(87), 165(99), 164(32), 156(22), 155(100), 154(31), 151(9), 150(69), 148(13), 147(5), 141(15), 140(26), 139(28), 138(100), 137(57), 136(94), 135(8), 134(6), 132(7), 128(9), 127(42), 126(51), 124(35), 123(96), 122(96), 121(11), 120(22), 113(9), 112(39), 111(37), 110(93), 109(96), 108(57), 106(5), 105(11), 101(6), 100(5), 99(17), 98(78), 97(8), 96(19), 95(14), 94(25), 93(15), 92(7), 91(10), 84(11), 83(93), 82(26), 81(26), 80(35), 79(11), 78(7), 77(18), 73(10), 71(11), 70(9), 69(21), 68(39), 67(46), 66(12), 65(11), 58(5), 57(21), 56(22), 55(82), 54(92), 53(56), 52(47), 51(11), 50(5), 45(15), 44(8,12), 43(62), 42(36), 41(94), 40(14), 39(53), 31(7), 30(15), 29(10,14), 27(93), 26(12), 15(7)
Ph	CO <sub>2</sub> Et	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub>	217	20	218(16), 217(100), 190(7), 189(39), 173(28), 172(78), 160(4), 161(13), 145(10), 144(8), 143(8), 133(5), 118(12), 117(27), 116(13), 115(13), 105(25), 104(17), 103(6), 88(4), 91(6), 90(13), 89(35), 77(14), 63(8), 29(12)
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	C <sub>11</sub> H <sub>10</sub> N <sub>3</sub> OCl	251	90	252(29), 251(100), 225(15), 224(7), 223(44), 221.5 *(251→236), 207(21), 206(97), 198.5 *(251→223), 196(5), 195(25), 180(6), 179(7), 178(7), 177(10), 172(9), 170.5*(223→195), 164(6), 154(7), 153(16), 152(17), 151(43), 150(16), 149(11), 140(6), 139(48), 138(19), 137(9), 128*(251→179), 126(5), 125(6), 124(12), 123(53), 115(11), 114(21), 113(5), 111(12), 102(8), 100.5 *(151→123), 90(7), 89(14), 88(8), 75(7), 73(9), 69(11), 63(6), 60(14), 57(9), 45(7), 43(7), 29(53), 27(12)
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	C <sub>11</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub>	262	88	263(17), 262(100), 235(9), 234(64), 218(18), 217(62), 209*(262→234), 206(20), 204(16), 190(22), 189(12), 188(12), 178(9), 172(8), 171(22), 170(12), 163(8), 162(20), 150(27), 143(6), 134(5), 132(10), 131(5), 116(10), 115(23), 114(16), 105(6), 104(13), 103(9), 90(7), 89(20), 88(16), 77(12), 76(10), 63(7), 29(23)
<i>m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	C <sub>11</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub>	262	60	263(16), 262(94), 245(15), 234(59), 218(31), 217(100), 209 *(262→234), 206(29), 201(31), 193(18), 190(16), 188(19), 187(15), 178(17), 176(27), 171(20), 170(25), 163(11), 162(26), 159(11), 150(68), 146(14), 143(13), 134(14), 116(24), 115(43), 114(35), 105(11), 104(21), 103(26), 102(21), 91(15), 90(13), 89(36), 88(36), 77(27), 76(21), 65(12), 63(14), 39(10), 29(59)
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	247	65	248(12), 247(76), 222(21) ?, 219(6), 206(25) ?, 202(14), 195 * ?, 194 *(247→219), 219→206, 191(8), 176(6), 161(28), 150(6), 147(10), 146(10), 145(11), 136(12), 135(100), 134(16), 133(13), 132(8), 119(17), 107(6), 92(11), 85.5 *(135→107), 77(16), 76(5), 29(9)
Me	COTMe	C <sub>7</sub> H <sub>8</sub> N <sub>6</sub> O	192	100	193(9), 192(67), 177(9), 164(23), 163(6), 136(10), 135(12), 122(8), 121(6), 114(6), 111(8), 110(100), 109(8), 108(17), 107(8), 93(10), 84(5), 83(15), 82(13), 81(14), 80(12), 69(20), 67(25), 66(16), 60.8 *(192→108), 56(21), 55(16), 54(56), 53(12), 52(15), 43(19), 42(62), 41(7), 39(8), 30(5), 29(6), 27(23)

TABLE 1 (Continued)

