Synthesis and Mass Spectra of 1-Arylideneamino-1,2,3-triazoles

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The synthesis of the title compounds is described. Their mass spectra upon electron impact are given and the main fragmentation pathways are described.

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It is well known that the carbon nitrogen double bond, C=N, undergoes a variety of cycloaddition reactions to give interesting heterocyclic products. Thus, it reacts in [2+3] cycloadditions with nitrilimines [1] giving 1,2,4-triazolines, with diazocompounds [2,3] giving 1,2,3-triazolines, and with nitriloxides [1] giving 1,2,4-oxadiazoline derivatives. It also reacts in [2+2] cycloadditions with ketenes [4] to give a variety of β-lactame derivatives.

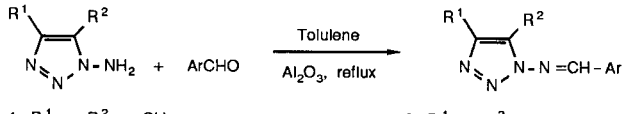
In connection to our studies on the 1-amino-1,2,3-triazole derivatives [5,6], we have prepared a series of 1-(α-aroyloxyarilidene)amino-1,2,3-triazoles and tried to react on their carbon-nitrogen double bond, C=N, with ketenes and nitriloxides in [2+2] and [2+3] cycloaddition reactions respectively. However all the efforts to get reaction products failed. Since the C=N bond in the above mentioned compounds is somewhat hindered by the bulky aroyloxy-group, which also lies out of the plain of the double bond [6], it was thought that the less hindered and more stable Schiff's bases of the 1-amino-1,2,3-triazole might be better representatives for such reactions. However many efforts to react these Schiff's bases with ketenes, in different reacting conditions, were unsuccessful. On the other hand, reaction of these compounds with nitrilimines and nitriloxides gave in low yields cycloaddition products, and these reactions are under further study.

The above experimental observations of these compounds upon cycloaddition reactions prompted us to prepare a series of them, in order to examine their spectroscopic characteristics, which might lead to understanding of the chemical behaviour of the C=N bond of these Schiff's bases.

In this study we present the preparation of the 1-arylideneamino-1,2,3-triazoles, most of them being new compounds, and examine the fragmentation pattern in their mass spectra.

Results and Discussion.

1-Arylideneamino-1,2,3-triazoles, **9-30**, have been prepared by condensation of 1-amino-1,2,3-triazoles **1-8** with the corresponding aldehydes in refluxing toluene, in the presence of aluminium oxide [7]. Their analytical and spectral data are in agreement with their structure and are



1 $R^1 = R^2 = CH_3$
2 R^1 = Ph, $R^2 = CH_3$
3 $R^1 = CH_3$, R^2 = Ph
4 R^1 = Ph, R^2 = H
5 R^1 = p-CH_3-C_6H_4, R^2 = H
6 R^1 = p-CH_3O-C_6H_4, R^2 = H
7 R^1 = p-Cl-C_6H_4, R^2 = H
8 R^1 = p-Br-C_6H_4, R^2 = H

9 $R^1 = R^2 = CH_3$, Ar = Ph
10 $R^1 = R^2 = CH_3$, Ar = p-CH_3-C_6H_4
11 $R^1 = R^2 = CH_3$, Ar = p-CH_3O-C_6H_4
12 $R^1 = R^2 = CH_3$, Ar = p-HO-C_6H_4
13 $R^1 = R^2 = CH_3$, Ar = p-Cl-C_6H_4
14 $R^1 = R^2 = CH_3$, Ar = p-O_2N-C_6H_4
15 $R^1 = R^2 = CH_3$, Ar = p-$(CH_3)_2N$-C_6H_4
16 $R^1 = R^2 = CH_3$, Ar = p-NC-C_6H_4
17 $R^1 = CH_3$, R^2 = Ph, Ar = Ph
18 $R^1 = CH_3$, R^2 = Ph, Ar = p-CH_3O-C_6H_4
19 R^1 = Ph, $R^2 = CH_3$, Ar = Ph
20 R^1 = Ph, $R^2 = CH_3$, Ar = p-CH_3O-C_6H_4
21 R^1 = Ph, R^2 = H, Ar = Ph
22 R^1 = Ph, R^2 = H, Ar = p-CH_3-C_6H_4
23 R^1 = Ph, R^2 = H, Ar = p-CH_3O-C_6H_4
24 R^1 = Ph, R^2 = H, Ar = p-Cl-C_6H_4
25 R^1 = Ph, R^2 = H, Ar = p-O_2N-C_6H_4
26 R^1 = Ph, R^2 = H, R^2 = pH, Ar = -$(CH_3)_2N$-C_6H_4
27 R^1 = p-CH_3-C_6H_4, R^2 = H, Ar = Ph
28 R^1 = p-CH_3O-C_6H_4, R^2 = H, Ar = Ph
29 R^1 = p-Cl-C_6H_4, R^2 = H, Ar = Ph
30 R^1 = p-Br-C_6H_4, R^2 = H, Ar = Ph

