

Electron Impact Ionization Mass Spectra of 2,4,5,5-
Tetrasubstituted 1,2,4-Triazolidine-3-thiones.
The Effect of the Ethoxycarbonyl Group at Position 4

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The electron impact ionization mass spectra of 2,4,5,5-tetrasubstituted 1,2,4-triazolidine-3-thiones studied confirmed that the substituent at position 4 has the most dramatic influence on the fragmentation pattern. When the substituent is a methylallyl group the molecular ions exhibit four main routes of fragmentation, but when it is an ethoxycarbonyl/acetyl or a methyl group these direct decompositions of the molecular ion become less abundant. Interestingly all 4-ethoxycarbonyl derivatives and the 4-acetyl derivative exhibited the ions $[M-R^4-COOC_2H_4]^+$ and $[M-R^4-COCH_3]^+$, respectively, with the same composition.

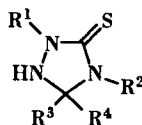
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Introduction.

In our earlier work [1] we examined the mass spectra of several 2,4,5,5-tetrasubstituted 1,2,4-triazolidine-3-thiones

mainly with methylallyl substitution at N-4. In this paper we describe the fragmentation of 22 new derivatives (Table 1) under electron impact ionization (Table 2). The

Table 1
The Structures of the Compounds Studied



No.	Mp, °C	R ¹	R ²	R ³	R ⁴
1	103-104	4-CH ₃ -C ₆ H ₄	CH ₂ -C(CH ₃)=CH ₂	CH ₃	CH ₃
2	117-121	4-CH ₃ -C ₆ H ₄	CH ₂ -C(CH ₃)=CH ₂	-CH ₂ -CH ₂ -C(Ph)=CH-	
3	118-120	4-CH ₃ -C ₆ H ₄	CH ₂ -C(CH ₃)=CH ₂	CH ₃	2-Pyridyl
4	119-122	4-CH ₃ -C ₆ H ₄	CH ₂ -C(CH ₃)=CH ₂	CH ₃	4-Pyridyl
5	102-105	CH ₃	CH ₂ -C(CH ₃)=CH ₂	CH ₃	C ₆ H ₅
6	180-186	CH ₃	CH ₂ -C(CH ₃)=CH ₂	CH ₃	4-Pyridyl
7	109-112	CH ₃	CH ₃	-(CH ₂) ₃ -CH(CH ₃)-CH ₂ -	
8	109-116	CH ₃	CH ₃	-(CH ₂) ₂ -CH(CH ₃)-(CH ₂) ₂ -	
9	108	C ₆ H ₅	COOEt	-(CH ₂) ₄ -	
10	133	C ₆ H ₅	COOEt	-(CH ₂) ₅ -	
11	119	C ₆ H ₅	COOEt	-(CH ₂) ₆ -	
12	99	C ₆ H ₅	COOEt	CH ₃	CH ₃
13	77	C ₆ H ₅	COOEt	CH ₃	C ₂ H ₅
14	81	C ₆ H ₅	COOEt	C ₂ H ₅	C ₂ H ₅
15	99	C ₆ H ₅	COOEt	CH ₃	C(CH ₃) ₃
16	118	4-CH ₃ -C ₆ H ₄	COOEt	CH ₃	CH ₃
17	101	4-CH ₃ -C ₆ H ₄	COOEt	C ₂ H ₅	C ₂ H ₅
18	105	CH ₃	COOEt		-(CH ₂) ₄ -
19	115	CH ₃	COOEt		-(CH ₂) ₅ -
20	90	CH ₃	COOEt		-(CH ₂) ₆ -
21	124	C ₆ H ₅	COCH ₃	CH ₃	CH ₃

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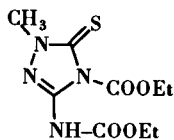


Table 2

The 70 eV Mass Spectra of Compounds **1-22**: m/z (relative abundance).
 (The results are ¹³C contribution corrected. Relative Abundances ≥ 5% are Included)