R	R'	Formula	Molecular weight	Probe temperature (°C)	<i>m/e</i> (relative intensity)
Me	COCCMe	C <sub>7</sub> H <sub>7</sub> N <sub>3</sub> O	149	40	150(7), 149(61), 148(8), 121(6), 120(24), 119*(121→120), 110(8), 109(16), 97* ± 1(149,148→121, 120), 93(9), 92(9), 80(10), 79(6), 68(9), 67(100), 66(22), 65(10), 56(7), 54(16), 53(9), 52(11), 51(6), 46.8*(93→67), 42(12), 40(6), 39(31), 27(9)
Ph	COTPh	C <sub>17</sub> H <sub>12</sub> N <sub>6</sub> O	316	170	318(8), 317(51), 316(99), 315(24), 314*(316→315), 299(5), 289(14), 288(65), 287(61), 286*(288→287), 262* ± 2(317, 316, 315→287, 288, 289) 261(8), 260(25), 259(19), 239(12), 234.5* ± 2(289, 288, 287→261, 260, 259), 233(10), 232(36), 231(36), 229(7), 217(8), 214(7), 213*(317→260, 316→259), 207*(216→232), 205(14), 204(32), 203(8), 190(8), 181.2*(232→205), 180*(233→205), 173(29), 172(100), 155(14), 144(10), 143(11), 130(11), 129(37), 128(18), 119(10), 118(22), 117(86), 116(44), 115(17), 105(51), 104(94), 103(15), 102(18), 93.5*(316→172), 91(15), 90(29), 89(95), 78(10), 77(51), 69(21), 68.5*(117→89, 116→89), 57*(104→77), 46.5* ± 1(232→104), 44(10)
Ph	COCCPh	C <sub>17</sub> H <sub>11</sub> N <sub>3</sub> O	273	100	274(6), 273(35), 272(100), 271*(273→272), 245(18), 244(16), 243(8), 242*(244→243), 220*(273→245), 219*(272→244), 217(12), 216(15), 192.2* ± 1(245, 244→217, 244→216), 190(9), 189(20), 165.7* ± 0.5(216→189), 142(6), 130(11), 129(90), 128(6), 121(6), 119(16), 117(16), 115(8), 114(7), 105(11), 104(7), 102(6), 101(9), 89(12), 85(16), 83(24), 82(6), 77(10), 75(9), 47(11)
Ph	COCHCHPh	C <sub>17</sub> H <sub>13</sub> N <sub>3</sub> O	275	65	276(20), 275(100), 274(86), 273*(275→274), 247(11), 246(34), 219(9), 218(13), 217(18), 198(6), 191(9), 172(11), 170(7), 158(8), 145(7), 132(8), 131(61), 117(12), 116(11), 115(15), 105(9), 104(27), 103(71), 102(15), 91(27), 90(8), 89(18), 78(29), 77(53), 76(5), 63(5), 52(6), 51(11), 44(6), 40(10), 39(5)
Ph	CHO	C <sub>9</sub> H <sub>7</sub> N <sub>3</sub> O	173	40	174(14), 173(100), 172(37), 171*(173→172), 145(19), 144(18), 118(18), 117(29), 116(11), 104(8), 92(5), 91(17), 90(26), 89(39), 103(5), 78(8), 77(14), 64(6), 63(10), 51(6), 39(5)
Ph	COCHC(Ph)NEt <sub>2</sub>	C <sub>21</sub> H <sub>22</sub> N <sub>4</sub> O	346	85	347(12), 346(46), 345(20), 330(30), 329(100), 318(6), 317(14), 313*(346→329), 301(7), 290(7), 289(14), 275(6), 247(6), 246(8), 204(5), 203(12), 202(64), 201(5), 200(6), 186(10), 184(7), 176(6), 175(14), 174(68), 173(10), 172(40), 170(6), 167(6), 158(8), 149(8), 146(22), 144(8), 143(6), 132(32), 131(8), 130(11), 129(6), 122(19), 117(13), 116(9), 115(9), 106(7), 105(60), 104(60), 103(40), 100(6), 91(14), 89(14), 78(16), 77(36), 74(16), 73(17), 72(44), 70(6), 59(28), 58(56), 57(6), 56(18), 51(14), 45(27), 44(28), 43(18), 42(11), 41(8), 31(46), 30(32), 29(29), 27(15)
Ph	COCHC(Ph)NHPh	C <sub>23</sub> H <sub>18</sub> N <sub>4</sub> O	366	100	367(15), 366(54), 350(6), 349(20), 337(11), 333* ± 1(366→349), 246(7), 223(15), 222(80), 206(7), 195(20), 194(100), 193(20), 180(30), 181(6), 172(26), 167(6), 144(9), 117(6), 116(9), 104(12), 89(6), 77(20)
Me	C <sub>3</sub> N <sub>2</sub> H <sub>2</sub> Me	C <sub>7</sub> H <sub>9</sub> N <sub>5</sub>	163	25	164(11), 163(100), 162(64), 134(8), 120(3), 108(17), 107(16), 93(5), 83(3), 77(4), 67(5), 56(6), 66(3), 52(4), 42(8), 39(4)
Ph	C <sub>3</sub> N <sub>2</sub> H <sub>2</sub> Ph	C <sub>17</sub> H <sub>13</sub> N <sub>5</sub>	287	40	288(40), 287(100), 286(40), 285(287→286), 259(11), 258(7), 234*(287→259), 231(14), 230(12), 226*? 203(6), 202(11), 187* ± 2(287, 286→231), 155(11), 143.5(6), 129(9), 128(11), 104(13), 103(7), 102(23), 91(5), 89(8), 77(17)
Me	C <sub>3</sub> NOHMe	C <sub>7</sub> H <sub>7</sub> N <sub>4</sub> O	164	62	165(16), 164(100), 163(7), 162*(164→163), 136(7), 135(9), 123(9), 110(45), 109(14), 107(8), 95(10), 92.5* 164→123), 82(42), 80(6), 69(8), 68(6), 67(11), 66(12), 56(13), 55(17), 54(28), 53(10), 52(12), 43(8), 42(26), 41(11), 40(5), 39(9), 27(16)
Ph	C <sub>3</sub> NOHPh	C <sub>17</sub> H <sub>12</sub> N <sub>4</sub> O	288	90	290(6), 289(35), 288(100), 287(78), 286*(288→287), 260(10), 259(7), 231(12), 235*(288→260), 204(8), 197(7), 185(25), 172(31), 156(8), 144(28), 129(12), 128(10), 117(23, 4), 116(17), 105(13), 104(20), 103(9), 102(17), 90(7), 89(25), 78(6), 77(46), 51(6)
Ph		C <sub>23</sub> H <sub>17</sub> N <sub>5</sub>	363	90	365(12), 364(82), 363(100), 362(39), 361*(362→361), 336(5), 335(18), 334(14), 333(6), 309* ± 1(363→335), 307(8), 306(5), 286(7), 273(12), 272(34), 271*(273→272), 259(6), 258(6), 245(8), 244(8), 232(12), 231(24), 230(7), 229(8), 217(7), 216(9), 205(6), 204(18), 203(8), 202(11), 190(7), 189(9), 181.5(11), 181(12), 180(74), 165(6), 160*(363→307), 155(6), 130(7), 129(38), 128(9), 116(8), 115(5), 105(11), 104(18), 103(7), 102(11), 91(18), 90(5), 89.2*(362→180), 89(11), 78(5), 77(41), 43(14)

