1,2,3- and 1,2,4-Triazolium Salts, Pyrazoles, and Quinoxalines from Diarylnitrilimines and Isocyanides: a Study of the Scope

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Dedicated to Professor A. R. Katritzky on the occasion of his 75th birthday.

Formation of the four title compounds has been found to be strongly dependent on substituents: 1,2,3-Triazolium salts **6** do not arise from nitrilimines **2** that have an electron-acceptor attached to either the *C*- or the *N*-phenyl group. Likewise *tert*-butyl and aryl isocyanides do not afford this class of compounds; from the former isocyanide, dequaternization products **7** are obtained instead, whereas from the latter 1,2,4-triazolium salts **11** are formed. Compounds **11** with a *tert*-butyl group at the ring are unstable too, giving rise to triazoles **13**. Pyrazole formation (analogues of **14**) is completely suppressed when both *tert*-butyl and aryl isocyanides are used, whereas access to this ring system works best with *sec*-alkyl isocyanides (the influence of substituents of **2** being almost negligible in this case). Formation of quinoxalines **23** which arise from intermediary 1,2-diazets **22** by ring expansion is much favoured on employment of **2** that bears a donator substituent at the *N*-phenyl group, and under this premise ring closure to **22** is virtually independent on the nature of the isocyanide. Formation of **23** is not observed with **2** having acceptor groups.

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Introduction.

Several years ago we have shown that diarylnitrilimines **2**, generated from **1**, are attacked by isocyanides **3** at the *C*-terminus to give linear intermediates **4** (Scheme 1) which undergo four competing reactions: (i) 1/5-cyclization (→ **5**; Scheme 2), (ii) addition of **2** (→ **10**; Scheme 3), (iii) addition of **3** (→ **14**; Scheme 4), and (iv) 1/4-cyclization (→ **22**; Scheme 5). These secondary species stabilize to afford the title compounds **6**, **11**, **17**, and **23** [1,2]. Since our findings originate from a limited number of reactants, *viz.* the parent diphenylnitrilimine (**2a**) (including the tolyl derivatives **2b,c**) and two types of alkyl isocyanides (**3a** and **3b,c**), the present study is extended to nitrilimines **2** that bear an electron-donator or -acceptor group at the phenyl substituent such as **2d-g** and to isocyanides **3** that have for Z a *tert*-alkyl (**3d,e**) or an aryl group (**3g-k**). The behaviour of **2** towards an isocyanide having an activated α-methylene group (**3f**) [3] and also complementary work on *C*-acyl-*N*-arylnitrilimines [4] has been reported recently. In both cases there are major deviations in reactivity so that products different from the title classes were obtained.

Results and Discussion.

Experiments were performed under the conditions originally applied (Scheme 1; method A and B). As it becomes apparent from Table 1, all pairs of reactants **2** and **3** (given in the form of **4**) produce complex mixtures, which is especially true of runs conducted after method B. To provide an overall picture, the results from previous work [1-3] are listed, too.

1,2,3-Triazolium Salts **6**.

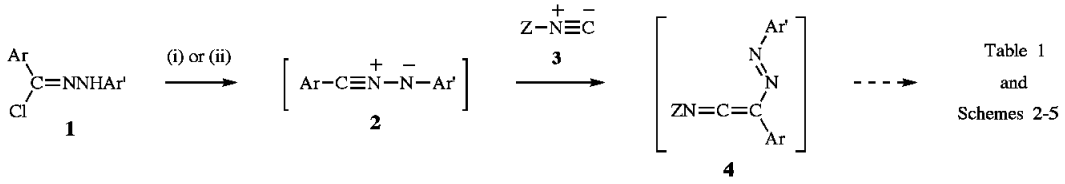
Access to this product class requires mild conditions (method A), because the precursor of **6**, *i.e.* the triazolium ylide **5**, reverts to **4** at higher temperature (a conspicuous exception concerns Z = Me [2]). Using cyclohexyl isocyanide (**3c**) as a standard probe, we found that the donator-substituted nitrilimines **2d** and **2e** afforded the desired products **6h,i** in reasonable yield (Table 1). However, when **3c** was reacted with the nitrophenyl representatives **2f** and **2g** under the same conditions, instead of compounds **6** considerable amounts of the pyrazole derivatives **17h,i** were obtained (Scheme 4), accompanied by the dihydrotetrazine **9b** and the α-hydrazonoamides **8b,c** which arise from the intermediates **4x,z** by action of moisture (*cf.* ref. [4]). The failure of **4z** to undergo 1/5-cyclization into the ylide **5** resembles unsuccessful attempts to prepare 1-aryl-2-(4-nitrophenyl)-1,2,3-triazolium salts by oxidative ring closure of the respective α-hydrazonoimines [5].

Efforts to make triazolium salts **6** with either a *tert*-butyl or a phenyl group at N(1) have been reported as being unrewarded [1]. Revisiting this finding, we observed the following:

(i) In the case of *tert*-butyl isocyanide (**3d**), 1,2,3-triazoles **7** were formed instead of **6**, perhaps *via* direct elimination of isobutene from the precursor **5**. Examples studied include the couples **2a** + **3d** and **2d** + **3d** (corresponding to intermediates **4d,q**), which afforded the derivatives **7a** and **7c**. Triazolium salts **6** having a 1-adamantyl group at N(1) were expected to be more stable, but our synthetic approach was vitiated, since under the usual conditions (method A) the isocyanide **3e** could not be kept in solution.

(ii) Aryl isocyanides such as **3g-i**, when reacted with the nitrilimines **2a,b** (intermediates **4f-h,m**), produced the 1,2,4-triazolium salts **11e-g,i** (Scheme 3). No triazolium salts **6** could be found. Their elusiveness is surprising, since congeners having aryl substituents attached to both

Scheme 1



1, 2a: Ar = Ar' = Ph
b: Ar = 4-MeC_6H_4, Ar' = Ph
c: Ar = Ph, Ar' = 4-MeC_6H_4
d: Ar = 4-$MeOC_6H_4$, Ar' = Ph
e: Ar = Ph, Ar' = 4-$MeOC_6H_4$
f: Ar = 4-$O_2NC_6H_4$, Ar' = Ph
g: Ar = Ph, Ar' = 4-$O_2NC_6H_4$

3a: Z = Me
b: Z = *i*-Pr
c: Z = *c*-C_6H_{11}
d: Z = *t*-Bu
e: Z = 1-Adamantyl
f: Z = CH_2CO_2Et

3g: Z = Ph
h: Z = 4-MeC_6H_4
i: Z = 4-$MeOC_6H_4$
j: Z = 4-$O_2NC_6H_4$
k: Z = 2,6-$Me_2C_6H_3$

4	Ar	Ar'	Z	from
a	Ph	Ph	Me	**2a** + **3a** [1,2]
b	Ph	Ph	*i*-Pr	**2a** + **3b** [1,2]
c	Ph	Ph	*c*-C_6H_{11}	**2a** + **3c** [1,2]
d	Ph	Ph	*t*-Bu	**2a** + **3d**
e	Ph	Ph	1-Adamantyl	**2a** + **3e**
f	Ph	Ph	Ph	**2a** + **3g**
g	Ph	Ph	4-MeC_6H_4	**2a** + **3h**
h	Ph	Ph	4-$MeOC_6H_4$	**2a** + **3i**
i	Ph	Ph	2,6-$Me_2C_6H_3$	**2a** + **3k**
j	4-MeC_6H_4	Ph	*i*-Pr	**2b** + **3b** [1]
k	4-MeC_6H_4	Ph	*c*-C_6H_{11}	**2b** + **3c** [1,2]
l	4-MeC_6H_4	Ph	*t*-Bu	**2b** + **3d**
m	4-MeC_6H_4	Ph	4-MeC_6H_4	**2b** + **3h**
n	Ph	4-MeC_6H_4	*i*-Pr	**2c** + **3b** [1,2]
o	Ph	4-MeC_6H_4	*c*-C_6H_{11}	**2c** + **3c** [1,2]
p	4-$MeOC_6H_4$	Ph	*c*-C_6H_{11}	**2d** + **3c**
q	4-$MeOC_6H_4$	Ph	*t*-Bu	**2d** + **3d**
r	Ph	4-$MeOC_6H_4$	*i*-Pr	**2e** + **3b**
s	Ph	4-$MeOC_6H_4$	*c*-C_6H_{11}	**2e** + **3c**
t	Ph	4-$MeOC_6H_4$	*t*-Bu	**2e** + **3d**
u	Ph	4-$MeOC_6H_4$	CH_2CO_2Et	**2e** + **3f** [3]
v	Ph	4-$MeOC_6H_4$	4-MeC_6H_4	**2e** + **3h**
w	Ph	4-$MeOC_6H_4$	2,6-$Me_2C_6H_3$	**2e** + **3k**
x	4-$O_2NC_6H_4$	Ph	*c*-C_6H_{11}	**2f** + **3c**
y	4-$O_2NC_6H_4$	Ph	*t*-Bu	**2f** + **3d**
z	Ph	4-$O_2NC_6H_4$	*c*-C_6H_{11}	**2g** + **3c**
z'	Ph	4-$O_2NC_6H_4$	*t*-Bu	**2g** + **3d**

Reagents and conditions: (i), Et_3N (1 eq.), acetonitrile (25 ml / mmol of **1**), 20 °C, 24 hours (method A; *cf.* ref. [1]); (ii), Et_3N (3-4 eqs.), benzene (3 ml / mmol of **1**), 80 °C, 1 hour (method B; *cf.* ref. [2]).

N(1) and N(2) are known to be reasonably stable compounds [6]. Whether **6** reacts rapidly with additional nitrilimine **2** (or the anion of **1**) in a manner earlier shown for 1-alkyl congeners [7], or whether **4** fails to cyclize at all (with the consequence of direct uptake of a second molecule of **2** to give **10**), remains open to discussion. Yet another point deserves a comment: Whereas under the mild conditions of method A only negligible amounts of **11** have been detected so far (*e.g.* the derivative **11b** [1,2]), the yields are remarkably high in the present case (see Table 1).

1,2,4-Triazolium Salts **11**.

For this class of compounds procedure B is the method of choice [2]. Using cyclohexyl isocyanide (**3c**), we accordingly found that the two donator-substituted nitrilimines **2d,e** as well as the *C*-acceptor-substituted one **2f** gave the salts **11l,n** and **11o**. The yield of **11n**, however, is reduced, because the precursor **4s** is more prone to 1/4-cyclization (Scheme 5), which will be discussed later. Thus, in the case of **2e** + **3b** (≈ **4r**) the yield of **11** is lower too (Table 1). Interestingly, a salt **11** did not result, when **3c** was reacted with the *N*-acceptor-substituted nitrilimine **2g**. Here the intermediate **10**, instead of undergoing protonation, reacts with additional nitrilimine to give the derivative **12**.