- 1** 275 (M⁺, 29), 260 (13), 259 (5), 220 (6), 218 (100), 217 (8), 186 (5), 185 (25), 163 (8), 162 (16), 161 (8), 159 (8), 150 (7), 149 (17), 147 (11), 145 (6), 132 (6), 131 (5), 122 (6), 121 (10), 120 (5), 107 (9), 106 (56), 105 (11), 104 (16), 100 (13), 89 (6), 87 (8), 79 (11), 77 (6), 70 (6), 65 (14), 58 (11), 56 (8), 55 (8), 53 (6), 45 (5), 41 (8), 39 (10)
- 2** 262 (100), 261 (8), 247 (5), 220 (5), 218 (77), 217 (17), 186 (12), 185 (18), 159 (9), 158 (28), 157 (13), 156 (42), 149 (36), 144 (7), 142 (7), 141 (7), 132 (11), 131 (8), 130 (10), 129 (5), 128 (8), 120 (6), 118 (6), 115 (7), 113 (10), 107 (23), 106 (56), 102 (10), 91 (32), 79 (18), 78 (17), 77 (17), 70 (8), 65 (10), 63 (7), 55 (54), 53 (5), 50 (7), 41 (5), 39 (16)
- 3** 338 (M⁺, 11), 323 (9), 260 (25), 228 (11), 225 (100), 224 (29), 219 (6), 218 (58), 217 (13), 210 (12), 209 (5), 208 (50), 207 (23), 186 (6), 185 (15), 181 (5), 170 (5), 149 (30), 147 (9), 132 (7), 121 (25), 120 (16), 119 (6), 113 (38), 112.5 (8), 112 (9), 107 (22), 106 (53), 105 (33), 104 (29), 91 (23), 80 (7), 79 (57), 78 (48), 77 (22), 72 (7), 71 (5), 70 (12), 69 (5), 65 (14), 57 (7), 55 (75), 54 (5), 53 (15), 52 (14)
- 4** 338 (M⁺, 11), 323 (6), 225 (80), 224 (10), 218 (74), 217 (16), 210 (7), 186 (13), 185 (16), 170 (6), 149 (35), 145 (5), 144 (8), 132 (7), 121 (8), 120 (17), 119 (7), 117 (5), 113 (13), 107 (6), 106 (100), 105 (16), 104 (14), 91 (16), 89 (6), 87 (6), 79 (21), 78 (21), 77 (16), 70 (11), 65 (15), 55 (40), 53 (9), 52 (5), 51 (12), 42 (11), 40 (5), 39 (16)
- 5** 261 (M⁺, 9), 246 (11), 184 (5), 148 (7), 147 (20), 145 (5), 143 (100), 142 (7), 127 (5), 120 (63), 118 (8), 109 (35), 104 (17), 103 (10), 101 (7), 78 (5), 77 (24), 75 (5), 74 (16), 70 (49), 55 (18), 51 (7), 42 (15), 41 (5), 39 (7)
- 6** 262 (M⁺, 21), 247 (21), 184 (12), 163 (9), 149 (13), 148 (17), 145 (5), 143 (100), 142 (24), 141 (8), 134 (7), 127 (9), 121 (83), 120 (8), 115 (11), 113 (8), 109 (85), 106 (10), 105 (15), 104 (11), 101 (14), 93 (5), 86 (6), 80 (5), 79 (11), 78 (33), 77 (7), 75 (11), 74 (33), 73 (6), 72 (5), 71 (6), 70 (41), 68 (7), 55 (42), 53 (11), 52 (6), 51 (18), 45 (7), 43 (5), 42 (29)
- 7** 213 (M⁺, 100), 212 (5), 198 (10), 184 (19), 170 (65), 157 (12), 156 (42), 149 (6), 143 (67), 142 (13), 125 (6), 74 (19), 71 (7), 70 (5), 69 (6), 68 (8), 57 (4), 56 (6), 55 (15), 54 (5), 43 (8), 42 (16), 41 (21), 39 (6)
- 8** 213 (M⁺, 81), 184 (12), 157 (5), 156 (100), 143 (65), 142 (9), 74 (14), 71 (5), 69 (9), 55 (13), 54 (8), 43 (5), 42 (12), 41 (11)
- 9** 305 (M⁺, 72), 277 (20), 276 (100), 259 (18), 248 (6), 232 (9), 230 (6), 204 (11), 191 (6), 174 (43), 173 (16), 151 (12), 150 (5), 146 (5), 145 (25), 135 (12), 132 (5), 131 (7), 123 (11), 119 (13), 118 (29), 117 (6), 115 (39), 109 (7), 107 (5), 106 (17), 93 (25), 92 (24), 91 (27), 86 (6), 83 (8), 82 (22), 81 (5), 80 (5), 77 (53), 69 (15), 67 (24), 66 (5), 65 (21), 64 (9), 59 (5), 58 (9), 57 (5), 55 (21), 54 (24), 53 (6), 51 (16), 46 (7), 45 (16), 43 (9), 41 (27), 39 (16)
- 10** 319 (M⁺, 70), 290 (9), 277 (5), 276 (100), 274 (5), 273 (4), 263 (8), 259 (5), 204 (6), 188 (35), 187 (9), 159 (5), 151 (6), 149 (12), 145 (16), 143 (5), 135 (8), 131 (5), 129 (14), 119 (8), 118 (22), 109 (5), 107 (5), 106 (9), 104 (5), 97 (5), 96 (24), 93 (35), 92 (13), 91 (15), 84 (5), 81 (16), 79 (7), 77 (37), 69 (15), 67 (6), 65 (11), 59 (6) 57 (5), 55 (20), 54 (16), 53 (6), 51 (11), 45 (10), 43 (6), 42 (8), 41 (27), 39 (12)