both these compounds the simultaneous loss of C and O on these and other breakdown paths implies considerable atom scrambling.

**4,5-Disubstituted Triazoles.**—To impose some order on a large number of compounds, we have arbitrarily divided them into three groups. Again, the early loss of  $N_2$  must compete with paths which begin with the substituents. Loss of HCN, which now depends on the ease of skeletal rearrangement, is now *less* probable (not improbable, however, since  $[\text{benzotriazole}]^+ \rightarrow [P - N_2]^+ \rightarrow [P - N_2 - \text{HCN}]^+$ ).<sup>4</sup>

A group of seven esters is placed in the first subgroup,  $\text{RTCOC}_2\text{X}$  (R = aryl, alkyl or  $\text{CO}_2\text{Me}$ ; X = Me or Et). Typically, the early steps of most members of this subgroup include:  $[P + 1]^+$ ,  $P^+$ ,  $[\text{R}]^+$ ,  $[\text{RC}]^+$ ,  $[\text{RCN}]^+$ ,  $[P - \text{XO}_2\text{CCNH}]^+$ ,  $[\text{R}']^+$ ,  $[P - \text{XO}]^+$ ,  $[P - N_2]^+$ , and  $[P - \text{XO}_2\text{C} - N_2]^+$ . Thus, there is evidence for initial cleavage outside of the ring and splitting of the ring in two *via* (3), as well as loss of  $N_2$ .

