

Nikolaos G. Argyropoulos\* and Ecaterini Corobili [1]

Aristotelian University of Thessaloniki, Department of Chemistry, Laboratory of Organic Chemistry, Thessaloniki 540 06 Greece

Ecaterini P. Raptopoulou

National Research Center of Physical Sciences, "DEMOCRITOS" 153 10, Aghia Paraskevi, Athens Greece

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Dedicated to the memory of Professor Nicholas Alexandrou

A new, unusual way to obtain polysubstituted 1*H*-*s*-triazole *N*-imine derivatives is described from reactions of the readily available 1,3,4-oxadiazin-6-one derivatives and nitrilimines. Besides an hydrazide derivative of phenylglyoxylic acid is also formed. Both adducts were characterised by X-ray crystal structure analysis.

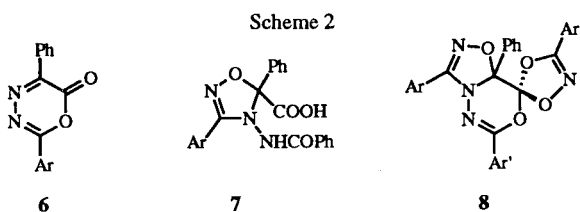
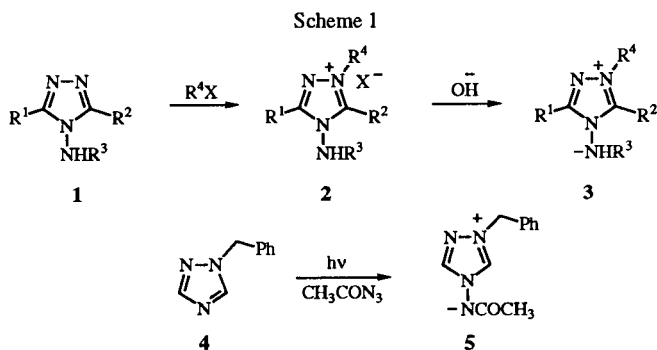
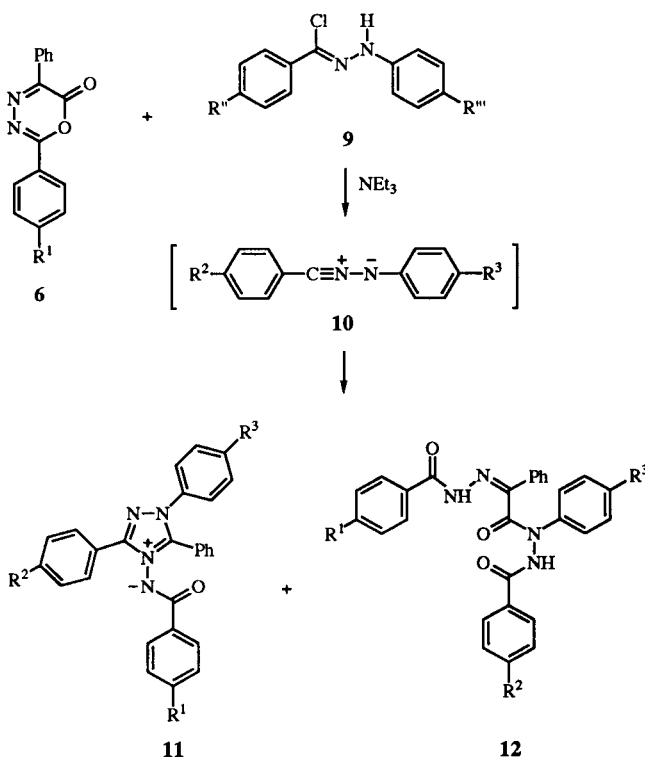
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The chemistry of heteroaromatic *N*-imines is closely related with their 1,3-dipolar azomethine *N*-imine functionality which makes them useful synthetic intermediates, particularly in heterocyclic synthesis. Many classes of these interesting compounds are known. In fact any heteroaromatic ring, with one or more nitrogen atom, with an amino group attached to ring nitrogen, is possible *N*-imine precursor. The most thoroughly studied *N*-imines are those of the pyridine ring. However many other classes with various nitrogen heteroaromatics, such as quinoline, triazoles, pyrazoles, imidazoles, diazines, etc. are also known. There is a rich chemistry concerning these compounds and at least two comprehensive review articles have already appeared [2,3].

An interesting class of *N*-imine derivatives is this of *s*-triazoles **3** which are stable compounds, except those

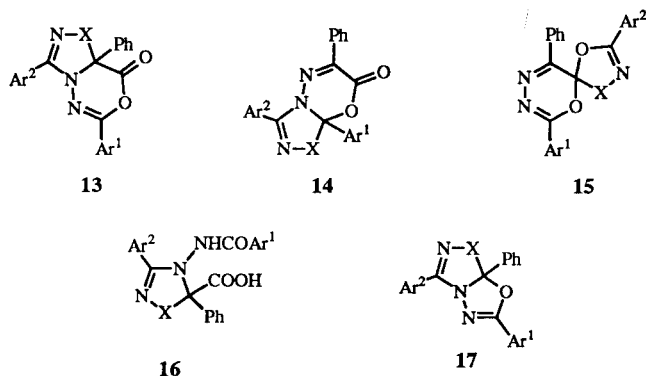
with an unsubstituted imino group. They are usually obtained from the corresponding *N*-aminoazoles **1** by quaternization and subsequent deprotonation of the resulting *N*-aminoazolium salts **2** [4-6], or by direct ami-