- 11** 333 (M⁺, 73), 290 (39), 277 (9), 276 (81), 273 (5), 263 (10), 232 (5), 204 (7), 202 (51), 186 (5), 171 (6), 170 (7), 156 (5), 149 (5), 145 (12), 143 (14), 135 (13), 130 (5), 129 (5), 123 (5), 119 (11), 118 (39), 115 (5), 110 (24), 109 (6), 108 (17), 107 (10), 106 (14), 95 (13), 93 (100), 92 (29), 91 (24), 86 (10), 83 (11), 82 (17), 81 (7), 80 (7), 77 (59), 69 (20), 68 (9), 67 (21), 65 (24), 64 (7), 60 (5), 59 (17), 57 (9), 56 (8), 55 (24), 54 (24), 51 (16), 50 (6), 46 (11), 45 (17), 43 (10), 42 (6), 41 (53), 39 (24)
- 12** 279 (M⁺, 49), 266 (5), 265 (12), 264 (100), 233 (8), 218 (6), 192 (16), 150 (5), 149 (5), 148 (30), 147 (15), 145 (17), 135 (7), 133 (22), 132 (11), 131 (9), 130 (8), 119 (6), 118 (25), 117 (5), 108 (5), 107 (21), 106 (33), 100 (17), 93 (14), 92 (36), 91 (26), 86 (6), 77 (40), 65 (11), 64 (8), 63 (6), 60 (13), 59 (6), 58 (6), 57 (15), 56 (37), 51 (19), 45 (11), 44 (5), 42 (39), 41 (18), 39 (10)
- 13** 293 (M⁺, 19), 278 (12), 266 (5), 264 (100), 247 (6), 236 (8), 218 (9), 192 (14), 162 (21), 151 (5), 149 (7), 147 (7), 145 (7), 135 (7), 133 (10), 120 (11), 118 (23), 109 (5), 107 (5), 106 (9), 93 (24), 92 (17), 91 (15), 77 (31), 71 (5), 70 (12), 65 (11), 64 (6), 59 (10), 58 (7), 57 (5), 55 (17), 51 (8), 45 (6), 43 (31), 42 (35), 41 (8), 39 (7)
- 14** 307 (M⁺, 13), 278 (100), 250 (8), 234 (6), 232 (8), 206 (14), 176 (11), 151 (5), 147 (7), 145 (5), 135 (5), 120 (9), 118 (21), 106 (5), 93 (22), 92 (11), 91 (14), 86 (5), 84 (6), 77 (23), 65 (9), 56 (33), 51 (6), 41 (10), 39 (5)
- 15** 321 (M⁺, 1), 264 (76), 263 (5), 236 (9), 220 (7), 218 (100), 192 (13), 190 (8), 151 (5), 150 (7), 149 (7), 145 (10), 135 (5), 132 (5), 118 (15), 109 (6), 93 (7), 92 (13), 91 (20), 77 (45), 65 (11), 59 (5), 57 (27), 55 (6), 51 (9), 45 (8), 43 (7), 42 (20), 41 (27), 39 (9)
- 16** 293 (M⁺, 46), 280 (5), 278 (100), 250 (6), 248 (6), 232 (8), 165 (7), 162 (41), 149 (7), 147 (21), 146 (7), 145 (5), 124 (5), 121 (13), 120 (17), 118 (5), 106 (68), 105 (11), 104 (8), 100 (11), 98 (7), 91 (16), 79 (6), 78 (9), 77 (15), 77 (15), 69 (9), 65 (11), 60 (5), 58 (9), 57 (8), 56 (34), 53 (5), 45 (6), 42 (11), 41 (9)
- 17** 321 (M⁺, 12), 292 (100), 264 (9), 248 (5), 246 (9), 220 (11), 190 (13), 165 (7), 161 (6), 134 (10), 132 (11), 131 (5), 107 (14), 106 (28), 105 (5), 91 (11), 84 (5), 65 (5), 56 (28), 41 (9)
- 18** 243 (M⁺, 67), 215 (12), 214 (100), 197 (6), 187 (8), 186 (12), 170 (11), 169 (7), 168 (12), 157 (6), 149 (16), 143 (8), 142 (26), 129 (19), 128 (8), 126 (5), 115 (25), 112 (8), 111 (13), 109 (5), 97 (6), 86 (6), 84 (6), 83 (14), 82 (15), 80 (6), 74 (5), 71 (7), 70 (5), 69 (9), 67 (16), 65 (5), 60 (8), 59 (7), 57 (20), 56 (11), 55 (23), 54 (24), 53 (6), 46 (9), 45 (12), 44 (5), 43 (21), 42 (11), 41 (31), 40 (6), 39 (15)
- 19** 257 (M⁺, 56), 228 (8), 214 (100), 212 (5), 201 (15), 186 (8), 170 (6), 168 (7), 149 (5), 142 (13), 129 (14), 126 (5), 125 (5), 97 (5), 96 (11), 83 (5), 81 (13), 72 (5), 69 (10), 67 (8), 60 (8), 57 (12), 55 (20), 54 (16), 53 (7), 45 (9), 43 (14), 42 (10), 41 (29), 39 (9)
- 20** 271 (M⁺, 55), 228 (38), 227 (5), 225 (34), 224 (7), 215 (11), 214 (100), 211 (13), 201 (6), 186 (7), 182 (7), 170 (10), 169 (6), 168 (10), 157 (5), 155 (5), 149 (5), 143 (13), 142 (13), 138 (7), 131 (21), 130 (7), 129 (5), 122 (7), 115 (6), 112 (7), 111 (6), 110 (7), 109 (7), 108 (7), 101 (7), 97 (5), 95 (44), 94 (5), 89 (7), 86 (8), 85 (7), 83 (18), 82 (20), 81 (13), 80 (8), 79 (7), 74 (7), 73 (9), 69 (11), 67 (20), 62 (6), 60 (7), 59 (8), 58 (7), 57 (26), 56 (9), 55 (21), 54 (13), 53 (8), 46 (14), 45 (21), 44 (5), 43 (33), 42 (13), 41 (44)

