# Tetrazole Compounds. 11 [1]. Electron Impact Mass Spectrometry of 1-Aryl-5-(1-acyl-2-dialkylaminovinyl)-1*H*-tetrazoles



Gerhard W. Fischer*

Institut für Organische Chemie, Universität Leipzig, Aussenstelle, Permoserstrasse 15, 04303 Leipzig, Germany

Michael Herrmann

Tarostrasse 1, 04103 Leipzig, Germany

Monika Möder

Umweltforschungszentrum Leipzig-Halle GmbH, Permoserstrasse 15, 04318 Leipzig, Germany

Received September 15, 1995

**In memory of Professor Nicholas Alexandrou**

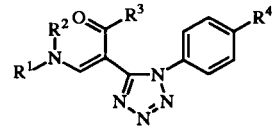
The mass spectrometric behaviour of 1-aryl-5-(1-acyl-2-dialkylaminovinyl)-1*H*-tetrazoles was studied, especially using 1-phenyl-5-(1-benzoyl-2-dimethylaminovinyl)-1*H*-tetrazole **1** and its *D*-and $^{15}N$-labeled derivatives. All tetrazoles investigated showed a clearly observable molecular ion and underwent as the main fragmentation the elimination of nitrogen followed by a number of various subsequent processes. Besides, primary fragments such as $[M - N_3^{\bullet}]^+$ and $[M - ArN_3]^{+\bullet}$ were also observed.

*J. Heterocyclic Chem.*, **33**, 815 (1996).

## Introduction.

1-Aryl-5-(1-acyl-2-dialkylaminovinyl)-1*H*-tetrazoles, *i.e.* tetrazolyl-substituted enamino ketones, recently proved to be useful intermediates in the synthesis of novel pyrazolyl- and isoxazolyltetrazoles [2] as well as tetrazolylpyrimidines [3]. At the same time they provide the possibility to investigate how the mass spectrometric behaviour of 1,5-disubstituted tetrazoles is influenced by a more complex substituent at position 5.

It is known from the literature [4] that the nature of substituents plays an important role for the preferred fragmentation pathways of 1,5-disubstituted tetrazoles. Thus, for example, in the case of 5-alkyl- or 5-aryl-1-methyl-1*H*-tetrazoles [5,6] the most significant process is the initial loss of $NH_2^{\bullet}$ followed by ejection of HCN, whereas the loss of $N_3^{\bullet}$ and $N_2$ is only of minor importance. However, important loss of $N_2$ upon electron impact is observed with a number of 1,5-disubstituted tetrazoles containing substituents such as $CO_2Me$ or aryl groups at both the 1- and 5-positions [7]. A similar behaviour involving some surprising rearrangements, especially the formation of a carbodiimide radical as an intermediate, we found for 1-aryl-5-(2-dialkylaminovinyl)-1*H*-tetrazoles [8]. Acylation of the latter leads to tetrazoles of type **1-26** which are the subject of the present paper. The enlargement of the substituent at position 5 opens additional possibilities for skeletal rearrangements. In the following we will discuss the electron impact mass spectra of **1-26** and propose mechanisms of the fragmentation pathways supported by MIKE spectra and comparative studies with isotope labeled derivatives.



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| **1** | $CH_3$ | $CH_3$ | $C_6H_5$ | H |
| **2** | $CH_3$ | $CH_3$ | $C_6H_5$ | $CH_3$ |
| **3** | $CH_3$ | $CH_3$ | $C_6H_5$ | $C_2H_5$ |
| **4** | $CH_3$ | $CH_3$ | $C_6H_5$ | $OCH_3$ |
| **5** | $CH_3$ | $CH_3$ | 3-F-$C_6H_4$ | H |
| **6** | $CH_3$ | $CH_3$ | $C_6H_5$ | F |
| **7** | $CH_3$ | $CH_3$ | 4-Cl-$C_6H_4$ | H |
| **8** | $CH_3$ | $CH_3$ | 3-Cl-$C_6H_4$ | H |
| **9** | $CH_3$ | $CH_3$ | $C_6H_5$ | Cl |
| **10** | $CH_3$ | $CH_3$ | $C_6H_5$ | Br |
| **11** | $CH_3$ | $CH_3$ | 4-$NO_2$-$C_6H_4$ | H |
| **12** | $CH_3$ | $CH_3$ | $CH_3$ | H |
| **13** | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ |
| **14** | $CH_3$ | $CH_3$ | $CH_3$ | $C_2H_5$ |
| **15** | $CH_3$ | $CH_3$ | $CH_3$ | $OCH_3$ |
| **16** | $CH_3$ | $CH_3$ | $CH_3$ | F |
| **17** | $CH_3$ | $CH_3$ | $CH_3$ | Cl |
| **18** | $CH_3$ | $CH_3$ | $CH_3$ | Br |
| **19** | $CH_3$ | $CH_3$ | $CH_3$ | I |
| **20** | $CH_3$ | $CH_3$ | $CH_3$ | $C_6H_5$ |
| **21** | $CH_3$ | $CH_3$ | $C_2H_5$ | H |
| **22** | $CH_3$ | $CH_3$ | $C_3H_7$ | H |
| **23** | $CH_3$ | $CH_3$ | $CH_2Cl$ | H |
| **24** | $(CH_2)_4$ | | $CH_3$ | H |
| **25** | $(CH_2)_5$ | | $CH_3$ | H |
| **26** | $(CH_2)_6$ | | $CH_3$ | H |

## Results and Discussion.

An immediately striking fragmentation in the mass spectrum of **1** and its derivatives is the loss of dinitrogen from the molecular ion. The resulting radical ion (ion *a*) undergoes a skeletal rearrangement to a carbodiimide structure. This is the only way to explain the composition

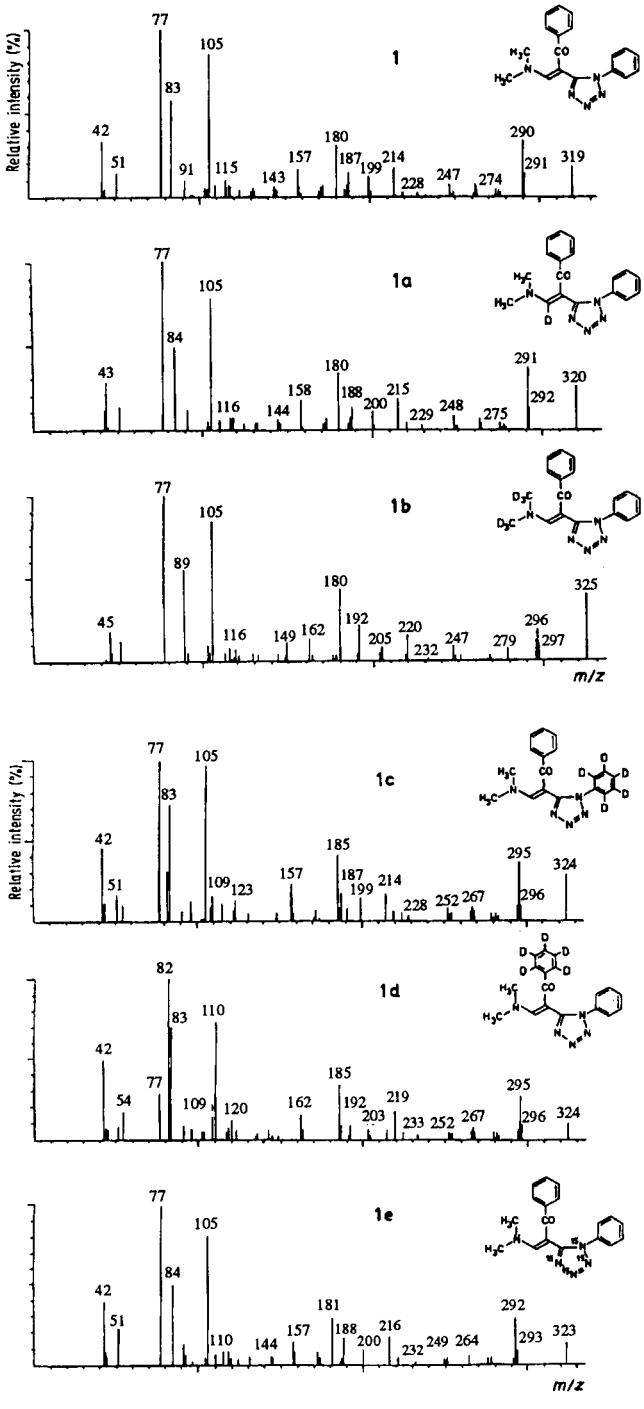



Figure 1. Mass spectra of compound **1** and its labeled derivatives **1a-1e**.