Scheme 3

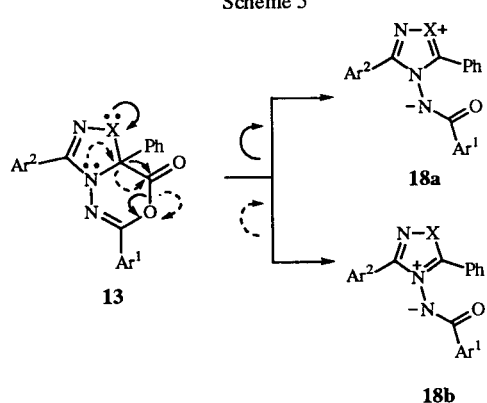


**6a**,  $\text{R}^1 = \text{H}$ ; **6b**,  $\text{R}^1 = \text{NO}_2$ ; **6c**,  $\text{R}^1 = \text{Me}$ ; **6d**,  $\text{R}^1 = \text{OMe}$ ; **6e**,  $\text{R}^1 = \text{Cl}$   
**9a**,  $\text{R}^2 = \text{R}^3 = \text{H}$ ; **9b**,  $\text{R}^2 = \text{Cl}$ ,  $\text{R}^3 = \text{H}$ ; **9c**,  $\text{R}^2 = \text{Me}$ ,  $\text{R}^3 = \text{H}$ ; **9d**,  $\text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{NO}_2$   
**11a**, **12a**,  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ; **11b**, **12b**,  $\text{R}^1 = \text{NO}_2$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ ; **11c**, **12c**,  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ ; **11d**, **12d**,  $\text{R}^1 = \text{R}^3 = \text{H}$ ,  $\text{R}^2 = \text{Cl}$ ; **11e**, **12e**,  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Cl}$ ,  $\text{R}^3 = \text{H}$ ;  
**10f**, **12f**,  $\text{R}^1 = \text{NO}_2$ ,  $\text{R}^2 = \text{Cl}$ ,  $\text{R}^3 = \text{Me}$ ; **11g**, **12g**,  $\text{R}^1 = \text{R}^3 = \text{H}$ ,  $\text{R}^2 = \text{Me}$ ; **11h**, **12h**,  $\text{R}^1 = \text{Cl}$ ,  $\text{R}^2 = \text{Me}$ ,  $\text{R}^3 = \text{H}$ ; **11i**, **12i**,  $\text{R}^1 = \text{NO}_2$ ,  $\text{R}^2 = \text{Me}$ ,  $\text{R}^3 = \text{H}$ ; **11j**, **12j**,  $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{NO}_2$

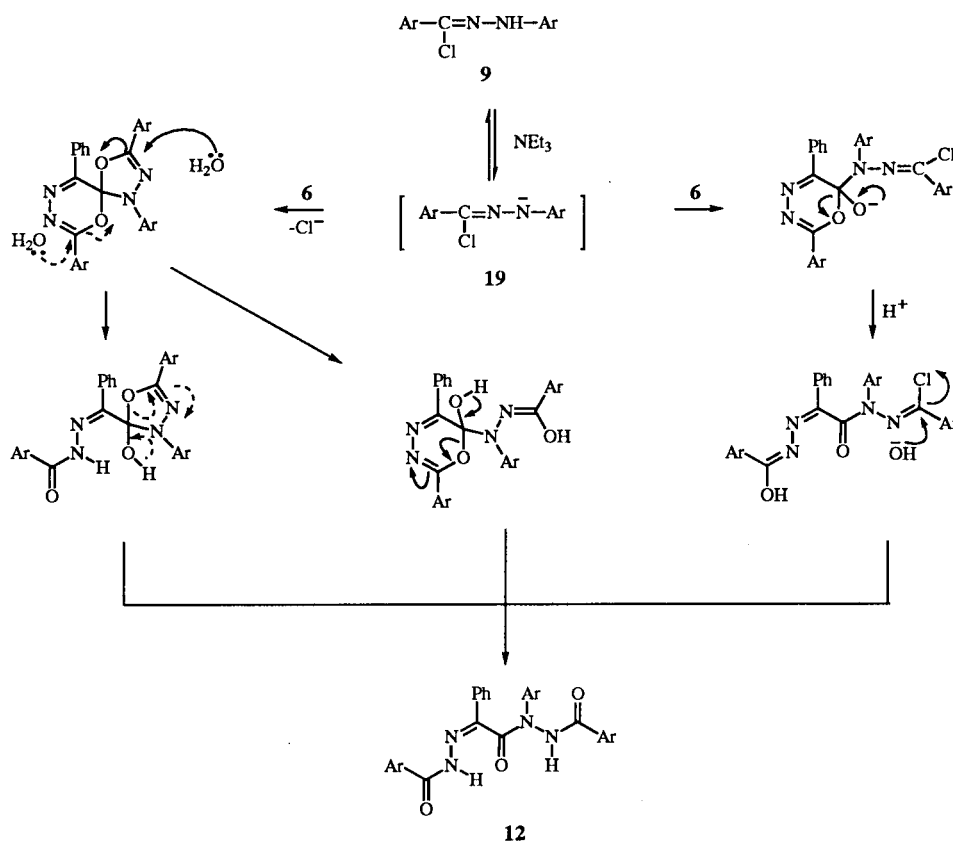
Scheme 4



Scheme 5



Scheme 6



nation of triazoles **4** with acyl azides upon irradiation. A nitrene intermediate is presumably involved [2] (Scheme 1). Some cycloaddition reactions of them with various dipolarophiles have been also described [7-10]. In this paper will be described an unusual and quite unexpected novel way for their preparation from 1,2,4-oxadiazin-6-ones and nitrilimines.

