

Neil G. Keats, Shyam K. Singh and Lindsay A. Summers*

Department of Chemistry, The University of Newcastle, 2308,
New South Wales, Australia
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4-Carboxy-5-methyl-2-aryl-2H-1,2,3-triazoles undergo considerable fragmentation on electron impact including loss of OH \cdot and H $_2$ O from the molecular ions and rupture of the triazole ring. 4-Carboxy-5-phenyl-2-aryl-2H-1,2,3-triazoles, on the other hand, show no loss of H $_2$ O from the molecular ions.

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The mass spectrum of 1,2,3-triazole has been reported. The base peak is due to the molecular ion at mass 69. The initial fragmentation route involves either loss of HCN to give a peak at mass 42 (42% of intensity of base peak) or loss of N $_2$ to give a peak at mass 41 (12%) [1]. The mass spectra of several 4- or 4,5-substituted 1,2,3-triazoles containing no substituents on the nitrogen atoms have also received attention [2-4]. A variety of 1-substituted 1H-1,2,3-triazoles have been studied. The loss of N $_2$ by rupture of the triazole ring is frequently the initial route of fragmentation [2,3,5-9]. Some work on the mass spectra of 2-substituted 2H-1,2,3-triazoles has also been reported including 4-hydroxy-2-methyl-2H-1,2,3-triazole [7] and several 4-substituted saccharide derivatives of 2-phenyl-2H-1,2,3-triazole [10,11]. This paper is concerned with the mass spectral fragmentation pattern of six 4-carboxy-5-methyl-2-aryl-2H-1,2,3-triazoles **I** (R = H), **I** (R = 3-CH $_3$), **I** (R = 4-CH $_3$), **I** (R = 2-Cl), **I** (R = 3-Cl) and **I** (R = 4-Cl), three 4-carboxy-5-phenyl-2-aryl-2H-1,2,3-triazoles **II** (R = H), **II** (R = CH $_3$) and **II** (R = Cl) and the corresponding nine

methyl esters **III** (R = H), **III** (R = 3-CH $_3$), **III** (R = 4-CH $_3$), **III** (R = 2-Cl), **III** (R = 3-Cl), **III** (R = 4-Cl), **IV** (R = H), **IV** (R = CH $_3$) and **IV** (R = Cl). Details of the principal peaks in the spectra are given in Tables 1-4 and the spectra of 4-carboxy-5-methyl-2-phenyl-2H-1,2,3-triazole **I** (R = H) and 4-carboxy-2,5-diphenyl-2H-1,2,3-triazole **II** (R = H) are given in Figures 1 and 2 respectively by way of illustration. The synthesis of the eighteen compounds has recently been reported [12].

The mass spectra of the six 4-carboxy-5-methyl-2-aryl-2H-1,2,3-triazoles (Table 1) are very interesting. With the parent member of the series, 4-carboxy-5-methyl-2-phenyl-2H-1,2,3-triazole **I** (R = H) the base peak is at 91 due to a C $_6$ H $_8$ N $^{+}$ species formed by rupture of the triazole ring as indicated in Scheme 1.

The base peak at mass 91 disintegrates by loss of HCN to give a peak at mass 64 of 22% of the intensity of the base peak due to a C $_5$ H $_4$ $^{+}$ species. A strong metastable peak for the 91 \rightarrow 64 transition at 45.0 was observed. The C $_5$ H $_4$ $^{+}$ species then loses H \cdot to afford the peak at mass 63

Scheme 1

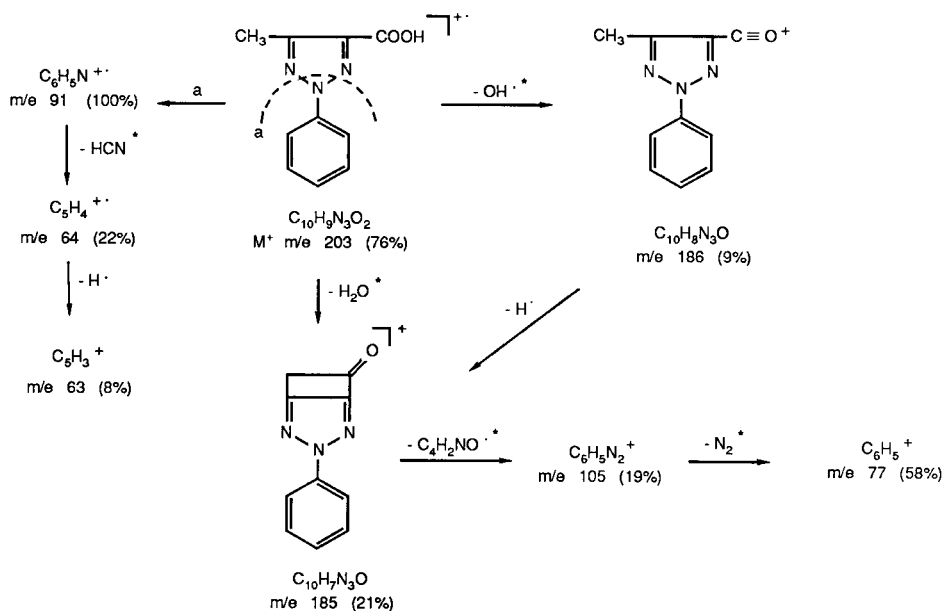


Table 1

Empirical Formula of Fragment Ions [a] in the Mass Spectra of 4-Carboxy-5-methyl-2-aryl-2*H*-1,2,3-triazoles I