of some succeeding ions, suddenly containing a nitrogen atom of the tetrazole ring system rather than its carbon atom. It can be best demonstrated by the example of ion m/z 83 (see Figure 1). The deuterated species **1a** and **1b** show the corresponding shift by one or six amu respectively for this ion. Thus, the dimethylaminovinyl side chain is involved in this fragment ion in any way.

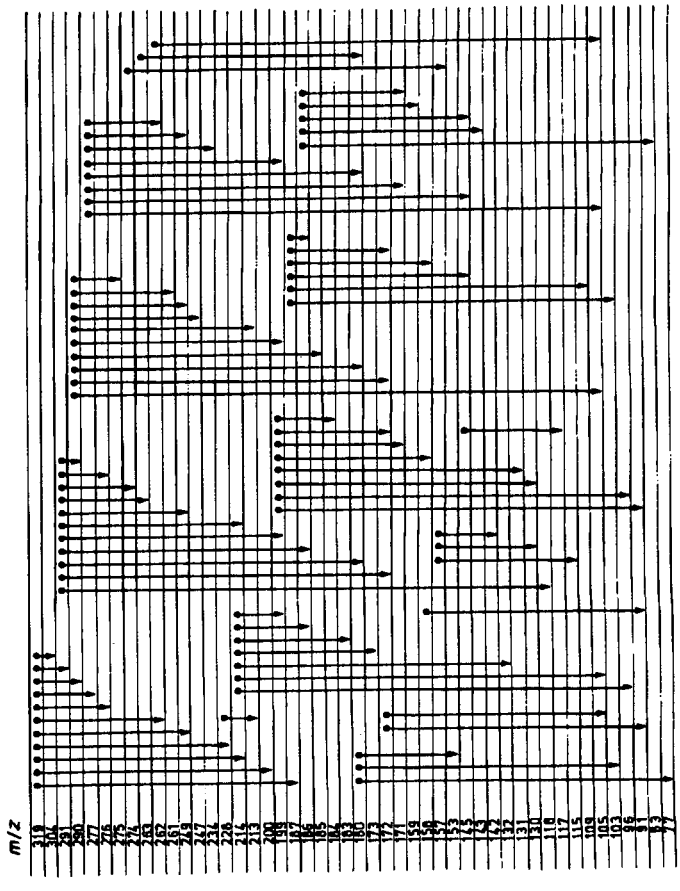
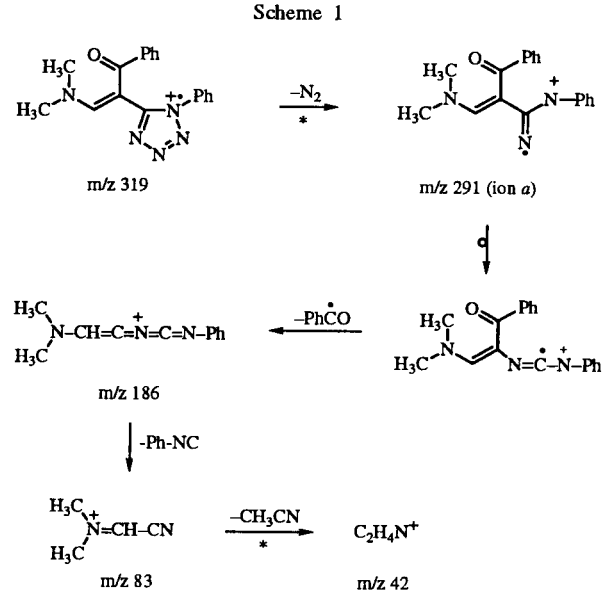



Figure 2. MIKE spectra of compound **1**.

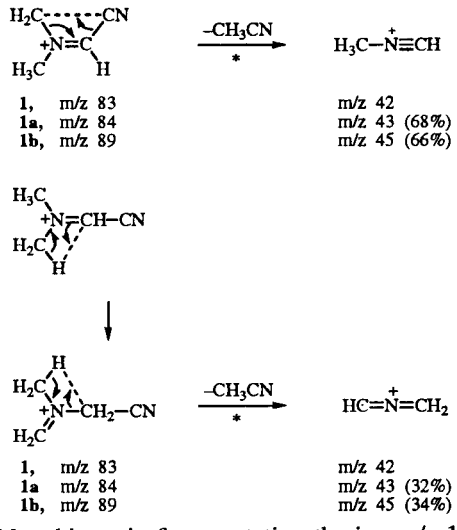
However, the $^{15}N$-labeled compound **1e** also exhibits a shift of 1 amu. Precursor of m/z 83 is the ion m/z 186 (see Figure 2). In accordance with all isotope shifts a fragmentation path shown in Scheme 1 can be proposed.

Scheme 1



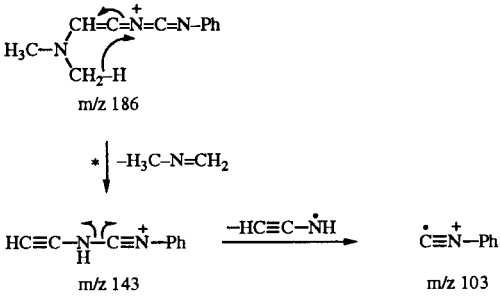
The further decay of ion m/z 83 occurs by the elimination of acetonitrile leading to ion m/z 42. Comparison between spectra **1, 1a** and **1b** respectively reveals two ways on which the split acetonitrile is formed: About two thirds originates from the transfer of a methyl group, the other third originates *via* a twofold hydrogen shifting (Scheme 2).

Scheme 2



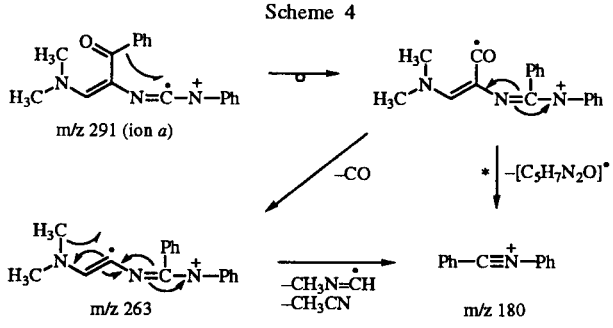

Besides this main fragmentation the ion m/z 186 decays in a second way to ion m/z 143 by loss of *N*-methylmethyleneimine. As to see in spectrum **1b** one hydrogen atom is transferred from the dimethylamino group to the resulting ion in this reaction (Scheme 3).