1,3,4-Oxadiazin-6-ones **6**, first described by Steglich and coworkers [11], are mainly known from their inverse electron demand Diels Alder reactions, acting as  $\pi_4$  component, with their 2,3-diaza-1,3-diene functionality [12-17]. In addition the presence of three dipolarophilic

centers makes this ring a suitable partner in dipolar cycloadditions. In this respect our interest in oxadiazinone chemistry was originally oriented to their dipolarophilic behaviour and we have already [18] studied the cycloaddition reactions of some derivatives with nitrile oxides. In that study a remarkable site selectivity was found for the adjacent carbonyl carbon-nitrogen double bond and for the carbonyl double bond itself, giving rise to compounds of type **7** and **8** respectively. The other carbon nitrogen double bond seems to be completely unreactive (Scheme 2).

Our next step was the study of analogous reactions with nitrilimines. Although both nitrile oxides and nitrilimines

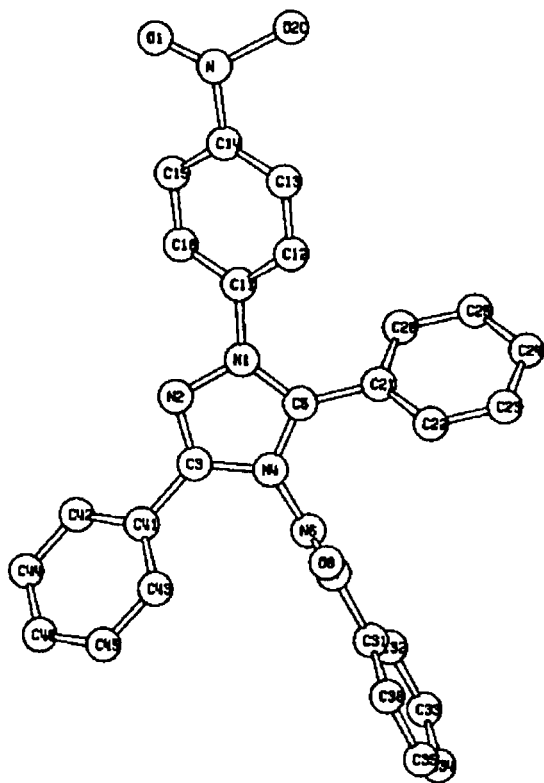


Figure 1. Crystal Structure of *s*-Triazole *N*-Imine 11j.

are two closely related classes of 1,3-dipoles [19], the reactions of nitrilimines in this particular case followed a quite different and unusual course. In all cases studied no one typical cycloadduct, analogous to those obtained from reactions with nitrile oxides, is obtained. Instead the main reaction product was the 1,2,4-triazole *N*-imine derivatives **11** and an open chain adduct **12**, an unusual poly-substituted hydrazide derivative of the aroylhydrazone of phenylglyoxylic acid (Scheme 3).

A typical experiment involves equimolar amounts of 2,5-diaryl-1,3,4-oxadiazin-6-ones **6**, prepared as reported [11,20] and diaryl nitrilimines **10**, which were liberated *in situ* from the corresponding hydrazoneyl chlorides **9** and triethylamine [21], in stirring benzene solution and at room temperature for 5 days. In some cases the reactions were performed in refluxing benzene solutions within 2 days. Work up of the reaction mixture on column chromatography (silica gel, hexane/ethyl acetate) gave compounds **12** followed by **11**, which was eluted with ethyl acetate.

Spectral and analytical data for compounds **11** and **12** are collected in Tables 1 and 2 respectively. The *N*-imines exhibit in the ir spectra a characteristic low frequency (~1600 cm<sup>-1</sup>) carbonyl absorption, quite similar to that observed from other analogous *s*-triazole *N*-acylimines [2]. In the mass spectra the molecular ion is usually not observed, but instead the most characteristic fragment is that of a triazole one formed by a N-N bond cleavage

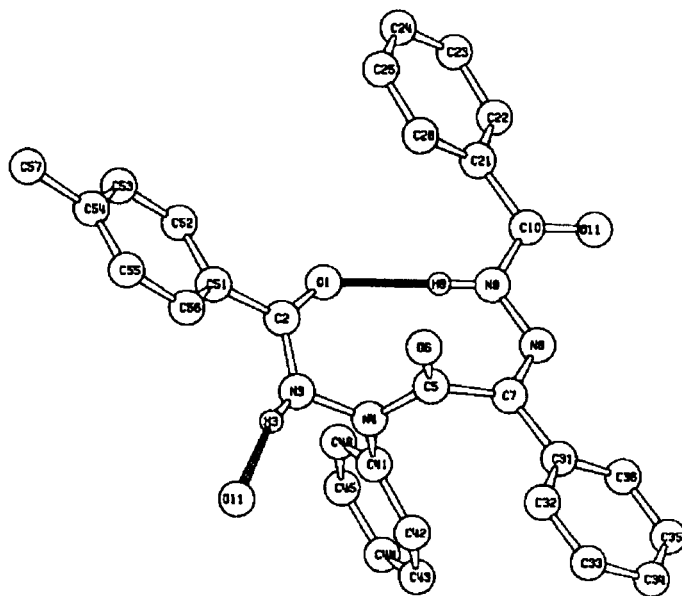


Figure 2. Crystal Structure of Hydrazide 12g.

analogous to that observed in other analogous cases [2,22]. As regards the open chain adduct it is noteworthy that in the <sup>1</sup>H nmr the chemical shifts for the NH protons and also for the methyl protons appear in some cases as two or three peaks, probably as a result of hindered rotation of amide bond and possibly from intramolecular hydrogen bonding.