Table 1

Analytical and Spectral Data of Compounds **9-30**

Compound	Mp (°C) (Solvent) [a]	Yield (%)	Formula M.W.	Analysis Found (Calcd) C%	H%	N%	IR ν, cm⁻¹	¹H-nmr, deuteriochloroform, δ ppm CH=N	CH_3-4	CH_3-5	arylidene-group o,o′	m, (p),m′	4- or 5-aryl-group o,o′	m, (p),m′	
9	76-78 EtOH/PE	90	$C_{11}H_{12}N_4$	lit [18]:80-81			1620 1610	9.37 (s, 1H)	2.31 (s, 3H)	2.36 (s, 3H)	7.84-8.90 (m, 2H)	7.44-7.53 (m, 3H)			
10	112-114 Et_2O/PE	86	$C_{12}H_{14}N_4$ 214.273	67.36 67.27	6.54 6.59	26.15 26.15	1605	9.31 (s, 1H)	2.33 (s, 3H)	2.37 (s, 3H)	7.78 (d, 2H)	7.28 (d, 2H)			2.43 [c] (s, 3H)
11	133-135 EtOH	61	$C_{12}H_{14}N_4O$ 230.272	62.34 62.59	6.03 6.13	24.38 24.33	1610	9.30 (s, 1H)	2.30 (s, 3H)	2.33 (s, 3H)	7.85 (d, 2H)	6.97 (d, 2H)			3.87 [d] (s, 3H)
12	234-235 EtOH	60	$C_{11}H_{12}N_4O$ 216.245	60.75 61.10	5.41 5.59	25.65 25.91	1595	insoluble in deuteriochloroform and DMSO-d_6							
13	143-144.5 EtOH	61	$C_{11}H_{11}N_4Cl$ 234.191	56.03 56.29	4.68 4.72	23.58 23.87	1595	9.34 (s, 1H)	2.31 (s, 3H)	2.35 (s, 3H)	7.84 (d, 2H)	7.45 (d, 2H)			
14	225-227 EtOH/MC	75	$C_{11}H_{11}N_5O_2$ 245.244	53.73 53.87	4.42 4.52	28.71 28.56	1600	9.55 (s, 1H)	2.35 (s, 3H)	2.41 (s, 3H)	8.13 (d, 2H)	8.32 (d, 2H)			
15	157.5-159 EtOH	95	$C_{13}H_{17}N_5$ 243.314	64.33 64.17	6.95 7.04	28.75 28.78	1615	9.18 (s, 1H)	2.31 (s, 6H)	2.31 (s, 6H)	7.74 (d, 2H)	6.69 (d, 2H)			3.04 [e] (s, 6H)
16	218-220 Et_2O/$CHCl_3$	93	$C_{12}H_{11}N_5$ 225.256	63.71 63.99	4.75 4.92	31.19 31.09	1590 2220	9.50 (s, 1H)	2.38 (s, 3H)	2.43 (s, 3H)	8.12 (d, 2H)	7.84 (d, 2H)			
17	117-120 PE		$C_{16}H_{14}N_4$ 262.317	72.99 73.26	5.63 5.38	21.36 21.36		9.48 (s, 1H)	2.47 (s, 3H)	—	7.75-8.10 (m, 2H)	7.41-7.58 (m, 3H)	7.52 (bs, 4H)	7.52 (bs, 4H)	
18	141-142 EtOH	60	$C_{17}H_{16}N_4O$ 292.344	69.38 69.85	5.43 5.52	19.22 19.16		9.42 (s, 1H)	2.47 (s, 3H)	—	7.79 (d, 2H)	6.97 (d, 2H)	7.51 (bs, 4H)	7.51 (bs, 4H)	3.87 [d] (s, 3H)
19	156-158 EtOH	78	$C_{16}H_{14}N_4$ 262.317	72.98 73.26	5.33 5.38	21.08 21.36		9.54 (s, 1H)	—	2.65 (s, 3H)	7.80-8.10 (m, 4H)	7.42-7.60 (m, 6H)	7.80-8.10 (m, 4H)	7.42-7.60 (m, 6H)	
20	143-145 EtOH	79	$C_{17}H_{16}N_4O$ 292.344	70.12 69.85	5.79 5.52	19.34 19.16		9.40 (s, 1H)	—	2.64 (s, 3H)	7.90 (d, 2H)	7.00 (d, 2H)	7.70-7.90 (m, 2H)	7.35-7.60 (m, 3H)	3.90 [d] (s, 3H)
21	134-135 $CHCl_3$/Et_2O	77	$C_{15}H_{12}N_4$ 248.290	72.61 72.56	4.77 4.87	22.42 22.57	3120 1620 1610	9.46 (s, 1H)	—	8.06 [b] (s, 1H)	7.82-8.02 (m, 4H)	7.37-7.63 (m, 6H)	7.82-8.02 (m, 4H)	7.37-7.63 (m, 6H)	
22	186-187 $CHCl_3$/MC	67	$C_{16}H_{14}N_4$ 262.317	73.11 73.26	5.27 5.38	21.45 21.36	3130 1620 1605	9.48 (s, 1H)		8.10 [b] (s, 1H)	7.87 (d, 2H)	7.37 (d, 2H)	7.80-8.03 (m, 2H)	7.42-7.58 (m, 3H)	2.45 [c] (s, 3H)
23	157-158 $CHCl_3$/PE	70	$C_{16}H_{14}N_4O$ 278.318	68.94 69.05	4.87 5.07	20.04 20.13	3120 1605 1600	9.45 (s, 1H)		8.10 [b] (s, 1H)	7.94 (d, 2H)	7.08 (d, 2H)	7.87-8.05 (m, 2H)	7.40-7.55 (m, 3H)	3.92 [d] (s, 3H)