Scheme 3




Another decay exclusively derivable *via* the carbodiimide is the formation of ion m/z 180. In this ion both phenyl substituents are involved as well as one nitrogen atom of the former tetrazole ring. The isotope shifts of m/z 180 in spectra **1c, 1d** and **1e** speak unequivocally for that composition and the explanation is a migration of phenyl from the benzoyl substituent in ion *a* (m/z 291) to the radical carbon atom, followed by the expelling of smaller particles either directly or across the intermediate ion m/z 263 (Scheme 4).

Scheme 4

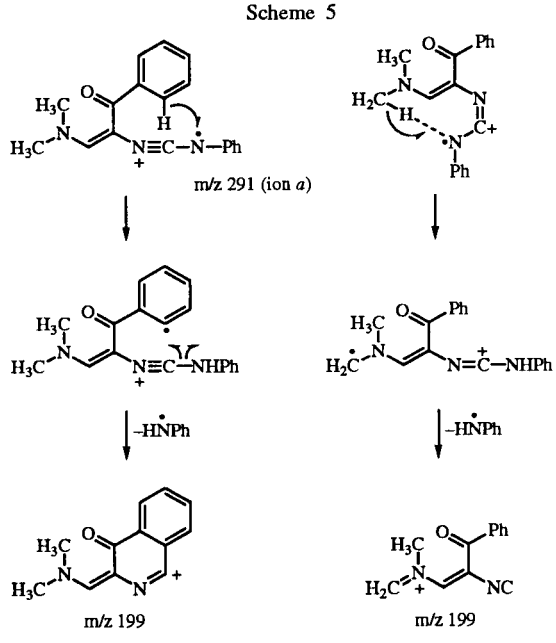



A further competitive fragmentation pathway takes its course *via* ion m/z 249. Its explanation requires a twofold hydrogen radical migration as well as tautomeric rearrangements. But the mean source of the phenylbenzonitrilium cation m/z 180 is another precursor (see below).

Besides this ion a methylbenzonitrilium cation m/z 118 is formed, obviously by migration of a methyl group in ion *a* to the radical carbon atom of the carbodiimide moiety and the subsequent decay of the intermediate in a benzoyl radical, a neutral part of 68 amu (presumably $CH_3$-N=CH-CN) and the ion $[CH_3\text{-}C{\equiv}N\text{-}C_6H_5]^+$ at m/z 118. The origin of methyl from the dimethylamino group is discernible by the shift of 3 amu in spectrum **1b**: About half of the peak intensity of m/z 118 is shifted to m/z 121. Thus, peak m/z 118 in **1** contains a second fragment ion, possibly the carbodiimide $[HN{=}C{=}N\text{-}C_6H_5]^{+\bullet}$. This would explain the behaviour of m/z 118 in spectrum **1e**: About half of it is shifted to m/z 119 as expected, the other half is shifted for two units to m/z 120, thus indicating the presence of two labeled nitrogen atoms from the tetrazole ring.

Somewhat more complicated is the loss of 92 amu from the carbodiimide radical ion m/z 291. The separated radical can be nothing else but $C_6H_5NH^{\bullet}$. One of the original tetrazole nitrogen atoms remains in the resulting ion m/z 199 as seen in spectrum **1e**. But the transferred hydrogen has two sources. An amount of 60% arises from the phenyl group of

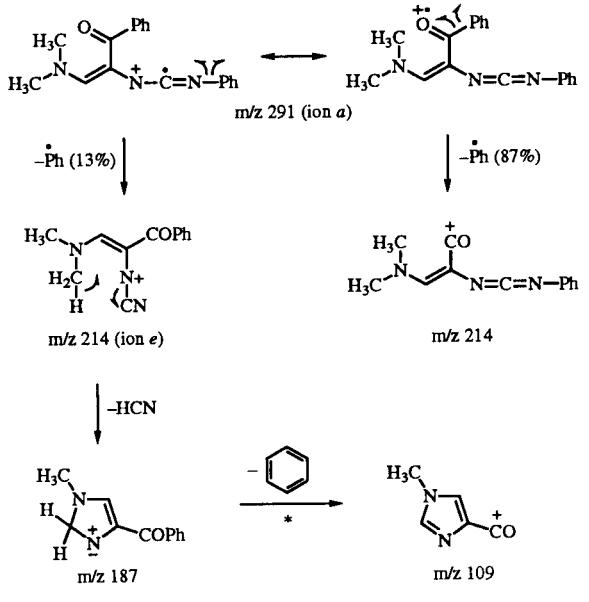
Scheme 5



the benzoyl substituent and 40% derives from the dimethylamino group. This is the reason for the division of the corresponding labeled fragments in two parts with different mass numbers. In spectrum **1b** the m/z 199 is shifted to m/z 204 and m/z 205, and in **1d** there is a shift to m/z 203 and m/z 204, respectively. Thus, peak m/z 199 is composed by two fragments with different structures, as demonstrated in Scheme 5. However, the evidences for the proposed structures are poor due to the small significance of further decays, consisting of loss of methyl, hydroxyl, water, hydrocyanic acid, carbon monoxide and acetonitrile.

A coincidence of two different structures exists also at m/z 214. The loss of phenyl from the ion m/z 291 takes place from the benzoyl substituent (87%) as well as from the carbodiimide moiety (13%). The percentages could be estimated analysing the MIKE spectra of **1c** and **1d**. In the normal mass spectra of both deuterated compounds a peak intensity comparison of m/z 214 and the correspondingly shifted m/z 219 would be erroneous, because a direct loss of 105 amu from the molecular ion m/z 319 also contributes to m/z 214. (At the first glance this mass difference seems to be the benzoyl radical, but a closer look at mass spectrum **1e** reveals for m/z 214 a shift of merely two mass units to m/z 216 rather than four. Thus, the tetrazole ring is decomposed, inclusively with the removal of the substituted phenyl group). Scheme 6 shows the descent of the ions at m/z 214.

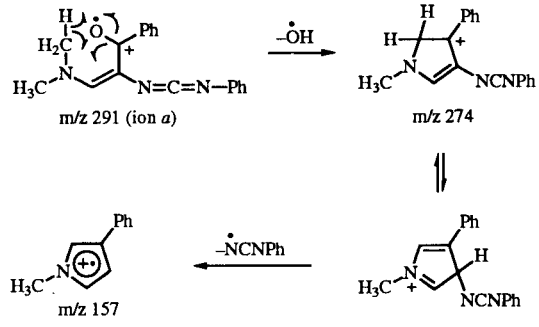
Scheme 6




The further decay could be elucidated only for one of the structures (see later discussion). For the other structure the MIKE spectra of **1c** and **1d** do not deliver a determined picture: The split mass differences like 16, 30, 31 and 39 amu might be seen as hints to other extensive rearrangements.

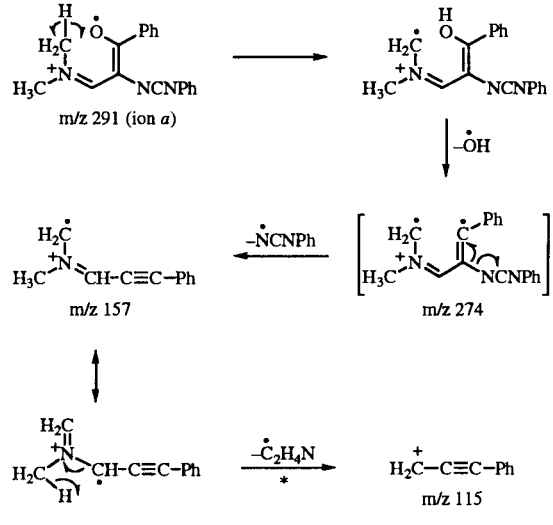
A rather unexpected fragmentation is the separation of a hydroxyl radical from the radical ion $[M - N_2]^{+\bullet}$ (ion *a*). A comparison between **1** and **1b** demonstrates the dimethylamino group as the source of the transferred hydrogen: The peak m/z 274 is shifted for only five mass units to m/z 279 in **1b**. During the next step we observed the loss of the phenylcarbodiimide radical yielding the ion m/z 157. At the first glance the formation of an aromatic ring structure like a pyrrolium cation seems to be the most plausible explanation (Scheme 7).

