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INFLUENCE OF ELECTRON-WITHDRAWING N-1 SUBSTITUENTS ON THE THERMAL BEHAVIOUR OF 5-AZIDO-1,2,3-TRIAZOLES

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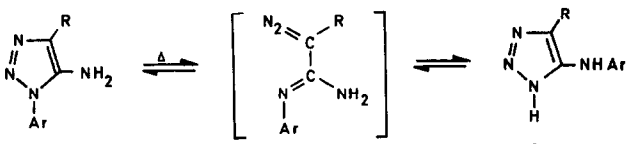
Abstract. 5-Amino-1,2,3-triazoles (7), possessing a strong electron-withdrawing N-1 substituent, cannot be converted into the corresponding azides by the diazotization method, but the diazo transfer on the conjugate bases with tosyl azide proceeds smoothly and was used in this work as a general method to obtain the azides 8. The latter thermolyze by two different pathways, depending on the nature of the R^4-substituent; i.e. rearrangement to diazoester substituted tetrazoles 12 when R^4 = COOR, and decomposition to alkylidenetriazenes 16 when R^4 = Ar. The diazoesters 12 can further thermolyze in benzene to norcaradienes 13, or in nitrile solution to imidazotetrazoles 14 and 15. The kinetics of the rearrangement 8 ⇄ 12 in different solvents at 50°C are discussed.

1,2,3-Triazoles can exist in thermal equilibrium with diazoimines,[1] and this constitutes the basis of the Dimroth rearrangement when an amine function is located at the 5-position (1 ⇄ 2).[2] Recently, we have discovered the thermal isomerization of 4-alkoxycarbonyl-5-azido-1,2,3-triazoles into 5-diazoalkyl substituted tetrazoles (3 ⇄ 4), a reaction which also proceeds by ring-opening of 3 to a diazoimine.[3] Whereas the Dimroth rearrangement is classified as a ring-degenerate rearrangement involving one side-chain atom,[2] the new ring transformation 3 → 4 involves the participation of three side-chain atoms. In contrast to 3, 5-azido-4-phenyltriazole 5 does not rearrange on thermolysis, but decomposes (at 50°C) to the alkylidenetriazene 6.[4,5]



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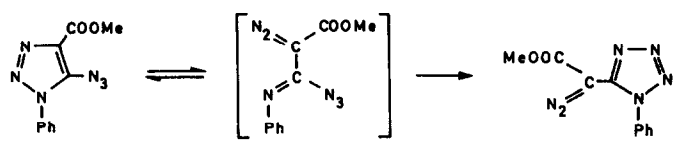

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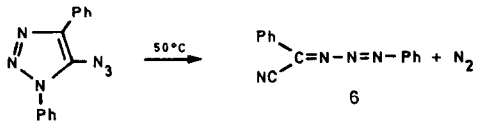


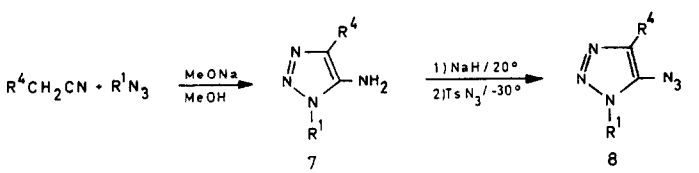
5 6

In a further phase of our research, we have introduced strong electron-withdrawing substituents at the N-1 position of 5-azidotriazoles for two main reasons. Firstly, since these substituents are known to accelerate both the Dimroth rearrangement 1 → 2 and the 1,3-dipolar rearrangement 3 → 4,[2,3] the question arises if they are capable of switching the thermolysis mechanism of 5-azido-4-aryltriazoles (5 → 6) from a decomposition to a rearrangement pathway. Secondly, the introduction of strong electron-withdrawing N-1 substituents would enable us to examine whether an equilibrium is involved at all in the isomerization of 3 to 4. In our previous work,[3] the observation of an equilibrium was prevented by slow decomposition of 4 during the rearrangement at 70-80°C. However, evidence for an equilibrium was found when formyl and phosphoryl substituents were introduced at the 4-position of 5-azidotriazoles.[5] This prompted us to undertake the present investigation in order to determine the kinetic parameters of the rearrangement.

SYNTHESIS OF THE AZIDOTRIAZOLES

The 5-aminotriazoles 7a-e used in this work were prepared by condensation of activated methylene nitriles (methyl cyanoacetate, phenylacetonitrile, p-chlorophenylacetonitrile) with 4-azidopyridine or p-nitrophenyl azide in methanol and in the presence of sodium methoxide (Scheme I).[6,7] Care was taken to avoid the Dimroth rearrangement (1 → 2) during the reaction by working at a lower temperature (0-20°C). Indeed, Brown and co-workers[8] were unable to isolate 7d (ethyl ester instead of methyl ester) from ethyl cyanoacetate and p-nitrophenyl azide, but obtained the rearranged product 2 (R = COOEt, Ar = p-$NO_2C_6H_4$) by gently heating the reagents in ethanol solution.