Table 1 (continued)

Compound	Mp (°C) (Solvent) [a]	Yield (%)	Formula M.W.	Analysis Found (Calcd) C%	H%	N%	IR ν, cm^{-1}	^{1}H-nmr, deuteriochloroform, δ ppm CH=N	CH_3-4	CH_3-5	arylidene-group o,o′	m, (p),m′	4- or 5-aryl-group o,o′	m, (p),m′
24	207-208	81	$C_{18}H_{11}N_4Cl$	63.72	3.69	19.65	3120	9.45		8.10 [b]	7.90	7.50	7.85-8.0	7.40-7.65
	EtOH		282.735	63.72	3.92	19.82	1610	(s, 1H)		(s, 1H)	(d, 2H)	(d, 2H)	(m, 2H)	(m, 3H)
25	257-259	55	$C_{18}H_{11}N_5O_2$	61.43	3.62	23.70	3120	insoluble in deuteriochloroform and DMSO-d_6						
			293.288	61.43	3.78	23.88	1610							
26	188-190	86	$C_{17}H_{17}N_3$	70.10	5.93	24.03	3120	9.33		8.03 [b]		6.78	7.87-8.03	7.35-7.50
	EtOH		291.359	70.08	5.88	24.14	1610	(s, 1H)		(s, 1H)		(d, 2H)	(m, 2H)	(m, 3H)
27	158-160	76	$C_{16}H_{14}N_4$	73.25	5.34	21.22	3130	9.53		8.08 [b]	7.87-8.03	7.51-7.70	7.86	7.33
	$CHCl_3/Et_2O$		262.317	73.26	5.38	21.36	1605	(s, 1H)		(s, 1H)	(m, 2H)	(m, 3H)	(d, 2H)	(d, 2H)
28	152-154	82	$C_{16}H_{14}N_4O$	69.17	4.96	20.02	3130	9.53		8.07 [b]	7.83-8.00	7.53-7.70	7.90	7.06
	Et_2O/MC		278.318	69.05	5.07	20.13	1620	(s, 1H)		(s, 1H)	(m, 2H)	(m, 3H)	(d, 2H)	(d, 2H)
29	194-196	35	$C_{15}H_{11}N_4Cl$	63.69	3.78	19.89	3120	9.45		8.05 [b]	7.87-8.03	7.50-7.64	7.83	7.42
	$CHCl_3$/PE		282.735	63.72	3.92	19.82	1610	(s, 1H)		(s, 1H)	(m, 2H)	(m, 3H)	(d, 2H)	(d, 2H)
30	198-200	74	$C_{15}H_{11}N_4Br$	55.10	3.33	16.99	3125	9.47		8.07 [b]	7.83-8.00	7.53-7.70	7.80	7.55
	$CHCl_3$		327.186	55.06	3.39	17.12	1610	(s, 1H)		(s, 1H)	(m, 2H)	(m, 3H)	(d, 2H)	(d, 2H)