Table 2 (continued)

21	249 (M ⁺ , 42), 236 (7), 234 (100), 193 (6), 192 (31), 151 (10), 149 (5), 148 (39), 147 (13), 133 (23), 132 (6), 119 (7), 118 (16), 108 (6), 107 (22), 106 (25), 104 (5), 100 (13), 93 (11), 92 (29), 82 (5), 77 (16), 71 (7), 69 (5), 65 (6), 64 (10), 63 (6), 57 (14), 56 (9), 51 (5), 43 (63), 42 (14), 41 (14), 39 (20)
22	274 (M ⁺ , 71), 246 (6), 230 (7), 229 (52), 228 (23), 202 (74), 201 (5), 200 (5), 185 (11), 183 (67), 160 (6), 157 (31), 156 (32), 149 (9), 132 (11), 130 (14), 127 (8), 118 (9), 116 (5), 112 (5), 104 (9), 101 (5), 99 (5), 97 (8), 91 (6), 88 (31), 87 (6), 86 (27), 83 (22), 73 (12), 71 (23), 70 (5), 69 (17), 61 (5), 60 (27), 59 (11), 58 (8), 57 (12), 56 (10), 55 (9), 46 (10), 45 (34), 44 (18), 43 (100), 42 (26), 41 (12), 40 (27), 39 (5)

substituent R¹ at N-2 is either a methyl or an aryl group and the substituent R² at N-4 a methylallyl (**1-6**), ethoxycarbonyl (**9-20**) or a methyl group (**7** and **8**). In compound **21** the N-4 substituent, however, is an acetyl group. Compound **22** differed substantially from the others; because of the C(5)-N(1) double bond it should actually be classified as a dihydrotriazole. The substitution at C-5 is also entirely different from that in the other compounds studied. Many 1,2,4-triazolidinethiones are important because of their herbicidal [2-5], fungicidal [6-10] or pharmacological [11] activities.

Compounds 1-8.

Compounds **1-4** which are most closely related to those derivatives studied in our earlier report [1] behaved also quite similarly. They fragmented through four major routes [1] (Scheme 1), although the intensities of the ions formed varied from compound to compound. The base

peak of compound **1** was caused by the ion [R¹R²CN₂S]⁺⁺ (B⁺⁺) formed *via* cleavage of the bonds N(1)-N(2) and N(4)-C(5). The ion of m/z 185 is obtained through loss of HS[•] from the ion B⁺⁺. A cleavage of the bonds N(1)-N(2) and C(3)-N(4) leads to the ion [R¹NCS]⁺⁺ (A⁺⁺) and that of the bonds N(2)-C(3) and N(4)-C(5) to the ion [R¹R³R⁴CHN₂]⁺⁺ (C⁺⁺). Also the ion [R³R⁴CN₂N]⁺ (D⁺) was observed. It is formed *via* dissociation of the bonds N(1)-N(2) and N(4)-C(5) accompanied by a hydrogen transfer. The ion of m/z 106 had an elemental composition [C₇H₈N]⁺ (and corresponded probably the structure [R¹NH]⁺).

The molecular ion of **2** was nearly nonexistent due to the influence of the conjugated spiro substituent [1]. In this case the ion C⁺⁺ gave the base peak and the ion B⁺⁺ was the next most favoured one. The peaks corresponding to the ions A⁺⁺, D⁺ and [B-SH]⁺ were also quite abundant (Scheme 1).

The ion C⁺⁺ was responsible for the base peak in the spectrum of **3**. Instead in the case of **4** that was given by the ion [C₇H₈N]⁺ (m/z 106). In addition to the ions A⁺⁺, B⁺⁺, [B-SH]⁺, C⁺⁺ and D⁺ (Scheme 1) mentioned above, the ion m/z 113 was quite abundant (especially in the spectrum of compound **3**) and had according to accurate mass measurements an elemental composition [C₃H₃N₃S]⁺⁺. In the case of compound **3** the abundant formation of the ion [C-NH₃]⁺⁺ (m/z 208) must be promoted by the 2-pyridyl substitution at C-5 since **4** showed practically no such ion.