Scheme 7




However, the further decay of m/z 157 to an ion m/z 115 takes place with a specific hydrogen transfer. In spectrum **1b** the m/z 115 shifts to 116 for only one mass unit. And the shifting of one unit in spectrum **1a** proves the undivided participation of the deuterated structure adjacent to the amino nitrogen in the formation of ion m/z 115. Moreover, the latter contains the phenyl part of the original benzoyl substituent, as seen in spectrum **1d**. For these reasons a formulation of ion m/z 274 as an open structure and, for better understanding, as temporary double radical ion is perhaps the better way to explain this fragmentation path (Scheme 8).

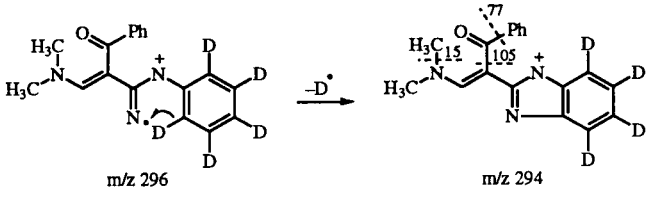
Scheme 8




It is difficult to explain the hydrogen cleavage from the radical ion m/z 291. The labeling experiments indicate

three different hydrogen sources within the molecule: The dimethylamino group and both phenyl substituents. The contribution of the latter amounts to about 20% each (see Figure 1, **1c** and **1d**). This result would fit to a conception of ten favoured positions for the hydrogen radical abstraction: Besides the six hydrogen atoms of the dimethylamino group the four *ortho* positions of both phenyls could come into question. But the contribution of the dimethylamino group to the hydrogen loss runs only to 33% rather than to the expected 60%. The apparent deficit can also be explained in another way; that of the origin of the ion m/z 290, *i.e.* the direct loss of 29 amu ($N_2$ and H$^\bullet$) from the molecule ion. Here the hydrogen is split off exclusively from the phenyl substituents. Indirect evidence delivers the mass spectrum of compound **4**: The introduction of a methoxy group into the phenyl ring suppresses by its stabilizing effect of the hydrogen radical loss, thus decreasing the intensity of ion *b* (see Table 1). This "ion *b*" consists in practice of three different structures or even more. An effort to assign these structures was attempted by comparing the MIKE spectra of the corresponding ions [M - $N_2$ - D$^\bullet$]$^+$ of **1b**, **1c** and **1d**. However, a differentiated inspection for significant fragmentation steps allowing conclusions to the structures did not deliver clear results. *E.g.*, the structure of m/z 294 in **1c** was supposed to be a benzimidazole system, formed before the carbodiimide rearrangement could take place (Scheme 9).

Scheme 9



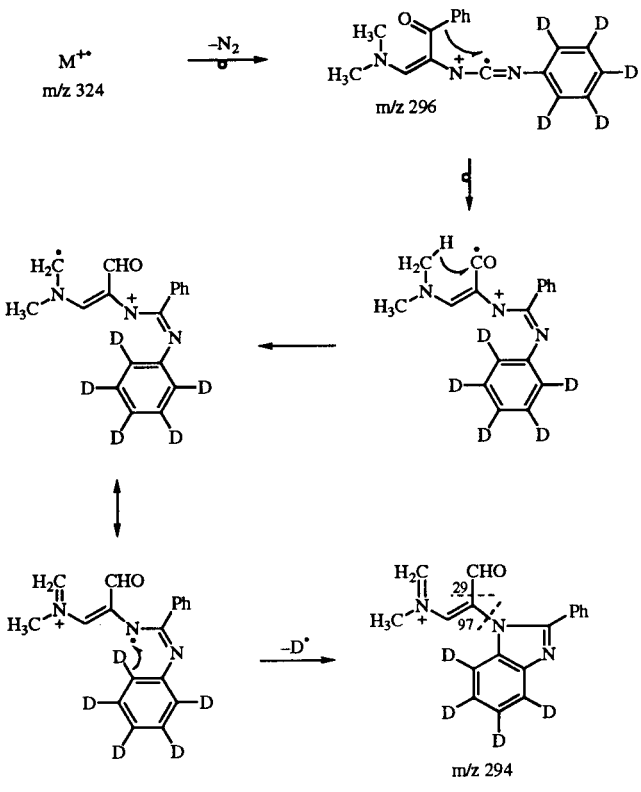

Such formation of benzimidazoles is described for the thermolytic decomposition of aryl tetrazoles [9], and the further decays by loss of a phenyl, benzoyl and methyl radical are plausible for this structure. However, mass differences like 29, 97 and 110 amu indicate the existence of further probable structures, possibly derivable from previously rearranged forms (Scheme 10).

Similarly, the MIKE spectrum of ion m/z 294 in **1d** with its mass differences of 29, 83 and 110 amu is to see it as a hint of a profoundly rearranged ion.

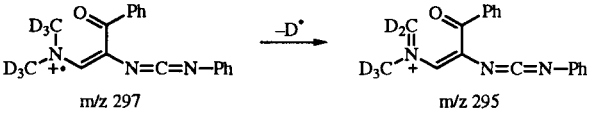
The third possible structure, caused by hydrogen loss from the dimethylamino group, has the ion [M - $N_2$]$^{+\bullet}$ (ion *a*) as the only precursor. For this reason the preceding carbodiimide rearrangement is taken into consideration (Scheme 11).

Besides the nitrogen expulsion as the predominant degradation under electron impact the molecule ion is also subjected to some not so striking fragmentations. Typical for

Scheme 10




Scheme 11




certain tetrazoles is the loss of an azide radical. In our case the resulting ion m/z 277 is quickly transformed by migration of the substituent $R^3$, *i.e.* the phenyl of the benzoyl group, and releasing of small neutrals to the obviously more stable phenylbenzonitrilium cation m/z 180, mentioned

Scheme 12

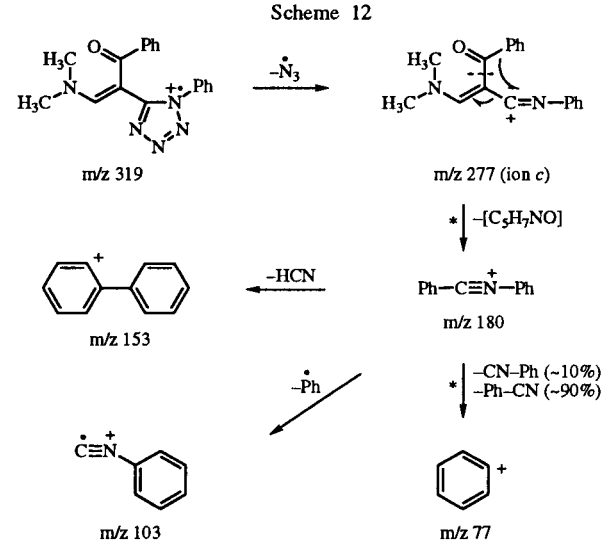


Table 1

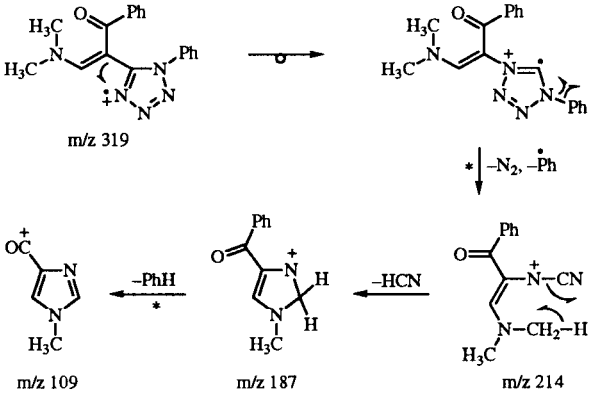
Key Ions in the Mass Spectra of Compounds **1-11** (m/z, % intensity) [a]

| | | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M^{+\bullet}$ | | 319 (18) | 333 (20) | 347 (20) | 349 (18) | 337 (25) | 337 (15) | 353 (12) | 353 (22) | 353 (20) | 397 (9) | 364 (14) |
| $[M - N_2]^{+\bullet}$ | (ion *a*) | 291 (14) | 305 (17) | 319 (17) | 321 (33) | 309 (16) | 309 (13) | 325 (9) | 325 (13) | 325 (13) | 369 (8) | 336 (13) |
| $[a - H^{\bullet}]^+$ | (ion *b*) | 290 (32) | 304 (33) | 318 (33) | 320 (16) | 308 (37) | 308 (36) | 324 (25) | 324 (32) | 324 (29) | 368 (21) | 335 (26) |
| $[M - N_3^{\bullet}]^+$ | (ion *c*) | 277 (3) | 291 (4) | 305 (5) | 307 (3) | 295 (2) | 295 (2) | 311 (2) | 311 (2) | 311 (2) | 355 (2) | 322 (3) |
| $[a - {}^{\bullet}CH_3]^+$ | | 276 (4) | 290 (6) | 304 (12) | 306 (38) | 294 (4) | 294 (3) | 310 (3) | 310 (6) | 310 (4) | 354 (5) | 321 (4) |
| $[a - {}^{\bullet}OH]^+$ | (ion *d*) | 274 (4) | 288 (5) | 302 (5) | 304 (3) | 292 (4) | 292 (4) | 308 (3) | 308 (5) | 308 (4) | 352 (3) | 319 (6) |
| $[a - CO]^+$ | | 263 (4) | 277 (6) | 291 (6) | 293 (3) | 281 (5) | 281 (4) | 297 (4) | 297 (6) | 297 (4) | 341 (2) | 308 (6) |
| $[a - C_2H_4N^{\bullet}]^+$ | | 249 (3) | 263 (6) | 277 (8) | 279 (4) | 267 (3) | 267 (2) | 283 (3) | 283 (4) | 283 (5) | 327 (4) | 294 (2) |
| $[b - CH_3NCH_2]^+$ | | 247 (7) | 261 (7) | 275 (8) | 277 (3) | 265 (5) | 265 (5) | 281 (4) | 281 (4) | 281 (4) | 325 (2) | 292 (3) |
| $[M - R^4C_6H_4CH_2^{\bullet}]^+$ | | 228 (2) | 228 (8) | 228 (2) | 228 (2) | 246 (2) | 228 (2) | 262 (1) | 262 (2) | 228 (4) | 228 (3) | 273 (3) |
| | | 219 (4) | 233 (5) | 247 (5) | 249 (3) | 237 (3) | 237 (3) | 253 (4) | 253 (2) | 253 (2) | 297 (1) | 264 (1) |
| $[a - {}^{\bullet}R^3]^+$ | | 214 (7) | 228 (8) | 242 (5) | 244 (4) | 214 (3) | 232 (5) | 214 (34) | 214 (29) | 248 (6) | 292 (3) | 214 (6) |
| $[a - {}^{\bullet}C_6H_4R^4]^+$ | (ion *e*) | 214 (7) | 214 (17) | 214 (20) | 214 (7) | 232 (12) | 214 (9) | 248 (12) | 248 (14) | 214 (52) | 214 (21) | 259 (14) |
| $[M - R^4C_6H_4N_3]^{+\bullet}$ | (ion *f*) | 200 (3) | 200 (10) | 200 (8) | 200 (3) | 218 (2) | 200 (2) | 234 (2) | 234 (4) | 200 (4) | 200 (4) | 245 (3) |
| $[a - R^4C_6H_4NH^{\bullet}]^+$ | | 199 (12) | 199 (11) | 199 (14) | 199 (7) | 217 (10) | 199 (16) | 233 (2) | 233 (9) | 199 (14) | 199 (17) | 244 (6) |
| $[e - HCN]^+$ | (ion *g*) | 187 (14) | 187 (20) | 187 (21) | 187 (21) | 205 (19) | 187 (14) | 221 (9) | 221 (18) | 187 (18) | 187 (17) | 232 (18) |
| $[a - R^3CO^{\bullet}]^+$ | (ion *h*) | 186 (7) | 200 (10) | 214 (20) | 216 (7) | 186 (7) | 204 (5) | 186 (7) | 186 (11) | 220 (4) | 264 (3) | 186 (15) |
| $[R^3\text{-}C{\equiv}N\text{-}C_6H_4R^4]^+$ | | 180 (30) | 194 (34) | 208 (35) | 210 (32) | 198 (24) | 198 (27) | 214 (34) | 214 (29) | 214 (52) | 258 (20) | 225 (10) |
| $[d - R^4C_6H_4NCN^{\bullet}]^{+\bullet}$ | (ion *i*) | 157 (16) | 157 (23) | 157 (17) | 157 (14) | 175 (14) | 157 (16) | 191 (11) | 191 (14) | 157 (20) | 157 (22) | 202 (10) |
| $[h - CH_3NCH_2]^+$ | | 143 (6) | 157 (23) | 171 (7) | 173 (14) | 143 (6) | 161 (4) | 143 (7) | 143 (8) | 177 (3) | 221 (<1) | 143 (10) |
| $[f - {}^{\bullet}R^3]^+$ | | 123 (3) | 123 (5) | 123 (6) | 123 (5) | 123 (64) | 123 (5) | 123 (5) | 123 (7) | 123 (4) | 123 (5) | 123 (6) |
| $[i - C_2H_4N^{\bullet}]^+$ | | 115 (10) | 115 (10) | 115 (9) | 115 (8) | 133 (9) | 115 (10) | 149 (10) | 149 (6) | 115 (9) | 115 (8) | 160 (6) |
| $[g - R^3H]^+$ | | 109 (7) | 109 (9) | 109 (8) | 109 (9) | 109 (7) | 109 (17) | 109 (10) | 109 (9) | 109 (8) | 109 (7) | 109 (4) |
| $R^3CO^+$ | (ion *j*) | 105 (86) | 105 (97) | 105 (81) | 105 (75) | 123 (64) | 105 (89) | 139 (77) | 139 (52) | 105 (100) | 105 (100) | 150 (13) |
| $[h - R^4C_6H_4NC]^+$ | (ion *k*) | 83 (58) | 83 (65) | 83 (56) | 83 (62) | 83 (100) | 83 (66) | 83 (100) | 83 (100) | 83 (62) | 83 (58) | 83 (100) |
| $[j - CO]^+$ | | 77 (100) | 77 (100) | 77 (100) | 77 (100) | 95 (64) | 95 (19) | 111 (59) | 111 (50) | 77 (90) | 77 (83) | 122 (1) |
| $[k - CH_3CN]^+$ | | 42 (33) | 42 (36) | 42 (32) | 42 (35) | 42 (43) | 42 (44) | 42 (53) | 42 (45) | 42 (33) | 42 (28) | 42 (37) |
| Further: | | | | | | | | | | | | |
| $R^4C_6H_4NCN^+$ | | 117 (8) | 131 (13) | 145 (9) | 147 (7) | 117 (6) | 135 (6) | 117 (8) | 117 (8) | 151 (5) | 195 (3) | 117 (8) |
| $R^4C_6H_4NC^+$ | | 103 (6) | 117 (10) | 131 (20) | 133 (8) | 103 (8) | 121 (8) | 103 (9) | 103 (8) | 137 (3) | 181 (2) | 103 (10) |
| $R^4C_6H_4N^+$ | | 91 (11) | 105 (97) | 119 (12) | 121 (30) | 91 (9) | 109 (17) | 91 (17) | 91 (15) | 125 (7) | 169 (4) | 91 (19) |
| $R^4C_6H_4^+$ | | 77 (100) | 91 (32) | 105 (81) | 107 (7) | 77 (35) | 95 (19) | 77 (41) | 77 (35) | 111 (11) | 155 (5) | 77 (30) |

