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SYNTHESIS AND THERMOLYSIS OF 4-SUBSTITUTED 5-AZIDO-1-PHENYL-1,2,3-TRIAZOLES

Gerrit L'abbé, Anna Vandendriessche, and Suzanne Toppet

Department of Chemistry, University of Leuven
Celestijnenlaan 200F, 3030 Heverlee, Belgium

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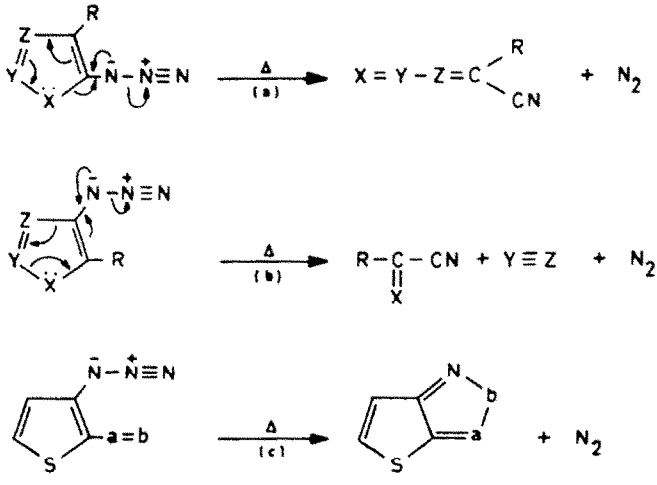
ABSTRACT. 5-Azido-1-phenyltriazoles (4) can thermally isomerize to diazo substituted tetrazoles (5) or decompose to alkylidenetriazenes (8) depending on the nature of the substituent at the 4-position. The former are obtained for electron-withdrawing substituents (CH=O, CH=NR', $PO(OEt)_2$, $PhSO_2$), whereas the latter are formed with aryl substituents. The diazo compounds 5 were stable and isolable when R = CHO or $PO(OEt)_2$, but they ring-closed to triazoles (6) when R = CH=NR', or they decomposed under the reaction conditions (refluxing benzene) to cycloheptatrienes (7) when R = $ArSO_2$. A kinetic study of the rearrangement has been carried out and the mechanism is discussed (Scheme IV).

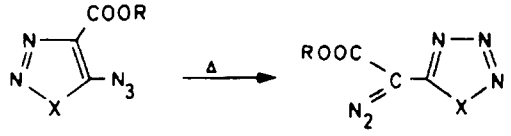
Thermolysis of five-membered heterocyclic azides can occur by two general pathways (a and b, Scheme I), depending on whether the azide function is located at the α or the β-position. Thus, 5-azidofurans,[1] 5-azidopyrazoles[2] and 5-azido-1,4-diphenyl-1,2,3-triazole[3] decompose by path (a), whereas 4-azidoisoxazoles,[4] 4-azidopyrazoles[5] and 4-azido-1,2,3-triazoles[5] follow path (b).

Scheme I



Alternative reaction routes have also been observed. For instance, the azide (or nitrene) can interact with a neighbouring function without cleavage of the heterocycle. This path (c) is known for 3-azidothiophenes bearing a carbonyl,[6] imine,[7] nitro[8] or vinyl group[9] at the 2-position.

In 1982, we discovered a new rearrangement based on the electrocyclic ring-opening of 1,2,3-thiadiazoles; namely the isomerization of 5-azido-4-ethoxycarbonyl-1,2,3-thiadiazole (1a) to ethyl α-thiatriazolyldiazoacetate (2a).[10] This type of rearrangement was also observed when 5-azido-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (1b) was heated at 60-80°, yielding methyl α-tetrazolyldiazoacetate (2b).[11] Thus, rearrangement of 1b occurs more rapidly than does thermal decomposition by path (a). In contrast, 5-azido-1,4-diphenyltriazole was shown by Smith et al.[3] to thermolyze at 50° to 1-phenyl-3-(α-cyano)benzylidenetriazene according to path (a) (X = NPh, R = Ph).



1 2

a : X = S ; b : X = NPh

From these results, it is evident that the outcome of the thermolysis of 5-azidotriazoles depends on the facility of ring-opening vs thermal stability of the azide. Since the nature of the 4-substituent is important in determining the reaction route, we have now introduced a variety of substituents in this position and studied the thermal behaviour.

SYNTHESIS OF THE AZIDOTRIAZOLES

The azidotriazoles 4 studied in this work (Scheme II) were prepared from the aminotriazoles 3, which themselves are available by known procedures.[12] Diazotization of 3 at 0/5°, followed by treatment of the diazonium salts with an excess of sodium azide at about -30° readily afforded the azides 4a,i,j,k,m,p. The direct conversion of 3n to 4n was less successful, since a mixture of the desired azide in low yield (3%) along with much 5-chloro-4-cyano-1-phenyltriazole (14%) was obtained. A convenient method for the synthesis of 4n, however, starts from the 5-amino-4-carbamoyltriazole 3m, by first transforming the amine function into an azide function (4m). The carboxamide function is then dehydrated with phosphoryl chloride in dimethylformamide to give a nitrile function.[13] The conversion of 3q into 4q by the diazotization method was also unsuccessful, but the diazo transfer reaction with tosyl azide under basic conditions[14] yielded 4q in 25% yield.