m/e	Formula	Intensity (%)					
		R = H	R = 3-CH ₃	R = 4-CH ₃	R = 2-Cl	R = 3-Cl	R = 4-Cl
239	C ₁₀ H ₈ ³⁷ ClN ₃ O ₂	—	—	—	18	23	29
237	C ₁₀ H ₈ ³⁵ ClN ₃ O ₂	—	—	—	54	71	89
222	C ₁₀ H ₇ ³⁷ ClN ₃ O	—	—	—	—	5	—
221	C ₁₀ H ₆ ³⁷ ClN ₃ O	—	—	—	11	11	—
220	C ₁₀ H ₇ ³⁵ ClN ₃ O	—	—	—	8	15	7
219	C ₁₀ H ₅ ³⁵ ClN ₃ O	—	—	—	37	29	—
217	C ₁₁ H ₁₁ N ₃ O ₂	—	100	100	—	—	—
203	C ₁₀ H ₉ N ₃ O ₂	76	—	—	—	—	—
200	C ₁₁ H ₁₀ N ₃ O	—	7	—	—	—	—
199	C ₁₁ H ₉ N ₃ O	—	12	6	—	—	—
186	C ₁₀ H ₈ N ₃ O	9	—	—	—	—	—
185	C ₁₀ H ₇ N ₃ O	21	—	—	—	—	—
141	C ₆ H ₄ ³⁷ ClN ₂	—	—	—	15	—	8
139	C ₆ H ₄ ³⁵ ClN ₂	—	—	—	41	15	22
127	C ₆ H ₄ ³⁷ ClN	—	—	—	37	32	32
125	C ₆ H ₄ ³⁵ ClN	—	—	—	100	100	100
119	C ₇ H ₇ N ₂	—	7	8	—	—	—
113	C ₆ H ₄ ³⁷ Cl	—	—	—	17	19	15
111	C ₆ H ₄ ³⁵ Cl	—	—	—	42	63	41
105	C ₆ H ₅ N ₂	19	—	—	—	—	—
	C ₇ H ₇ N	—	72	83	—	—	—
104	C ₇ H ₆ N	—	27	14	—	—	—
101	C ₆ H ₄ ³⁷ Cl	—	—	—	5	—	—
99	C ₅ H ₄ ³⁵ Cl	—	—	—	18	5	—
98	C ₅ H ₃ ³⁵ Cl	—	—	—	—	6	—
91	C ₆ H ₅ N	100	—	—	—	—	—
	C ₇ H ₇	—	64	46	—	—	—
90	C ₆ H ₄ N	—	—	—	42	46	24
89	C ₆ H ₃ N	—	—	—	7	11	5
85	C ₆ H ₂ ³⁵ Cl	—	—	—	—	6	—
79	C ₅ H ₅ N	—	8	—	—	—	—
78	C ₆ H ₆	—	15	13	—	—	—
77	C ₆ H ₅	58	10	10	—	—	—
76	C ₆ H ₄	—	—	—	—	9	—
75	C ₆ H ₃	—	—	—	26	44	15
74	C ₆ H ₂	—	—	—	—	10	—
73	C ₅ H ₂ ³⁵ Cl	—	—	—	—	6	—
65	C ₅ H ₅	—	19	14	—	—	—
64	C ₅ H ₄	22	—	—	—	—	—
	C ₆ H ₂ N	—	—	—	7	13	6
63	C ₅ H ₃	8	6	—	24	40	13
62	C ₅ H ₂	—	—	—	5	10	—

[a] Only those ions of mass >60 and of intensity ≥5% of the base peak are recorded. Peaks due to ¹³C species are omitted from the table.

due to a C₅H₃⁺ ion (8% intensity). The molecular ion of 4-carboxy-5-methyl-2-phenyl-2*H*-1,2,3-triazole I (R = H) (C₁₀H₉N₃O₂⁺) gives a peak at mass 203 of 76% of the intensity of the base peak. Apart from rupture of the triazole ring to afford the base peak, the molecular ion of 4-carboxy-5-methyl-2-phenyl-2*H*-1,2,3-triazole disintegrates by at least two other routes. One route involves loss of OH[·] to afford the peak at mass 186 due to the C₁₀H₈N₃O⁺ ion of 9% of the intensity of the base peak. A metastable for 203 → 186 transition was observed. A second route of disintegration of the molecular ion involves loss of H₂O to give a C₁₀H₇N₃O⁺ species which gives rise to a peak at mass 185