[a] PE = petroleum ether, MC = CH_2Cl_2. [b] H-5 of the triazole ring. [c] $-C_6H_4-CH_3$. [d] $-OCH_3$. [e] $-N(CH_3)_2$.

given in Table 1. It is worth mentioning the proton absorption peak of the CH=N group in their ^{1}H nmr spectra, where it appears at δ 9.2-9.5, whereas in the arylidene=anilines [8] resonates at δ 8.2-8.5. The downfield shift, ~1 ppm, of the methine proton in the arylidenetriazoles **9-30**, in respect to that of the arylideneanilines should be rather the result of electronic effects on the carbon-nitrogen double bond of the triazole ring, although conformation differences around the tr-N=CH and Ar-CH=N bonds of these compounds could be included.

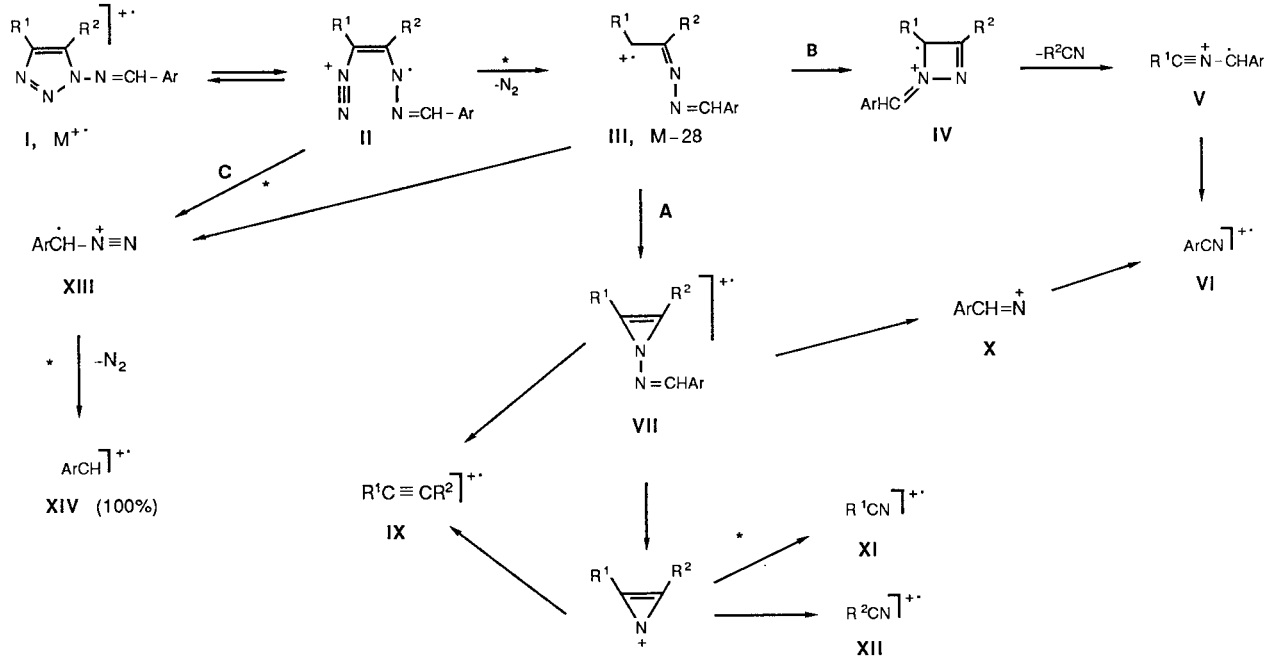
1-Arylideneamino-1,2,3-triazoles **9-30** showed in their mass spectra the general fragmentation pattern of other 1,2,3-triazole derivatives [9-11]. Thus, except of a low intensity (0.2-12%) molecular ion peak, $M^{+\cdot}$, they all showed the M-28$^{]+\cdot}$ ion, which corresponds to N_2 elimination from the molecular ion and is very characteristic of the 1-substituted-1,2,3-triazoles [9-11]. The M-28$^{]+\cdot}$ ion is further split to give ions corresponding to the azirine structure **VIII** and to the acetylenes **IX**, as well as the nitriles $R^1CN^{]+\cdot}$ and $R^2CN^{]+\cdot}$ and to the ion $ArCH=\overset{+}{N}\cdot$ (Scheme, path **A**). This fragmentation pattern was almost the main pathway of splitting of the 4-methyl-5-phenyl-derivatives **17** and **18**, where ion **VIII** corresponded to the base peak of the spectrum.