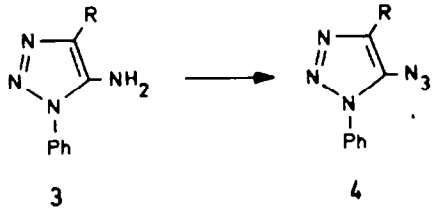
Since 5-aminotriazoles bearing an imine function at the 4-position (3b-g) are prone to undergo a ring-degenerate rearrangement at ambient temperature,[15] the synthesis of the azides 4b-h was achieved by treating the azido-aldehyde 4a with amines (or hydroxylamine). This furnished 4b,c,d,h in the pure crystalline state, whereas 4e,f,g rearranged during the condensation and subsequent crystallization processes at room temperature (vide infra).

THERMOLYSIS

Although all the azidotriazoles 4a-g decomposed more or less easily when gently heated in solution (< 80°), the R-substituent has a decisive influence on the nature

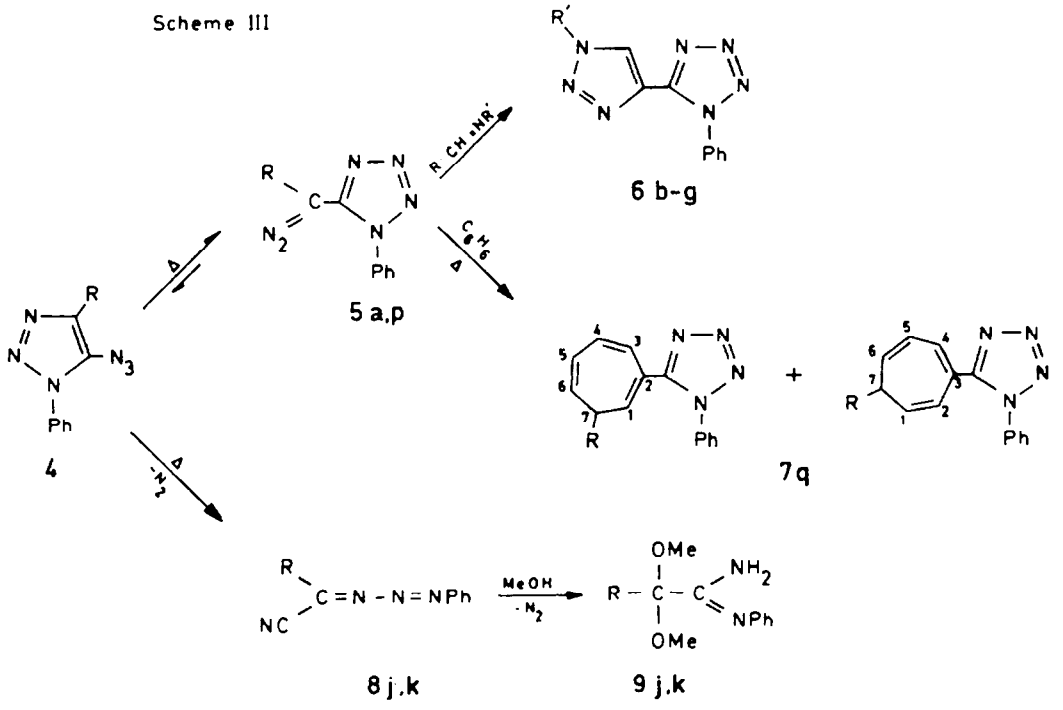
3-9	R
a	CH=O
b	CH=NPh
c	CH=NC$_6$H$_4$OMe(p)
d	CH=NC$_6$H$_4$Cl(p)
e	CH=NEt
f	CH=NCMe$_3$
g	CH=NCH$_2$Ph
h	CH=NOH
i	CH=CPhCN
j	C$_6$H$_4$Cl(p)
k	C$_6$H$_4$NO$_2$(p)
m	CONH$_2$
n	CN
p	PO(OEt)$_2$
q	SO$_2$Ph

Scheme II



3 4

Scheme III



4 5 a,p 6 b-g 7q 8 j,k 9 j,k

of the reaction products (see Scheme III). Those with the strong electron-withdrawing formyl and phosphoryl substituents (4a,p) rearranged cleanly to the diazo substituted tetrazoles 5a,p. This isomerization also occurred with the phenylsulfonyl derivative 4q, but the resulting diazo compound 5q decomposed further in benzene solution via a carbene intermediate to give a mixture of the 2,7- and 3,7-disubstituted cycloheptatrienes 7q in a ratio of 1:4. Apparently, the sulfonyl group had migrated during the reaction as a result of steric repulsion by the tetrazolyl substituent. The structures of the isomers of 7q were established on the basis of a detailed analysis of the ^{1}H NMR spectrum recorded on a 250 MHz instrument (see Experimental Section).[16]

The 1,3-dipolar isomerization of 4 to 5 was also observed for the 4-imino substituted azidotriazoles 4b-q, but here a subsequent electrocyclization reaction between the resulting diazo and imine functions yielded the triazolyl substituted tetrazoles 6b-q. This isomerization already occurred during the synthesis and/or crystallization of 4e-q. In contrast, 4h failed to isomerize but gave intractable tars on thermolysis in benzene.