[a] Values are not isotope corrected. For halogen containing compounds only the main isotope fragment is given. In case of coincidences the mass number appears twice with the same intensity for both.

above. This way is the main path of its formation, and it is completely consistent with all isotope shifts of compounds **1a-1e** (Figure 1). In the course of further decay the labeled compounds also reveal the portions of neutral benzonitrile and phenylisonitrile split off from ion m/z 180 (MIKES). The observed percentages found are nearly the same in the fragmentation of benzylideneaniline [10]. In case of taking over the positive charge by the nitrogen atom exclusively, the phenylisonitrilium ion m/z 103 comes out (Scheme 12).

Scheme 13




A third way that the tetrazole ring degraded is in the loss of $PhN_2^{\bullet}$, presumably as simultaneous separations of the nitrogen and phenyl radical. Before this step a rearrangement is supposed to have taken place, similar to the migration leading to the carbodiimide. In this case the migration leads to a 1,4-disubstituted tetrazolium radical ion and the succeeding decay yields an ion m/z 214 from which the cleavage of hydrocyanic acid is explainable, found among other steps by MIKES. The resulting ion m/z 187 lacks one hydrogen atom of the dimethylamino group, disclosed by comparison of spectra **1** and **1b**: The m/z 187 is shifted to m/z 192 (where it is superimposed by ion m/z 186-$d_6$). The structure of ion m/z 187 is supposed to be an imidazolinium ion. This provides perhaps the best explanation for the fragmentation step which follows: The surprising elimination of neutral benzene, leading to an imidazoyl cation m/z 109 (Scheme 13). Thus we have another aroyl

Table 2

Key Ions in the Mass Spectra of Compounds **12-22** (m/z, % intensity) [a]

| | | **12** | **13** | **14** | **15** | **16** | **17** | **18** | **19** | **20** | **21** | **22** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M^{+\bullet}$ | | 257 (22) | 271 (22) | 285 (30) | 287 (22) | 275 (11) | 291 (5) | 335 (2) | 383 (7) | 333 (28) | 271 (12) | 285 (20) |
| $[M - N_2]^{+\bullet}$ | (ion *a*) | 229 (4) | 243 (7) | 257 (11) | 259 (20) | 247 (7) | 263 (3) | 307 (1) | 355 (4) | 305 (29) | 243 (6) | 257 (6) |
| $[a - H^{\bullet}]^{+}$ | (ion *b*) | 228 (27) | 242 (20) | 256 (24) | 258 (12) | 246 (25) | 262 (12) | 306 (5) | 354 (13) | 304 (20) | 242 (20) | 256 (19) |
| $[M - N_3^{\bullet}]^{+}$ | (ion *c*) | 215 (4) | 229 (10) | 243 (8) | 245 (9) | 233 (3) | 249 (2) | 293 (2) | 341 (2) | 291 (6) | 229 (3) | 243 (6) |
| $[a - {}^{\bullet}CH_3]^{+}$ | | 214 (11) | 228 (14) | 242 (25) | 244 (48) | 232 (9) | 248 (5) | 292 (2) | 340 (5) | 290 (17) | 228 (6) | 242 (18) |
| $[a - {}^{\bullet}OH]^{+}$ | (ion *d*) | 212 (3) | 226 (3) | 240 (3) | 242 (3) | 230 (2) | 246 (1) | 290 (1) | 338 (1) | 288 (2) | 226 (1) | 240 (1) |
| $[a - C_2H_4N^{\bullet}]^{+}$ | | 187 (3) | 201 (4) | 215 (5) | 217 (5) | 205 (3) | 221 (2) | 265 (1) | 313 (2) | 263 (7) | 201 (<1) | 215 (2) |
| $[b - CH_3NCH_2]^{+}$ | | 185 (5) | 199 (4) | 213 (5) | 215 (2) | 203 (3) | 219 (1) | 263 (1) | 311 (<1) | 261 (7) | 199 (3) | 213 (3) |
| $[M - R^4C_6H_4CH_2^{\bullet}]^{+}$ | | 166 (3) | 166 (4) | 166 (4) | 166 (1) | 166 (2) | 166 (3) | 166 (2) | 166 (5) | 166 (16) | 180 (2) | 194 (3) |
| $[a - {}^{\bullet}R^3]^{+}$ | | 214 (11) | 228 (14) | 242 (25) | 244 (48) | 232 (9) | 248 (5) | 292 (2) | 340 (5) | 290 (17) | 214 (9) | 214 (14) |
| $[a - {}^{\bullet}C_6H_4R^4]^{+}$ | (ion *e*) | 152 (25) | 152 (23) | 152 (31) | 152 (7) | 152 (21) | 152 (20) | 152 (21) | 152 (26) | 152 (40) | 166 (12) | 180 (15) |
| $[M - R^4C_6H_4N_3]^{+\bullet}$ | (ion *f*) | 138 (5) | 138 (7) | 138 (12) | 138 (4) | 138 (5) | 138 (7) | 138 (4) | 138 (5) | 138 (5) | 152 (3) | 166 (3) |
| $[a - R^4C_6H_4NH^{\bullet}]^{+}$ | | 137 (3) | 137 (4) | 137 (7) | 137 (4) | 137 (5) | 137 (9) | 137 (3) | 137 (4) | 137 (4) | 151 (3) | 165 (3) |
| $[e - HCN]^{+}$ | (ion *g*) | 125 (31) | 125 (40) | 125 (54) | 125 (41) | 125 (25) | 125 (29) | 125 (19) | 125 (26) | 125 (46) | 139 (11) | 153 (14) |
| $[a - R^3CO^{\bullet}]^{+}$ | (ion *h*) | 186 (8) | 200 (8) | 214 (12) | 216 (9) | 204 (8) | 220 (4) | 264 (2) | 312 (4) | 262 (15) | 186 (7) | 186 (11) |
| $[R^3\text{-}C{\equiv}N\text{-}C_6H_4R^4]^{+}$ | | 118 (7) | 132 (9) | 146 (9) | 148 (10) | 136 (8) | 152 (20) | 196 (2) | 244 (3) | 194 (11) | 132 (2) | 146 (1) |
| $[d - R^4C_6H_4NCN^{\bullet}]^{+\bullet}$ | (ion *i*) | 95 (10) | 95 (11) | 95 (13) | 95 (9) | 95 (30) | 95 (10) | 95 (10) | 95 (10) | 95 (8) | 109 (3) | 123 (13) |
| $[h - CH_3NCH_2]^{+}$ | | 143 (11) | 157 (10) | 171 (10) | 173 (7) | 161 (9) | 177 (5) | 221 (2) | 269 (4) | 219 (7) | 143 (5) | 143 (6) |
| $[f - {}^{\bullet}R^3]^{+}$ | | 123 (13) | 123 (11) | 123 (13) | 123 (11) | 123 (15) | 123 (14) | 123 (16) | 123 (16) | 123 (6) | 123 (11) | 123 (13) |
| $R^3CO^{+}$ | (ion *j*) | 43 (45) | 43 (56) | 43 (42) | 43 (49) | 43 (54) | 43 (73) | 43 (78) | 43 (50) | 43 (33) | 57 (11) | 71 (6) |
| $[h - R^4C_6H_4NC]^{+}$ | (ion *k*) | 83 (100) | 83 (100) | 83 (100) | 83 (100) | 83 (100) | 83 (100) | 83 (100) | 83 (100) | 83 (100) | 83 (100) | 83 (100) |
| $[k - CH_3CN]^{+}$ | | 42 (58) | 42 (63) | 42 (48) | 42 (52) | 42 (68) | 42 (88) | 42 (90) | 42 (62) | 42 (35) | 42 (30) | 42 (35) |
| Further: | | | | | | | | | | | | |
| $R^4C_6H_4NCN^{+}$ | | 117 (7) | 131 (9) | 145 (8) | 147 (11) | 135 (8) | 151 (4) | 195 (2) | 243 (3) | 193 (10) | 117 (3) | 117 (5) |
| $R^4C_6H_4NC^{+}$ | | 103 (6) | 117 (6) | 131 (8) | 133 (7) | 121 (10) | 137 (9) | 181 (2) | 229 (2) | 179 (9) | 103 (5) | 103 (6) |
| $R^4C_6H_4N^{+}$ | | 91 (11) | 105 (18) | 119 (18) | 121 (31) | 109 (19) | 125 (29) | 169 (4) | 217 (4) | 167 (35) | 91 (6) | 91 (8) |
| $R^4C_6H_4^{+}$ | | 77 (27) | 91 (26) | 105 (12) | 107 (10) | 95 (30) | 111 (15) | 155 (6) | 203 (5) | 153 (15) | 77 (14) | 77 (14) |