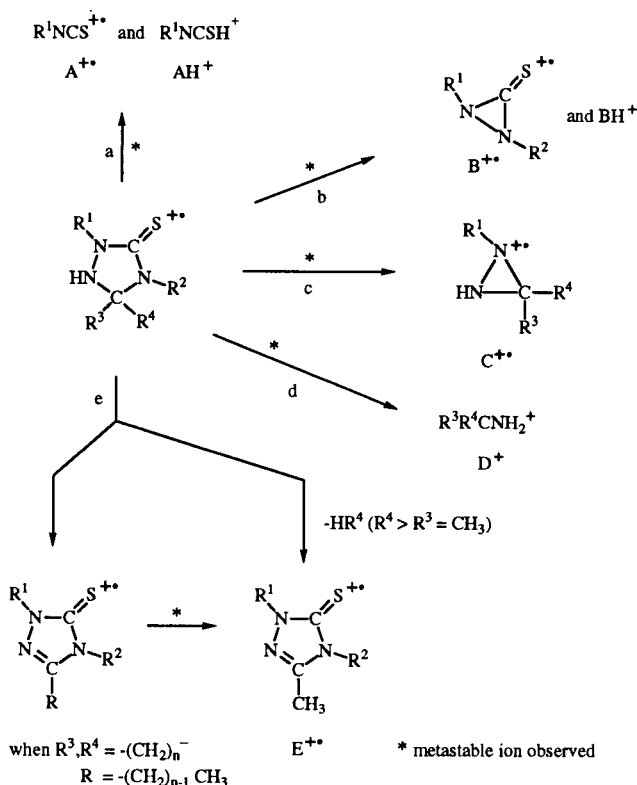
Replacing the aromatic substituent R¹ with methyl [1] changes the fragmentation pattern so that instead of the ions A⁺⁺ and B⁺⁺ the ions AH⁺ and BH⁺ appear. This situation also prevailed in compounds **5** and **6**. Additionally an ion [C-H]⁺ was formed (relative abundance, 15-20%). The ion of m/z 103 corresponded to a composition [C₈H₇]⁺ and the ion of m/z 104 [C₇H₆N]⁺.