The unusual reaction course was associated with uncertainties regarding structure elucidation of the isolated products. From the available data both reaction products were characterized as a 1:1 adduct and from that point of view of typical cycloadducts (Scheme 4), according to a dipolar cycloaddition mode, structures **13-15** (X = NAr) were the most probable. The absence of a typical carbonyl absorption for compound **11**, suggesting a cycloaddition across the carbonyl double bond (structure **15**, X = NAr), is not supported by either analytical or ms data. As previously noted all these compounds exhibit a very strong peak, in the mass spectra, corresponding to a benzonitrile-nitrilimine fragment, which could not account for any compound related to structure **15**. On the other hand structure **17** (X = NAr) might be considered, since all available spectral data support **17**.

With respect to the open chain adduct **12**, analytical data suggest structure **16**, an adduct quite analogous to that obtained from all reactions of nitrile oxides and oxadiazinones (X = O) [18]. However comparing spectral data of both classes, there are notable differences. The ir spectra of compounds **12** show an amide carbonyl absorption (~1680 cm<sup>-1</sup>), instead of that of the triazolincarboxylic acid, which is expected to absorb at higher frequencies. In the mass spectra fragments corresponding to the triazole ring were not observed. For the above reasons

Table 1  
Analytical and Spectral Data of Compounds 11

Compound	Mp °C	Yield %	Molecular Formula M.W.	Analysis %			Spectral Data
				Calcd.	Found		
11a	195-197	28	C <sub>27</sub> H <sub>20</sub> N <sub>4</sub> O M.W. 416.46	77.86 77.71	4.84 4.84	13.45 13.28	ir (nujol): 3080, 1610 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 7.21-7.76 (m, 16H), 7.88-8.15 (m, 2H), 8.15-8.39 (m, 2H); ms: m/z (%) 416 [M <sup>+</sup> ], (2), 297 (37), 194 (46), 119 (23), 105 (21), 103 (18), 91 (100)
11b	227-229	38	C <sub>27</sub> H <sub>19</sub> N <sub>5</sub> O <sub>3</sub> M.W. 461.46	70.27 70.36	4.15 4.03	15.18 15.13	ir (nujol): 3040, 1605 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 7.16-7.83 (m, 13H), 8.08-8.46 (m, 6H); ms: m/z (%) 429 (8), 297 (14), 224 (57), 207 (68), 194 (17), 163 (8), 150 (9), 103 (31)
11c	198-200	44	C <sub>28</sub> H <sub>22</sub> N <sub>4</sub> O M.W. 430.49	78.12 77.91	5.15 5.20	13.02 13.12	ir (nujol): 3040, 1590 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.3 (s, 3H), 7.0-7.75 (m, 15H), 7.8-8.0 (d, 2H, J = 8 Hz), 8.1-8.4 (m, 2H); ms: m/z (%) 429 [M <sup>+</sup> ], (5), 297 (31), 194 (37), 133 (11), 119 (23), 103 (17), 91 (100)
11d	189-191	49	C <sub>27</sub> H <sub>19</sub> N <sub>4</sub> OCl M.W. 450.91	71.91 71.68	4.25 4.31	12.42 12.35	ir (nujol): 3040, 1600, 1590; <sup>1</sup> H nmr (deuteriochloroform): δ 7.2-7.8 (m, 15H), 7.9-8.1 (m, 2H), 8.35 (d, 2H, J = 8 Hz); ms: m/z (%) 449 (1), 331 (22), 297 (1), 228 (20), 119 (50), 105(4), 103 (21), 91 (100)
11e	198-200	28	C <sub>28</sub> H <sub>21</sub> N <sub>4</sub> OCl M.W. 464.94	72.33 72.20	4.55 4.44	12.05 12.23	ir (nujol): 1580 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.33(s, 3H), 7.09-7.68 (m, 14H), 7.9 (d, 2H, J = 8 Hz), 8.25 (d, 2H, J = 8 Hz); ms: m/z (%) 463 (n), 429 (n) 331 (59), 228 (36), 133 (79), 103 (9), 91 (100)
11f	190-192	50	C <sub>27</sub> H <sub>18</sub> N <sub>5</sub> O <sub>3</sub> Cl M.W. 495.91	65.39 65.60	3.66 3.67	14.12 14.19	ir (nujol): 3050, 1610, 1580 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 7.15-7.75 (m, 12H), 8.0-8.3 (m, 6H); ms: m/z (%) 326 (22), 228 (10), 164 (2) 150 (2) 137 (15), 103 (100), 91 (25)
11g	191-194	46	C <sub>28</sub> H <sub>22</sub> N <sub>4</sub> O M.W. 430.49	78.12 78.31	5.15 4.99	13.02 13.14	ir (nujol): 3040, 1590 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.35 (s, 3H), 7.2-7.8 (m, 15H), 7.95-8.10 (m, 2H), 8.18 (d, 2H, J = 8 Hz); ms: m/z (%) 311 (4), 207 (14), 119 (61), 116 (15), 103 (56), 91 (100)
11h	197-198	24	C <sub>28</sub> H <sub>21</sub> N <sub>4</sub> OCl M.W. 464.94	72.33 72.48	4.55 4.61	12.05 12.08	ir (nujol): 3040, 1595; <sup>1</sup> H nmr (deuteriochloroform): δ 2.4 (s, 3H), 7.0-7.7 (d, 2H, J = 8 Hz), 8.15 (d, 2H, J = 8 Hz); ms: m/z (%) 311 (34), 208 (31), 155 (100), 139 (5), 103 (8), 91 (98)
11i	214-216	68	C <sub>28</sub> H <sub>21</sub> N <sub>5</sub> O <sub>3</sub> M.W. 475.49	70.72 71.02	4.45 4.58	14.73 14.80	ir (nujol): 3060, 1610 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.3 (s, 3H), 7.2-7.8 (m, 14H), 7.9-8.2 (m, 4H); ms: m/z (%) 311 (100), 208 (92), 164 (80), 150 (4), 103 (26), 91 (90)
11j	211-213	17	C <sub>27</sub> H <sub>19</sub> N <sub>5</sub> O <sub>3</sub> M.W. 461.46	70.27 70.01	4.15 4.01	15.18 15.01	ir (nujol): 3040, 1595 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform) 7.25-7.78 (m, 13H), 7.09-8.08 (m, 2H), 8.17-8.42 (m, 4 H); ms: m/z (%) 461, [M <sup>+</sup> ], (1) 342 (60), 239 (40), 119 (100), 105 (28), 103 (42), 91 (99)