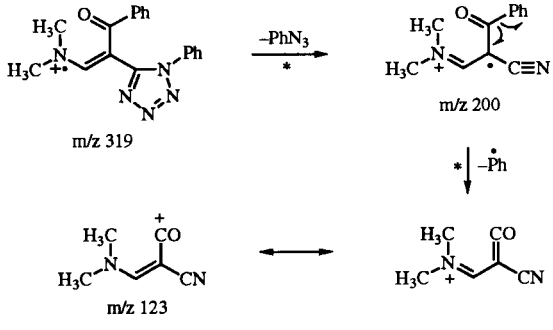
[a] See Table 1.

ion similar and as stable as the benzoyl cation. The latter is also present among the decay products of ion m/z 187, but in a very low scale. All isotope shifts in spectra **1a-1e** are in accordance with these fragmentation steps, of course.

The ejection of phenylazide is the fourth way leading to tetrazole ring degradation. This leads to the unpretentious ion m/z 200, which looses then the substituent $R^3$, here the phenyl residue of the benzoyl substituent, forms ion m/z 123 (Scheme 14). The complete preservation of the dimethylamino group shows spectrum **1b** with a shift of 6 amu to m/z 129, and the presence of one original tetrazole nitrogen demonstrates spectrum m/z with the shift to m/z 124 for this ion.

The only fragmentation without cleaving the tetrazole ring at the first step is the loss of 91 amu in the form of a benzyl radical. The resulting ion m/z 228 appears shifted in spectrum **1e** to m/z 232, thus proving unequivocally the maintenance of all four tetrazole nitrogen atoms. The shift of 4 amu in spectrum **1b** instead of 6 amu demonstrates the participation of a methyl group in this fragmentation. Spectrum **1c** reveals the origin of the phenyl in the split benzyl radical. Because ion m/z 228 keeps its place at the mass scale the phenyl in question can only be the substituent of the tetrazole ring. The second evidence delivers spectrum **1d**, in which mass number 228 is shifted to m/z 233. Scheme 15 illustrates the fragmentation concluded from these findings.

Scheme 14




Scheme 15

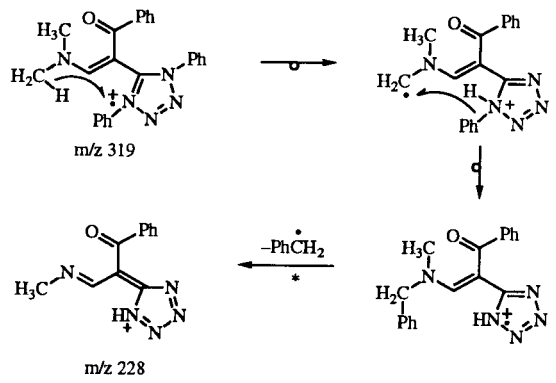


Table 3

Key Ions of Compound **23** and Compounds **24-26** (m/z, % intensity) [a]