The aryl substituted azidotriazoles 4j,k decomposed in benzene at 50° with loss of nitrogen to give the red alkylidenetriazenes 8j,k in a manner analogous to the 4-phenyl derivative studied by Smith et al.[3] In methanol, the red colour of 8j,k disappeared with formation of the acetal-amidines 9j,k. The other azidotriazoles 4i,m,n decomposed thermally to intractable tars.

KINETICS AND MECHANISM OF THE REARRANGEMENT

In order to get more insight into the mechanistic details of the rearrangement, the rate of the reaction 4a ⇌ 5a was studied by NMR techniques, and the results are summarized in Table I. From this table it is apparent that the rearrangement is enhanced by the use of less polar solvents; a phenomenon already noticed for the ester derivative.[11] Furthermore, the same order of reactivity was found for the Dimroth rearrangement of 3a which yields 5-anilino-4-formyltriazole ($k = 27.8 \times 10^{-5}$ s^{-1} in DMSO-d_6 at 70°).

Table I. Kinetics of the reaction 4a ⇌ 5a at 70°

Solvent	CCl_4	C_6D_6	CD_3CN
10^5 k, s^{-1}	78.3	64.6	21.7

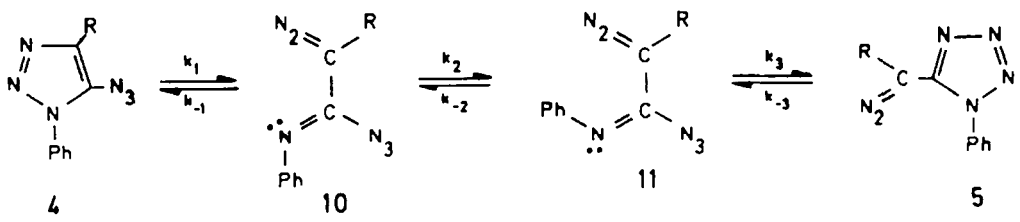
More relevant was the observation that an equilibrium is reached in the three solvents at 70°, containing the diazo isomer 5a for 90%, 94% and 82% respectively. These values are only estimates, since the determination of the exact equilibrium positions was rendered difficult by the slow decomposition of 5a at the end of the reaction. The isomerization of 4p also reached an equilibrium since 10% of the starting azide was recovered after being heated at 60° for 24 h. In the case of 1b, studied previously,[11] the rate of rearrangement was much slower and decomposition of the resulting diazo 2b prevented the observation of an equilibrium.

The imine substituted azidotriazoles 4b-q rearranged completely and faster than did the aldehyde 4a. For instance, 4c reacted in chloroform solution at 70° with a rate constant $k = 124.7 \times 10^{-5}$ s^{-1}, which is twice as fast as 4a in the less polar solvent benzene, and almost six times faster than 4a in acetonitrile. Moreover, the aliphatic imines 4e-q could not be isolated pure, since they isomerized readily, even at room temperature. In order to compare the reactivity of three selected imines (4c,d,e), we have carried out kinetic measurements in dimethyl sulfoxide solution, in which all three samples were soluble. The results, recorded in Table II, indicate that the rate increases in the order: 4c < 4e < 4d.

Table II. Substituent effect on the rearrangement 4 ⇌ 6 in $(CD_3)_2SO$ solution at 70°

Azide	4c	4d	4e
10^5 k, s^{-1}	27.0	48.4	34.6

Scheme IV



We can rationalize these results on the basis of the mechanistic Scheme IV, which comprises the sequence of a reversible ring-opening of 4, syn-anti isomerization of the azido-imine 10, and reversible ring-closure to the tetrazole 5. The experimentally determined first-order rate constant of the forward reaction (k) is given by the following equation:[17]

$$k = \frac{k_1 \frac{k_2}{k_{-1} + k_2} \times \frac{k_3}{k_{-2} + k_3}}{1 - \frac{k_2}{k_{-1} + k_2} \times \frac{k_{-2}}{k_3 + k_{-2}}}$$

The diazo function of 10 can reclose to 4 by k_{-1}, thus reducing the overall rate. This is counteracted by introducing an imine function at the 4-position (R = CH=NR') which competes with C=NPh for electrocyclization with the diazo function, so that the reaction rate increases. The electron-withdrawing nature of the imine substituent also affects k_1 to some extent, giving the observed reactivity sequence of Table II.

Finally, a comment on the stereochemistry of ring-opening of 4 to the azido-imine, and its ring-closure to 5, is in order. The indicated stereochemistry is deduced from ab-initio calculations carried out for the isomerization of azidoazomethine to 1H-tetrazole.[18] According to Leroy and co-workers, the cyclization reaction proceeds by a bending of the azido function, due to the formation of a lone electron pair on the central nitrogen atom (Fig.1). This is accompanied by a π-electron flow towards the imine function and the formation of a σ-bond at the expense of the lone pair on the imine nitrogen. The important feature of the process is the role of the lone pair on the imine nitrogen which permits the formation of a sigma bond without the NH group having to rotate. This has been corroborated by experimental facts.[19] As a result, the tetrazole 5 is formed from the azido-imine having the E-configuration (11), whereas ring-opening of 4 gives the azido-imine in the Z-configuration (10).