both structures were unambiguously determined by an X-ray crystal structure analysis of compounds 11j and 12g, respectively.

The established molecular geometry and the labelling sequences of these compounds are given in Figures 1 and 2 respectively. Selected values of bond distances and bond angles and positional parameters of non-hydrogen atoms are given in Tables 3 and 4. Imines 11 have an almost planar triazole ring with a characteristic long length (~1.25 Å) carbonyl double bond, substantially longer than a typical amide carbonyl double bond observed in amides (~1.21 Å). The open chain adduct has a *Z* configuration around the carbon nitrogen double bond and a folded geometry as a result of an intramolecular hydrogen bond between O(1)1 and H(9).

In a plausible mechanistic assumption for the *N*-imine formation, it is reasonable to assume, that a non isolable mono adduct 13 (X = NAr<sup>3</sup>) is initially formed, from a cycloaddition across the adjacent carbonyl-carbon nitrogen double bond. This, in turn, undergoes a CO abstraction,

which might be formulated as a [ $\pi 6_s + \omega 2_a$ ] retrochelotropic cycloreversion, resulting in the delocalized triazolium heteroaromatic ring 18a,b (X = NAr) (Scheme 5). On the other hand the analogous non isolable primary adduct 13 (X = O) obtained from nitrile oxides is ring opened into the oxadiazoline carboxylic acid [18]. This apparent different behaviour between these possible primary adducts might be explained as a result of the enhanced aromaticity of triazole ring (X = NAr<sup>3</sup>) [23,24] over that of a possible oxadiazole ring 18 (X = O) [24,25].

The open chain adduct 12 was apparently formed from an intermediate of a reaction at the carbonyl double bond of oxadiazinone. Depending on the mode of initial attack, two alternative mechanistic pathways may be proposed. The first one involves the formation of a typical non isolable cycloadduct from the carbonyl double bond 15, which in turn is hydrolysed by ring opening, either of the 6*H*-oxadiazine ring or the oxadiazoline ring. The other pathway may involve a nucleophilic attack to the carbonyl double bond, which is susceptible to nucleophilic