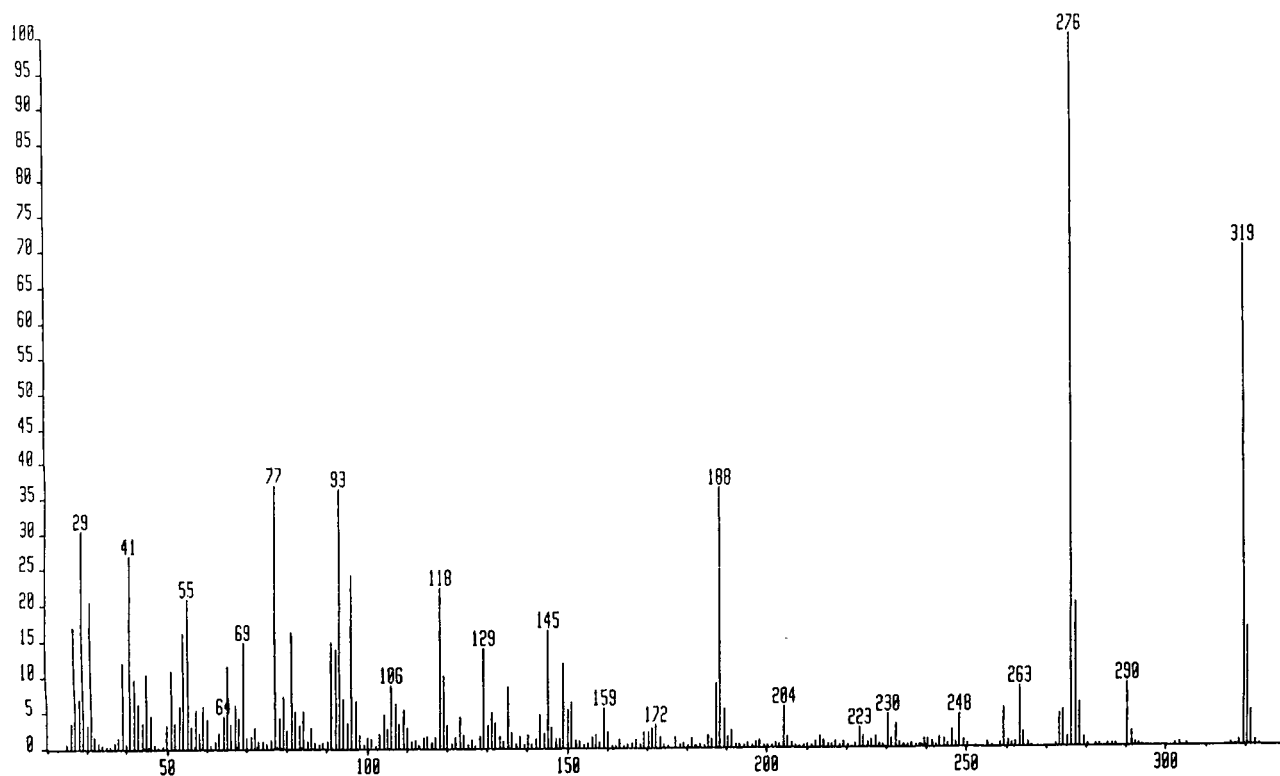
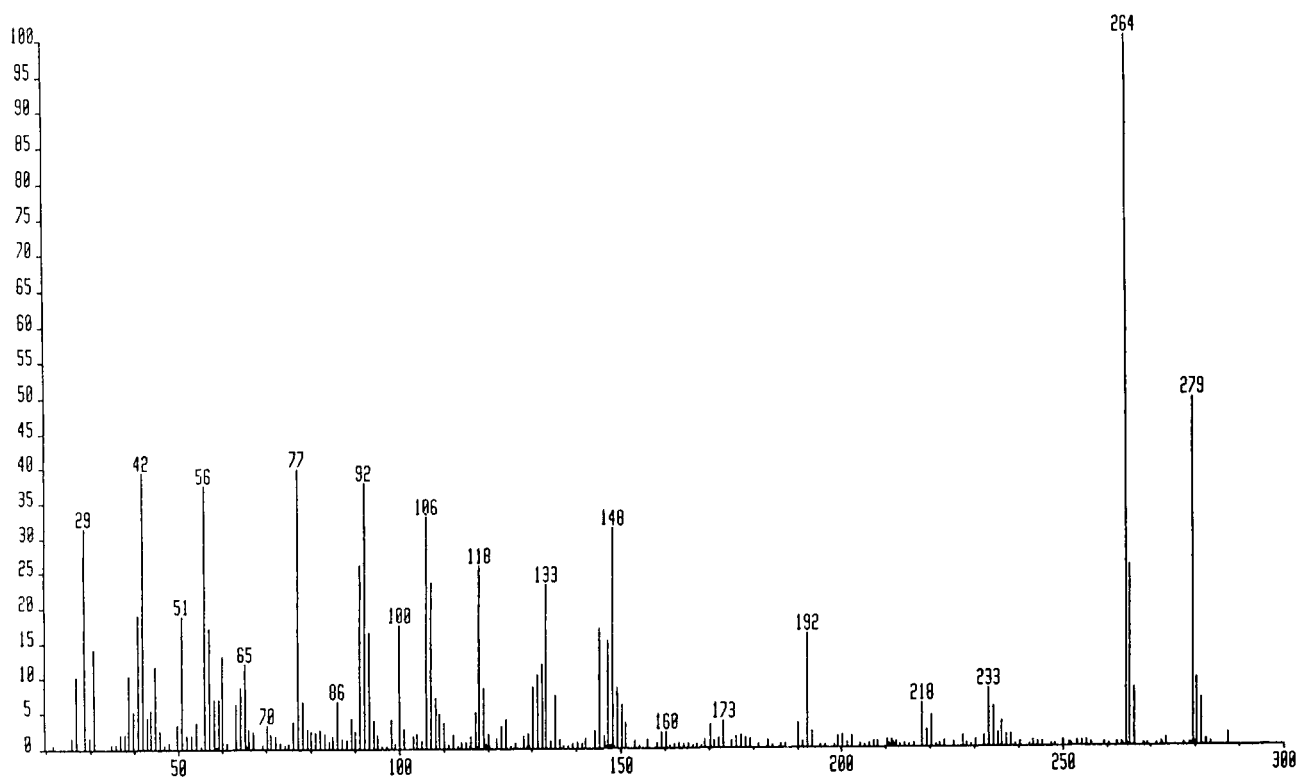
In accordance with our earlier results [1] the abundance of the ion [R¹R²C₃H₃N₃S]⁺⁺ (E⁺⁺) was remarkable when R² was a methyl group (compounds **7** and **8**). The other important fragment ions originated by loss of alkyl radicals from the molecular ions.

Compounds 9-11.

The ethoxycarbonyl group as the substituent R² at N-4 changed the fragmentation patterns totally. The molecular

Scheme 1



Figure 1. 70 eV mass spectrum of **10**.Figure 2. 70 eV mass spectrum of **12**.

ion of **9-11** is always very stable (relative abundance, *ca.* 70%). Compounds **10** (Figure 1) and **11** showed some formation of the product E^{++} (m/z 263, Scheme 1). The ions B^{++} and D^+ were not observed at all. Appreciable amounts (relative abundance, 30-50%) of the ion C^{++} (m/z 174, 188 or 202, respectively) were formed and the ion A^{++} (m/z 135) in a lesser amount. Loss of alkyl radicals from the spiro ring ($-R^3-R^4$) became very abundant. The ions $[M-Et]^+$ and $[M-Pr]^+$ (m/z 276) characteristic for spiro compounds formed the base peaks of the spectra of compounds **9** and **10**, respectively. Similarly, the ion $[M-Bu]^+$ was the second most intensive peak in the spectrum of **11**. The abundances of all the other fragment ions obtained directly from the molecular ion were at a much lower level.