The second subgroup,  $\text{RTCOR}''$ , consists of seven ketones and one aldehyde. In all cases the favoured cleavage steps involve bonds to the carbonyl group and the formation of one or more of  $[\text{RT}]^+$ ,  $[\text{R}'\text{CO}]^+$ ,  $[\text{COR}']^+$ , and  $[\text{R}']^+$ . This aspect of the pattern, which is not obvious in Table 1, is the substance of Table 2: at

TABLE 2

Mass-spectral analogy between triazolylcarbonyl compounds,  $\text{RTCOR}''$ , and triazolylisoxazoles. The figures are relative intensities<sup>a</sup>

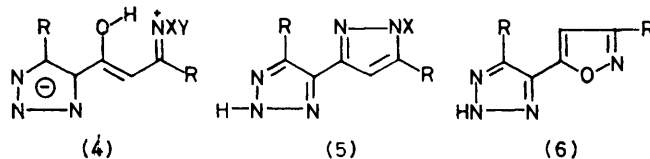
R	R''	$[\text{RT}]^+$	$[\text{R}'\text{CO}]^+$	$[\text{R}']^+$	$[\text{R}'\text{CO}]^+$	$[P - 28]^+$	$[\text{R}]^+$
Me	Me	13	100	13	100	23	3
Me	$\text{C}_2\text{Me}$	4	8	31	100	6	1
Ph	TPh	10	100	10	100	65	51
Ph	$\text{C}_2\text{Ph}$	<1	<1	9	90	16	10
Ph	CHCHPh	3	11	71	61	11	53
Ph	H	18	37	<i>b</i>	<1	19	14
Ph	CHCPh(NEt) <sub>2</sub>	8	40	68	64	6	36
Ph	CHCPhNHPPh	9	26	100	80	5	20
Me	$\text{C}_2\text{NHMe}^c$	42	45	28	42	7	3
Ph	$\text{C}_2\text{NHP}^c$	28	31	17	31	10	46

<sup>a</sup> Statistical factors of 2 were not included. <sup>b</sup> Not measured.

<sup>c</sup> These are isoxazoles (6) formulated here for convenience as the isomeric ketones.

least one of the carbonyl bonds cleaves in preference to other processes such as formation of  $[P - 28]^+$ ,  $[\text{R}]^+$ , etc. The driving force here, of course, is the relative stability of acyl radicals or cations. Secondly, elimination of  $[\text{R}]^+$  and  $[\text{RCN}]^+$  and splitting of  $\text{R}''$  are definitely competitive with loss of  $N_2$  or CO. It is interesting, however, that the sequence which might be regarded as typical of 1,2,3-triazoles, *i.e.*  $P^+ \rightarrow [P - N_2, \text{HCN}]^+$ , should be altered for most members of this group to  $P^+ \rightarrow [P - N_2, \text{CO}, \text{HCN}]^+$ . Formally, CO and HCN are lost by extrusion from the backbone of the molecule which, of course, implies considerable rearrangement of the original framework.<sup>6</sup> The last two members of this group, the triazolylketoenamines, are peculiar in that the formation of  $[P - \text{OH}]^+$  becomes important. The presence of an ylide tautomer (4), probably with intramolecular hydrogen bonding, could account for  $[P - \text{OH}]^+$  [as well as the absence of  $\nu(\text{CO})$

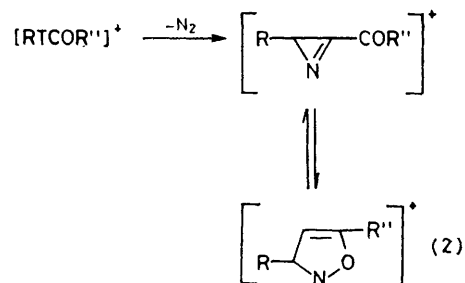
and the unexpected decrease in acidity of these triazoles].<sup>5</sup> At this stage the fact that the elimination of  $N_2$  comes relatively late can no longer be regarded as special or unusual for a triazole.



The third subgroup consists of the bisheterocycles, triazolylpyrazoles (5) and triazolylisoxazoles (6). Simons *et al.* report that the 3,4-diphenylpyrazole has  $[P - \text{HCN}]^+$  and  $[P - \text{C}_2\text{H}_3\text{N}_2]^+$  as major fragments;<sup>7</sup> other pyrazoles behave in the same way.<sup>8</sup> Diphenyl and other isoxazoles rearrange and extrude CO.<sup>7,9</sup> Such patterns signal potential complexity for (5) and (6).