No triazolium salts **11** could be made from *tert*-butyl isocyanide (**3d**) under the routine conditions of method B. Again dequaternization took place so that the 1,2,4-triazoles **13** were obtained as final products. This was demonstrated by reactions of the nitrilimines **2b,d,f,g**. From these experiments arose, in addition to **13b-e**, the respective 1,2,3-triazoles **7** (see starting adducts **4l,q,y,z'** in Table 1). Loss of the *tert*-butyl group from the precursor **5** must be rapid so as to prevent ring opening into the starting adduct **4**. In contrast to the foregoing, a triazole of type **13** did not arise from the *N*-donator-substituted nitrilimine **2e** (see **4t**), although the corresponding derivative **7d** was found. Here, for lack of reactivity, major quantities of **1e**/**2e** were transformed into the dihydrotetrazine **9a** (*cf.* ref. [8]).

Whereas method B proved to be inappropriate for making *tert*-butyl-substituted salts **11**, modified conditions as defined in Table 1 allowed for preparation of the derivative **11c**. However, when this material was dissolved in chloroform, it gradually decomposed into **13a**. Attempts to synthesize analogues from the nitrilimines **2b** and **2d** failed but, interestingly, gave enhanced yields of the respective 1,2,3-triazoles **7** (Table 1, footnote [b]). Easy access to the

Table 1

Synopsis of Products (Yield, %) Obtained from Intermediate **4** [a]

4	**6**	**7** [b]	**11**	**13**	**17**	**23**	**25** [c]	**27**
a	**a** (63) [1]					**a** (<1) [2]	**a** (<5) [2]	**a** (<5) [2]
b	**b** (57) [1]		**a** (20) [2]		**a** (12) [2]	**b** (3) [2]	**b** (5) [2]	**a** (5) [2]
c	**c** (73) [1]		**b** (32) [2]		**b** (34) [2]	**c** (2) [2]	**c** (9) [2]	**a** (4) [2]
d		**a** (44)	**c** (20 [d])	**a** (12 [d])				
e [e]			**d** (15)					
f			**e** (25/ 66)					
g			**f** (44/ 87)					
h			**g** (20/ 51)					
i							**d** (52)	**a** (6)
j	**d** (53) [1]							
k	**e** (73) [1]		**h** (25) [2]		**c** (29) [2]	**d** (2) [2]	**c** (9) [2]	**b** (7) [2]
l		**b** (20)		**b** (13)				
m			**i** (70/ 57)					
n	**f** (70) [1]		**j** (10) [2]		**d** (<5) [2]	**e** (5) [2]	**e** (14) [2]	**c** (<5) [2]
o	**g** (58) [1]		**k** (21) [2]		**e** (25) [2]	**f** (<1) [2]	**f** (9) [2]	**c** (<5) [2]
p	**h** (39)		**l** (24)		**f** (17)	**g** (4)	**c** (17)	**d** (7)
q		**c** (42/ 57)		**c** (6)				
r			**m** (8)			**h** (15)	**g** (49)	**e** (2)
s [f]	**i** (50)		**n** (10)		**g** (6)	**i** (25)	**h** (43)	**e** (2)
t [g]		**d** (27)				**j** (3)	**i** (19)	
u [h]						**k** (18) [3]		
v						**l** (21)	**j** (37)	**e** (6)
w						**m** (17)	**k** (62)	**e** (5)
x [i]			**o** (22)		**h** (28/ 30)			
y		**e** (74)		**d** (10)				
z [j]					**i** (16/ 34)			
z'		**f** (<1)		**e** (84)				

[a] Yield figures refer to method B or, if underlined, to method A; products obtained by the latter are not listed, if yield is below 5%; [b] with modified method B (20 °C and reaction time of 24 hours) yields are as follows: **7a** (20), **7b** (44), and **7c** (88); [c] yields are based on the respective urea; [d]modified conditions as with [b]; [e] also isolated: **8a** (4); [f] also isolated: **9a** (2); [g] also isolated: **9a** (33); [h] for further products, see ref. [3]; [i] also isolated: **8b** (19); [j] alsoisolated: **8c** (13/ 5), **9b** (20/ 5), **12** (21), **16** (8), and **18** (<1).

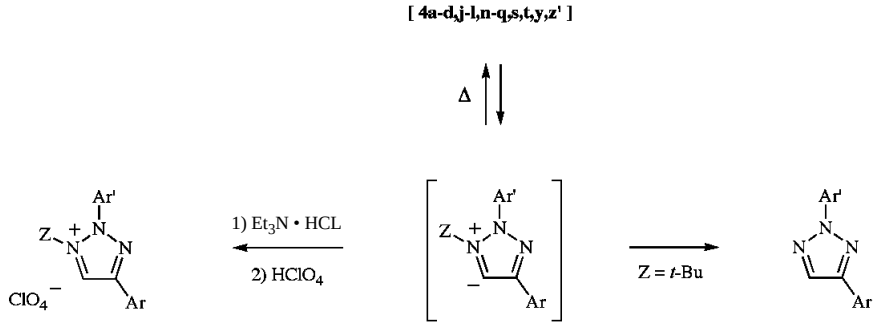
starting materials and handiness of the preparative procedure makes this reaction an attractive route to 2,4-diaryl-1,2,3-triazoles, which are normally obtained from α-diketone derivatives [9]. No proclivity towards dequaternization was of course shown by the adamantyl-substituted triazolium salt **11d**; this compound could therefore be prepared under the standard conditions of method B.

When the aryl isocyanides **3g-i** and nitrilimines **2a,b** (which, as shown, produced considerable amounts of triazolium salts **11e-g,i** even under mild conditions) were reacted also at higher temperature (method B), the yields of these salts were largely enhanced. As it is evident from Table 1, there were no products formed in addition. Remarkably, formation of **11** was not observed with both the *N*-donator- and *N*-acceptor-substituted nitrilimines **2e** and **2g**. In the first case, the process was suppressed by competitive 1/4-cyclization (as exemplified by the behaviour of the species **4v,w**); in the second instance (**2g** + **3g**), no definite material could be isolated. Also the aryl isocyanides **3j,k** failed to give a triazolium salt **11**: the nitrophenyl derivative **3j** turned out to be too weak a nucleophile for attacking the nitrilimine carbon, whereas with the bulky isocyanide **3k** (reacted with the parent **3g**) only 1/4-cyclization of the linear adduct **4i** occurred.

Pyrazoles **17**.

Formation of this type of compound proceeds through the [4 + 1] cycloadduct **14**. This species readily undergoes aromatization by 1/→5/hydrogen-migration to give **15** whose new imine function takes up a nitrilimine to afford the final product **17** [2]. The specific direction of the proton shift is rationalized in terms of a higher basicity of N^5 which formally belongs to an amidrazone function. Since our previous experiments had shown **3c** to be the most propitious isocyanide for making **17**, we used it for studying the behaviour towards the donator- and acceptor-substituted

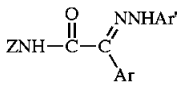
Scheme 2



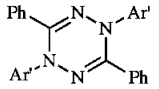
6a: Ar = Ar' = Ph, Z = Me [1]
b: Ar = Ar' = Ph, Z = *i*-Pr [1]
c: Ar = Ar' = Ph, Z = *c*-C_6H_{11} [1]
d: Ar = 4-MeC_6H_4, Ar' = Ph, Z = *i*-Pr [1]
e: Ar = 4-MeC_6H_4, Ar' = Ph, Z = *c*-C_6H_{11} [1]
f: Ar = Ph, Ar' = 4-MeC_6H_4, Z = *i*-Pr [1]
g: Ar = Ph, Ar' = 4-MeC_6H_4, Z = *c*-C_6H_{11} [1]
h: Ar = 4-$MeOC_6H_4$, Ar' = Ph, Z = *c*-C_6H_{11}
i: Ar = Ph, Ar = 4-$MeOC_6H_4$, Z = *c*-C_6H_{11}

5

7a: Ar = Ar' = Ph
b: Ar = 4-MeC_6H_4, Ar' = Ph
c: Ar = 4-$MeOC_6H_4$, Ar' = Ph
d: Ar = Ph, Ar' = 4-$MeOC_6H_4$
e: Ar = 4-$O_2NC_6H_4$, Ar' = Ph
f: Ar = Ph, Ar' = 4-$O_2NC_6H_4$

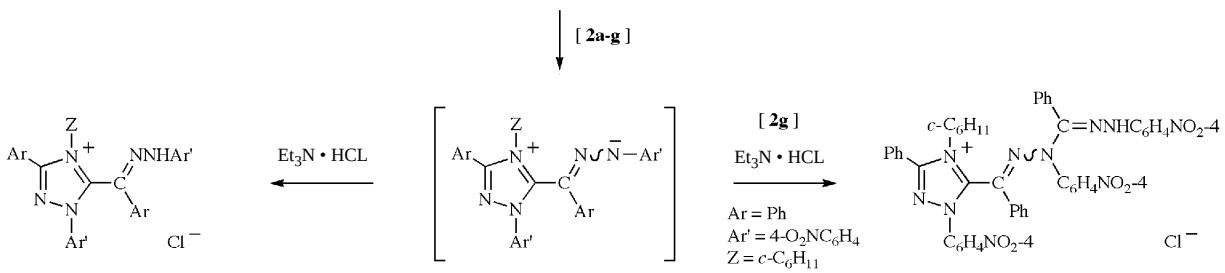


8a: Ar = Ar' = Ph, Z = 1-Adamantyl
b: Ar = 4-$O_2NC_6H_4$, Ar' = Ph, Z = *c*-C_6H_{11}
c: Ar = Ph, Ar' = 4-$O_2NC_6H_4$, Z = *c*-C_6H_{11}



9a: Ar' = 4-$MeOC_6H_4$
b: Ar' = 4-$O_2NC_6H_4$

Scheme 3



11a: Ar = Ar' = Ph, Z = *i*-Pr [2]
b: Ar = Ar' = Ph, Z = *c*-C_6H_{11} [2]
c: Ar = Ar' = Ph, Z = *t*-Bu
d: Ar = Ar' = Ph, Z = 1-Adamantyl
e: Ar = Ar' = Z = Ph
f: Ar = Ar' = Ph, Z = 4-MeC_6H_4
g: Ar = Ar' = Ph, Z = 4-$MeOC_6H_4$
h: Ar = 4-MeC_6H_4, Ar' = Ph, Z = *c*-C_6H_{11} [2]
i: Ar = Z = 4-MeC_6H_4, Ar' = Ph
j: Ar = Ph, Ar' = 4-MeC_6H_4, Z = *i*-Pr [2]
k: Ar = Ph, Ar' = 4-MeC_6H_4, Z = *c*-C_6H_{11} [2]
l: Ar = 4-$MeOC_6H_4$, Ar' = Ph, Z = *c*-C_6H_{11}
m: Ar = Ph, Ar' = 4-$MeOC_6H_4$, Z = *i*-Pr
n: Ar = Ph, Ar' = 4-$MeOC_6H_4$, Z = *c*-C_6H_{11}
o: Ar = 4-$O_2NC_6H_4$, Ar' = Ph, Z = *c*-C_6H_{11}