of 21% of the intensity of the base peak. A strong metastable at 168.6 corresponding to the 203 → 185 transition was observed. The C₁₀H₇N₃O⁺ species at mass 185 is depicted as a fused cyclobutanone-triazole structure in Scheme 1. Strong support for the involvement of a hydrogen of the 5-methyl group of 4-carboxy-5-methyl-2-phenyl-2*H*-1,2,3-triazole I (R = H) in the loss of H₂O from the molecular ion comes from the observation that the similar loss of H₂O is not seen in the spectrum of 4-carboxy-2,5-diphenyl-2*H*-1,2,3-triazole II (R = H) (see later and Scheme 2). The C₁₀H₇N₃O⁺ species at mass 185 may also be formed from the C₁₀H₈N₃O⁺ ion at mass 186 by loss of H[·]. The

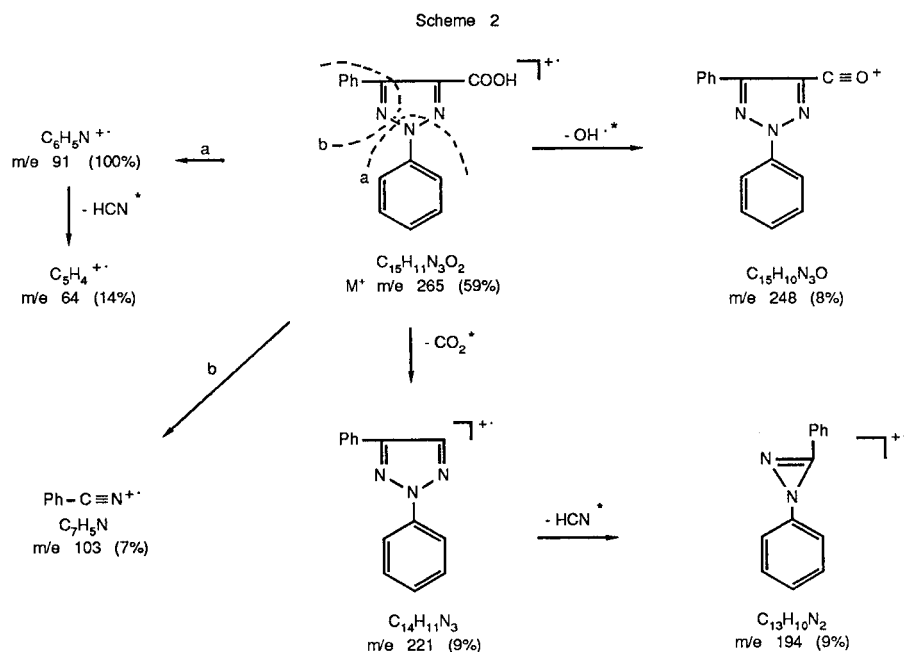
$C_{10}H_7N_3O^+$ species further disintegrates by loss of C_4H_2NO to give a $C_6H_5N_2^+$ ion which is responsible for a peak at mass 105 of 19% of the intensity of the base peak.

A strong metastable at 59.6 corresponding to the 185 \rightarrow 105 transition was present in the spectrum. The $C_6H_5N_2^+$ ion at mass 105 then loses N_2 to afford a peak at mass 77 of 58% intensity due to a $C_6H_5^+$ ion. A metastable for the 105 \rightarrow 77 transition at 56.5 was observed. The $C_6H_5^+$ ion at mass 77 is presumably also formed directly from the molecular ion and the $C_{10}H_8N_3O^+$ and $C_{10}H_7N_3O^+$ species. The representations in Scheme 1, therefore, account for all the prominent peaks in the spectrum of 4-carboxy-5-methyl-2-phenyl-2H-1,2,3-triazole **I** ($R = H$).

The fragmentation patterns of the two 2-(methylphenyl) analogues of **I** ($R = H$), namely 4-carboxy-5-methyl-2-(3-methylphenyl)-2H-1,2,3-triazole **I** ($R = 3-CH_3$) and 4-carboxy-5-methyl-2-(4-methylphenyl)-2H-1,2,3-triazole **I** ($R = 4-CH_3$) (Table 1) are very similar to that discussed for **I** ($R = H$) with only minor differences being noted. The principal differences is that the molecular ions at mass 217 ($C_{11}H_{11}N_3O_2^+$) are the base peaks with **I** ($R = 3-CH_3$) and **I** ($R = 4-CH_3$) while the $C_7H_7N^+$ species at mass 105, analogous to the $C_6H_5N^+$ species which is the base peak with **I** ($R = H$), account for peaks of 72-83% of the intensity of the molecular ions with **I** ($R = 3-CH_3$) and **I** ($R = 4-CH_3$). Otherwise the fragmentations routes are much the same and are analogous to the routes depicted in Scheme 1. Loss of OH from the molecular ion to give a peak at mass 200 ($C_{11}H_{10}N_3O^+$, 7%) is observed with the 3-methylphenyl derivative **I** ($R = 3-CH_3$) but with the 4-methylphenyl analogue **I** ($R = 4-CH_3$) the corresponding peak is less than