Consider the pyrazoles (5) first. Other than  $[P + 1]^+$ ,  $[P]^+$ , and  $[P - 1]^+$ , which are relatively intense, the three compounds display different preferences in their major peaks:  $[\text{C}_8\text{H}_6]^+$ ,  $[\text{C}_6\text{H}_5]^+$ , and  $[P - N_4]^+$  (R = Ph, X = H);  $[P - \text{C}_2\text{H}_3\text{N}_2]^+$  or  $[P - \text{CN}_3\text{H}]^+$ ,  $[P - N_4]^+$  or  $[P - \text{CN}_3\text{H}_2]^+$ ,  $[P - N_2\text{H}]^+$ , and  $[\text{C}_2\text{H}_4\text{N}]^+$  (R = Me, X = H); and  $[\text{Ph}_2\text{CN}]^+$ ,  $[\text{PhCN}_2]^+$ ,  $[P - 91]^+$ , and  $[P - \text{C}_7\text{N}_3]^+$  (R = X = Ph). Clearly  $[P - N_2]^+$  is of secondary importance. In fact, the triazoles (5; X = H) show metastables for  $[P - 56]^+$  which are most plausibly interpreted as the simultaneous elimination of two  $N_2$ . These must come from an ion with paired nitrogens! For (5; R = X = Ph), the dominant fragment at  $m/e$  180 may arise in a sequence such as (364, 362)  $\xrightarrow{-ca. 90}$  (273, 272)  $\xrightarrow{-ca. 90}$  (181, 180). Both these paths appear to involve N-N bond cleavage in (5) and the elimination of PhN. The remaining important steps appear simply to permute three or four eliminations of  $m/e$  ca. 28, ca. 102, and ca. 129.

The isoxazoles (6) differ in composition from the appropriate bistriazolyl ketones simply by  $N_2$  [equation (2)]. Previous workers have also suggested that isoxazoles rearrange to the azirine under electron impact and



may lose CO or HCN.<sup>7,9</sup> Moreover,  $[P - \text{NO}]^+$  does not appear to be significant nor does it appear here. As a result, it is not surprising that the bistriazolyl ketones and triazolylisoxazoles (6) have similar fragmentation patterns, *e.g.*  $[\text{RC}_2\text{HCOC}_2\text{NOHR}]^+$ ,  $[\text{R}'\text{CO}]^+$ ,  $[\text{RT}]^+$ ,  $[\text{RC}_2\text{NHC}]^+$ ,  $[\text{R}_2\text{C}_2\text{NH}]^+$ , etc. Given  $(\text{MeT})_2\text{CO}$  (192),

for example, its isoxazole (6; R = Me) 'begins' at  $m/e$  164. On the path which produces  $[P - 56]^+$ , we again expect to fall in with the processes already described for the bistriazolyl ketones. Differences in detail presumably arise because the paths through the common azirene ketone [equation (2)] are neither identical nor exclusive. The ketone analogy, however, seems sufficiently strong so that we have listed isoxazole data in Table 2 with the carbonyl compounds.

**Cleavage Comparisons.**—Although the final products of pyrolysis and photolysis of 1,2,3-triazoles may differ, both begin with ejection of  $N_2$ .<sup>1,10</sup> It should be evident that this is often important in the mass spectra work but other routes, e.g., the loss of HCN, RCN, R'CNH [from (3)], among others which depend on the ring substituents, may compete. Thus, it is possible that other pyrolytic cleavage routes remain to be found when a variety of triazoles are studied.

#### EXPERIMENTAL

All but one of the compounds have been described elsewhere.<sup>5</sup> 4-*n*-Pentyl-5-ethoxycarbonyl-H-1,2,3-triazole, m.p. 80–81 °C, was prepared (by M. Tuffano) according to a standard method<sup>5</sup> (Found: C, 56.55; H, 8.4.  $C_{10}H_{17}N_3O_2$  requires C, 56.84; H, 8.11%).

Mass spectra were obtained on a Varian MAT CH7 spectrometer, typically at an ionizing potential of 55 eV and  $10^{-4}$  A. Probe temperatures are given in Table 1. The relative intensities (RI) in our Tables are, of course, rounded figures and low values, usually < 3–10%, have been omitted. Likewise, peaks at  $m/e$  32, 28, 18, and 17 have been excluded. In chloro-compounds, peaks attributed to ions containing  $^{35}Cl$  (corrected, if need be, for  $^{37}Cl$ ) are listed;  $^{37}Cl$  species have been deleted. Occasionally the intensities of a resolved doublet are given in parenthesis  $F^+(x, y)$ ; the first figure corresponds to the higher  $m/e$ . Fairly complete breakdown diagrams, including RIs, were

constructed for the triazoles but are not included here. To distinguish details such as timing, competitive *versus* sequential paths, extrusion, rearrangement, etc., the reader would have to reconstruct these schemes from Table 1. Admittedly, further studies, e.g., precise mass measurements, metastable searches, and isotopic labelling would limit the mechanistic possibilities.

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