Table 2  
Analytical and Spectral Data of Compounds 12

Compound	Mp °C	Yield %	Molecular Formula	Analysis %			Spectral Data
				Calcd./Found			
<b>12a</b>	185-188	41	C <sub>28</sub> H <sub>22</sub> N <sub>4</sub> O <sub>3</sub> M.W. 462.49	72.71 72.88	4.79 4.89	12.12 12.28	ir (nujol): 3280, 1660, 1635 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 6.89-8.27, (m, 20H), 9.90, (s, 1H), 10.49, 11.29 (s, 1H); ms: m/z (%) 327 (3), 251 (10), 223 (32), 213 (11), 211 (64), 194 (5), 105 (100)
<b>12b</b>	196-199	12	C <sub>28</sub> H <sub>21</sub> N <sub>5</sub> O <sub>5</sub> M.W. 507.49	66.26 66.08	4.17 4.31	13.80 13.95	ir (nujol): 3250, 1690, 1600 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 4.7-8.4 (m, 19H), 9.24 (s, 1H), 11.6 (s, 1H); ms: m/z (%) 427 (2), 356 (1), 328 (2), 316 (5), 241 (12), 211 (35), 185 (100), 150 (13), 120 (9), 105 (65), 91 (23)
<b>12c</b>	222-225	35	C <sub>29</sub> H <sub>24</sub> N <sub>4</sub> O <sub>3</sub> M.W. 476.51	73.09 73.28	5.08 5.18	11.76 11.91	ir (nujol): 3250, 1675, 1640, 1600 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.3, 2.4 (s, 3H), 6.9-8.1 (m, 19H), 9.22 (s, 1H), 11.1, 11.22 (s, 1H); ms: m/z (%) 368 (16), 296 (36), 239 (8), 237 (5), 211 (5), 194 (6), 134 (99), 120 (9), 119 (18), 105 (32), 103 (17)
<b>12d</b>	216-219	48	C <sub>28</sub> H <sub>21</sub> N <sub>4</sub> O <sub>3</sub> Cl M.W. 496.94	67.67 67.49	4.26 4.26	11.27 11.18	ir (nujol): 3200, 1680, 1650, 1630 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): 6.99-8.10 (m, 19H), 9.90 (s, 1H), 10.48, 11.2, (s, 1H); ms: m/z (%) 331 (1), 273 (1), 245 (20), 228 (20), 168 (14), 154 (4), 139 (70), 105 (100)
<b>12e</b>	194-197	23	C <sub>29</sub> H <sub>23</sub> N <sub>4</sub> O <sub>3</sub> Cl M.W. 510.96	68.16 68.15	4.53 4.63	10.96 10.78	ir (nujol): 3140, 1690, 1660, 1640, 1595 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.28, 2.41 (s, 3H), 6.87-8.06 (m, 18H), 9.95 (s, 1H), 10.39, 11.12 (s, 1H); ms: m/z (%) 410 (1), 285 (1), 273 (4), 265 (3), 245 (19), 237 (5), 228 (15), 168 (4), 154 (6), 139 (51), 119 (100), 103 (45)
<b>12f</b>	208-211	10	C <sub>28</sub> H <sub>20</sub> N <sub>5</sub> O <sub>5</sub> Cl M.W. 541.94	62.05 61.98	3.72 4.00	12.92 13.08	ir (nujol): 3250, 1690, 1670, 1645, 1590 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 6.98-8.51 (m, 18H), 9.78 (s, 1H), 11.5 (s, 1H); ms: m/z (%) 267 (60), 245 (45), 228 (57), 168 (Cl), (12), 165 (90), 154 (12), 150 (44), 139 (98), 105 (59), 103 (100)
<b>12g</b>	202-205	34	C <sub>29</sub> H <sub>24</sub> N <sub>4</sub> O <sub>3</sub> M.W. 476.51	73.09 73.18	5.08 5.28	11.76 11.89	ir (nujol): 3200, 1680, 1660, 1650, 1615, 1600 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.1, 2.3 (s, 3H), 6.7-8.2 (m, 19H), 9.38 (s, 1H), 11.32 (s, 1H); ms: m/z (%) 251 (3), 223 (16), 222 (35) 208 (26), 180 (21), 166 (20), 165 (50), 149 (29), 119 (86), 105 (100), 103 (98)
<b>12h</b>	198-201	38	C <sub>29</sub> H <sub>23</sub> N <sub>4</sub> O <sub>3</sub> Cl M.W. 510.96	68.16 68.11	4.53 4.38	10.96 10.73	ir (nujol): 3180, 1675, 1615, 1600 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.18, 2.4 (s, 3H), 6.8-8.1 (m, 18H), 9.1 (s, 1H), 11.3 (s, 1H); ms: m/z (%) 284 (2), 257 (10), 226 (10), 210 (10), 208 (16), 153 (11), 139 (49), 119 (74), 103 (100)
<b>12i</b>	164-167	11	C <sub>29</sub> H <sub>23</sub> N <sub>5</sub> O <sub>5</sub> M.W. 521.51	66.78 66.63	4.45 4.63	13.43 13.34	ir (nujol): 3280, 1690, 1675, 1650, 1605 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 2.32, 2.4 (s, 3H), 7.18-8.38 (m, 18H), 9.25 (s, 1H), 11.6 (s, 1H); ms: m/z (%) 280 (15), 268 (21), 225 (35), 165 (17), 150 (30), 119 (100), 105 (52), 103 (56), 91 (61)
<b>12j</b>	212-215	34	C <sub>28</sub> H <sub>21</sub> N <sub>5</sub> O <sub>5</sub> M.W. 507.5	66.26 66.61	4.17 3.99	13.80 13.89	ir (nujol): 3240, 1690, 1650, 1595 cm <sup>-1</sup> ; <sup>1</sup> H nmr (deuteriochloroform): δ 7.2- 8.4 (m); ms: m/z (%) 397 (n), 343 (n), 251 (15), 239 (n), 223 (38), 120 (9), 105 (100), 91 (11)

ring opening [12]. One possible nucleophile may be the hydrazoneyl chloride anion **19**, since it is known [26] that the triethylamine dehydrochlorination of hydrazoneyl chlorides to nitrilimines, proceeds *via* a rapid proton abstraction, followed by the rate determining step of chloride anion removal. Both processes could finally afford the open chain adduct **12** as exemplified in Scheme 6. However there is not any evidence supporting these assumptions, or others such as that the possibility of the starting hydrazoneyl chloride **9** may be the actual nucleophile.

## EXPERIMENTAL

All melting points are uncorrected and they are obtained with a Kofler hot stage apparatus. The ir spectra were obtained with a Perkin-Elmer 297 spectrophotometer. The <sup>1</sup>H nmr spectra, reported in δ units, were obtained in deuteriochloroform solutions, with tetramethylsilane as the internal standard, and recorded with a Bruker AW 80 spectrometer, whereas mass spectra were measured with a Hitachi-Perkin-Elmer RMU-6L or VG TS-250 spectrometer with an ionization energy of 70 eV. Elemental analyses were performed with a Perkin-Elmer 240B automatic analyzer.