5% of the intensity of the base peak. Peaks in the spectra of **I** ($R = 3-CH_3$) and **I** ($R = 4-CH_3$) at mass 199 ($C_{11}H_9N_3O$, 6-12%), 119 ($C_7H_7N_2$, 7-8%), 105 (C_7H_7N , 72-83%), 91 (C_7H_7 , 46-64%), 78 (C_6H_6 , 13-15%) and 77 (C_6H_5 , 10%) are analogous to those of **I** ($R = H$) at mass 185 ($C_{10}H_7N_3O$, 21%), 105 ($C_6H_5N_2$, 19%), 91 (C_6H_5N , 100%), 77 (C_6H_5 , 58%), 64 (C_5H_4 , 22%) and 63 (C_5H_3 , 8%) respectively. Metastable peaks were present in most cases. A few peaks in the mass spectra of **I** ($R = 3-CH_3$) and **I** ($R = 4-CH_3$) which do not have a corresponding peak in the spectrum of **I** ($R = H$) deserve comment. The peaks at mass 104 (C_7H_6N , 14-27%) clearly arise by loss of H from the $C_7H_7N^+$ species at mass 105. The peak at mass 79 due to a $C_5H_5N^+$ species (8%) in the spectrum of **I** ($R = 3-CH_3$) is obtained by the loss of C_2H_2 from the $C_7H_7N^+$ species at mass 105. A metastable at 59.4 was present corresponding to the 105 \rightarrow 79 transition. Likewise the peaks at mass 65 due to $C_5H_5^+$ ions (14-19%) in the spectra of **I** ($R = 3-CH_3$) and **I** ($R = 4-CH_3$) arise by loss of C_2H_2 from $C_7H_7^+$ ions at mass 91. A strong metastable at 46.4 due to the 91 \rightarrow 65 transition was present in the spectra.

The fragmentation patterns of the three 2-(chlorophenyl) analogues of **I** ($R = H$), namely 4-carboxy-5-methyl-2-(2-chlorophenyl)-2H-1,2,3-triazole **I** ($R = 2-Cl$), 4-carboxy-5-methyl-2-(3-chlorophenyl)-2H-1,2,3-triazole **I** ($R = 3-Cl$) and 4-carboxy-5-methyl-2-(4-chlorophenyl)-2H-1,2,3-triazole **I** ($R = 4-Cl$) (Table 1) likewise are very similar to that of **I** ($R = H$). With all three chlorophenyl derivatives the base peak is at mass 125 due to a $C_6H_4^{35}ClN^+$ species analogous to the $C_6H_5N^+$ species which is the base peak with **I** ($R = H$). The molecular ions of the chlorophenyl derivatives account for peaks at mass 237 of 54-89% of the



intensity of the base peak. All the peaks in the spectra of the three chlorophenyl derivatives above mass 101 are analogous to peaks in the spectrum of **I** ($R = H$) as depicted in Scheme 1. The peaks at and below mass 101 in the spectra of the three chlorophenyl derivatives are readily accounted for by further disintegration of higher mass species and deserve little comment. For example, the base peak at mass 125 due to $C_6H_4^{35}ClN^+$ species may lose CN to afford $C_5H_4^{35}Cl^+$ ions at mass 99 (5-18%) or HCN to afford $C_5H_3^{35}Cl^+$ species at mass 98 (6%). The base peaks also readily lose Cl to afford high intensity peaks at mass 90 ($C_6H_4N^+$, 24-46%). Likewise the $C_6H_4^{35}Cl^+$ ions at mass 111 may lose HCl to afford $C_6H_3^+$ ions at mass 75 (15-44%) or C_2H_2 to afford $C_4H_2^{35}Cl^+$ ions at mass 85 (6%). Moreover, the $C_6H_4N^+$ ions at mass 90 may further disintegrate by loss of HCN to afford $C_5H_3^+$ ions at mass 63 (13-40%) or by loss of C_2H_2 to give $C_4H_2N^+$ ions at mass 64 (6-13%). Metastables for most of these transitions were observed.

The mass spectral fragmentation pattern of 4-carboxy-2,5-diphenyl-2*H*-1,2,3-triazole **II** ($R = H$) is also an interesting one (Table 2, Scheme 2) showing some similarity to the spectrum of 4-carboxy-5-methyl-2-phenyl-2*H*-1,2,3-triazole **I** ($R = H$) but also some important differences. Like **I** ($R = H$), the base peak in the spectrum of **II** ($R = H$) is at mass 91 due to a $C_6H_5N^+$ species resulting from rupture of the triazole ring. Another fragment from rupture of the triazole ring survives in the form of the $C_7H_5N^+$ species at mass 103 which is responsible for a peak of 7% of the intensity of the base peak. This species of mass 103 is almost certainly the benzonitrile molecular ion as indicated in Scheme 2. The analogous fragment, namely the acetonitrile molecular ion at mass 41, was not detected in the spectrum of 4-carboxy-5-methyl-2-phenyl-2*H*-1,2,3-triazole **I** ($R = H$) possibly due to its low mass. The base peak at mass 91 in the spectrum of **II** ($R = H$) further disintegrates by loss of HCN to give a peak at mass 64 due to a $C_5H_4^+$ species (14%). A metastable at 45.0 corresponding to the 91 \rightarrow 64 transition was observed in the spectrum. The molecular ion of 4-carboxy-2,5-diphenyl-2*H*-1,2,3-triazole **II** ($R = H$) gives a peak at mass 265 ($C_{15}H_{11}N_3O_2^+$) of 59% of the intensity of the base peak. Like **I** ($R = H$), the molecular ion of **II** ($R = H$) loses OH to give a peak at