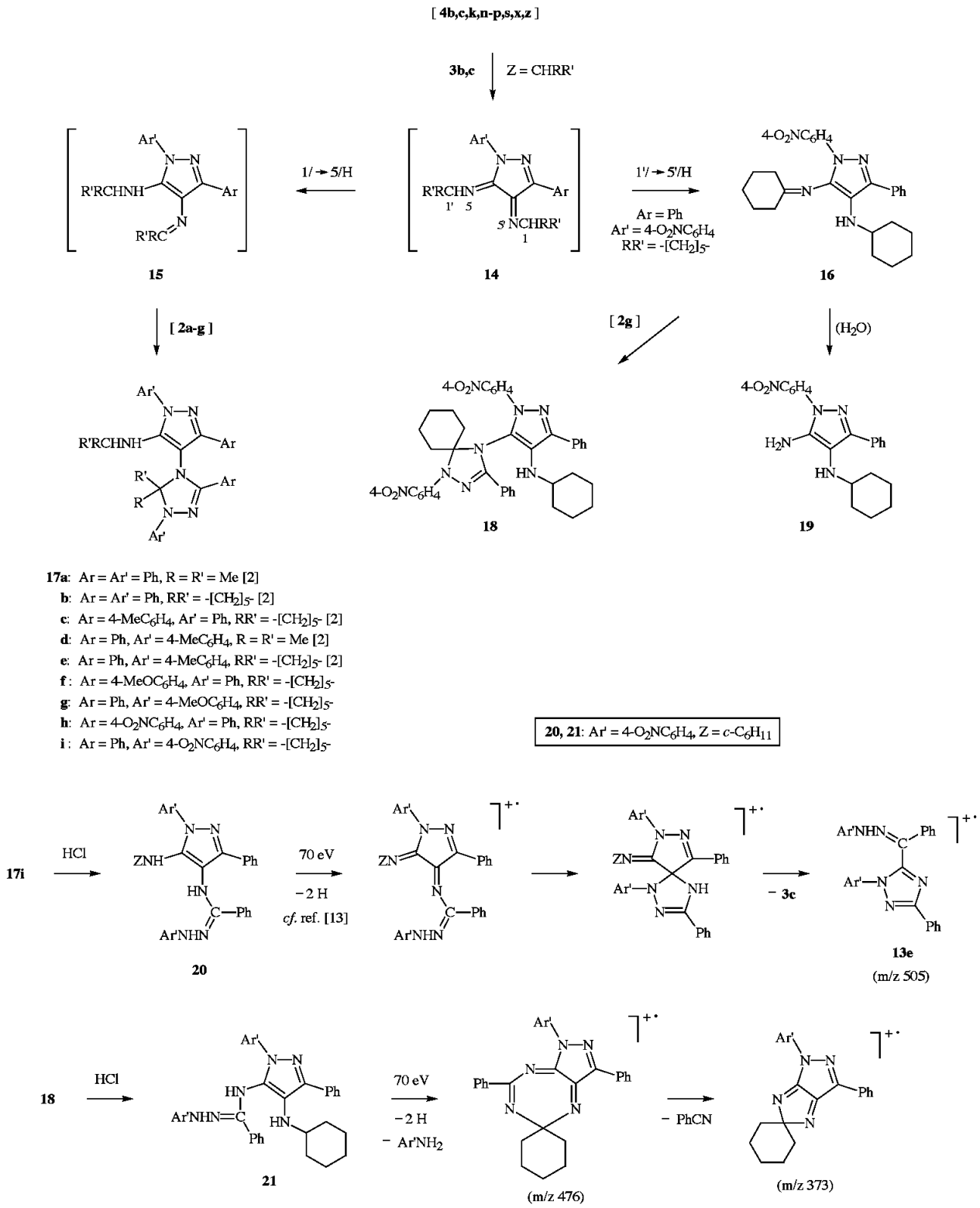
10

12

13a: Ar = Ar' = Ph
b: Ar = 4-MeC_6H_4, Ar' = Ph
c: Ar = 4-$MeOC_6H_4$, Ar' = Ph
d: Ar = 4-$O_2NC_6H_4$, Ar' = Ph
e: Ar = Ph, Ar' = 4-$O_2NC_6H_4$

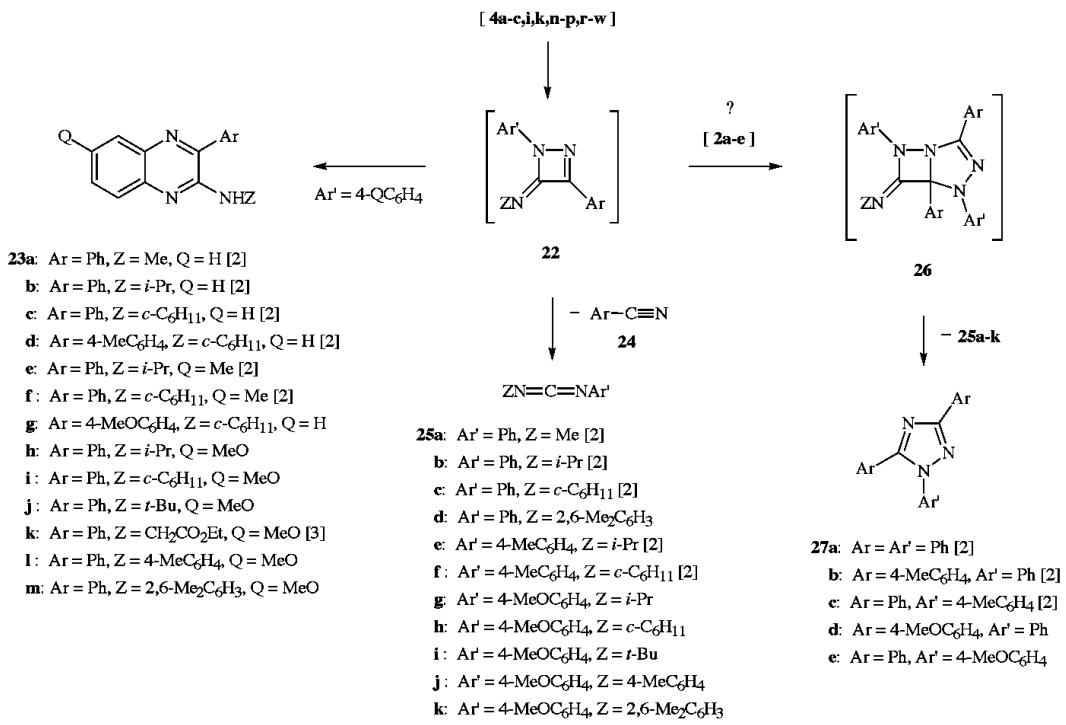
nitrilimines **2d-g**. In all cases the envisaged products could be isolated (**17f-i**), though of the derivative **17g** (formed from **4s**) we obtained only minor quantities (*cf.* the low yield of **11n**). More interestingly, aromatization of the 1-(4-nitrophenyl)-substituted cycloadduct **14** turned out to be a criss-cross process: here also 1′/→5′/hydrogen-

Scheme 4



migration occurred to give the imine **16**. The acceptor group at the adjacent ring position obviously reduces the basicity of N^5 so as to prevent prototropy from taking a specific course. In contrast to the respective isomer **15**, the

Scheme 5



imine **16** could be separated from the reaction mixture, and only very little was transformed into the derivative **18**.

Cycloadducts **14** having for CHRR′ a *tert*-alkyl or an aryl group should be sufficiently stable for isolation and were expected to arise from intermediates such as **4e-i,l,m,q,t,v,w,y,z**′. However, we had no indications for their occurrence in any of these cases, although analogous ring systems have been prepared from the respective isocyanides and heteroallenes comparable to **4** [10,11].

A final comment applies to structural proof of the isomers **17i** and **18**. In the NMR experiment pyrazole-4,5-diamines display the N^5–H signal downfield from the N^4–H one (*cf.* ref. [12]). For the said compounds we found δ 4.22 (**17i**) and 3.04 ppm (**18**). To confirm this assignment, both isomers were hydrolyzed to give the (4-pyrazolyl)- and (5-pyrazolyl)-substituted amidrazones **20** and **21**, respectively. Amidrazones of the former type are known to undergo ring transformation into 1,2,4-triazoles of type **13** when kept in ethanolic solution or submitted to mass spectrometry [13]. In the present instance (**20**) the first method failed, because pyrazole-4,5-diamine units that have a 4-nitrophenyl group attached to the ring nitrogen resist the initial oxidation step [14], but when we applied the MS method, the reaction could be induced to proceed down to **13e**. The isomeric amidrazone **21**, however, produced a pyrazolo[3,4-*f*][1,3,5]triazepine (m/z 476) which split out benzonitrile to give an imidazo[4,5-*c*]pyrazole (m/z 373).

Quinoxalines **23**.

1/4-Cyclization of the linear adduct **4** has been shown to give a 1,2-diazet derivative (**22**) which, as expected for structures of this kind [15], underwent [2 + 2] cycloreversion into a nitrile (**24**) and a carbodiimide (**25**) (Scheme 5). A second mode of stabilization consisted in ring expansion to afford a quinoxaline (**23**) [2]. Comparing the yields of **23b-d,f** and **25b,c,f** with those of **11a-c,h,k** and **17a-c,e** (Table 1), the formation of **22** from **4** appeared as a negligible process [2]. Experiments with the *N*-donator-substituted nitrilimine **2e** now demonstrated that 1/4-cyclization could be the predominant step which completely suppressed the other conversions **4** is capable to undergo. This was exemplified by reactions of **2e** with the isocyanides **3b,c,h,k** (see Table 1 for precursors **4r,s,v,w**). Also on employment of the isocyanide **3f** formation of **22** was shown to be important [3]; and using *tert*-butyl isocyanide (**3d**), this route was still favoured to some extent, if one compares species such as **4d,l,q** which were not transformed at all (in contrast to their cyclohexyl congeners **4c,k,o** [2]). Generally no cyclization of **4** into **22** was observed with derivatives having 4-$O_2NC_6H_4$ for Ar or Ar′ (**4x-z**′). This applied also to intermediates **4** that have for Z an aryl substituent but are devoid of the 4-$MeOC_6H_4$ group (**4f-h,m**); a conspicuous exception constitutes the adduct **4i** which like **4r,s,v,w** (see above) underwent 1/4-cyclization only.