The M-28$^{]+\cdot}$ ion peak was of lower intensity than the molecular ion $M^{+\cdot}$ in the 4,5-dimethyl-derivatives **9-16**, but of about equal intensity with the $M^{+\cdot}$ peak in the 4- or 5-phenyl-derivatives **17-30**. This is rather expected, since the phenyl group can stabilize both, the open, **III**, and the azirine, **VII**, form (Scheme), that can take the M-28$^{]+\cdot}$ ion.

The M-28$^{]+\cdot}$ ion was accompanied by a loss of an acetonitrile fragment, CH_3CN, in the 4,5-dimethyl- **9-16** and in the 4-phenyl-5-methyl-derivatives **19-20**, or of an hydrogen cyanide, HCN, in the 4-aryl-derivatives **21-30**, the M-69$^{]+\cdot}$ and M-55$^{]+\cdot}$ ion peaks being of higher intensity and most characteristics in the 4-aryl-derivatives **19-30**. The peaks corresponding to the above fragmentation were almost absent or of very low intensity in the 4-methyl-5-phenyl-derivatives **17** and **18**.

The above fragmentation could be explained by the formation of a diazetine intermediate **IV** (Scheme, path **B**), which is further split with a cyanide elimination giving the ion **V**. Other diazetine derivatives show an analogous fragmentation in their mass spectra [11b]. The diazetine intermediate **IV** may be formed from the open imidoyl-carbene form **III**, together with the azirine **VII**, that most authors [9-11] have accepted for the structure of the M-28$^{]+\cdot}$ ion. Fragmentation path **B** is prevailed in the 4-aryl-derivatives **19-30**, whereas fragmentation path **A** is mainly observed in the 4-methyl-5-phenyl-derivatives **17** and **18**. It should be noticed that the above fragmentation pattern

Scheme



Main fragmentation pattern of compounds **9-30**

(path **B**) has also been found in the mass spectra of other 1-amino-1,2,3-triazole-derivatives, such as the 1-(α-aroyloxyarylidene)amino-1,2,3-triazoles [12] and the 1-aroylamino-1,2,3-triazoles [13].

Another interesting ion fragment was that corresponding to the aryldiazomethane structure, $ArCHN_2^{+\cdot}$, which was further split with a N_2 elimination to give the ion $ArCH^{+\cdot}$, (Scheme, path **C**). The latter was the base peak in almost all the mass spectra studied. The aryldiazomethane fragment **XIII** could be generated either from the open form of the $M\text{-}28^{+\cdot}$ fragment **III**, or from the open form of the molecular ion **II**. Form **II** can be considered as the intermediate in the N_2 elimination, and is the open tautomer in the Dimroth-like rearrangement that occurs in the 5-amino- or 5-hydroxy-1,2,3-triazole-derivatives [14-15]. It should be mentioned that the fragmentation of the molecular ion to the aryldiazomethane fragment **XIII** was supported by metastable ion peaks.

In the mass spectra of the 4-methyl-5-phenyl-derivatives **17** and **18**, the peaks corresponding to ions of the above fragmentation (path **C**), were of very low intensity, indicating again their differentiation in respect to the 4-phenyl derivatives **19-30**. This is attributed to the phenyl ring at

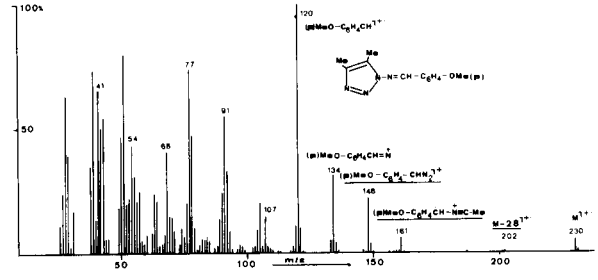


Figure 1. The 70 eV mass spectrum of compound **11**.