mass 248 due to a $C_{15}H_{10}N_3O^+$ ion (8%). A metastable peak for the transition 265 \rightarrow 248 at 232.0 was present. The most notable difference in the fragmentation route of **II** ($R = H$) compared with **I** ($R = H$) is that the loss of H_2O is not observed from the molecular ion of **II** ($R = H$). Instead the molecular ion of **II** ($R = H$) loses CO_2 to give a $C_{14}H_{11}N_3^+$ species at mass 221 (9%) as shown in Scheme 2. A small metastable for the 265 \rightarrow 221 transition at 184.3 was observed. The $C_{14}H_{11}N_3^+$ species at mass 221 then loses HCN to give a $C_{13}H_{10}N_2^+$ species at mass 194 (9%) depicted as a diphenyldiazirine in Scheme 2. A strong

metastable for the transition 221 \rightarrow 194 at 170.2 was noted in the spectrum. The only other prominent peak in the spectrum of **II** ($R = H$) (Table 2) not accounted for is the one at mass 77 due to the $C_6H_5^+$ ion which gives a peak of 22% of the intensity of the base peak. It clearly can arise by loss of the phenyl group from the 2- and/or 5-positions of the molecular ion of **II** ($R = H$) or some of the subsequent fragments. Unlike the formation of some of the $C_6H_5^+$ ion in the spectrum of **I** ($R = H$) (Scheme 1) no clear metastables were observed, however, in the spectrum of **II** ($R = H$) to account for the formation of the $C_6H_5^+$ ion.

Table 2

Empirical Formula of Fragment Ions [a] in the Mass Spectra of 4-Carboxy-5-phenyl-2-aryl-2*H*-1,2,3-triazoles **II**

m/e	Formula	Intensity (%)		
		R = H	R = CH ₃	R = Cl
301	$C_{15}H_{10}^{37}ClN_3O_2$	—	—	33
299	$C_{15}H_{10}^{35}ClN_3O_2$	—	—	100
279	$C_{16}H_{13}N_3O_2$	—	100	—
265	$C_{15}H_{11}N_3O_2$	59	—	—
248	$C_{15}H_{10}N_3O$	8	—	—
221	$C_{14}H_{11}N_3$	9	—	—
194	$C_{13}H_{10}N_2$	9	—	—
127	$C_6H_4^{37}ClN$	—	—	31
125	$C_6H_4^{35}ClN$	—	—	99
113	$C_6H_4^{37}Cl$	—	—	5
111	$C_6H_4^{35}Cl$	—	—	12
105	C_7H_7N	—	74	—
104	C_7H_6N	—	16	—
103	C_7H_5N	7	—	—
91	C_6H_5N	100	—	—
	C_7H_7	—	10	—
90	C_6H_4N	—	—	27
89	C_6H_3N	—	—	9
78	C_6H_6	—	12	—
77	C_6H_5	22	9	—
76	C_6H_4	—	—	5
65	C_5H_5	—	9	—
64	C_5H_4	14	—	—
63	C_5H_3	—	—	15
62	C_5H_2	—	—	5

[a] Only those ions of mass > 60 and of intensity $\geq 5\%$ of the base peak are recorded. Peaks due to ^{13}C species are omitted from the table.

The fragmentation pattern of the 2-(4-methylphenyl) analogue of **II** ($R = H$), namely 4-carboxy-5-phenyl-2-(4-methylphenyl)-2*H*-1,2,3-triazole **II** ($R = CH_3$) (Table 2), although similar to that of **II** ($R = H$) is much simpler. One difference is that the molecular ion at mass 279 ($C_{16}H_{13}N_3O_2^+$) is the base peak in the spectrum of **II** ($R = CH_3$) while the $C_7N_7N^+$ species at mass 105, analogous to the $C_6H_5N^+$ species at mass 91 which is the base peak in the spectrum of **II** ($R = H$), accounts for a peak of 74% of the intensity of the base peak. The $C_7H_7N^+$ species at mass 105 in the spectrum of **II** ($R = CH_3$) may lose H to