Table 2

Melting Points, IR Spectra, and Elemental Analyses (Calcd./Found) of New Compounds

N°	Mp °C (solvent)	IR (KBr) ν cm^{-1}	Formula	C	H	N
6h	159-162 (CH_2Cl_2/Et_2O) [a]	3132, 1613, 1090	$[C_{21}H_{24}N_3O]ClO_4$	58.13	5.58	9.68
				57.98	5.63	9.51
6i	145 (Me_2CO/Et_2O) [a]	3129,1603, 1090	$[C_{21}H_{24}N_3O]ClO_4$	58.13	5.58	9.68
				57.81	5.63	9.40
7d	75-76 (EtOH)	1516	$C_{15}H_{13}N_3O$	71.70	5.21	16.72
				71.88	5.10	16.46
7e	209-210 (EtOH)	1597	$C_{14}H_{10}N_4O_2$	63.15	3.79	21.04
				63.10	3.78	21.05
8b	212-213 (EtOH)	3278, 1626, 1517	$C_{20}H_2N_4O_3$	65.56	6.05	15.29
				65.60	6.20	15.18
8c	219-221 (EtOH)	3280, 1625, 1550	$C_{20}H_2N_4O_3$	65.56	6.05	15.29
				65.68	6.17	15.36
9a	213-214 (EtOH)	1508	$C_{28}H_{24}N_4O_2$	74.99	5.39	12.49
				75.10	5.39	12.52
11c	223-227 (EtOH) [a]	2979,1600	$[C_{31}H_{30}N_5]Cl$	73.29	5.95	13.78
				73.45	5.81	13.62
11d	162-163 (Me_2CO/Et_2O) [a]	2913,1600	$[C_{37}H_{36}N_5]Cl$	75.81	6.19	11.95
				75.54	6.08	11.83
11e	310-316 (AcOH) [a]	2807, 1597, 1491	$[C_{33}H_{26}N_5]Cl$	75.06	4.96	13.26
				75.11	5.12	12.90
11f	314-320 (AcOH) [a]	2856, 1598, 1491	$[C_{34}H_{28}N_5]Cl$	75.33	5.21	12.91
				75.33	5.17	12.57
11g	294-296 (AcOH) [a]	2853, 1599, 1511	$[C_{34}H_{28}N_5O]Cl$	73.17	5.06	12.55
				73.48	4.89	12.42
11i	297-298 (AcOH) [a]	2851, 1600, 1511	$[C_{36}H_{32}N_5]Cl$	75.84	5.66	12.28
				75.56	5.26	12.56
11l	262-263 (Me_2CO/Et_2O) [a]	2934, 1604, 1499, 1253	$[C_{35}H_{36}N_5O_2]Cl$	70.75	6.11	11.79
				70.69	6.19	11.80
11m	164-165 (Me_2CO/Et_2O) [a]	2834, 1605, 1504, 1443	$[C_{32}H_{32}N_5O_2]Cl$	69.37	5.82	12.64
				68.94	5.68	12.71
11n	228-229 (Me_2CO/AcOEt) [a]	2932, 1546, 1503	$[C_{35}H_{36}N_5O_2]Cl$	70.75	6.11	11.79
				70.75	6.10	11.79
11o	256-258 (Me_2CO) [a]	2938, 1600, 1525, 1339	$[C_{33}H_{30}N_7O_4]Cl$	63.51	4.84	15.71
				62.98	4.65	15.64
12	198-199 (AcOEt) [a]	2929, 1594, 1492, 1329	$[C_{46}H_{39}N_{10}O_6]Cl$	64.02	4.52	16.22
				63.87	4.52	16.20
13c	164-166 (EtOH)	1597	$C_{29}H_{25}N_5O_2$	73.25	5.30	14.73
				73.32	5.29	14.72
13e	248-251 (EtOH)	1598	$C_{27}H_{19}N_7O_4$	64.16	3.79	19.40
				63.65	3.72	19.46
16	148-152 (EtOH)	3297, 2927, 1653, 1595	$C_{27}H_{31}N_5O_2$	70.88	6.83	15.30
				70.80	6.82	15.38
17f	193-195 (EtOH) [a]	3273, 2931, 1608, 1250	$C_{42}H_{46}N_6O_2$	75.65	6.95	12.60
				75.79	7.06	12.58
17g	205-207 (EtOH)	3245, 2925, 1565, 1507, 1249	$C_{42}H_{46}N_6O_2$	75.65	6.95	12.60
				75.69	7.02	12.61
17h	218-221 (EtOH)	3285, 1595	$C_{40}H_{40}N_8O_4$	68.95	5.79	16.08
				68.34	5.73	16.01
17i	148-152 (CH_2Cl_2/light petroleum)	3328, 2930, 1590, 1495, 1339	$C_{40}H_{40}N_8O_4$	68.95	5.79	16.08
				68.95	5.77	16.03
18	199-201 (EtOH)	3373, 2928, 1586, 1493, 1339	$C_{40}H_{40}N_8O_4$	68.95	5.79	16.08
				68.80	5.71	16.37
19	144-145 (CH_2Cl_2/light petroleum)	3390, 3320	$C_{21}H_{23}N_5O_2$	66.83	6.14	18.55
				66.61	6.17	18.69
23g	oil	3426 (neat)	$C_{21}H_{23}N_3O$	75.65	6.95	12.60
				75.58	7.38	12.30
23h	oil	3424 (neat)	$C_{18}H_{19}N_3O$	73.70	6.53	14.32
				73.34	6.45	14.21
23i	oil [b]	3424 (neat)	$C_{27}H_{26}N_6O_8$ [f]	57.65	4.66	14.93
				57.62	4.68	14.92
23j	oil [c]	3436 (neat)	$C_{25}H_{24}N_6O_8$ [f]	55.97	4.51	15.66
				55.57	4.69	15.13

Table 2 (continued)

N°	Mp °C (solvent)	IR (KBr) ν cm^{-1}	Formula	C	H	N
23l	176-178 (EtOH)	3375	$C_{22}H_{19}N_3O$	77.40	5.61	12.31
				77.52	5.60	12.18
23m	181-182 (EtOH)	2856, 1598, 1491	$C_{23}H_{21}N_3O$	77.72	5.96	11.82
				77.50	5.76	12.04
25′h [d]	179-180 (Me_2CO) [e]	3304, 2932, 1629	$C_{14}H_{20}N_2O_2$	67.72	8.12	11.28
				67.48	8.20	11.30
25′i [d]	142-145 (EtOH)	3295	$C_{12}H_{18}N_2O_2$	64.84	8.16	12.60
				64.71	8.05	12.42
25′k [d]	248-251 (EtOH)	3282, 1638	$C_{16}H_{18}N_2O_2$	71.11	6.71	10.36
				71.38	6.52	10.18

[a] With dec; [b] picrate: mp 167-168 °C (EtOH); [c] picrate: mp 109-111 °C (EtOH); [d] urea derived from **25**; [e] no mp reported in ref. [36], HRMS data given in place of elemental analysis; [f] data refer to picrate.

The pronounced propensity of **4** to give **22** when Ar′ = 4-$MeOC_6H_4$ can be ascribed to an enhanced nucleophilicity of the terminal azo nitrogen. But although a derivative such as **4t** was observed spectroscopically (ir: ν 2000 cm^{-1}; *cf.* ref. [16]), there is no need for the exclusiveness of a pathway *via* **4**; rather, an alternate mode of combining **2** with **3** might be operative in this case: A donator group at the *N*-terminus of a nitrilimine favours its allenic structure [17] so that the isocyanide carbon may attack that position. The resulting transition state can pass to **22** as well, but can also, prior to ring closure, fragment into nitrile and carbodiimide.

As side products we found almost throughout the 1,2,4-triazoles **27**. Their way of formation is subject to speculation. The well known [3 + 2] cycloaddition of **2** onto **24** [18] is not the main source, because a model experiment with **2a** and benzonitrile (conditions of method B) produced much less **27a** than did the respective nitrilimine/isocyanide reactions (see Table 1). We already assumed [2] that the nitrilimine adds onto the ArC=N double bond of **22** to give the bicyclic intermediate **26** which in turn fragments into **25** and **27** (*cf.* ref. [19]). As shown by the relatively constant yields of **27a-e**, the process is almost insusceptible to substituent effects.

EXPERIMENTAL

Melting points were determined on a Kofler microscope. Elemental analyses were obtained on a Carlo-Erba C-H-N-O Elemental Analyser 1106. The ir spectra were recorded on a Pye-Unicam SP 1100 or Philips PU-9800 FTIR instrument. The ^{1}H nmr spectra were run on a Varian EM-390 or Bruker DRX-400 spectrometer; the ^{13}C nmr spectra were taken on a Bruker DRX-400 instrument (tetramethylsilane or $CDCl_3$ as internal standard). The uv/vis spectra were determined on a Philips PU-8730 spectrometer. The fluorescence spectra were measured on a Kontron SFM 25 instrument. The mass spectra were taken on a Finnigan MAT 8430 or MAT 90 machine. Chromatography was carried out on silca gel using dichloromethane or (with **25**′) ethyl acetate as eluent.

The hydrazonoyl chlorides **1a,b,d-g** [20] and the isocyanides **3b,c** [21], **3d** [22], **3e** [23], and **3g-k** [24] were prepared according to (or by adopting) literature procedures. Known products were identified by means of authentic samples and/or literature data, as were the 1,2,3-triazoles **7a** [25] and **7b,c** [26], the 1,2,4,5-tetrazine **9b** [27], the 1,2,4-triazoles **13a** [7] and **13b** [13], the ureas **25′c** [28], **25′d** [29], **25′g** [30], and **25′j** [31], the 1,2,4-triazoles **27a** [32], **27d** [33], and **27e** [34].

General Procedure for the Reaction of Hydrazonoyl Chlorides **1** with Isocyanides **3** in the Presence of an Equimolar Amount of Triethylamine (Method A).

To a solution of **1** and **3** (4 mmol each) in anhydrous acetonitrile (100 mL) was added triethylamine (0.40 g, 4 mmol), and the mixture was allowed to stand at ambient temperature for 24 hours. After concentration *in vacuo* work-up was as follows:

(i) Starting pairs **1d** + **3c** and **1e** + **3c** (≈ intermediates **4p,s**): The residual solid was washed with diethyl ether (20 mL) and dissolved in a small amount of water. Addition of a few drops of 2 *N* $HClO_4$ precipitated the 2,4-diaryl-1-cyclohexyl-1,2,3-triazolium perchlorate **6h** or **6i** which was collected by filtration after 2 hours. For data, see Tables 1−3.

(ii) Starting pairs **1f** + **3c** and **1g** + **3c** (≈ intermediates **4x,z**): The ethereal washings of the solid (which was discarded) were concentrated and chromatographed to give, after some starting material, 1,4-bis-(4-nitrophenyl)-3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine (**9b**), the 1,3-diaryl-*N*-cyclohexyl-4-(1,3-diaryl-1,2,4-triaza-spiro[4.5]dec-2-en-4-yl)pyrazol-5-amine **17h** or **17i**, and finally the 2-aryl-2-(arylhydrazono)-*N*-cyclohexylacetamide **8b** or **8c**. For data, see Tables 1−4. – Hydrolysis of **17i**: 0.17 g (*ca.* 0.25 mmol) of the substrate was stirred with 12 *N* HCl/anhydrous ethanol (5 mL; 1/3) at ambient temperature for 6 hours. After filtration of some starting material, the mixture was diluted with water (100 mL) and neutralized with sodium hydrogencarbonate to precipitate the amidrazone **20** as an amorphous solid that was collected by filtration, thoroughly washed with water and submitted to mass spectrometry without further purification. For data, see Table 4.

(iii) Starting pairs **1a** + **3d** and **1d** + **3d** (≈ intermediates **4d,q**): The ethereal washings of the solid (which was discarded) were concentrated and chromatographed to yield, besides starting material **1**, the corresponding 2,4-diaryl-1,2,3-triazole **7a** or **7c**; full separation of **7a** from **1a** (*ca.* 1:1 mixture) could not be accomplished. For data, see Table 1.