In many fragmentations of compounds **9-11** the substituent $R^2 = COOEt$ played an important role. The ion $[M-R]^+$ was very weak except for **9** (m/z 232/9%). Loss of $C_3H_5^{\cdot}$ from that ion gave the ion m/z 191. Only the M^{++} ions of **9** and **10** showed some loss of EtOH giving rise to ions m/z 259 and 273, respectively. The peak m/z 230 was formed through two pathways: from the ion m/z 276 *via* loss of ethanol or from the ion $[M-EtOH]^{++}$ *via* elimination of an alkyl radical. Loss of C_2H_4 from the ion m/z 276 gave the peak at m/z 248 (McLafferty) and loss of $COOC_2H_4$ (or the elements of C_2H_4 and CO_2) the ions at m/z 204.

The peak at m/z 145 was a triplet, whose main component had a composition $[C_4H_5N_2O_2S]^+$. The ions m/z 118,

106, 93 (which corresponded to the base peak in the spectrum of **11**), 92 and 91 had elemental compositions $[C_7H_6N_2]^+$, $[C_7H_8N]^+$, $[C_6H_7N]^+$, $[C_6H_6N]^+$ and $[C_6H_5N]^+$, respectively, and could undoubtedly be born by many mothers. The routes of formation for the ions $[C_4H_7N_2O_2]^+$ (m/z 115; from **9**), $[C_5H_9N_2O_2]^+$ (m/z 129; from **10**) and $[C_6H_{11}N_2O_2]^+$ (m/z 143; from **11**) remained slightly unclear although most obviously consist of the consecutive losses of $C_4H_7^{\cdot}$ and PhNCS from the M^{++} ions.

Compounds **12-17**.

The molecular ions of compounds **12** (Figure 2) and **16** were relatively abundant, but less so for compounds **13-15** and **17** since the larger the substituents at C-5 the easier they are lost. That is why the relative abundance of the molecular ion of compound **15** was only *ca.* 1%. The very easy loss of the *tert*-butyl group is due to the steric crowding and strain it causes in its environment and on the other hand to the stability of the *tert*-butyl cation (m/z 57). The latter is reflected also in the appearance of the mass spectrum of **15** where $[M-(CH_3)_3C-EtOH]^+$ ion represents the base peak whereas in the spectra of compounds **12-14** and **16-17** the base peaks (m/z 264, 278, or 292) correspond to loss of the substituent R^4 .

Parallel to compounds **9** and **10**, the molecular ion of **12** and **13** lost some ethanol giving rise to the peaks m/z 233 and 247, respectively. For compounds **14-17** the $[M-$

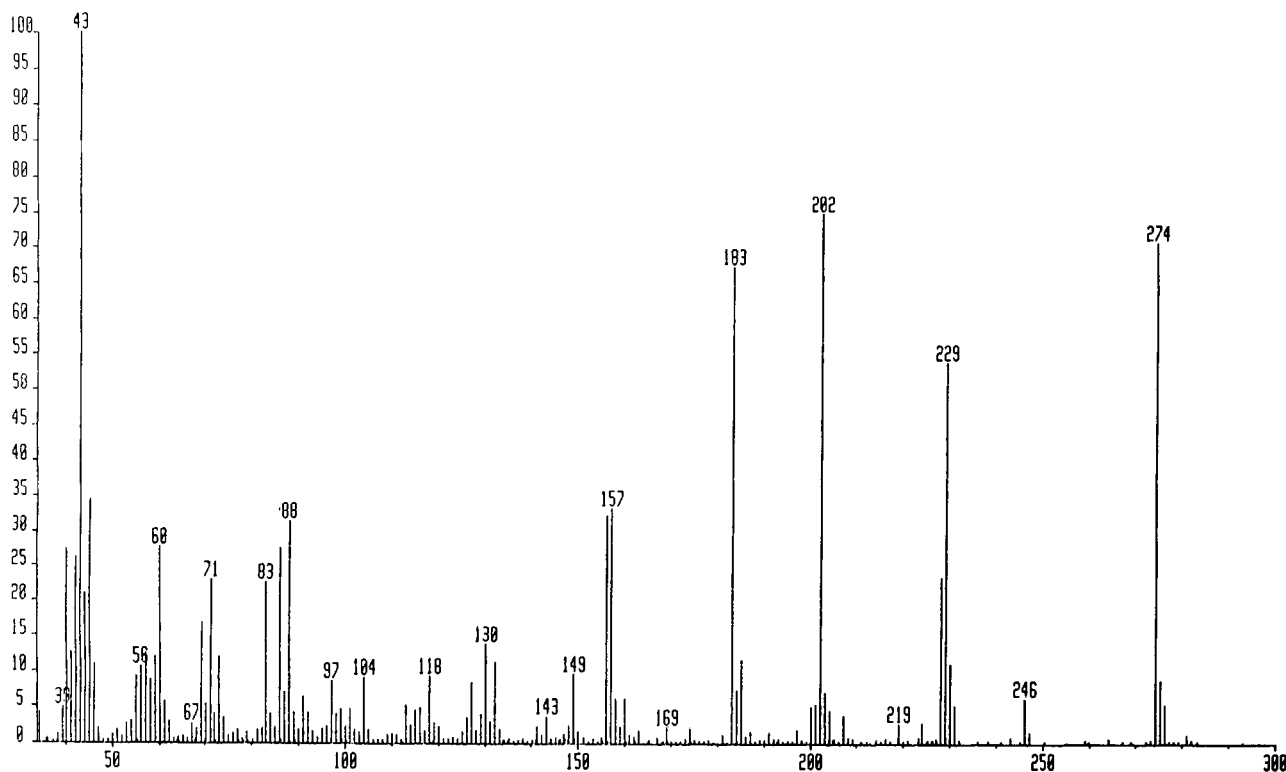


Figure 3. 70 eV mass spectrum of **22**.

