Mass Spectral Study of *N*-(1,2,3-Triazol-1-yl)-*N'*-arylureas

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The fragmentation pattern upon electron impact at 70 eV of several *N*-(1,2,3-triazol-1-yl)ureas as well as of the corresponding *N'*-aryl substituted is studied. The spectra examined contain the molecular ion peak in very low intensity and in some cases is absent, whereas the ion $ArNCO^{+\cdot}$ is the base peak or one of the most prominent. The principal fragmentation pathway takes place *via* the $[M-28]^+$ ion.

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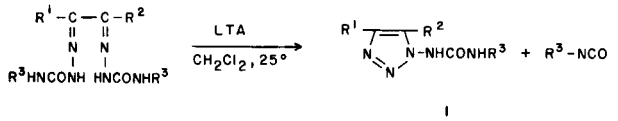
Although there are several studies on the mass spectra of 1,2,3-triazole derivatives [2-6] and substituted ureas [7,8], there is no study on the fragmentation pattern of the title compounds, which contain these two biologically interesting groups.

The compounds I are prepared [9] in moderate yields (25-55%) from bis-semicarbazones of α-dicarbonyl compounds by lead tetraacetate (LTA) oxidative cyclization in methylene chloride, at room temperature (Table 1).



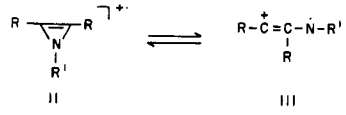
I

I	R^1	R^2	R^3
a	CH_3	CH_3	H
b	CH_3	CH_3	C_6H_5
c	C_6H_5	C_6H_5	H
d	C_6H_5	C_6H_5	C_6H_5
e	C_6H_5	CH_3	p-BrC_6H_4
f	C_6H_5	CH_3	p-$CH_3C_6H_4$
g	p-$CH_3C_6H_4$	CH_3	C_6H_5
h	p-$CH_3C_6H_4$	H	H
i	p-$CH_3C_6H_4$	H	C_6H_5
j	p-$CH_3C_6H_4$	H	p-BrC_6H_4

The structure of 4,5-unsymmetrically substituted ($R^1 \neq R^2$) triazolylureas (Ie-j) was confirmed after acid hydrolysis to the corresponding 1-aminotriazole derivatives [1,9] and by nmr spectroscopy [10].

In the mass spectra of compounds I (Table 2) the molecular ion $M^{+\cdot}$ appears with a very low relative intensity (0.1-7%), whereas in the compounds (Id, Ie, Ii, Ij) this ion peak is absent and they appear as the corresponding $[M-28]^+$ ion.

This ion fragment is present in all spectra with a variable relative intensity (2-35%), and it is formed from the molecular ion upon elimination of nitrogen of the triazole ring. This transition in several cases is accompanied by the appropriate metastable peak and it is very characteristic for the spectra of triazole derivatives [2,4,6]. On the other hand an analogous nitrogen elimination is also observed photochemically [11] or thermally [12]. In respect to the structure of $[M-N_2]^{+\cdot}$ ion an equilibirium between azirine ring II and open form III has been proposed [6].



II III

Another interesting fragmentation pathway arises by scissions of the urea function which mainly occur *via* the $[M-28]^+$ ion.

Thus, in the mass spectra studied two prominent ions IV and V are always observed, which are formed by scission of the urea in ^1NH-^2CO bond followed by an [1.3] hydrogen transfer. These transitions in several cases are followed by the corresponding metastable ion peak.