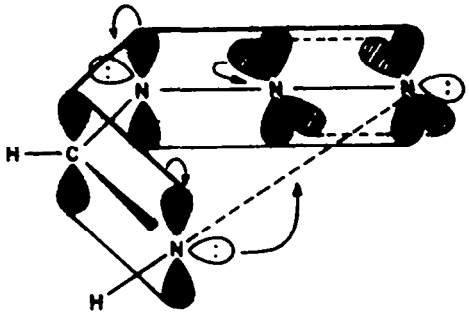


Fig.1. Electronic reorganization during the ring-closure of azidoazomethine

EXPERIMENTAL

Synthesis of the azidotriazoles 4a,i,j,k,m,p; exemplified for 4a. 5-Amino-4-formyl-1-phenyl-1,2,3-triazole, prepared by the method of Albert,[20] was diazotized by slow addition of sodium nitrite in water (0.76 g, 11 mmol) to a solution of 3a (1.88 g, 10 mmol) in 120 mL of concentrated hydrochloric acid at 0/-5°C. Then, a tenfold excess of sodium azide in water was added dropwise at about -30°C. After dilution with water, the reaction mixture was extracted with ether and the combined ether extracts were dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed on silica gel with dichloromethane as the eluent.

5-Azido-4-formyl-1-phenyl-1,2,3-triazole (4a) was obtained in 62% yield after crystallization from chloroform/ether, mp 97°C (dec.); IR (KBr) 2140 (s, N_3), 1690 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 7.4-7.7 (m, 5 aromatic H), 10.15 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 129.5 (C-4), 136.8 (C-5), 185.0 (CO). Anal. Calcd for $C_9H_6N_6O$ (mol wt 214): C, 50.46; H, 2.80. Found: C, 50.59; H, 2.74.

5-Azido-4-(α-cyanostyryl)-1-phenyl-1,2,3-triazole (4i) was similarly prepared from 3i[21] (conditions: 5 equiv. $NaNO_2$, 10 equiv. NaN_3, extraction with chloroform and crystallization from the same solvent), yield 56%, mp 125°C (dec.); IR (KBr) 2220 (m, CN), 2140 cm^{-1} (s, N_3); ^1H NMR (DMSO-d_6) δ 7.5-7.9 (m, vinyl and aromatic H); ^{13}C NMR (DMSO-d_6) δ 110.5 and 126.9 (vinyl α- and β-carbon atoms), 117.0 (CN, $^3J_{H,CN}$ = 14 Hz), 132.3 (C-4), 134.1 (C-5), 124.5, 125.7, 129.3, 129.4, 129.6, 130.1, 133.5, 134.0 (Ph C-atoms). Anal. Calcd for $C_{17}H_{11}N_7$ (mol wt 313): C, 65.17; H, 3.54. Found: C, 65.23; H, 3.64.

5-Azido-4-(p-chlorophenyl)-1-phenyl-1,2,3-triazole (4j) was similarly prepared from 3j (conditions: 1.1 equiv. $NaNO_2$, 5 equiv. NaN_3, extraction with ether and crystallization from the same solvent), yield 21%, mp 96°C (dec.); IR (KBr) 2140 cm^{-1} (s, N_3); ^1H NMR ($CDCl_3$) δ 7.4 and 7.7 (two d, 4 aromatic H), 7.4-7.6 (m, 5 aromatic H). Anal. Calcd for $C_{14}H_9ClN_6$ (mol wt 296): C, 56.66; H, 3.06. Found: C, 56.82; H, 3.12.

5-Azido-4-(p-nitrophenyl)-1-phenyl-1,2,3-triazole (4k) was similarly prepared from 3k (conditions: 1 equiv. $NaNO_2$, 13 equiv. NaN_3, purification of the precipitate by column chromatography on silica gel with dichloromethane as the eluent, followed by crystallization from ether), yield 32%, mp 92°C (dec.); IR (KBr) 2110 cm^{-1} (s, N_3); ^1H NMR ($CDCl_3$) δ 7.6 (s, 5 aromatic H), 8.10 and 8.35 (two d, 4 aromatic H). Anal. Calcd for $C_{14}H_9N_7O_2$ (mol wt 307): C, 54.71; H, 2.95. Found: C, 54.61; H, 3.02.

5-Azido-4-carbamoyl-1-phenyl-1,2,3-triazole (4m) was similarly prepared from 3m (conditions: 1 equiv. $NaNO_2$, 10 equiv. NaN_3, purification of the precipitate by crystallization from methanol), yield 90%, mp 138°C (dec.); IR (KBr) 3280, 3250, 3140 (m, NH_2), 2120 (s, N_3), 1680, 1655 cm^{-1} (s, CO); ^1H NMR (DMSO-d_6) δ 7.4-7.75 (m, 5 aromatic H), 7.8-8.1 (two br NH). Anal. Calcd for $C_9H_7N_7O$ (mol wt 229): C, 47.15; H, 3.08. Found: C, 47.27; H, 3.16.