Table 3

Selected Bond Distances (Å) and Bond Angles (°) of Compounds <b>11j</b> and <b>12g</b>				b: Angles (°)			
a: Bond Distances (Å)				Compound <b>11j</b>	Compound <b>12g</b>		
Compound <b>11j</b>		Compound <b>12g</b>					
N(1)-N(2)	1.376(5)	O(1)-C(2)	1.224(2)	N(2)-N(1)-C(5)	112.2(3)	O(1)-C(2)-N(3)	121.1(1)
N(1)-C(5)	1.337(5)	C(2)-N(3)	1.357(2)	N(2)-N(1)-C(11)	116.9(3)	O(1)-C(2)-C(51)	121.9(1)
N(1)-C(11)	1.432(5)	C(2)-C(51)	1.480(2)	C(5)-N(1)-C(11)	130.8(4)	N(3)-C(2)-C(51)	117.0(1)
N(2)-C(3)	1.308(5)	N(3)-N(4)	1.397(1)	N(1)-N(2)-C(3)	104.1(3)	C(2)-N(3)-N(4)	117.1(1)
C(3)-N(4)	1.375(5)	N(4)-C(5)	1.372(2)	N(2)-C(3)-N(4)	110.8(4)	N(3)-N(4)-C(5)	115.4(1)
C(3)-C(41)	1.364(6)	N(4)-C(41)	1.437(2)	N(2)-C(3)-C(41)	124.1(4)	N(3)-N(4)-C(41)	117.5(1)
N(4)-C(5)	1.347(5)	C(5)-O(6)	1.212(2)	N(4)-C(3)-C(41)	125.1(4)	C(5)-N(4)-C(41)	125.5(1)
N(4)-N(6)	1.408(5)	C(5)-C(7)	1.513(2)	C(3)-N(4)-C(5)	107.9(3)	N(4)-C(5)-O(6)	122.7(1)
C(5)-C(21)	1.464(5)	C(7)-N(8)	1.285(2)	C(3)-N(4)-N(6)	125.2(3)	N(4)-C(5)-C(7)	116.8(1)
N(6)-C(7)	1.347(5)	C(7)-C(31)	1.470(2)	C(5)-N(4)-N(6)	125.3(3)	O(6)-C(5)-C(7)	120.3(1)
C(7)-O(8)	1.248(5)	N(8)-N(9)	1.376(2)	N(1)-C(5)-N(4)	105.0(3)	C(5)-C(7)-N(8)	121.4(1)
C(7)-C(31)	1.500(6)	N(9)-C(10)	1.363(2)	N(1)-C(5)-C(21)	128.5(4)	C(5)-C(7)-C(31)	120.1(1)
		C(10)-O(11)	1.221(2)	N(4)-C(5)-C(21)	126.4(4)	N(8)-C(7)-C(31)	118.1(1)
		C(10)-C(21)	1.490(2)	N(4)-N(6)-C(7)	111.6(3)	C(7)-N(8)-N(9)	118.9(1)
				N(6)-C(7)-C(31)	112.0(4)	N(8)-N(9)-C(10)	117.3(1)
				N(6)-C(7)-O(8)	126.9(4)	N(9)-C(10)-O(11)	122.4(1)
				O(8)-C(7)-C(31)	121.1(4)	N(9)-C(10)-C(21)	116.0(1)

Table 4

Positional Parameters ( $\times 10^4$ ) of non-Hydrogen Atoms of Compounds **11j** and **12g**

<b>11j</b>				<b>12g</b>			
Atom	x	y	z	Atom	x	y	z
N(1)	3027(3)	3053(1)	9906(4)	O(1)	7605(1)	4054(1)	10382(1)
N(2)	1862(4)	2794(1)	9882(4)	C(2)	7698(1)	3460(1)	11014(1)
C(3)	2302(4)	2338(2)	9633(5)	N(3)	7124(1)	2545(1)	10989(1)
N(4)	3699(3)	2306(1)	9494(4)	C(5)	7298(1)	1932(1)	9598(1)
C(5)	4154(4)	2763(2)	9658(4)	O(1)	8262(8)	1813(1)	9825(6)
C(11)	2840(4)	3568(2)	10254(5)	C(7)	6807(1)	1883(1)	8642(1)
C(12)	3462(5)	3782(2)	11243(5)	N(8)	6845(1)	2682(1)	8134(1)
C(13)	3189(6)	4273(2)	11641(6)	N(9)	7258(1)	3628(1)	8486(1)
C(14)	2282(6)	4525(2)	11073(6)	C(10)	7428(1)	4412(1)	7920(1)
C(15)	1662(5)	4315(2)	10090(5)	O(11)	7198(1)	4307(1)	7130(1)
C(16)	1969(5)	3832(2)	9647(5)	C(51)	8438(1)	3703(1)	11835(1)
C(21)	5589(4)	2903(2)	9533(5)	C(52)	8713(1)	4754(1)	12019(10)
C(22)	6280(4)	2638(2)	10367(5)	C(53)	9457(2)	5009(2)	12744(1)
C(23)	7636(5)	2764(2)	10244(6)	C(54)	9954(1)	4238(2)	13301(1)
C(24)	8288(5)	3150(2)	9303(7)	C(55)	9676(1)	3193(2)	13111(1)
C(25)	7598(5)	3416(2)	8472(6)	C(56)	8926(1)	2925(1)	12387(1)
C(26)	6236(5)	3294(2)	8588(5)	C(57)	10787(2)	4528(2)	14074(1)
N(6)	4570(4)	1894(1)	8911(4)	C(21)	7934(1)	5403(1)	8320(1)
C(7)	4688(4)	1606(2)	10071(5)	C(22)	7697(2)	6346(1)	7875(1)
O(8)	4129(3)	1677(1)	11505(3)	C(23)	8210(2)	7272(2)	8185(2)
C(31)	5566(5)	1157(2)	9451(6)	C(24)	8962(2)	7269(2)	8927(2)
C(32)	6378(5)	1114(2)	7876(6)	C(25)	9192(2)	6352(2)	9370(1)
C(33)	7174(6)	692(2)	7351(9)	C(26)	8683(1)	5412(2)	9074(1)
C(34)	7148(7)	313(2)	8350(10)	C(31)	6384(1)	874(1)	8252(1)
C(35)	6362(7)	354(2)	9924(9)	C(32)	6600(1)	-77(1)	8693(1)
C(36)	5574(6)	775(2)	10465(7)	C(33)	6181(2)	-1021(1)	8330(1)
C(41)	1410(4)	1919(2)	9540(5)	C(34)	5559(2)	-1022(2)	7517(1)
C(42)	494(5)	1974(2)	8999(6)	C(35)	5339(2)	-85(2)	7073(1)
C(43)	1442(5)	1480(2)	10299(6)	C(36)	5737(1)	863(1)	7431(1)
C(44)	-378(6)	1585(3)	8615(7)	C(41)	5474(1)	2359(1)	9943(1)
C(45)	560(6)	1096(2)	10210(7)	C(42)	4816(1)	1522(1)	9620(1)
C(46)	-334(6)	1155(3)	9374(8)	C(43)	3721(1)	1673(2)	9401(1)
N	1920(10)	5042(2)	11579(8)	C(44)	3277(2)	2642(2)	9520(1)
O(1)	927(6)	5228(2)	11339(5)	C(45)	3923(2)	3471(2)	9868(1)
O(2A)	2520(30)	5244(9)	12150(50)	C(46)	5029(1)	3338(1)	10074(1)
O(2B)	1780(30)	5100(10)	13030(30)				
O(2C)	3230(20)	5317(9)	11730(40)				