(iv) Starting pairs **1a** + **3g**, **1a** + **3h**, **1a** + **3i**, and **1b** + **3h** (≈ intermediates **4f-h,m**): The solid was thoroughly washed with diethyl ether and water to give the 3,4-diaryl-1-phenyl-5-[aryl(phenylhydrazono)methyl]-1,2,4-triazolium chloride **11e**, **11f**, **11g** or **11i**. For data, see Tables 1−4.

Table 3

NMR Spectra of New Compounds

N°	NMR ($CDCl_3$) δ ppm
6h	^{1}H [a]: 1.19-1.28 (m, 3H), 1.61-1.72 (m, 1H), 1.82-1.94 (m, 4H), 2.23-2.26 (m, 2H), 3.87 (s, 3H), 4.51 (m_c, 1H), 7.20 (part of AA'BB', N = 9 Hz, 2H), 7.80-7.91 (m, 3H), 7.99-8.02 (m, 4H), 9.99 (s, 1H) ^{13}C [a]: 24.1 (t), 24.2 (t, 2C), 32.0 (t, 2C), 55.5 (q), 63.2 (d), 114.9 (d, 2C), 118.6 (s), 127.4 (d, 2C), 127.5 (d), 127.7 (d, 2C), 130.4 (d, 2C), 133.2 (d), 133.5 (s), 148.3 (s), 161.2 (s)
6i	^{1}H: 1.16-2.22 (m, 10 H), 3.94 (s, 3H), 4.52 (m_c, 1H), 7.17/7.68 (AA'BB', N = 9 Hz, 4H), 7.40-7.42 (m, 3H), 7.95-7.98 (m, 2H), 9.35 (s, 1H) ^{13}C: 23.8 (t), 25.0 (t, 2C), 32.3 (t, 2C), 56.0 (q), 64.7 (d), 115.7 (d, 2C), 125.6 (s), 125.8 (s), 126.7 (d, 2C), 127.6 (d), 128.7 (d, 2C), 129.2 (d, 2C), 130.9 (d), 149.8 (s), 163.0 (s)
7d	^{1}H: 3.87 (s, 3H), 7.01/8.04 (AA'BB', N = 9 Hz, 4H), 7.36-7.38 (m, 1H), 7.40-7.46 (m, 2H), 7.88-7.90 (m, 2H), 8.02 (s, 1H) ^{13}C: 55.6 (q), 114.4 (d, 2C), 120.3 (d, 2C), 126.1 (d, 2C), 128.7 (d), 128.9 (d, 2C), 130.2 (s), 132.1 (d), 133.8 (s), 148.5 (s), 159.0 (s)
7e	^{1}H: 7.36-7.43 (m, 1H), 7.51-7.56 (m, 2H), 8.07/8.34 (AA'BB', N = 9 Hz, 4H), 8.15 (s, 1H), 8.16-8.18 (m, 2H) ^{13}C: 119.0 (d, 2C), 124.4 (d, 2C), 126.6 (d, 2C), 128.1 (d), 129.4 (d, 2C), 133.2 (d), 136.2 (s), 139.6 (s), 146.6 (s), 147.8 (s)
8b	^{1}H: 1.13-1.80 (m, 8H), 1.92-2.02 (m, 2H), 3.95 (m_c, 1H), 5.68 (d, J = 9 Hz, 1H), 6.96-7.31 (m, 5H), 7.74/8.25 (AA'BB', N = 9 Hz, 4H), 12.64 (s, 1H) ^{13}C: 24.7 (t, 2C), 25.3 (t), 32.8 (t, 2C), 48.5 (d), 114.0 (d, 2C), 122.5 (d), 124.1 (d, 2C), 128.6 (d, 2C), 128.9 (s), 129.3 (d, 2C), 143.0 (s), 143.2 (s), 147.0 (s), 162.5 (s)
8c	^{1}H: 0.9-2.1 (m, 10H), 3.7-4.05 (m, 1H), 5.8 (d, J = 9 Hz, 1H), 7.17/8.14 (AA'BB', N = 9 Hz, 4H), 7.30-7.55 (m, 5H), 12.98 (s, 1H)
9a	^{1}H: 3.74 (s, 6H), 6.74/7.12 (AA'BB', N = 9 Hz, 8H), 7.22-7.36 (m, 10H)
11c	^{1}H: 1.64 (s, 9H), 6.92-6.96 (m, 2H), 7.11-7.16 (m, 2H), 7.20-7.62 (m, 8H), 7.64-7.68 (m, 2H), 7.74-7.80 (m, 2H), 8.06-8.14 (m, 2H), 8.26-8.36 (m, 2H), 12.79 (s, 1H); additional signals observed after 24 h: 1.62 (s), 1.73 (s), 4.66 (s)
11d	^{1}H: 1.36-1.39 (m, 3H), 1.46-1.49 (m, 3H), 1.98-2.06 (m, 3H), 2.23-2.26 (m, 3H), 2.54-2.57 (m, 3H), 6.92-6.95 (m, 1H), 7.24-7.75 (m, 17H), 8.12-8.14 (m, 2H), 12.80 (s, 1H) ^{13}C: 29.9 (d, 3C), 34.9 (t, 3C), 40.8 (t, 3C), 69.8 (s), 115.2 (d, 2C), 119.3 (s), 122.0 (d), 124.3 (d, 2C), 125.4 (d, 2C), 127.9 (s), 128.5 (d, 3C), 128.9 (d, 2C), 129.2 (d, 2C), 129.3 (d, 2C), 131.36 (d, 2C), 131.44 (d), 135.0 (s), 137.0 (s), 144.2 (s), 146.5 (s), 156.4 (s)
11e	^{1}H: 7.01-7.53 (m, 25H), 12.96 (s, 1H)
11f	^{1}H: 2.36 (s, 3H), 7.08-7.12 (m, 2H), 7.18-7.20 (m, 3H), 7.24-7.27 (m, 2H), 7.36-7.46 (m, 5H), 7.54-7.57 (m, 10H), 7.62-7.64 (m, 2H), 13.09 (s, 1H)
11g	^{1}H: 3.68 (s, 3H), 6.73/7.71 (AA'BB', N = 9 Hz, 4H), 6.89-6.93 (m, 1H), 7.17-7.31 (m, 8H), 7.35-7.53 (m, 9H), 7.84-7.88 (m, 2H), 13.06 (s, 1H)
11i	^{1}H: 2.20 (s, 3H), 2.28 (s, 3H), 2.31 (s, 3H), 6.84-6.87 (m, 1H), 7.01 (part of AA'BB', N = 8 Hz, 2H), 7.08 (part of AA'BB', N = 8 Hz, 2H), 7.13 (part of AA'BB', N = 8 Hz, 2H), 7.15-7.19 (m, 5H), 7.30-7.38 (m, 4H), 7.52 (part of AA'BB', N = 8 Hz, 2H), 7.57 (part of AA'BB', N = 8 Hz, 2H), 7.82 (part of AA'BB', N = 8 Hz, 2H), 12.92 (s, 1H) ^{13}C: 20.96 (q), 21.02 (q), 21.3 (q), 114.7 (d, 2C), 116.1 (s), 119.8 (s), 121.5 (d), 123.9 (d, 2C), 124.0 (d, 2C), 126.1 (d), 128.1 (s), 128.4 (d, 2C), 128.6 (d), 129.3 (d, 2C), 129.4 (d, 2C), 129.5 (d, 2C), 129.7 (d, 2C), 130.1 (d, 2C), 131.0 (d), 132.4 (s), 134.9 (s), 138.2 (s), 141.6 (s), 142.2 (s), 143.7 (s), 147.5 (s), 155.6 (s)
11l	^{1}H: 0.81-0.87 (m, 1H), 1.03-1.09 (m, 2H), 1.39-1.45 (m, 2H), 1.48-1.77 (m, 3H), 2.11-2.15 (m, 1H), 2.55-2.58 (m, 1H), 3.81 (s, 3H), 3.86 (s, 3H), 4.15-4.21 (m, 1H), 6.89-6.93 (m, 3H), 7.05 (part of AA'BB', N = 8 Hz, 2H), 7.21-7.37 (m, 7H), 7.69 (part of AA'BB', N = 8 Hz, 2H), 7.76 (part of AA'BB', N = 8 Hz, 2H), 7.99 (part of AA'BB', N = 8 Hz, 2H), 12.69 (s, 1H) ^{13}C: 24.6 (t), 25.7 (t), 25.8 (t), 31.2 (t), 32.3 (t), 55.4 (q), 55.5 (q) 61.8 (d), 114.4 (d, 2C), 114.7 (d, 2C), 114.9 (d, 2C), 115.8 (s), 116.8 (s), 121.7 (d), 124.7 (d, 2C), 125.8 (d, 2C), 128.7 (s), 128.8 (d, 2C), 129.5 (d, 2C), 131.1 (d), 132.5 (d, 2C), 135.1 (s), 144.3 (s), 146.1 (s), 156.4 (s), 159.9 (s), 162.3 (s)
11m	^{1}H: 1.36 (d, J = 7 Hz, 3H), 1.56 (d, J = 7 Hz, 3H), 3.71 (s, 3H), 3.77 (s, 3H), 4.60 (m_c, 1H), 6.80 (part of AA'BB', N = 9 Hz, 2H), 6.83 (part of AA'BB', N = 9 Hz, 2H), 7.25-7.40 (m, 5H), 7.57-7.64 (m, 3H), 7.66 (part of AA'BB', N = 9 Hz, 2H), 7.69 (part of AA'BB', N = 9 Hz, 2H), 8.06-8.10 (m, 2H), 12.82 (s, 1H) ^{13}C: 21.3 (q), 21.9 (q), 53.9 (d), 55.4 (q), 55.5 (q), 114.2 (d, 2C), 114.6 (d, 2C), 114.6 (s), 116.2 (d, 2C), 123.8 (d, 2C), 124.0 (s), 126.0 (d, 2C), 127.7 (s), 127.9 (d), 128.9 (d, 2C), 129.1 (d, 2C), 130.8 (d, 2C), 131.8 (d), 136.0 (s), 137.8 (s), 146.1 (s), 155.2 (s), 155.8 (s), 161.3 (s)
11n	^{1}H: 0.79-0.85 (m, 1H), 1.02-1.07 (m, 2H), 1.37-1.41 (m, 2H), 1.44-1.74 (m, 3H), 2.10-2.16 (m, 1H), 2.53-2.59 (m, 1H), 3.71 (s, 3H), 3.77 (s, 3H), 4.13-4.19 (m, 1H), 6.78-6.80 (m, 4H), 7.20-7.40 (m, 5H), 7.56-7.71 (m, 7H), 8.05-8.07 (m, 2H), 12.81 (s, 1H) ^{13}C: 24.5 (t), 25.7 (t), 25.8 (t), 31.2 (t), 32.4 (t), 55.5 (q), 55.6 (q), 61.8 (d), 114.3 (d, 2C), 114.6 (d, 2C), 114.9 (s), 116.4 (d, 2C), 124.0 (d, 2C), 124.2 (s), 126.2 (d, 2C), 127.8 (s), 128.0 (d), 129.0 (d, 2C), 129.1 (d, 2C), 130.9 (d, 2C), 131.9 (d), 136.4 (s), 138.0 (s), 146.2 (s), 155.3 (s), 156.1 (s), 161.4 (s)
11o	^{1}H: 0.79-0.97 (m, 1H), 1.01-1.20 (m, 2H), 1.36-1.60 (m, 2H), 1.61-1.81 (m, 3H), 2.22-2.32 (m, 1H), 2.58-2.72 (m, 1H), 4.16 (m_c, 1H), 7.04-7.08 (m, 1H), 7.28-7.31 (m, 4H), 7.39-7.42 (m, 1H), 7.62-7.68 (m, 2H), 7.72 (part of AA'BB', N = 8 Hz, 2H), 7.77 (part of AA'BB', N = 8 Hz, 2H), 8.21 (part of AA'BB', N = 8 Hz, 2H), 8.28-8.36 (m, 2H), 8.45 (part of AA'BB', N = 8 Hz, 2H), 13.48 (s, 1H) ^{13}C: 24.3 (t), 25.5 (t), 25.6 (t), 31.5 (t), 32.7 (t), 62.5 (d), 113.4 (s), 115.9 (d, 2C), 123.9 (d, 2C), 124.2 (d, 2C), 124.5 (d, 3C), 124.6 (d, 2C), 129.1 (d, 2C), 129.8 (d, 2C), 130.0 (s), 131.9 (d), 132.7 (d, 2C), 134.4 (s), 141.7 (s), 143.1 (s), 145.7 (s), 146.7 (s), 150.0 (s), 154.6 (s)
12	^{1}H: 0.79-0.98 (m, 2H), 1.24-1.38 (m, 1H), 1.54-1.62 (m, 2H), 1.60-1.86 (m, 3H), 2.02-2.18 (m, 2H), 4.99 (m_c, 1H), 6.68-6.80 (m, 4H), 7.04-7.16 (m, 3H), 7.20-7.28 (m, 2H), 7.60-7.71 (m, 8H), 7.72-7.74 (m, 2H), 8.06 (part of AA'BB', N = 9 Hz, 2H), 8.14 (part of AA'BB', N = 9 Hz, 2H), 8.16-8.22 (m, 4H), 12.14 (s, 1H) ^{13}C: 24.2 (t), 25.4 (t), 25.9 (t), 32.2 (t), 33.2 (t), 62.6 (d), 123.8 (s), 128.4 (s), 131.9 (s), 132.5 (s), 138.7 (s), 141.0 (s), 144.5 (s), 147.5 (s), 148.9 (s), 149.7 (s), 150.4 (s), 155.3 (s); dublets of Ph and 4-$O_2NC_6H_4$ omitted
13c	^{1}H: 3.70 (s, 3H), 3.89 (s, 3H), 6.64/7.03 (AA'BB', N = 9 Hz, 4H), 6.89-6.94 (m, 1H), 7.15-7.37 (m, 10H), 7.42-7.55 (m, 1H), 8.22 (part of AA'BB', N = 9 Hz, 2H), 10.18 (s, 1H) [b] ^{13}C: 55.2 (q), 55.4 (q), 113.56 (d, 2C), 113.61 (d, 2C), 114.2 (d, 2C), 121.0 (d), 122.8 (s), 123.9 (d, 2C), 127.7 (d, 2C), 128.1 (d, 2C), 128.5 (d), 128.7 (s), 128.9 (d, 2C), 129.3 (d, 2C), 129.6 (s), 137.4 (s), 144.1 (s), 146.8 (s), 159.4 (s), 161.0 (s), 161.9 (s)