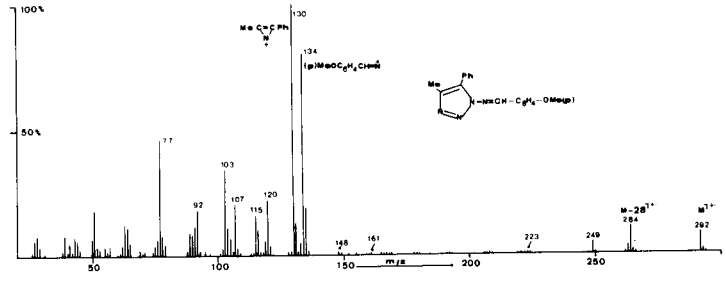


Figure 2. The 70 eV mass spectrum of compound **18**.

Table 2

Main Fragment Ions in the Mas Spectra of Compounds **9-30**, m/z, (% Relative Intensities).

9	200 (M^+, 7.4), 185 (1), 172 (M-28$^+$, 0.4), 131 (M-69$^+$, 4.3), 130 (2.5), 118 (35), 104 (23), 103 (1.5), 90 (100), 89 (25), 77 (43), 68 (18), 54 (3), 41 (7.5)
10	214 (M^+, 3.3), 186 (M-28$^+$, 0.2), 171 (0.3), 145 (M-69$^+$, 2), 144 (2), 132 (28), 118 (22), 117 (2), 116 (2), 105 (10), 104 (100), 103 (29), 91 (44), 77 (18), 68 (27), 54 (4), 41 (17)
11	230 (M^+, 5.3), 202 (M-28$^+$, 0.5), 187 (0.5), 161 (M-69$^+$, 6), 160 (1), 148 (22), 134 (32), 133 (5), 120 (100), 107 (15), 105 (20), 92 (33), 91 (56), 90 (24), 77 (74), 76 (20), 68 (41), 54 (43), 41 (66)
12	216 (M^+, 6), 188 (M-28$^+$, 1.7), 147 (M-69$^+$, 11), 146 (6), 134 (29), 120 (38), 119 (23), 107 (10), 106 (100), 105 (29), 93 (25), 78 (81), 77 (40), 68 (35), 54 (95), 41 (33)
13	236/234 (M^+, 19), 208/206 (M-28$^+$, 0.9), 193/191 (1), 167/165 (M-69$^+$, 4), 164 (2), 154/152 (41), 140/138 (32), 137 (5), 126/124 (100), 113/111 (33), 89 (56), 75 (30), 68 (65), 54 (27), 41 (6)
14	245 (M^+, 6.5), 217 (M-28$^+$, 2), 216 (1), 202 (2), 176 (M-69$^+$, 4), 175 (1), 163 (39), 149 (20), 148 (5), 135 (43), 133 (2), 103 (13), 89 (100), 77 (12), 76 (20), 68 (57), 54 (45), 41 (30)
15	243 (M^+, 10.5), 215 (M-28$^+$, 6), 214 (9), 174 (M-69$^+$, 6), 173 (2), 161 (6), 147 (31), 146 (13), 145 (18), 143 (16), 133 (100), 132 (61), 120 (13), 119 (13), 118 (61), 117 (21), 105 (15), 104 (12), 103 (12), 91 (31), 89 (22), 78 (31), 77 (15), 68 (18), 54 (95), 41 (33)
16	225 (M^+, 2), 197 (M-28$^+$, 0.8), 156 (M-69$^+$, 2.5), 155 (5), 143 (20), 129 (15), 128 (14), 116 (11), 115 (100), 114 (15), 102 (18), 89 (7), 77 (26), 76 (12), 68 (52), 54 (74), 41 (37)
17	262 (M^+, 4.4), 234 (M-28$^+$, 4.4), 233 (2), 193 (M-69$^+$, 0.7), 192 (0.3), 131 (17) 130 (100), 118 (2), 117 (3.5), 116 (30), 115 (40), 104 (23), 103 (45), 90 (26), 89 (23), 77 (39), 76 (10), 41 (81)
18	292 (M^+, 8), 264 (M-28$^+$, 11), 263 (3), 223 (M-69$^+$, 0.5), 222 (0.3), 161 (0.6), 148 (1), 135 (19), 134 (80), 133 (5), 131 (17), 130 (100), 120 (21), 119 (5), 116 (10), 115 (15), 107 (20), 105 (7), 104 (11), 103 (34), 92 (18), 91 (16), 89 (9), 77 (46), 41 (5)
19	262 (M^+, 6.3), 234 (M-28$^+$, 0.9), 193 (M-69$^+$, 47), 192 (3), 191 (4), 165 (3), 131 (10), 130 (53), 119 (8), 118 (68), 116 (7), 115 (16), 104 (11), 103 (6), 91 (20), 90 (100), 77 (15), 41 (6)
20	292 (M^+, 3), 264 (M-28$^+$, 5), 223 (M-69$^+$, 27), 222 (1), 208 (3.5), 161 (6.5), 148 (19), 134 (2), 133 (3), 131 (4), 130 (31), 121 (10), 120 (100), 117 (8), 116 (74), 115 (84), 105 (15), 104 (7), 103 (7), 92 (11), 91 (32), 77 (27), 41 (13)