Table 1

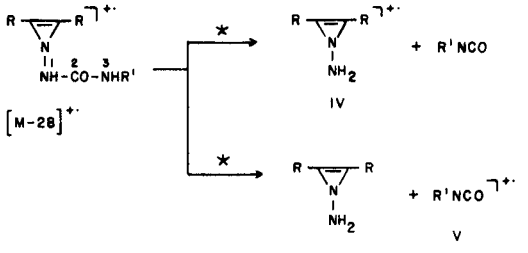
Analytical Data for the *N*-(1,2,3-Triazol-1-yl)-*N'*-arylureas I

Compound No.	Mp, °C	Yield %	Formula	Molecular Weight	Analysis, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
Ia	225-226 [9]	30	$C_5H_9N_5O$	155.2						
Ib	164-165	43	$C_{11}H_{13}N_5O$	231.2	57.13	5.61	30.29	57.44	5.60	29.88
Ic	209-211 [9]	40	$C_{15}H_{13}N_5O$	279.3						
Id	206-208	25	$C_{21}H_{17}N_5O$	355.4	70.96	4.82	19.71	71.01	4.85	19.67
Ie	248-249	45	$C_{16}H_{14}BrN_5O$	372.2	51.63	3.79	18.81	51.44	3.83	19.14
If	206-208	25	$C_{17}H_{17}N_5O$	307.3	66.43	5.58	22.79	66.46	5.59	22.78
Ig	213-216	40	$C_{17}H_{17}N_5O$	307.3	66.43	5.58	22.79	66.02	5.54	22.69
Ih	224-225	32	$C_{10}H_{11}N_5O$	217.2	55.29	5.10	32.24	55.41	5.20	32.34
Ii	203-205	55	$C_{16}H_{15}N_5O$	293.3	65.51	5.15	23.88	65.78	5.14	24.30
Ij	222-223	43	$C_{16}H_{14}BrN_5O$	372.2	51.63	3.79	18.81	51.26	3.87	19.05

Table 2

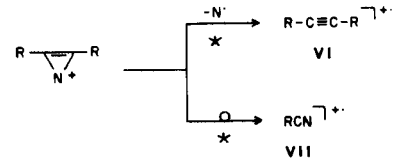
Principal Fragment Ions in the Mass Spectra of the 1,2,3-Triazolylureas I, m/z (% Relative Intensities)

Ia	155 (0.5) $M^{+\cdot}$, 127 (20), 112 (3), 97 (5), 69 (20), 68 (93), 54 (10), 44 (80), 43 (100), 41 (84)
Ib	231 (7) $M^{+\cdot}$, 203 (35), 120 (32), 119 (100), 112 (4), 97 (3), 93 (47), 91 (27), 84 (4), 69 (5), 68 (80), 54 (4), 41 (23)
Ic	279 (0.5) $M^{+\cdot}$, 251 (30), 236 (3), 221 (5), 208 (15), 193 (25), 192 (76), 178 (90), 103 (100), 44 (15), 43 (65)
Id	327 (5) $[M-28]^{+\cdot}$, 236 (0.5), 221 (8), 208 (4), 193 (8), 192 (26), 178 (40), 120 (16), 119 (100), 103 (70), 93 (68), 92 (13)
Ie	345/343 (3) $[M-28]^{+\cdot}$, 200/198 (10), 199/197 (100), 174 (92), 173/171 (35), 159 (2.5), 146 (4), 130 (12), 116 (12), 103 (52), 41 (20)
If	307 (0.5) $M^{+\cdot}$, 279 (13), 174 (3), 159 (18), 146 (6), 134 (13), 133 (100), 116 (30), 107 (32), 103 (38), 41 (20)
Ig	307 (0.1) $M^{+\cdot}$, 279 (6), 188 (0.1), 173 (6), 160 (5), 144 (12), 130 (15), 120 (11), 119 (100), 117 (29), 93 (23), 41 (19)
Ig	217 (1) $M^{+\cdot}$, 189 (15), 174 (2), 159 (7), 146 (17), 130 (22), 118 (100), 117 (90), 116 (66), 43 (60)
Ii	265 (30) $[M-28]^{+\cdot}$, 174 (2), 159 (6), 146 (30), 130 (25), 120 (30), 119 (100), 117 (70), 116 (65), 93 (80), 92 (40)
Ij	345/343 (1) $[M-28]^{+\cdot}$, 200/198 (8), 199/197 (100), 174 (3), 173/171 (30/50), 159 (9), 146 (8), 130 (8), 117 (25), 116 (21)



The abundance of the ion V is much higher than IV and the isocyanate ion usually corresponds to the base peak of the spectrum, especially when R' is an aryl. A similar scission in $^{2}CO\text{-}^{3}NHR'$ bond followed by a hydrogen transfer leads to the formation of the $R'NH_2]^{+\cdot}$ with a high relative intensity.