5-Azido-4-diethylphosphoryl-1-phenyl-1,2,3-triazole (4p) was similarly prepared from 3p[22] (conditions: 1.1 equiv. $NaNO_2$, 5 equiv. NaN_3, extraction with chloroform, purification by column chromatography on alumina with ethyl acetate as the eluent, crystallization from ether), yield 55%, mp 98°C (dec.); IR (KBr) 2140 cm^{-1} (s, N_3); ^1H NMR ($CDCl_3$) δ 1.3 (t, 6H, two CH_3), 4.3 (m, 4H, two CH_2), 7.55 (s, 5 aromatic H); ^{13}C NMR ($CDCl_3$) δ 16.3 and 63.4 (C_2H_5), 126.6 (C-4, $^1J_{CP}$ = 243 Hz), 140.4 (C-5, $^2J_{CP}$ = 32 Hz), 124.3, 129.4, 129.8, 134.3 (Ph C-atoms). Anal. Calcd for $C_{12}H_{15}N_6O_3P$ (mol wt 322): C, 44.73; H, 4.69. Found: C, 44.85; H, 4.72.

Synthesis of 5-azido-4-cyano-1-phenyl-1,2,3-triazole (4n). Phosphoryl chloride (0.85 mL, 10 mmol) was added to a suspension of 4m (1.15 g, 5 mmol) in 5 mL of DMF at 0°C. The solution was stirred for 5 min at 0°C, 10 min at 25°C and finally 15 min at 80°C. Then, 5 mL of hydrochloric acid (1N) was added and the mixture was heated at 80°C for 5 min. After cooling, 4n was isolated in 61% yield and recrystallized from methanol/water, mp 88-90°C (dec.); IR (KBr) 2220 (m, CN), 2120 cm^{-1} (s, N_3); ^1H NMR ($CDCl_3$) δ 7.60 (s, aromatic H); ^{13}C NMR ($CDCl_3$) δ 110.2 and 111.4 (CN and C-4), 139.6 (C-5), 123.8, 129.7, 130.9, 133.6 (Ph C-atoms). Anal. Calcd for $C_9H_5N_7$ (mol wt 211): C, 51.17; H, 2.38. Found: C, 51.03; H, 2.50.

Synthesis of 5-azido-1-phenyl-4-phenylsulfonyl-1,2,3-triazole (4q). Compound 3q (1.5 g, 5 mmol) (prepared by reacting equimolar amounts of phenylsulfonylacetonitrile, phenyl azide and sodium

methoxide in methanol at 20°C for 1 day) was added in several portions to a suspension of sodium hydride (140 mg, 80%) in 30 mL of dry tetrahydrofuran. When hydrogen evolution has ceased (ca 30 min), tosyl azide (0.98 g, 5 mmol) was added dropwise and the reaction mixture was stirred for 5 h at room temperature. Then, 20 mL of water was added and the whole mixture was evaporated, extracted with ether and the ether extracts dried over Na_2SO_4. This furnished a crude product (4q) which was purified by column chromatography on silica gel with n-hexane/ethyl acetate (ratio 2:1) as the eluent, yield 25%, mp 125°C (dec.); IR (KBr) 2150 (s, N_3), 1330 and 1155 cm^{-1} (s, SO_2); ^1H NMR ($CDCl_3$) δ 7.50 (s, 5H, Ph), 7.5-7.7 (m, 3 aromatic H), 8.1-8.2 (d, 2 aromatic H); ^{13}C NMR ($CDCl_3$) δ 135.5 and 136.5 (C-4 and C-5), 124.5, 127.9, 129.5, 130.4, 133.5, 134.3, 139.7 (Ph C-atoms). Anal. Calcd for $C_{14}H_{10}N_6O_2S$ (mol wt 326): C, 51.53; H, 3.03. Found: C, 51.39; H, 3.13.

Synthesis and thermolysis of the azidotriazoles 4b-h. Equimolar amounts (2.3 mmol) of 4a and aniline were allowed to react in ethanol (20 mL) at room temperature for 10 min. Then, the precipitate was filtered off and crystallized from chloroform/ether (without warming).

5-Azido-1-phenyl-4-phenyliminomethyl-1,2,3-triazole (4b) was obtained in 71% yield; IR (KBr) 2140 (s, N_3), 1640 cm^{-1} (m, C=N); ^1H NMR ($CDCl_3$) δ 7.3-7.8 (m, 10 aromatic H), 8.85 (s, 1H, CH=N). Anal. Calcd for $C_{15}H_{11}N_7$ (mol wt 289): C, 62.28; H, 3.83. Found: C, 62.16; H, 3.86.