21	248 (M^+, 2), 220 (M-28$^+$, 0.6), 193 (M-55$^+$, 8.4), 191 (2), 119 (3), 118 (36), 117 (1.5), 116 (5.5), 115 (1.3), 103 (1.6), 102 (10), 91 (8), 90 (100), 89 (36), 77 (7), 76 (8)
22	262 (M^+, 1), 234 (M-28$^+$, 1), 207 (M-55$^+$, 4), 206 (1.5), 191 (1), 133 (2.5), 132 (25), 118 (8.5), 117 (4.5), 116 (25), 115 (2), 105 (12), 104 (100), 103 (38), 102 (62), 90 (17), 89 (18), 78 (40), 77 (22), 76 (23)
23	278 (M^+, 5), 250 (M-28$^+$, 7), 223 (M-55$^+$, 12), 222 (4), 208 (4), 207 (5.5), 180 (3), 179 (4), 149 (6), 148 (37), 135 (2), 134 (5), 133 (3), 121 (12), 120 (100), 119 (7), 117 (2.3), 116 (5), 115 (1.3), 107 (2.2), 105 (17), 103 (3), 102 (19), 91 (32), 90 (15), 89 (13), 77 (25), 76 (9)
24	284/288 (M^+, 3.3), 256/254 (M-28$^+$, 2.7), 229/227 (M-55$^+$, 13), 192 (4), 191 (4), 154/152 (37), 139 (1), 138 (1), 137 (1.5), 126/124 (100), 116 (9), 115 (1), 113/111 (4), 103 (2), 102 (16), 90 (9), 89 (80), 77 (2), 76 (7), 75 (10)
25	293 (M^+, 4), 265 (M-28$^+$, 6), 239 (5), 238 (M-55$^+$, 24), 237 (1), 165 (10), 164 (7), 163 (66), 150 (4), 149 (24), 148 (4), 136 (8), 135 (67), 134 (4), 133 (3), 120 (4), 118 (4), 117 (7), 116 (14), 115 (4), 105 (12), 104 (5), 103 (12), 102 (89), 91 (10), 90 (17), 89 (100), 77 (17), 76 (34), 75 (32)
26	291 (M^+, 11), 263 (M-28$^+$, 15), 236 (M-55$^+$, 9), 235 (4), 220 (3), 192 (1.3), 161 (11), 147 (5), 146 (3), 145 (6), 133 (100), 132 (46), 131 (7), 119 (8), 118 (45), 117 (17), 116 (6), 105 (11), 103 (11), 102 (60), 92 (55), 91 (84), 89 (20), 77 (22), 76 (23)
27	262 (M^+, 2.6), 234 (M-28$^+$, 4.6), 207 (M-55$^+$, 16), 206 (3), 191 (2), 131 (3), 130 (4), 118 (23), 117 (5), 116 (30), 115 (34), 105 (3), 104 (5), 103 (8), 91 (14), 90 (100), 89 (30), 77 (10), 76 (6)
28	278 (M^+, 4), 250 (M-28$^+$, 6), 235 (2.5), 223 (M-55$^+$, 22), 222 (2), 208 (8), 207 (3), 192 (3), 191 (2), 165 (4), 147 (5), 146 (3), 145 (3), 133 (11), 132 (96), 131 (4), 118 (16), 117 (36), 116 (3), 115 (4), 105 (11), 104 (12), 103 (28), 102 (8), 91 (24), 90 (100), 89 (84), 77 (24), 76 (20)
29	284/282 (M^+, 1.1), 256/254 (M-28$^+$, 0.7), 229/227 (M-55$^+$, 4.4), 191 (2), 153 (0.4), 152 (0.7), 151 (0.5), 150 (1.7), 138/136 (42), 118 (3), 106 (4), 105 (5), 104 (2), 103 (7), 101 (16), 90 (100), 89 (25), 77 (12), 75 (17)
30	328/326 (M^+, 0.7), 300/298 (M-28$^+$, 1.3), 273/271 (M-55$^+$, 2.6), 197 (0.9), 196 (0.9), 195 (0.9), 194 (0.9), 192 (1), 191 (2), 182/180 (26), 118 (26), 116 (2), 115 (2), 104 (2), 103 (6), 101 (26), 90 (100), 89 (24), 77 (6), 75 (22)

the 5-position of the triazole ring in compounds **17** and **18**.