Table 3 (continued)

16	^{1}H: 0.94-1.02 (m, 2H), 1.06-1.24 (m, 3H), 1.52 (s, 1H), 1.62-1.72 (m, 6H), 1.82-1.89 (m, 4H), 2.22-2.30 (m, 3H), 2.56-2.62 (m, 2H), 2.70 (m_c, 1H), 7.35-7.47 (m, 3H), 7.84-8.00 (m, 4H), 8.25 (part of AA'BB', N = 9 Hz, 2H) ^{13}C: 24.9 (t, 2C), 25.4 (t), 25.9 (t), 26.9 (t), 27.6 (t), 33.7 (t), 34.1 (t, 2C), 39.3 (t), 55.8 (d), 117.6 (s), 120.9 (d, 2C), 124.6 (d, 2C), 127.2 (d, 2C), 128.2 (d), 128.6 (d, 2C), 132.9 (s), 140.2 (s), 144.5 (s), 145.2 (s), 146.9 (s), 182.6 (s)
17f	^{1}H: 0.59-0.61 (m, 2H), 0.79-1.02 (m, 4H), 1.07-1.58 (m, 8H), 1.62-1.80 (m, 2H), 1.81-2.37 (m, 4H), 2.42-2.58 (m, 1H), 3.73 (s, 3H), 3.84 (s, 3H), 5.17 (d, J = 9.8, 1 H), 6.72 (part of AA'BB', N = 9 Hz, 2H), 6.97 (part of AA'BB', N = 9 Hz, 2H), 7.15-7.17 (m, 1H), 7.23-7.44 (m, 7H), 7.68 (part of AA'BB', N = 8 Hz, 2H), 7.78 (part of AA'BB', N = 8 Hz, 2H), 8.26 (m, 2H) ^{13}C: 21.8 (t), 22.7 (t), 24.8 (t, 2C), 25.2 (t), 25.3 (t), 30.2 (t), 32.0 (t), 33.7 (t), 34.2, (t), 54.6 (d), 55.2 (q, 2C), 87.8 (s), 107.8 (s), 113.5 (d, 4C), 122.3 (s), 124.0 (d, 2C), 124.3 (d, 2C), 124.5 (d), 126.0 (s), 127.1 (d), 128.6, 128.8 (d, 2C), 128.9 (d, 2C), 129.1 (d, 2C), 140.8 (s), 144.8 (s), 146.9 (s), 147.7 (s), 152.6 (s), 159.4 (s), 160.4 (s)
17g	^{1}H: 0.48-0.76 (m, 2H), 0.81-1.07 (m, 4H), 1.19-1.38 (m, 7H), 1.40-1.58 (m, 2H), 1.61-1.81 (m, 3H), 2.02-2.08 (m, 1H), 2.10-2.18 (m, 1H), 2.46-2.54 (m, 1H), 3.81 (s, 3H), 3.82 (s, 3H), 5.05 (d, J = 9.9 Hz, 1H), 6.88 (part of AA'BB', N = 9 Hz, 2H), 6.93 (part of AA'BB', N = 9 Hz, 2H), 7.16-7.23 (m, 3H), 7.24-7.35 (m, 3H), 7.40-7.49 (m, 2H), 7.52-7.56 (m, 2H), 7.80-7.82 (m, 2H), 8.24-8.26 (m, 2H) ^{13}C: 21.7 (t), 22.6 (t), 24.8 (t, 2C), 25.2 (t, 2C), 30.1 (t), 32.1 (t), 33.8 (t), 34.1 (t), 54.3 (d), 55.4 (q), 55.5 (q), 87.7 (s), 107.4 (s), 113.8 (d, 2C), 114.0 (d, 2C), 125.8 (d, 2C), 126.7 (d, 2C), 127.4 (d, 2C), 127.7 (d, 2C), 127.8 (d), 128.0 (d, 2C), 128.1 (d, 2C), 129.0 (d), 129.8 (s), 133.3 (s), 133.8 (s), 137.6 (s), 146.9 (s), 147.6 (s), 152.6 (s), 157.3 (s), 158.7 (s)
17h	^{1}H: 0.49-0.61 (m, 2H), 0.78-1.80 (m, 15H), 1.85-1.99 (m, 1H), 2.09-2.30 (m, 2H), 2.40-2.60 (m, 1H), 5.15 (d, J = 9.9 Hz, 1H), 7.21-7.31 (m, 1H), 7.32-7.48 (m, 7H), 7.64-7.72 (m, 2H), 7.94 (part of AA'BB', N = 9 Hz, 2H), 8.05 (part of AA'BB', N = 9 Hz, 2H), 8.32 (part of AA'BB', N = 9 Hz, 2H), 8.63 (part of AA'BB', N = 9 Hz, 2H) ^{13}C: 22.0 (t), 22.9 (t), 24.5 (t), 24.6 (t), 25.2 (t, 2C), 30.1 (t), 31.4 (t), 33.7 (t), 34.6 (t), 54.6 (d), 89.2 (s), 108.0 (s), 123.5 (d, 2C), 123.7 (d, 2C), 124.2 (d, 2C), 124.4 (d, 2C), 125.6 (d), 127.5 (d, 2C), 127.6 (d, 2C), 128.1 (d), 129.0 (d, 2C), 129.1 (d, 2C), 135.7 (s), 139.3 (s), 140.2 (s), 143.2 (s), 144.8 (s), 147.3 (s), 147.4 (s), 147.7 (s), 150.0 (s)
17i	^{1}H [c]: 0.4-2.8 (m, 21H), 4.22 (d, J = 9 Hz, 1H), 7.2-7.5 (m, 8H), 7.75-7.95 (m, 4H), 8.05-8.35 (m, 6H) ^{13}C: 21.8 (t), 22.7 (t), 24.1 (t), 24.7 (t), 24.99 (t), 25.02 (t), 31.4 (t), 32.0 (t), 33.7 (t), 33.9 (t), 55.4 (d), 88.4 (s), 108.2 (s), 116.8 (d, 2C), 123.4 (d, 2C), 124.6 (d, 2C), 125.2 (d, 2C), 127.5 (d, 2C), 127.8 (d, 2C), 128.2 (s), 128.4 (d, 2C), 128.5 (d, 2C), 128.9 (d), 130.1 (d), 132.1 (s), 140.5 (s), 145.2 (s), 145.8 (s), 146.9 (s), 148.6 (s), 150.1 (s), 151.9 (s)
18	^{1}H: 0.38-0.48 (m, 1H), 0.61-0.88 (m, 5H), 1.02-1.18 (m, 2H), 1.22-1.42 (m, 6H), 1.54-1.60 (m, 1H), 1.62-1.74 (m, 1H), 1.97-2.16 (m, 2H), 2.38-2.46 (m, 2H), 2.70-2.84 (m, 1H), 3.04 (s, 1H), 7.31-7.49 (m, 8H), 7.64-7.78 (m, 4H), 8.12-8.20 (m, 4H), 8.25-8.28 (m, 2H) ^{13}C: 21.8 (t), 22.6 (t), 23.8 (t), 24.9 (t), 25.0 (t), 25.3 (t), 31.3 (t), 32.2 (t), 34.2 (t), 34.8 (t), 54.4 (d), 89.5 (s), 115.8 (d, 2C), 121.9 (d, 2C), 124.7 (d, 2C), 125.3 (d, 2C), 125.9 (s), 126.9 (d, 2C), 127.5 (s), 127.7 (d, 2C), 128.6 (d, 2C), 128.7 (d), 128.8 (d, 2C), 130.47 (d), 130.50 (s), 132.6 (s), 140.3 (s), 144.4 (s), 145.2 (s), 145.5 (s), 147.7 (s), 148.2 (s)
19	^{1}H: 1.05-1.19 (m, 5H), 1.55-1.85 (m, 5H), 2.32 (s, 1H), 2.66-2.71 (m, 1H), 3.90 (s, 2H), 7.34-7.45 (m, 3H), 7.80-7.82 (m, 2H), 7.99/8.26 (AA'BB', N = 9 Hz, 4H) ^{13}C: 24.7 (t, 2C), 25.9 (t), 34.0 (t, 2C), 57.8 (d), 113.5 (s), 121.2 (d, 2C), 124.9 (d, 2C), 126.8 (d, 2C), 128.2 (d), 128.6 (d, 2C), 132.9 (s), 142.6 (s), 144.76 (s), 144.78 (s), 149.0 (s)
23g	^{1}H: 1.16-1.40 (m, 5H), 1.58-1.78 (m, 3H), 2.02-2.08 (m, 2H), 3.88 (s, 3H), 4.16 (m_c, 1H), 5.05 (d, J = 8 Hz, 1H), 7.06/7.67 (AA'BB', N = 9 Hz, 4H), 7.28-7.36 (m, 1H), 7.50-7.58 (m, 3H) ^{13}C: 24.7 (t, 2C), 25.8 (t), 32.8 (t, 2C), 49.1 (d), 55.4 (q), 114.7 (d), 123.9 (d), 128.66 (d), 128.74 (d, 2C), 129.2 (d), 129.8 (d, 2C), 132.4 (s), 136.9 (s), 141.7 (s), 146.4 (s), 149.5 (s), 160.6 (s)
23h	^{1}H: 1.24 (d, J = 7 Hz, 6H), 3.88 (s, 3H), 4.37 (m_c, 1H), 4.78 (d, J = 7 Hz, 1H), 7.22-7.25 (m, 1H), 7.30-7.32 (m, 1H), 7.48-7.55 (m, 3H), 7.63-7.65 (m, 1H), 7.68-7.69 (m, 1H), 7.70-7.71 (m, 1H) ^{13}C: 22.7 (q, 2C), 42.5 (d), 55.5 (q), 107.7 (d), 121.3 (d), 126.9 (d), 128.3 (d, 2C), 129.2 (d, 2C), 129.4 (d), 137.06 (s), 137.09 (s), 137.4 (s), 146.2 (s), 148.5 (s), 156.6 (s)
23i	^{1}H: 1.13-1.26 (m, 3H), 1.40-1.57 (m, 2H), 1.62-1.78 (m, 3H), 2.02-2.08 (m, 2H), 3.88 (s, 3H), 4.11 (m_c, 1H), 4.85 (d, J = 8 Hz, 1H), 7.18-7.30 (m, 2H), 7.41-7.58 (m, 3H), 7.62-7.65 (m, 1H), 7.69-7.72 (m, 2H) ^{13}C: 24.8 (t, 2C), 25.9 (t), 32.9 (t, 2C), 49.3 (d), 55.6 (q), 107.8 (d), 121.4 (d), 126.9 (d), 128.4 (d, 2C), 129.3 (d, 2C), 129.5 (d), 137.16 (s), 137.22 (s), 137.5 (s), 146.3 (s), 148.6 (s), 156.6 (s)
23j	^{1}H: 1.49 (s, 9H), 3.86 (s, 3H), 4.91 (s, 1H), 7.20-7.26 (m, 1H), 7.41-7.54 (m, 4H), 7.62-7.70 (m, 3H)
23l	^{1}H: 2.32 (s, 3H), 3.89 (s, 3H), 6.87 (s, 1H), 7.13 (part of AA'BB', N = 8 Hz, 2H), 7.27-7.33 (m, 2H), 7.51-7.61 (m, 5H), 7.73-7.77 (m, 3H) ^{13}C: 20.8 (q), 55.6 (q), 107.4 (d), 119.3 (d, 2C), 121.9 (d), 127.5 (d), 128.6 (d, 2C), 129.3 (d, 2C), 129.5 (d, 2C), 129.8 (d), 132.2 (s), 136.1 (s), 136.6 (s), 137.0 (s), 138.4 (s), 146.2 (s), 146.6 (s), 157.6 (s)
23m	^{1}H: 2.21 (s, 6H), 3.87 (s, 3H), 6.23 (s, 1H), 7.10-7.12 (m, 3H), 7.17-7.22 (m, 1H), 7.32-7.36 (m, 1H), 7.50-7.60 (m, 4H), 7.83-7.85 (m, 2H) ^{13}C: 18.9 (q, 2C), 55.5 (q), 107.4 (d), 121.6 (d), 126.4 (d), 127.6 (d), 128.1 (d, 2C), 128.3 (d, 2C), 129.4 (d, 2C), 129.6 (d), 135.4 (s, 2C), 136.0 (s), 136.8 (s), 137.0 (s), 138.2 (s), 146.0 (s), 147.4 (s), 157.2 (s)
25′h	^{1}H [a]: 1.02-1.18 (m, 3H), 1.20-1.36 (m, 2H), 1.42-1.60 (m, 1H), 1.60-1.72 (m, 2H), 1.76-1.82 (m, 2H), 3.44 (m_c, 1H), 3.68 (s, 3H), 5.92 (d, J = 8 Hz, 1H), 6.79/7.26 (AA'BB', N = 9 Hz, 4H), 8.07 (s, 1H) [d]
25′i	^{1}H: 1.47 (s, 9H), 3.71 (s, 3H), 6.01 (s, 1H), 6.77/7.25 (AA'BB', N = 9 Hz, 4H), 8.03 (s, 1H)
25′k	^{1}H [a]: δ = 2.19 (s, 6H), 3.88 (s, 3H), 6.77/7.28 (AA'BB', N = 8 Hz, 2H), 6.86-6.93 (m, 1H), 7.40-7.44 (m, 2H), 7.79 (s, 1H), 8.84 (s, 1H)