When 4b (30 mg) was heated in benzene (5 mL) at 70°C for 10 min, a crystalline precipitate of 1-phenyl-5-(1-phenyl-1,2,3-triazol-4-yl)tetrazole (6b) was formed in 75% yield, mp 224°C; IR (KBr) 3130 (m, =CH), 1620, 1600 cm^{-1} (m); ^1H NMR (DMSO-d_6) δ 7.50-7.75 (m, 8 aromatic H), 7.90-8.00 (m, 2 aromatic H), 9.60 (s, 1H, triazole H); ^{13}C NMR (DMSO-d_6) δ 125.1 (triazole C-5), 133.2 (triazole C-4), 146.6 (tetrazole C-atom). Anal. Calcd for $C_{15}H_{11}N_7$ (mol wt 289): C, 62.28; H, 3.83. Found: C, 62.26; H, 3.91.

5-Azido-4-(p-methoxyphenyl)iminomethyl-1-phenyl-1,2,3-triazole (4c) was similarly obtained from 4a and p-anisidine (reaction time 10 min) as a red-orange precipitate in 64% yield; IR (KBr) 2120 cm^{-1} (s, N_3); ^1H NMR ($CDCl_3$) δ 3.85 (s, 3H, OCH_3), 6.9 and 7.3 (two d, 4 aromatic H), 7.5-7.7 (m, 5 aromatic H), 8.8 (s, 1H, CH=N).

Compound 4c rearranged partially into 6c upon crystallization from chloroform/ether at room temperature. Rearrangement was complete when 4c was heated in benzene, chloroform or ethanol for a short period.

5-(1-p-methoxyphenyl-1,2,3-triazol-4-yl)-1-phenyltetrazole (6c) was obtained in quantitative yield, mp 204°C (chloroform/ether); IR (KBr) 3110 (m, =CH), 1610, 1595 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 3.9 (s, 3H, OCH_3), 7.05 (d, 2 aromatic H), 7.6-7.7 (m, 7 aromatic H), 8.6 (s, 1H, triazole H); ^{13}C NMR ($CDCl_3$) δ 55.7 (OCH_3), 123.7 (triazole C-5), 134.0 (triazole C-4), 146.6 (tetrazole C-atom). Anal. Calcd for $C_{16}H_{13}N_7O$ (mol wt 319): C, 60.18; H, 4.10. Found: C, 60.32; H, 4.22.

5-Azido-4-(p-chlorophenyl)iminomethyl-1-phenyl-1,2,3-triazole (4d) was similarly obtained from 4a and p-chloroaniline (reaction time 10 min) as a yellow-orange precipitate in 64% yield; IR (KBr) 2140 cm^{-1} (s, N_3); ^1H NMR ($CDCl_3$) δ 7.5-7.8 (m, 5 aromatic H), 7.2 and 7.4 (two d, 4 aromatic H), 8.8 (s, 1H, CH=N).

Compound 4d rearranged partially into 6d upon crystallization from chloroform/ether at room temperature. Rearrangement was complete when 4d was heated in benzene, chloroform or ethanol for a short period.

5-(1-p-chlorophenyl-1,2,3-triazol-4-yl)-1-phenyltetrazole (6d) was obtained in quantitative yield, mp 238°C; IR (KBr) 3110 (m, =CH), 1605, 1590 cm^{-1} (m); ^1H NMR (DMSO-d_6) δ 7.6-7.9 and 8.0-8.2 (two m, 9 aromatic H), 9.6 (s, 1H, triazole H); ^{13}C NMR (DMSO-d_6) δ 125.2 (triazole C-5), 134.0 (triazole C-4), 146.4 (tetrazole C-atom). Anal. Calcd for $C_{15}H_{10}ClN_7$ (mol wt 324): C, 55.65; H, 3.11. Found: C, 55.52; H, 3.19.

5-(1-Ethyl-1,2,3-triazol-4-yl)-1-phenyltetrazole (6e) was obtained directly as a precipitate from the condensation of 4a (0.5 g) with an equivalent of ethylamine in ethanol (20 mL) at room temperature for 2 days, yield 54% after crystallization from chloroform/ether, mp 177°C; IR (KBr) 3100 (m, =CH), 1620, 1595 cm^{-1} (m); ^1H NMR ($CDCl_3$ + DMSO-d_6) δ 1.5 (t, 3H, CH_3), 4.45 (q, 2H, CH_2), 7.6 (s, 5 aromatic H), 8.65 (s, 1H, triazole H); ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ 14.9 and 44.9 (C_2H_5), 125.9 (triazole C-5), 131.8 (triazole C-4), 146.6 (tetrazole C-atom). Anal. Calcd for $C_{11}H_{11}N_7$ (mol wt 241): C, 54.76; H, 4.59. Found: C, 54.56; H, 4.46.

Note: When the reaction of 4a and ethylamine was stopped after 15 min at room temperature, a crude red oil of 4e was obtained (IR: 2135 cm^{-1}) which was used for the kinetic measurements.

5-Azido-4-(t-butyl)iminomethyl-1-phenyl-1,2,3-triazole (4f) was similarly obtained from 4a and tert-butylamine (reaction time 2 days) as a precipitate (IR: 2150 cm^{-1}) contaminated with 25% of 6f.