Thus, in conclusion, the fragmentation pattern upon electron impact of the 1-arylideneamino-1,2,3-triazoles can be used, along with spectroscopic methods [16,17], for distinguishing between the 4,5-unsymmetrically substituted derivatives, provided that one of the substituents is an aryl group. It should be noticed however, that other 1-substituted 4- or 5-phenyl-1,2,3-triazoles have been reported [15b] to give undistinguishable, identical fragments in their mass spectra.

A general fragmentation pattern in the mass spectra of compounds **9-30** is presented in the Scheme, whereas the main fragments with the relative intensities are given in Table 2. Figures 1-4 represent typical mass spectra of the compounds **11**, **18**, **20** and **24** respectively.

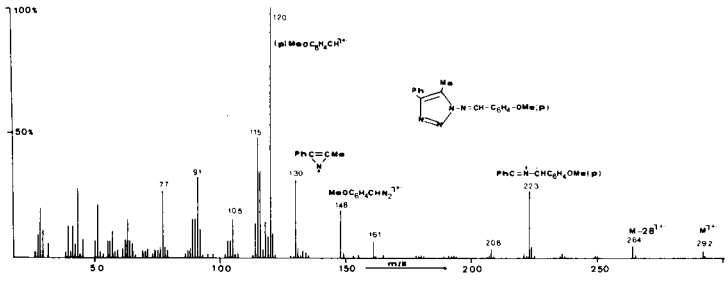


Figure 3. The 70 eV mass spectrum of compound **20**.

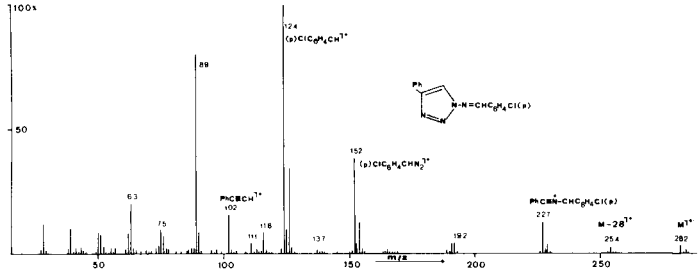


Figure 4. The 70 eV mass spectrum of compound **24**.

EXPERIMENTAL

Melting points are uncorrected and they were obtained with a Kofler hot stage apparatus. The ir spectra were obtained with a Perkin-Elmer 297 spectrometer, and the ^{1}H-nmr spectra, reported in δ units, were obtained with a Varian A-60A spectrometer with TMS as internal reference, in deuteriochloroform solutions. The mass spectra were measured with a Hitachi-Perkin-Elmer model RMU-6L spectrometer, with an ionization energy of 70 eV, at temperatures in the ion source between 180-200°. Elemental micro analyses were performed with a Perkin-Elmer 240 CHN analyser.

1-Amino-1,2,3-triazoles **1-8** were prepared by acid hydrolysis of the corresponding 1-(α-benzoyloxybenzylidene)amino-1,2,3-triazoles [6] or of the 1-ureido-1,2,3-triazoles [5b], and their analytical and spectral data were in agreement with those given in the literature and with their structure.

1-Arylideneamino-1,2,3-triazoles **9-30** were prepared by the following procedure [7]:

An equimolecular amount of 1-amino-1,2,3-triazole (10 mmoles) and of the corresponding benzaldehyde (10 mmoles) and alumina (Aluminium oxide 90, neutral, 70-230 mesh, Merk) (0.5 g), in toluene (5 ml), were refluxed for 4-10 hours. The reaction mixture was filtered and the aluminium oxide was washed on the filter several times with methylene chloride or hot chloroform, in the case of dissoluble derivatives. The combined filtrates were evaporated to give the 1-arylideneamino-1,2,3-triazole, which was recrystallized from the appropriate solvent. The yields were between 60-95%. Analytical and spectral data of the compounds thus prepared are given in Table 1. The main ion fragments in their mass spectra are given in Table 2.

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