| | | **23** | | | **24** | **25** | **26** |
|---|---|---|---|---|---|---|---|
| $M^{+\bullet}$ | | 291 (4) | $M^{+\bullet}$ | | 283 (65) | 297 (38) | 311 (30) |
| $[M - N_2]^{+\bullet}$ | (ion *a*) | 263 (1) | $[M - N_2]^{+\bullet}$ | (ion *a*) | 255 (11) | 269 (11) | 283 (12) |
| $[a - H^{\bullet}]^+$ | | 262 (2) | $[a - H^{\bullet}]^+$ | (ion *b*) | 254 (55) | 268 (30) | 282 (16) |
| $[M - Cl^{\bullet}]^+$ | (ion *b*) | 256 (5) | $[M - N_3^{\bullet}]^+$ | | 241 (14) | 255 (8) | 269 (11) |
| $[M - HCl]^{+\bullet}$ | (ion *c*) | 255 (5) | $[a - {}^{\bullet}R^3]^+$ | (ion *c*) | 240 (34) | 254 (16) | 268 (15) |
| $[M - N_3^{\bullet}]^+$ | | 249 (<1) | $[a - {}^{\bullet}OH]^+$ | (ion *d*) | 238 (6) | 252 (10) | 266 (14) |
| $[a - Cl^{\bullet}]^+$, $[b - N_2]^+$ | | 228 (5) | $[a - C_2H_4]^{+\bullet}$ | | 227 (46) | 241 (5) | 255 (5) |
| $[a - HCl]^{+\bullet}$, $[c\text{-}N_2]^{+\bullet}$ | (ion *d*) | 227 (4) | $[b - C_2H_4]^+$ | | 226 (28) | 240 (19) | 254 (17) |
| $[d - H^{\bullet}]^+$ | | 226 (7) | $[a - C_3H_6]^{+\bullet}$ | | 213 (25) | 227 (10) | 241 (15) |
| $[a - {}^{\bullet}R^3]^+$ | | 214 (5) | $[b\text{-}C_3H_6]^+$ | | 212 (42) | 226 (28) | 240 (85) |
| $[d - CO]^{+\bullet}$ | | 199 (4) | $[a - C_4H_8]^{+\bullet}$ | | | 213 (28) | 227 (19) |
| $[a - R^4C_6H_4{}^{\bullet}]^+$ | (ion *e*) | 186 (3) | $[b - C_4H_8]^+$ | | | 212 (19) | 226 (7) |
| $[a - R^3CO^{\bullet}]^+$ | (ion *f*) | 186 (3) | | | | | 213 (25) |
| $[d - C_2H_4N^{\bullet}]^+$ | | 185 (2) | | | | | 212 (23) |
| $[M - R^4C_6H_4N_3]^{+\bullet}$ | (ion *g*) | 172 (2) | $[a - R^3CO^{\bullet}]^+$ | (ion *e*) | 212 (42) | 226 (28) | 240 (85) |
| $[e - HCN]^+$ | | 159 (5) | | | 186 (18) | 186 (16) | 186 (17) |
| $[R^3\text{-}C{\equiv}N\text{-}C_6H_4R^4]^+$ | | 152 (0) | | | 184 (18) | | |
| $[d - {}^{\bullet}C_6H_4R^4]^+$ | (ion *h*) | 150 (1) | | | 179 (36) | | |
| $[f - CH_3NCH_2]^+$ | | 143 (3) | $[a - R^4C_6H_4{}^{\bullet}]^+$ | (ion *f*) | 178 (15) | 192 (3) | 206 (2) |
| $[d - R^4C_6H_4NH^{\bullet}]^+$ | | 135 (1) | $[M - R^4C_6H_4N_3]^{+\bullet}$ | (ion *g*) | 164 (10) | 178 (15 ) | 192 (22) |
| $[g - {}^{\bullet}R^3]^+$ | | 123 (10) | $[a - R^4C_6H_4NH^{\bullet}]^+$ | | 163 (29) | 177 (19) | 191 (19) |
| $[h - HCN]^+$ | | 123 (10) | $[f - HCN]^+$ | | 151 (18) | 165 (18) | 179 (6) |
| $[f - R^4C_6H_4NC]^+$ | (ion *i*) | 83 (100) | $[g - {}^{\bullet}R^3]^+$ | | 149 (12) | 163 (6) | 177 (7) |
| $[i - CH_3CN]^+$ | | 42 (40) | $[e - C_4H_7N]^+$ | | 143 (98) | | |
| | | | $[e - C_5H_9N]^+$ | | | 143 (55) | |
| | | | $[e - C_6H_{11}N]^+$ | | | | 143 (30) |
| | | | $[d - R^4C_6H_4NCN^{\bullet}]^+$ | | 121 (17) | 135 (19) | 149 (16) |
| | | | $[R^3\text{-}C{\equiv}N\text{-}C_6H_4R^4]^+$ | | 118 (15) | 118 (7) | 118 (4) |
| | | | $[e - R^4C_6H_4NC]^+$ | (ion *h*) | 109 (100) | 123 (63) | 137 (49) |
| | | | $[e - R^4C_6H_4NCNCCH]^+$ | | 70 (64) | 84 (100) | 98 (34) |
| | | | $[h - C_3H_6]^+$ | | 67 (53) | | |
| | | | $[h - C_4H_8]^+$ | | | 67 (35) | |
| | | | $[h - C_5H_{10}]^+$ | | | | 67 (35) |
| | | | $R^3CO^+$ | | 43 (80) | 43 (69) | 43 (95) |
| Further: | | | | | | | |
| $R^4C_6H_4NCN^+$ | | 117 (3) | $R^4C_6H_4NCN^+$ | | 117 (11) | 117 (7) | 117 (10) |
| $R^4C_6H_4NC^+$ | | 103 (6) | $R^4C_6H_4NC^+$ | | 103 (21) | 103 (14) | 103 (17) |
| $R^4C_6H_4N^+$ | | 91 (10) | $R^4C_6H_4N^+$ | | 91 (15) | 91 (13) | 91 (14) |
| $R^4C_6H_4^+$ | | 77 (20) | $R^4C_6H_4^+$ | | 77 (64) | 77 (47) | 77 (54) |
| | | | $C_4H_7^+$ | | 55 (69) | 55 (47) | 55 (85) |
| | | | $C_3H_5^+$ | | 41 (35) | 41 (90) | 41 (100) |

[a] See Table 1.

All results found up until now are confirmed best by the analogous fragmentation of compounds **2-11**, summarized with **1** in Table 1.

In the case of compounds **12-22**, which have an aliphatic substituent $R^3$, the fragmentation follows the rules as described above on the whole. For this reason, and for an easier comparison, we used the same subdivisions as in Table 1 for the fragmentation survey of **12-22** in Table 2. Comparing the intensities, there are some significant differences. *E.g.*, the formation of the nitrilium cation $[R^3\text{-}C{\equiv}N\text{-}C_6H_4R^4]^+$ is nearly omitted. A fragmentation step like [m/z 187 - $HR^3$], *i.e.* the loss of benzene in compound **1**, (Scheme 6), has no aliphatic pendant in form of methane separation. Therefore, the relative intensities of ion *g* in the acetyl series **12-22** are higher than in the benzoyl series **1-11**.

In the chloroacetyl compound **23** the expelling of chlorine competes with the loss of nitrogen as the primary fragmentation step (Table 3); the disubstituted nitrilium cation does not occur at all.

The substitution of the dimethylamino group by a pyrrolidino, piperidino or hexamethyleneimino group brings remarkable new features into the fragmentation pattern, as seen in Table 3, compounds **24-26**. After loss of dinitrogen from the tetrazole, there are as usual, on the one hand, stepwise decomposition reactions of the cyclic amino substitutents by ejection of small alkene molecules as it is well known after onium cleavage of such heterocyclic rings. On the other hand, the cyclic amino groups are stable enough to appear as ions of high intensity in the

mass spectra; in compound **25** the piperidinium cation m/z 84 is even the base peak. Their easy separation as cyclic imines, comparable to the fragmentation in Scheme 3, gives rise to a noteworthy intensive ion m/z 143.

## EXPERIMENTAL

The syntheses of compounds **1-26** are described in [11]; the labeled compounds have been prepared as prescribed there by using labeled starting components.

The mass spectra were recorded on a Varian MAT CH6 mass spectrometer at 70 eV. The samples were directly introduced and evaporated between 110° and 140°, depending on the molecular weight. The ion source temperature was about 200°. The MIKE spectra were recorded on a Finnigan MAT 95 instrument.

Acknowledgements.

G. W. F. wishes to thank the Fonds der Chemischen Industrie for financial support.

## REFERENCES AND NOTES

[1] Part **10**: G. W. Fischer, *J. Heterocyclic Chem.*, **32**, 1557 (1995).

[2] G. W. Fischer, *J. Prakt. Chem.*, **336**, 79 (1994).

[3] G. W. Fischer, *J. Heterocyclic Chem.*, **30**, 1517 (1993).

[4] For reviews see R. N. Butler, in Advances in Heterocyclic Chemistry, Vol **21**, Academic Press, New York, 1972, pp 324-435; Comprehensive Heterocyclic Chemistry, A. R. Katritzky and C. W. Rees, eds, Vol **5**, Pergamon, Oxford, 1984, pp 792-823; Q. N. Porter, Mass Spectrometry of Heterocyclic Compounds, Wiley Interscience, New York, 1985.

[5] D. M. Forkey and W. R. Carpenter, *Org. Mass Spectrom.*, **2**, 433 (1969).

[6] G. Ainsworth, *J. Heterocyclic Chem.*, **3**, 470 (1966).

[7] R. M. Moriarty, J. M. Kliegman and C. Shovlin, *J. Am. Chem. Soc.*, **89**, 5958 (1967).

[8] M. Herrmann and G. W. Fischer, *Org. Mass Spectrom.*, **24**, 829 (1989).

[9] D. Srzić, N. Čevizović and Z. Meić, *Org. Mass Spectrom.*, **22**, 400 (1987).

[10] P. A. S. Smith and E. Leon, *J. Am. Chem. Soc.*, **80**, 4647 (1958).

[11] G. W. Fischer, *J. Prakt. Chem.*, **332**, 977 (1990).