Oxadiazinones **6** were prepared as reported [12,20] from the corresponding glyoxylic acid arylhydrazones and dicyclohexylcarbodiimide, in dry benzene. Nitrilimines **10** were liberated *in situ* from the corresponding arylhydrazonoyl chlorides **9** with triethylamine [21].

General Procedure for the Reaction of Oxadiazinones with Nitrilimines.

To a solution of equimolar amounts of hydrazonoyl chloride (2 mmoles) and oxadiazinones in dry benzene (25 ml) triethylamine (2 mmoles) was added and then the solution was stirred at room temperature for 5-6 days. The reaction course was monitored by tlc. The insoluble triethylamine hydrochloride was filtered off and the crude reaction mixture was chromatographed on a silica gel column using a 30% ethyl acetate-hexane mixture as the eluant. The hydrazide was eluted first while the *N*-imine was eluted with ethyl acetate. Analytical samples were obtained after recrystallization from dichloromethane-hexane mixtures. Analytical data for the *N*-imines are given in Table 1 and for the hydrazides in Table 2. The reactions between 2,5-diphenyloxadiazin-6-one **6a** and *C*-(*p*-chlorophenyl)-*N*-phenylhydrazonoyl chloride **9b**, 2-(*p*-nitrophenyl)-5-phenyl-3,4-oxadiazin-6-one **6b** and *C,N*-diphenylhydrazonoyl chloride **9a** and 2-(*p*-methylphenyl)-5-phenyl-3,4-oxadiazin-6-one **6c** with *C,N*-diphenylhydrazonoyl chloride **9a** and *C*-(*p*-chlorophenyl)-*N*-phenylhydrazonoyl chloride **9b** were carried out in refluxing benzene solutions for about 2 days. Workup is essentially the same as that described above.

Crystal Data.

Compound **11j** (C<sub>27</sub>H<sub>19</sub>N<sub>5</sub>O<sub>3</sub>, monoclinic, Space group *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 10.0833(6), *b* = 27.111(1), *c* = 9.0596(5) Å, β = 70.494(4)° *V* = 2334.4(2) Å<sup>3</sup>, *Z* = 4, *F*(000) = 940, μ = 0.57 cm<sup>-1</sup>. Compound **12g** (C<sub>29</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>, monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*c* *a* = 12.557(2), *b* = 12.595(2), *c* = 15.550(2) Å, β = 99.58(1)°, *V* = 2425.1(7) Å<sup>3</sup>, *Z* = 4, *F*(000) = 1000, μ = 6.15 cm<sup>-1</sup>. Data were collected on a Syntex P2, four-circle diffractometer upgraded by CRYSTAL LOGIC, using Nb-filtered Mo-Kα (**11j**) and Ni-filtered Cu-Kα (**12g**) radiation. Using Θ-2Θ scans 3658 (**11j**) and 3806 (**12g**) unique reflections were collected and 2603 with *F*<sub>o</sub> > 2.0 σ(*F*<sub>o</sub>) (**11j**) and 3561 with *F*<sub>o</sub> > 1.5 σ(*F*<sub>o</sub>) (**12g**) were considered as observed. The structures were solved by direct methods using SIR 88 [26] (**11j**) and SHELX 76 [27] (**12g**) programs. The least square refinement converged with *R* = 0.0679 and *R*<sub>w</sub> = 0.0659 (**11j**), and *r* = 0.0409 and *R*<sub>w</sub> = 0.0468 (**12g**). All non-hydrogens were refined anisotropically. In (**11j**) hydrogen atoms were inserted at calculated positions (C-H distance 0.96 Å). The function minimized was ΣωΔ*F*<sup>2</sup> where ω = 1 (**11j**) and [*s*<sub>2</sub>(*F*<sub>o</sub> + 0.00012*F*<sub>o</sub>)<sup>2</sup>]<sup>-1</sup> (**12g**). The structures were refined by using SHELX 76 [27].

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