afford the $C_7H_6N^+$ ion at mass 104 (16%). The fragmentation of **II** ($R = CH_3$) affords peaks at mass 91 ($C_7H_7^+$, 10%) and 78 ($C_6H_6^+$, 12%) which have counterparts in the spectrum of **II** ($R = H$) at mass 77 ($C_6H_5^+$, 22%) and 64 ($C_5H_4^+$, 14%) respectively (see Scheme 2). The only other peaks in the spectrum of **II** ($R = CH_3$) not explained are the peaks at mass 77 ($C_6H_5^+$, 9%) clearly largely derived from the 5-phenyl substituent and at mass 65 ($C_5H_5^+$, 9%) which is formed from the $C_7H_7^+$ ion at mass 91 by loss of C_2H_2 . Unlike **II** ($R = H$) the loss of CO_2 from the molecular ion of **II** ($R = CH_3$) is not a significant fragmentation route and there is no peak in the spectrum of **II** ($R = CH_3$) at mass 103 corresponding to the benzonitrile molecular ion ($C_7H_5N^+$).

The fragmentation pattern of the 2-(4-chlorophenyl) analogue of **II** ($R = H$), namely 4-carboxy-5-phenyl-2-(4-chlorophenyl)-2*H*-1,2,3-triazole **II** ($R = Cl$) (Table 2), likewise is simpler than that of the parent compound **II** ($R = H$). In this case the molecular ion at mass 299 ($C_{15}H_{10}^{35}ClN_3O_2^+$) is responsible for the base peak in the spectrum. The $C_6H_4^{35}ClN^+$ species at mass 125, analogous to the $C_6H_5N^+$ species which gives rise to the base peak in the spectrum of **II** ($R = H$), gives a high intensity peak amounting to 99% of the intensity of the base peak. Loss of CO_2 from the molecular ion of **II** ($R = Cl$) does not occur to any significant extent and a peak due to the benzonitrile molecular ion at mass 103 was not observed in the spectrum of **II** ($R = Cl$). The peak at mass 111 in the spectrum of **II** ($R = Cl$) due to a $C_6H_4^{35}Cl^+$ ion clearly origi-

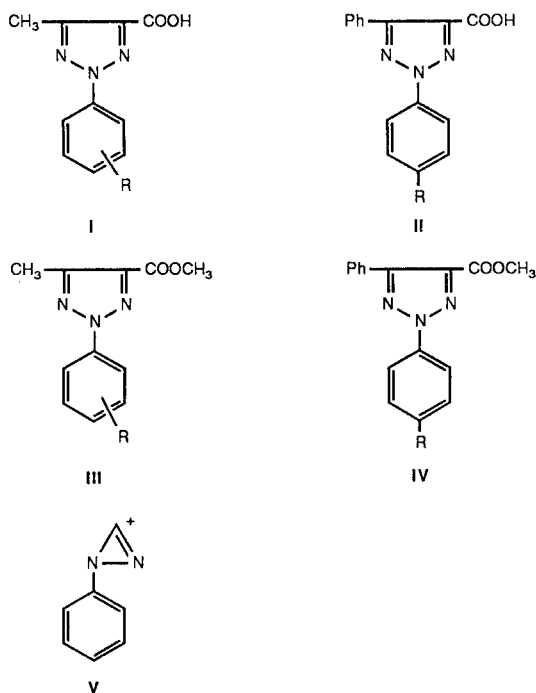
Table 3

Empirical Formula of Fragment Ions [a] in the Mass Spectra of 4-Methoxycarbonyl-5-methyl-2-aryl-2*H*-1,2,3-triazoles **III**

m/e	Formula	Intensity (%)					
		R = H	R = 3-CH ₃	R = 4-CH ₃	R = 2-Cl	R = 3-Cl	R = 4-Cl
253	$C_{11}H_{10}^{37}ClN_3O_2$	—	—	—	23	27	32
251	$C_{11}H_{10}^{35}ClN_3O_2$	—	—	—	72	77	100
231	$C_{12}H_{13}N_3O_2$	—	100	100	—	—	—
222	$C_{10}H_7^{37}ClN_3O$	—	—	—	16	28	16
221	$C_{10}H_6^{37}ClN_3O$	—	—	—	28	34	19
220	$C_{10}H_7^{35}ClN_3O$	—	—	—	67	86	44
219	$C_{10}H_6^{35}ClN_3O$	—	—	—	100	88	72
217	$C_{11}H_{11}N_3O_2$	100	—	—	—	—	—
200	$C_{11}H_{10}N_3O$	—	55	39	—	—	—
199	$C_{11}H_9N_3O$	—	41	25	—	—	—
186	$C_{10}H_8N_3O$	80	—	—	—	—	—
185	$C_{10}H_7N_3O$	80	—	—	—	—	—
184	$C_{10}H_8N_3O$	—	—	—	—	5	—
141	$C_6H_4^{37}ClN_2$	—	—	—	6	9	5
139	$C_6H_4^{35}ClN_2$	—	—	—	14	24	20
127	$C_6H_4^{37}ClN$	—	—	—	25	32	26
125	$C_6H_4^{35}ClN$	—	—	—	73	100	83
119	$C_7H_7N_2$	—	7	10	—	—	—
117	$C_7H_5N_2$	7	—	—	—	—	—
113	$C_6H_4^{37}Cl$	—	—	—	23	38	23
111	$C_6H_4^{35}Cl$	—	—	—	40	96	50
105	$C_6H_5N_2$	21	—	—	—	—	—
	C_7H_7N	—	69	77	—	—	—
104	C_7H_6N	—	26	15	—	—	—
99	$C_6H_4^{35}Cl$	—	—	—	5	6	—
91	C_6H_5N	98	—	—	—	—	—
	C_7H_7	—	76	52	—	—	—
90	C_6H_4N	—	—	—	26	40	18
89	C_6H_3N	—	—	—	—	8	—
79	C_6H_5N	—	8	—	—	—	—
78	C_6H_6	—	15	15	—	—	—
77	C_6H_5	81	12	16	—	—	—
76	C_6H_4	—	—	—	—	9	—
75	C_6H_3	—	—	—	22	42	17
65	C_5H_5	—	23	21	—	—	—
64	C_4H_2N	—	—	—	—	12	—
63	C_5H_3	—	6	—	10	30	11