Other prominent ion fragments are VI and VII which are arisen as follows although some other routes are also possible.



A general fragmentation pattern for the compound Ib is given in Scheme 1, whereas a typical mass spectrum for the same compound is shown in Figure 1.

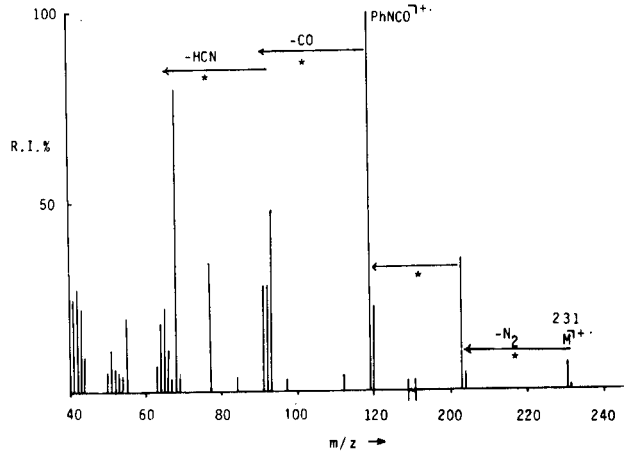
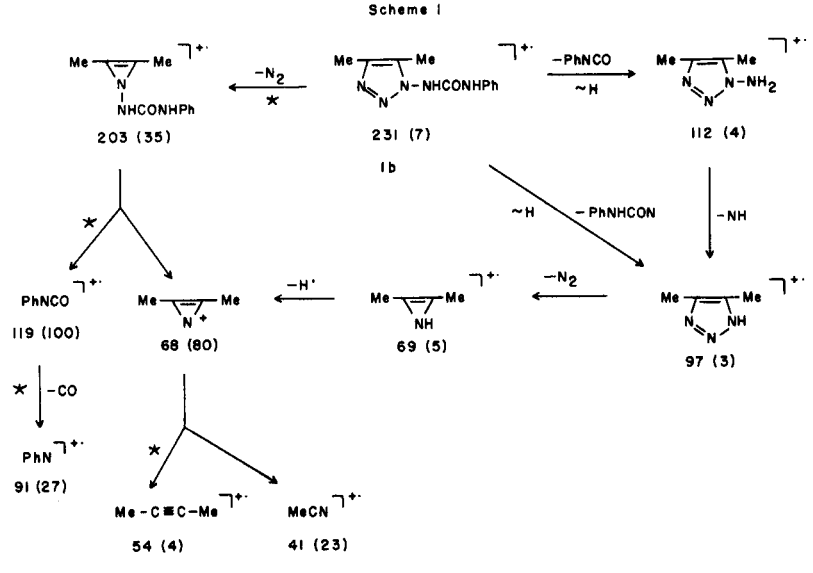


Figure 1. Mass spectrum of the compound Ib.

Scheme I



EXPERIMENTAL

All melting points are uncorrected and were obtained with a hot stage apparatus. The mass spectra were run at 70 eV on a RMU-6L Hitachi-Perkin-Elmer spectrometer, using the direct insertion probe of the samples in the range of 140-180°. Analyses were performed with a Perkin-Elmer Model 240 CHN Analyzer.

General Procedure for Preparation of *N*-(1,2,3-Triazol-1-yl)-*N'*-arylureas I.

To a suspension of bis-semicarbazonne of the corresponding α-dicarbonyl compound (0.2 mole), prepared according to a general procedure [13], in dichloromethane (100 ml) lead tetraacetate (0.021 ml) was added and the mixture was stirred at room temperature for 3-5 hours. The reaction mixture was filtered and the precipitate was treated with methanol. Evaporation of the solvent gave the triazolylurea I which recrystallized from methanol. For the analytical data of the compounds I see Table 1.

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