[a] $(CD_3)_2SO$ as solvent; [b] in case of the congener **13e**, low-field singlet observed at δ11.70 (remaining signals of this compound not clearly distinguished because of insufficient solubility); [c] 90 MHz; [d] data in part different from those reported in ref. [36].

General Procedure for the Reaction of Hydrazonoyl Chlorides **1** with the Isocyanide **3d** in the Presence of Excess Triethylamine at Room Temperature (Modified Method B).

To a solution of **1** (10 mmol) and **3d** (0.83 g, 10 mmol) in anhydrous benzene (25 mL) was added triethylamine (5 mL, *ca.* 36 mmol), and the mixture was kept at ambient temperature for

24 hours. Work-up was as follows:

(i) Starting pair **1a** + **3d** (≈ intermediate **4d**): The solid was collected by filtration, washed with light petroleum and water to give 4-*tert*-butyl-1,3-diphenyl-5-[phenyl(phenylhydrazono)-methyl]-1,2,4-triazolium chloride (**11c**). For data, see Tables 1−3. The filtrate and organic washings from **11c** were concentrated *in vacuo*, the residue was dissolved in the minimum amount of ethanol to allow crystallization of a trace of 4,8-bis(*tert*-butylimino)-1,3,5,7-tetraphenyl-1,4,5,8a-tetrahydro-1,2,5,6-tetrazocine [35] and thereupon was chromatographed to yield, successively, 2,4-diphenyl-1,2,3-triazole (**7a**) and 1,3-diphenyl-1,2,4-triazol-5-yl phenyl ketone phenylhydrazone (**13a**). For data, see Table 1.

(ii) Starting pairs **1b** + **3d** and **1d** + **3d** (≈ intermediates **4l,q**): The filtrate and organic washings from the solid (which was discarded) were concentrated; the residue was chromatographed to afford the 4-aryl-2-phenyl-1,2,3-triazole **7b** or **7c**. For data, see Table 1.

General Procedure for the Reaction of Hydrazonoyl Chlorides **1** with Isocyanides **3** in the Presence of Excess Triethylamine at Elevated Temperature (Method B).

To a stirred solution of **1** and **3** (10 mmol each) in anhydrous benzene (25 mL) was added triethylamine (5 mL, *ca.* 36 mmol). The mixture was heated under reflux for 1 hour, cooled to room temperature, diluted with light petroleum (25 mL), and allowed to stand for another 3-4 hours. Work-up was as follows:

(i) Starting pairs **1b** + **3d** and **1d** + **3d** (≈ intermediates **4l,q**): The solid was filtered off, washed with light petroleum, and discarded. The filtrate was concentrated and chromatographed to yield, successively, the 4-aryl-2-phenyl-1,2,3-triazole **7b** or **7c** and the aryl 3-aryl-1-phenyl-1,2,4-triazol-5-yl ketone phenylhydrazone **13b** or **13c**. For data, see Tables 1−3.

(ii) Starting pair **1e** + **3d** (≈ intermediate **4t**): Removal of the solid and concentration of the filtrate gave a residue that was dissolved in the minimum amount of diethyl ether to deposite 1,4-bis-(4-methoxyphenyl)-3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine (**9a**) which was collected by filtration. The concentrated filtrate from **9a** which showed a trace of *tert*-butyl-[(4-methoxyphenylazo)phenylvinylidene]amine (**4t**) [ir (neat) ν 2000 cm^{-1} (w)] was chromatographed to afford, successively, a mixture (0.59 g) consisting of a small amount of benzonitrile (**24**: R = Ph) and *N*-*tert*-butyl-*N*′-(4-methoxyphenyl)carbodiimide (**25i**) [ir (neat) ν 2211 (w) / 2105 cm^{-1} (s)], 2-(4-methoxyphenyl)-4-methyl-1,2,3-triazole (**7d**), and *N*-*tert*-butyl-6-methoxy-3-phenylquinoxalin-2-amine (**23j**); the latter was purified through its picrate according to the procedure given in ref. [2]. For data, see Tables 1−4.

(iii) Starting pairs **1f** + **3d** and **1g** + **3d** (≈ intermediates **4y,z**′): In the case of **1f**, the solid was collected by filtration, washed with light petroleum and water to give, after crystallization from ethanol, 4-(4-nitrophenyl)-2-phenyl-1,2,3-triazole (**7e**; from the organic filtrate and washings a second crop was obtained); for data, see Tables 1−4. The mother liquor of **7e** showed the presence of some 4-nitrophenyl 3-(4-nitrophenyl)-1-phenyl-1,2,4-triazol-5-yl ketone phenylhydrazone **13d** which was not isolated. In the case of **1g**, the same procedure afforded 1-(4-nitrophenyl)-3-phenyl-1,2,4-triazol-5-yl phenyl ketone (4-nitrophenyl)hydrazone (**13e**); the concentrated mother liquor of **13e** showed a trace of 2-(4-nitrophenyl)-4-phenyl-1,2,3-triazole (**7f**) which was not isolated (ms: m/z 266). For data, see Tables 1−4.