[a] Only those ions of mass >60 and of intensity $\geq 5\%$ of the base peak are recorded. Peaks due to ^{13}C species are omitted from the table.

nates from the 2-(4-chlorophenyl) substituent and the peaks at mass 90 ($C_6H_4N^+$, 27%) and 89 ($C_6H_3N^+$, 9%) are derived from the $C_6H_4^{35}ClN^+$ species at mass 125 by loss of Cl^- and HCl respectively. The peak at mass 76 ($C_6H_4^+$, 5%) comes from the $C_6H_4^{35}Cl^+$ ion at mass 111 by loss of Cl^- while the peak at mass 63 (C_5H_3 , 15%) is derived from the $C_6H_4N^+$ ion at mass 90 by loss of HCN . Further loss of H^- accounts for the peak at mass 62 due to a $C_5H_2^+$ species (5%). Metastable peaks for most of these transitions were present in the spectrum.



The principal peaks in the mass spectra of the six 4-methoxycarbonyl-5-methyl-2-aryl-2*H*-1,2,3-triazoles **I** ($R = H$), **II** ($R = 3-CH_3$), **III** ($R = 4-CH_3$), **III** ($R = 2-Cl$), **III** ($R = 3-Cl$) and **III** ($R = 4-Cl$) are given in Table 3. The fragmentation patterns, as expected, bear very close resemblance to those of the corresponding acids (Table 1) apart from the loss of OCH_3^- and CH_3OH from the molecular ions with the esters instead of the loss of OH^- and H_2O from the molecular ions of the acids. The resultant peaks in the spectra of the esters are almost identical to those of the acids although there are sometimes differences in the intensity of the peaks between the two series. Indeed only two peaks in Table 3 below mass 200 have not got their counterpart in Table 1. The peak at mass 184 due to a $C_{10}H_6N_3O^+$ ion (5%) in the spectrum of **III** ($R = 3-Cl$) results from loss of Cl^- from the $C_{10}H_6^{35}ClN_3O$ peak at mass 219 (88%), while the peak at mass 117 due to a $C_7H_5N_2^+$ species (7%) in the spectrum of **III** ($R = H$) is depicted as a phenyldiazirine structure (**V**) formed by fragmentation of the triazole ring.

The principal peaks in the mass spectra of the three 4-methoxycarbonyl-5-phenyl-2-aryl-2*H*-1,2,3-triazoles **IV** ($R = H$), **IV** ($R = CH_3$) and **IV** ($R = Cl$) are given in Table 4. The fragmentation patterns of the esters are very similar to those of the corresponding acids (Table 2) although the intensity of the resultant peaks may differ between the two series. As expected, the molecular ions of the esters lose OCH_3^- instead of OH^- which is lost from the molecular ions of the acids. There are only four peaks in Table 4 below mass 250 which do not have their counterpart in Table 2 and all of these are readily accounted for.

The peak at mass 103 ($C_7H_5N^+$, 7%) in the spectrum of **IV** ($R = CH_3$) clearly results from the loss of H^- from the $C_7H_6N^+$ ion at mass 104, the peak at mass 77 ($C_6H_5^+$, 6%) in the spectrum of **IV** ($R = Cl$) is derived from the 5-phenyl group, the peak at mass 65 ($C_5H_5^+$, 7%) in the spectrum of **IV** ($R = H$) arises from the base peak at mass 91 ($C_6H_5N^+$, 100%) by loss of CN^- , while the peak at mass 63 ($C_5H_3^+$, 8%) comes from the species $C_5H_4^+$ at mass 64 by loss of H^- . One other peak in Table 4 deserves comment. The peak at mass 194 ($C_{13}H_{10}N_2^+$, 6%) in the spectrum of **IV** ($R = H$) probably arises directly from the molecular ion by rupture of the triazole ring. In the spectrum of the