5-(1-t-Butyl-1,2,3-triazol-4-yl)-1-phenyltetrazole (6f) was obtained in 64% yield when the previous mixture was crystallized from chloroform/ether at room temperature, mp 128°C; IR (KBr) 3160 (m, =CH), 1620, 1595 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.7 (s, 9H, CMe_3), 7.6 (s, 5 aromatic H), 8.4 (s, 1H, triazole H); ^{13}C NMR ($CDCl_3$) δ 29.9 and 60.6 (CMe_3), 123.2 (triazole C-5, $^1J_{CH}$ = 196.6 Hz), 132.6 (triazole C-4, $^2J_{CH}$ = 9.5 Hz), 146.9 (tetrazole C-atom). Anal. Calcd for $C_{13}H_{15}N_7$ (mol wt 269): C, 57.98; H, 5.61. Found: C, 57.84; H, 5.48.

5-Azido-4-benzyliminomethyl-1-phenyl-1,2,3-triazole (4g) was similarly obtained from 4a and benzylamine (reaction time 1 day) as a white precipitate (IR: 2140 cm^{-1}) contaminated with much 6g. Crystallization of this mixture from chloroform/ether at room temperature yielded pure 6g.

5-(1-Benzyl-1,2,3-triazol-4-yl)-1-phenyltetrazole (6g) was obtained in 21% yield, mp 176°C; IR (KBr) 3100 (s, =CH), 1620, 1600 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 5.6 (s, 2H, CH_2), 7.3-7.45 (m, 5 aromatic H), 7.6 (s, 5 aromatic H), 8.15 (s, 1H, triazole H); ^{13}C NMR ($CDCl_3$) δ 54.6 (CH_2), 125.6 (triazole C-5, $^1J_{CH}$ = 200 Hz), 133.6 (triazole C-4, $^2J_{CH}$ = 9.2 Hz), 146.6 (tetrazole C-atom). Anal. Calcd for $C_{16}H_{13}N_7$ (mol wt 303): C, 63.36; H, 4.32. Found: C, 63.19; H, 4.36.

5-Azido-4-oximinomethyl-1-phenyl-1,2,3-triazole (4h) was obtained by adding an aqueous solution of $NH_2OH.HCl$ (385 mg in 5 mL), containing 5% NaOH, to an ethanol solution of 4a (0.5 g in 20 mL). After stirring for 10 min at room temperature, the precipitate was filtered off and crystallized from ethanol, yield 62%, mp 122°C (dec.); IR (KBr) 3220 (br, OH), 2140 cm^{-1} (s, N_3); ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 7.4-7.7 (m, 5 aromatic H), 8.2 (s, 1H, CH=N), 11.5 (s, 1H, OH); ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ 131.8 (C-5), 132.0 (C-4), 140.0 (CH=N). Anal. Calcd for $C_9H_7N_7O$ (mol wt 229): C, 47.16; H, 3.08. Found: C, 47.34; H, 3.22.

Thermolysis of the azidotriazoles 4a,p,q. A solution of 4a (1.5 g) in dry benzene was heated at 70°C for 3 h. Then, the solvent was removed in vacuo and the residue was chromatographed on silica gel with ethyl acetate/cyclohexane (15:85) as the eluent. This furnished 5-(α-formyl)diazomethyl-1-phenyltetrazole (5a) as a pale-yellow oil in 60% yield; IR (neat) 2110 (s, CN_2), 1660 cm^{-1} (s, CH=O); ^{1}H NMR ($CDCl_3$) δ 7.3-7.7 (m, 5 aromatic H), 9.60 (s, 1H, CH=O); ^{13}C NMR ($CDCl_3$) δ 66.8 (CN_2), 144.2 (C-5), 180.1 (C=O), 124.3, 129.8, 130.4, 132.1 (Ph C-atoms). Anal. Calcd for $C_9H_6N_6O$ (mol wt 214): C, 50.47; H, 2.82. Found: C, 50.73; H, 2.98.

A solution of 4p (0.5 g) in 20 mL of chloroform was heated at 60°C for 24 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel with ethyl acetate/n-hexane (70:30) as the eluent. This furnished unreacted 4p (10%) and 5-(α-diethylphosphoryl)diazomethyl-1-phenyltetrazole (5p) as a yellow oil in 70% yield; IR (neat) 2110 cm^{-1} (s, CN_2); ^{1}H NMR ($CDCl_3$) δ 1.3 (t, 6H, two CH_3), 4.2 (m, 4H, two CH_2), 7.4-7.7 (two m, 5 aromatic H); ^{13}C NMR ($CDCl_3$) δ 16.0 and 64.1 (C_2H_5), 145.1 (C-5), 125.5, 129.1, 129.7, 133.0 (Ph C-atoms); the diazo resonance was not detected due to coupling with the P-atom. Anal. Calcd for $C_{12}H_{15}N_6O_3P$ (mol wt 322): C, 44.73; H, 4.69. Found: C, 44.50; H, 4.75.

A solution of 4q (0.5 g) in 20 mL of benzene was refluxed for 24 h. The solvent was evaporated and the residue was chromatographed on silica gel with ethyl acetate/n-hexane (1:1) as the eluent. After crystallization from methanol 7q was obtained as a 1:4 mixture of the 2,7- and 3,7-phenylsulfonyl substituted isomers (overall yield 28%).