(iv) Starting pair **1a** + **3e** (≈ intermediate **4e**): The solid was collected by filtration, washed with light petroleum and water to give 4-(1-adamantyl)-1,3-diphenyl-5-[phenyl(phenylhydrazono)methyl]-1,2,4-triazolium chloride (**11d**). Chromatography of the concentrated filtrate and organic washings from **11d** afforded crude *N*-(1-adamantyl)-2-phenyl-2-(phenylhydrazono)-acetamide (**8a**; 0.17 g, 4%), mp 151-153 °C (from ethanol); ir (KBr): ν 3201, 2909, 1694, 1601 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.58 (s, 1H, NH), 12.73 (s, 1H, NH); this compound could not be obtained analytically pure. For data, see Tables 1−3.

(v) Starting pairs **1a** + **3g**, **1a** + **3h**, **1a** + **3i**, **1b** + **3h**, **1d** + **3c**, and **1e** + **3c** (≈ intermediates **4f-h,m,p,s**): The solid was collected by filtration, washed with light petroleum and water to give the 4-substituted 1,3-diaryl-5-[aryl(phenylhydrazono)methyl]-1,2,4-triazolium chloride **11e**, **11f**, **11g**, **11i, 11l** or **11n**. The filtrates and organic washings from **11l** and **11n** were concentrated and chromatographed to yield, after elution of some starting material and a trace of **9a**, a mixture (0.45 g or 1.14 g) consisting of very little 4-methoxybenzo- (**24**: Ar = 4-$MeOC_6H_4$) or benzonitrile (**24**: Ar = Ph) and the respective *N*-aryl-*N*′-cyclohexylcarbodiimide **25c** or **25h** [ir (neat) ν 2224 cm^{-1} (w) / 2128 (s) or 2211 (w) / 2102 cm^{-1} (s)] and in turn the 1,3-diaryl-*N*-cyclohexyl-4-(1,3-diaryl-1,2,4-triazaspiro[4.5]dec-2-en-4-yl)pyrazol-5-amine **17f** or **17g** which was crystallized by trituration with ethanol. The filtrate from **17** was concentrated and the residue was dissolved in 12 *N*

Table 4

Complementary Spectra of Selected New Compounds

N°	UV and *Fluorescence* (EtOH) λ nm (log ε)
17f	202 (4.55), 259 (4.26), 325 (3.72); *468*
17g	251 (4.42), 340 (3.88); *490*
17h	223 (4.39), 264 (4.40), 308 (4.22), 407 (3.98)
17i	235 (4.52), 320 (4.82), 438 (4.24)
18	232 (4.84), 295 (3.88), 401 (4.29)
23g	232 (4.42), 264 (4.29), 397 (3.95); *450*
23h	236 (4.40), 268 (4.29), 402 (3.95); *471*
23i	237 (4.41), 266 (4.30), 401 (3.96); *468*
23l	227 (4.51), 291 (4.45), 411 (4.01); *487* [a]
23m	230 (4.43), 271 (4.33), 397 (3.94); *462* [a]
	MS (m/z, %) [b]
7d	251 (M^+, 100)
7e	266 (M^+, 100)
11f	506 (100) [c]
11g	522 (100) [c]
12	827 (100), 587 (6), 504 (14), 451 (57) [c]
13c	475 (M^+, 58), 474 (100)
13e	505 (M^+, 63), 504 (100)
16	457 (M^+, 100), 375 (28)
17f	666 (M^+, 100), 623 (90), 584 (48), 452 (8)
17g	666 (M^+, 98), 623 (100), 584 (52)
17h	696 (M^+, 70), 653 (100), 614 (64), 558 (69)
17i	696 (M^+, 63), 653 (36), 614 (31), 558 (39), 481 (60), 96 (100)
18	696 (M^+, 4), 551 (14), 475 (2), 225 (100)
19	378 (26), 377 (M^+, 100), 294 (68)
20	616 (M^+, 1), 511 (63), 505 (36), 504 (24), 428 (100), 103 (81); 617 (M^+ + 1, 18), 154 (100) [c]
21	476 (56) [476.1942, calcd. for $C_{28}H_{24}N_6O_2$:476.1961], 373 (59), 185 (100); 617 (M^+ + 1, 92), 55 (100) [c]
23g	333 (M^+, 60), 251 (100)
23i	333 (M^+, 58), 251 (100)
23l	341 (M^+, 100), 340 (83)
23m	355 (M^+, 10), 340 (16), 327 (44), 121 (100)

[a] CH_2Cl_2 as solvent; [b] EI (70 eV); [c] FAB (pos.).

HCl/Ethanol (10 mL; 1/4). After standing at 20 °C for 4-5 hours the mixture was poured into water (100 mL), neutralized, and extracted with dichloromethane. Chromatography of the concentrated organic phase afforded the 1,3,5-triaryl-1,2,4-triazole **27d** or **27e** and then the 3-aryl-(6-methoxy)-*N*-cyclohexylquinoxalin-2-amine **23g** or **23i** which was purified through its picrate according to the procedure given in ref. [2]. For data, see Tables 1−4.

(vi) Starting pair **1e** + **3b** (≈ intermediate **4r**): The solid treated as above gave 4-isopropyl-1-(4-methoxyphenyl)-5-{[(4-methoxyphenyl)hydrazono]phenylmethyl}-3-phenyl-1,2,4-triazolium-chloride (**11m**). Chromatography of the filtrate from **11m** afforded a mixture (0.96 g) consisting of very little benzonitrile (**24**: Ar = Ph) and *N*-isopropyl-*N*′-(4-methoxyphenyl)carbodiimide (**25g**) [ir (neat) ν 2206 (w) / 2100 cm^{-1} (s)]. Continued elution gave *N*-isopropyl-6-methoxy-3-phenylquinoxalin-2-amine (**23h**) and 1-(4-methoxyphenyl)-3,5-diphenyl-1,2,4-triazole (**27e**). For data, see Tables 1−4.

(vii) Starting pairs **1f** + **3c** and **1g** + **3c** (≈ intermediates **4x,z**): The solid was separated and purified as above to give 4-cyclohexyl-3-(4-nitrophenyl)-5-[(4-nitrophenyl)(phenylhydrazono)-methyl]-1-phenyl-1,2,4-triazolium-chloride (**11o**) or 4-cyclohexyl-1-(4-nitrophenyl)-5-[(4-nitrophenyl-{[(4-nitrophenyl)-hydrazono]phenylmethyl}hydrazono)phenylmethyl]-3-phenyl-1,2,4-triazolium-chloride (**12**). The filtrates and organic washings from **11o** and **12** were concentrated and chromatographed to yield, in the case of **11o**, the pyrazolamine **17h**. In the case of **12**, elution gave, successively, the dihydrotetrazine **9b**, the amide **8c**, the pyrazolamine **17i**, and finally N^4-cyclohexyl-N^5-cyclohexylidene-1-(4-nitrophenyl)-3-phenylpyrazole-4,5-diamine (**16**). The filtrate from **12** showed a trace of *N*-cyclohexyl-1-(4-nitrophenyl)-5-[1-(4-nitrophenyl)-3-phenyl-1,2,4-triazaspiro[4.5]-dec-2-en-4-yl]-3-phenylpyrazol-4-amine (**18**) which could not be separated (identified through an authentic sample; preparation see below). For data, see Tables 1−4.

(viii) Starting pair **1e** + **3h** (≈ intermediate **4v**): The solid was collected by filtration and dissolved in the minimum amount of ethanol to allow crystallization of 6-methoxy-*N*-(4-methylphenyl)-3-phenylquinoxalin-2-amine (**23l**). The concentrated filtrate from **23l** was chromatographed to yield a mixture (1.13 g) consisting of very little benzonitrile (**24**: Ar = Ph) and *N*-(4-methoxyphenyl)-*N*′-(4-methylphenyl)carbodiimide (**25j**) [ir (neat) ν 2210 (w) / 2120 cm^{-1} (s)]. Continued elution gave a second crop of **23l** and 1-(4-methoxyphenyl)-3,5-diphenyl-1,2,4-triazole (**27e**). For data, see Tables 1−4.

(ix) Starting pairs **1a** + **3k** and **1e** + **3k** (≈ intermediates **4i,w**): The solid was filtered off, washed with light petroleum, and discarded. The filtrate was concentrated and chromatographed to yield a mixture (1.77 g or 1.90 g) consisting of a small amount of benzonitrile (**24**: Ar = Ph) and the *N*-aryl-*N*′-(2,6-dimethylphenyl)-carbodiimide **25d** or **25k** [ir (neat) ν 2210 (w) / 2120 cm^{-1} (s); either mixture]. Continued elution gave, in the case of **1a**, 1,3,5-triphenyl-1,2,4-triazole (**27a**) and, in the case of **1e**, a mixture consisting of *N*-(2,6-dimethylphenyl)-6-methoxy-3-phenylquinoxalin-2-amine (**23m**) and 1-(4-methoxyphenyl)-3,5-diphenyl-1,2,4-triazole (**27e**) which were separated by fractional crystallization from ethanol. For data, see Tables 1−4.

General Procedure for the Conversion of the Carbodiimides **25** into the *N*,*N*′-Disubstituted Ureas **25**′.

The oily mixture consisting of the nitrile **24** and the carbodiimide **25** was dissolved in 12 *N* HCl/1,1-dimethoxyethane (5 mL; 1/3) and allowed to stand at room temperature for 12 hours. Evaporation under reduced pressure gave a residue which was chromatographed to yield the *N*,*N*′-disubstituted urea **25′c, 25′d, 25′g, 25′h, 25′i, 25′j** or **25′k**. For data, see Tables 1−3.

Reactions of N^4-Cyclohexyl-N^5-cyclohexylidene-1-(4-nitrophenyl)-3-phenylpyrazole-4,5-diamine (**16**).

(i) Reaction with **1g** / triethylamine: The substrate **16** (0.11 g, 0.25 mmol) was dissolved in anhydrous benzene (5 mL) and, after addition of triethylamine (0.2 mL), heated under reflux for 10 minutes. The cooled mixture was diluted with light petroleum (5 mL), and the solid was filtered off and washed with light petroleum (10 mL). The filtrate was concentrated and the residue was chromatographed to give, after trituration with ethanol, 0.07 g (40%) *N*-cyclohexyl-1-(4-nitrophenyl)-5-[1-(4-nitrophenyl)-3-phenyl-1,2,4-triazaspiro[4.5]dec-2-en-4-yl]-3-phenylpyrazol-4-amine (**18**). For data, see Tables 2−4. – Hydrolysis of **18**: The substrate was treated as described for the pyrazole **17i** (see above) to give the amidrazone **21** as an amorphous solid that was submitted to mass spectrometry without further purification. For data, see Table 4.

(ii) Hydrolysis: The substrate **16** (0.11 g, 0.25 mmol) was dissolved in ethanol (25 mL) and kept at room temperature for 24 hours to allow crystallization of 0.07 g (74%) N^4-cyclohexyl-1-(4-nitrophenyl)-3-phenylpyrazole-4,5-diamine (**19**) which was collected by filtration. For data, see Tables 2−4.

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