Table 4

Empirical Formula of Fragment Ions [a] in the Mass Spectra of 4-Methoxycarbonyl-5-phenyl-2-aryl-2*H*-1,2,3-triazoles **IV**

m/e	Formula	Intensity		
		R = H	R = CH ₃	R = Cl
315	$C_{16}H_{12}^{37}ClN_3O_2$	—	—	35
313	$C_{16}H_{12}^{35}ClN_3O_2$	—	—	100
293	$C_{17}H_{15}N_3O_2$	—	100	—
284	$C_{15}H_9^{37}ClN_3O$	—	—	9
282	$C_{15}H_9^{35}ClN_3O$	—	—	32
279	$C_{16}H_{13}N_3O_2$	81	—	—
262	$C_{16}H_{12}N_3O$	—	22	—
248	$C_{15}H_{10}N_3O$	35	—	—
194	$C_{13}H_{10}N_2$	6	—	—
127	$C_6H_4^{37}ClN$	—	—	25
125	$C_6H_4^{35}ClN$	—	—	83
113	$C_6H_4^{37}Cl$	—	—	7
111	$C_6H_4^{35}Cl$	—	—	17
105	C_7H_7N	—	85	—
104	C_7H_6N	—	15	—
103	C_7H_5N	—	7	—
91	C_6H_5N	100	—	—
	C_7H_7	—	16	—
90	C_6H_4N	—	—	20
89	C_6H_3N	—	—	8
78	C_6H_6	—	13	—
77	C_6H_5	44	11	6
76	C_6H_4	—	—	5
75	C_6H_3	—	—	13
65	C_5H_5	7	13	—
64	C_5H_4	19	—	—
63	C_5H_3	8	—	10

[a] Only those ions of mass >60 and of intensity $\geq 5\%$ of the base peak are recorded. Peaks due to ^{13}C species are omitted from the table.

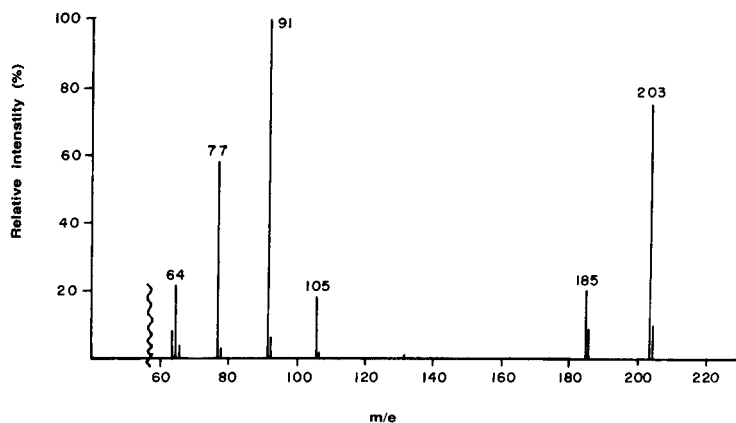


Figure 1. Mass spectrum of 4-carboxy-5-methyl-2-phenyl-2H-1,2,3-triazole **I** (R = H).

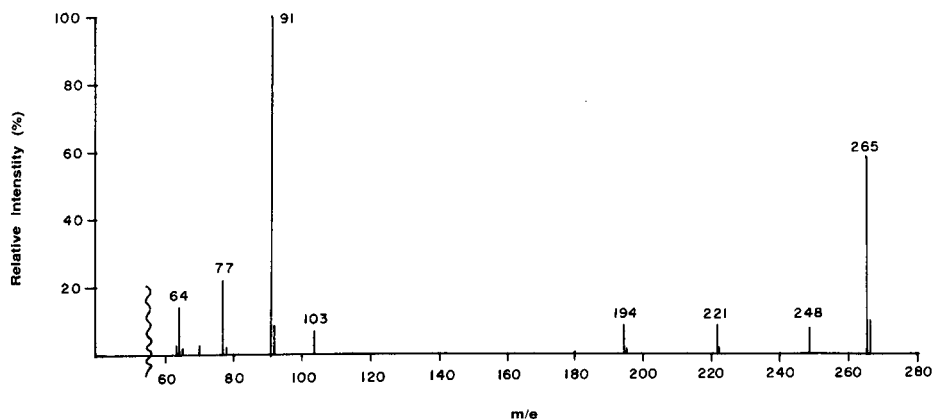


Figure 2. Mass spectrum of 4-carboxy-2,5-diphenyl-2H-1,2,3-triazole **II** (R = H).

corresponding acid **II** (R = H) (see Scheme 2) the $C_{13}H_{10}N_2^+$ species was shown to be derived from the $C_{14}H_{11}N_3^+$ species at mass 221 by loss of HCN. However no significant peak at mass 221 is observed in the spectrum of the ester **IV** (R = H).

EXPERIMENTAL

The spectra were determined with an AEI MS-30 mass spectrometer. The samples were analysed by a direct insertion probe at an ionising current of 70 eV. The ion source temperature was 200°.

The eighteen compounds were analytically pure [12].

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