Spectral data of the 2,7-disubstituted isomer: ^{1}H NMR (DMSO-d_6) δ 3.92 (t, 1H, H-7), 5.54 (dd, 1H, H-6), 5.84 (d, 1H, H-1), 6.43 (ddd, 1H, H-5), 6.6 (m, 1H, H-4).

Spectral data of the 3,7-disubstituted isomer: ^{1}H NMR (DMSO-d_6) δ 4.1 (t, 1H, H-7), 5.4 (dd, 1H, H-1), 5.79 (dd, 1H, H-6), 6.31 (d, 1H, H-2), 6.60 (dd, 1H, H-5), 7.25 (d, 1H, H-4), 7.35-7.95 (m, aromatic H); ^{13}C NMR (DMSO-d_6) δ 63.2 (C-7, $^1J_{CH}$ = 143 Hz, $^2J_{CH}$ = 3.5 Hz, $^3J_{CH}$ = 10 Hz), 117.7 (C-1), 120.1 (C-6), 127.0 (C-2), 128.1 (C-5), 135.0 (C-4), 137.2 (C-3)(the CH resonances were assigned on the basis of a H,C 2D correlation), 153.6 (tetrazole C-5), 125.4, 125.8, 128.6, 129.5, 130.2, 133.6, 134.3 (Ph C-atoms).

Thermolysis of the azidotriazoles 4j,k. Compound 4j was heated in benzene (treated with alumina) at 50°C for 4 h. After removal of the solvent, the residue was chromatographed on silica gel with dichloromethane as the eluent. This furnished 1-phenyl-3-(α-cyano)(p-chloro)benzylidenetriazene (8j) in 60% yield, mp 137°C (ether); IR (KBr) 2210 (vw, CN), 1590 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.4-7.6 and 7.8-8.1 (two m, 7 aromatic H), 8.20 (d, 2 aromatic H); ^{13}C NMR ($CDCl_3$) δ 110.2 (C≡N), 149.3 (C=N), 129.5, 129.8, 130.1, 130.2, 133.2, 141.2, 148.6 (aryl C-atoms).

When 8j was treated with dry methanol at room temperature, gas evolution occurred and N-phenyl-α,α-dimethoxy-(p-chloro)phenylacetamidine (9j) was obtained in 65% yield after crystallization from ether/petroleum ether, mp 112-115°C; IR (KBr) 3460 and 3300-3250 (m, NH_2), 1630-1590 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.30 (s, 6H, two CH_3), 5.3-5.7 (br, 2H, NH_2), 6.9-7.25 (m, 5 aromatic H), 7.3 and 7.6 (two d, 4 aromatic H). Anal. Calcd for $C_{16}H_{17}ClN_2O_2$ (mol wt 304): C, 63.04; H, 5.62. Found: C, 63.27; H, 5.69.

Note: This compound was also obtained when 4j was refluxed in dry methanol for 2 h.

1-Phenyl-3-(α-cyano)(p-nitro)benzylidenetriazene (8k) was similarly prepared from 4k as red crystals in 63% yield, mp 153°C (ether); IR (KBr) 2220 (w, CN), 1550, 1530, 1340 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.3-7.6 and 7.9-8.1 (two m, 5 aromatic H), 8.50 (s, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 109.8 (C≡N), 150.95 (C=N), 124.4, 124.8, 129.7, 133.8, 135.4, 147.5, 148.4 (aryl C-atoms). Anal. Calcd for $C_{14}H_9N_5O_2$ (mol wt 279): C, 60.21; H, 3.23; N, 25.09. Found: C, 60.05; H, 3.36; N, 24.99.

When 8k (0.3 g) was treated with 10 mL of dry methanol at room temperature, the red colour disappeared while nitrogen evolution occurred. After 30 min, the solvent was evaporated and the residue was crystallized from ether/n-pentane to give N-phenyl-α,α-dimethoxy-(p-nitro)phenylacetamidine (9k) as pale yellow crystals in 53% yield, mp 141°C; IR (KBr) 3480 and 3370 (m, NH_2), 1660 cm^{-1} (s, C=N); ^1H NMR ($CDCl_3$) δ 3.25 (s, 6H, two CH_3), 5.15 (br, 2H, NH_2), 6.7-7.4 (two m, 5 aromatic H), 7.75 and 8.20 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 100.9 (quat. C-atom), 155.3 (C=N). Anal. Calcd for $C_{16}H_{17}N_3O_4$ (mol wt 315): C, 60.94; H, 5.43. Found: C, 61.05; H, 5.33.

Kinetic measurements. Solutions of the azides 4a,c,d,e (ca 1 mmol in 3 mL of solvent) were placed in NMR tubes at 70°C (± 0.1°) for decomposition. At several time intervals, the NMR tubes were cooled to 0°C and analyzed by ^1H NMR spectroscopy. The rates of decomposition were followed by integration of the R-singlets (δ 8-10) in the spectra. By plotting log |azide|(%) vs time, linear plots were obtained up to a high degree of conversion (70-80%), all having a correlation coefficient of better than -0.995. Thus, the effect of the reverse reactions in the case of 4a could be neglected. The first order rate constants were determined from the slopes of the linear plots and the results are given in Tables I and II.

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