EtOH]⁺ ions were even less significant. Ethanol was lost much easier from the ion [M-R^q]⁺ (m/z 264 for **12**, **13** and **15**, 278 for **13**, **14** and **16** and 292 for **17**) and the ions m/z 218, 232 and 246, respectively, were produced. A minor fraction of these ions could also be formed from the ion [M-EtOH]⁺ through loss of R⁴. An interesting group of ions at m/z 192 (**12**, **13**, **15**), 206 (**13**, **14**, **16**) and 220 (**15**, **17**) had the composition [R¹(R³ or R⁴)C₂H₂N₃S]⁺ mainly corresponding to loss of COOC₂H₄⁺ from the ions [M-R^q]⁺ or [M-R³]⁺ (Table 2).

The spectra of compounds **12-15** showed also the ions A⁺ (m/z 135) and C⁺ (m/z 148, 162, 176 or 190) and the spectra of **16** and **17** the ion C⁺ (m/z 162 or 190). The ion C⁺ in turn lost one or the other of the substituents R³, R⁴ and gave rise to ions m/z 133 (**12**, **13**, **15**), 147 (**13**, **14**, **16**), 161 (**17**), and 175 (**15**).

In contrast to the situation in compounds **9-11**, in the case of **12** the main component of the doublet at m/z 145 had a composition [C₈H₅N₂O]⁺. The ions of m/z 107, 106, 100, 92 and 91 had compositions [C₇H₉N]⁺, [C₇H₈N]⁺, [C₄H₆NS]⁺, [C₆H₆N]⁺ and [C₆H₅N]⁺.

Compounds **18-20**.

Compounds **18-20** behave quite similarly to compounds **9-11**. For instance, **18** gave no E⁺ ion (Scheme 1) whereas **19** and **20** showed such ions at m/z 201. However, between compounds **20** and **11** some significant differences do exist. Compound **20** gave rise to a fairly intense [M-EtOH]⁺ ion (relative abundance, ca. 35%), whereas **11** gave no such ion. In addition the ions [C₇H₁₁]⁺ (m/z 95), [C₃H₅N₃OS]⁺ (m/z 131), [C₈H₁₂NO]⁺ (m/z 138), [C₅H₉N₃O₂]⁺ (m/z 143), and [C₇H₈N₃OS]⁺ (m/z 182) were characteristic for compound **20**.

Compound **21**.

This compound is obtained from **12** by replacing the ethoxycarbonyl group at N-4 by an acetyl group. The spectra of both compounds are very much alike (Table 2). Compound **21** gave the ion [M-R⁴-COCH₂]⁺ as **12** gave the ion [M-R⁴-COOC₂H₄]⁺ both ions at m/z 192 having the same composition. The only major differences at m/z values below 192 in the spectra of **12** and **21** were the ions m/z 145 (only **12**) and the abundant m/z 43, CH₃CO⁺ in the spectrum of **21**.

Compound **22**.

The fragmentation pattern of compound **22** (Figure 3) differs dramatically from those cases discussed above. The molecular ion was stable (relative abundance, ca. 70%). It released C₂H₄ in a McLafferty type rearrangement typical for ethyl esters giving rise to the ion of m/z 246 of relative-

ly low intensity. Instead the ions [M-EtO]⁺ (m/z 229), [M-EtOH]⁺ (m/z 228) and [M-COOC₂H₄]⁺ or [M-C₂H₄-CO₂]⁺ (m/z 202) were more abundant. When the ion [M-EtO]⁺ lost a further ethanol molecule, the ion corresponding to the peak at m/z 183 was formed. Accurate mass measurements revealed that the ions m/z 156 and 157 had elemental compositions of [C₅H₄N₂O₄]⁺ and [C₅H₅N₂O₄]⁺, respectively. The peaks at m/z 83, 86, 88, 97 and 130 corresponded to the compositions [C₃H₃N₂O]⁺, [C₂NOS]⁺, [C₂H₄N₂S]⁺, [C₃H₃N₃O]⁺ and [C₃H₆N₄S]⁺, respectively.

EXPERIMENTAL

The compounds studied (Table 1) were synthesized similarly to our earlier 1,2,4-triazolidine derivatives [12]. The EI mass spectra (Table 2) were recorded at 70 eV on a VG Analytical 7070E instrument equipped with a VG II-250 data system. The accelerating voltage was 6 kV, the temperature of the ion source ca. 453 K and the trap current 100 μA. The samples were introduced into the mass spectrometer through the solid inlet system below 330 K (for compounds **2-4** at ca 420 K) for low resolution (R = 1000), high resolution (R = 2500-4000) and metastable (B/E) measurements.

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