Scheme I



7 8

7/8	a	b	c	d	e
R^1	4-pyridyl	4-pyridyl	4-pyridyl	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$
R^4	COOMe	C_6H_5	p-ClC_6H_4	COOMe	C_6H_5

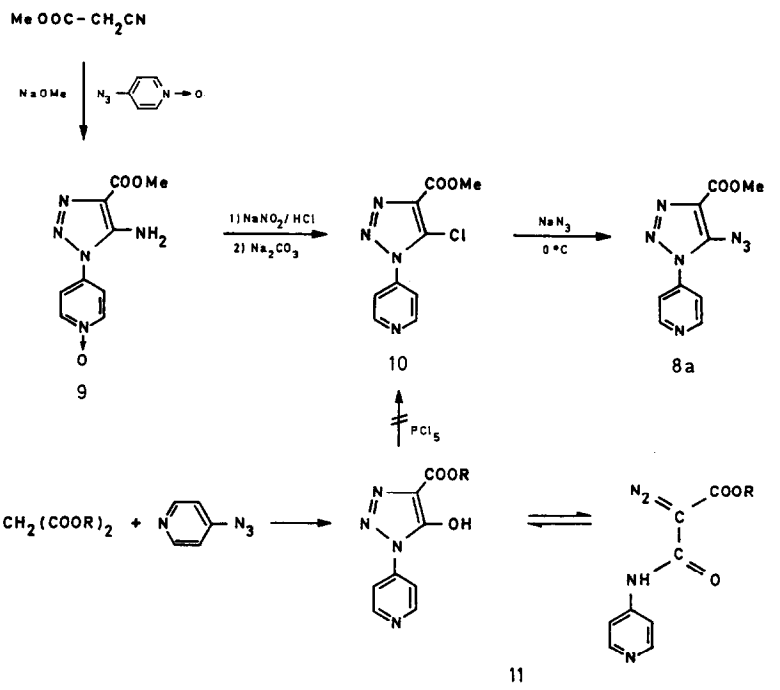
The classical diazotization method failed to prepare 8a from 7a, probably due to the low basicity of the amine function since no reaction was observed. Therefore, we explored other methods and found that the conjugate base of 7a, generated by reaction with sodium hydride, underwent a diazo transfer reaction with tosyl azide at -30°C to give 8a in reasonable yield (35%). The other azidotriazoles 8b-e were similarly prepared.

An alternative method of obtaining 8a is by using 4-azidopyridine-N-oxide which was condensed with methyl cyanoacetate to give the aminotriazole 9. During the diazotization reaction in hydrochloric acid, this compound is converted into the

chloride 10 which is a precursor of the azide 8a. Attempts to prepare 10 (ethyl instead of methyl ester) directly from 11 by reaction with phosphorus pentachloride, both in the presence and the absence of solvent (toluene) failed. Compound 11 (triazole form) is readily available by condensation of 4-azidopyridine with malonic ester, but undergoes ring-opening to the diazo isomer upon crystallization from chloroform/ether.

Since the diazo transfer method (Scheme I) offers the advantage of a simple, time-saving two-step synthesis, the second method (Scheme II) was abandoned.

Scheme II



THERMOLYSIS PRODUCTS

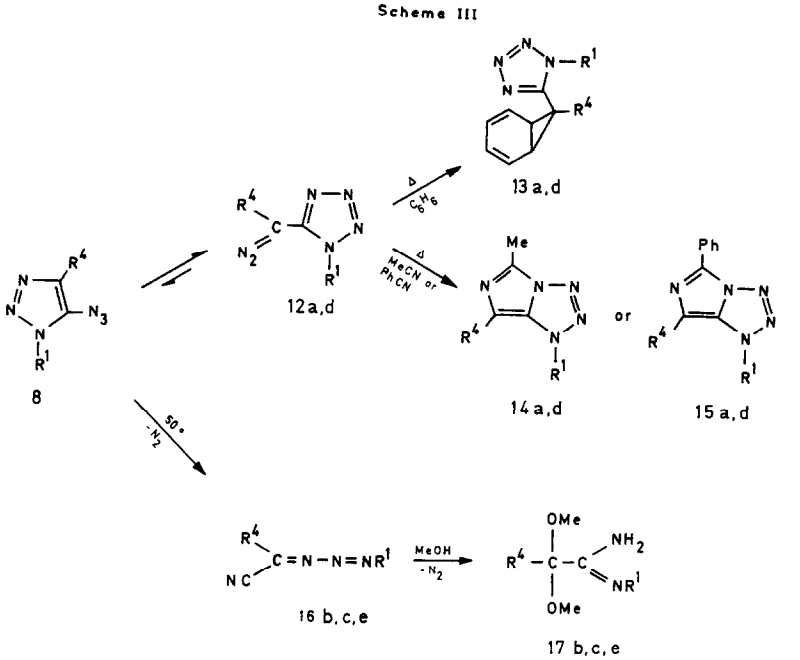
The azidotriazoles 8a,d rearranged smoothly in solution at 50°C to give the diazoester substituted tetrazoles 12a,d as the sole reaction products. These compounds were further thermolyzed in benzene, acetonitrile or benzonitrile to give the norcaradienes 13a,d and the imidazotetrazoles 14a,d and 15a,d respectively. Since the structures of analogous products (with R^1 = Ph) have already been discussed in our previous account,[3] we defer the spectral data to the Experimental Section.

The 4-aryl substituted 5-azidotriazoles 8b,c,e also decomposed at or below 50°C, but yielded the alkylidenetriazenes 16b,c,e which were transformed by methanol in the acetal-amidines 17b,c,e. Hence, we conclude that the introduction of a strong electron-withdrawing substituent at the N-1 position does not alter the thermolysis mechanism of 5-azido-4-aryltriazoles.

KINETICS OF THE REARRANGEMENT

The azides 8a,d were heated at 50°C in the appropriate solvents and the rates of isomerization were measured spectroscopically by following the methyl ester singlets in the ^{1}H NMR spectra. No noticeable decomposition of 12a,d was observed when

Scheme III



	a	b	c	d	e
R^1	4-pyridyl	4-pyridyl	4-pyridyl	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$
R^4	COOMe	C_6H_5	p-ClC_6H_4	COOMe	C_6H_5

the equilibrium positions were reached. From the measured over-all rate constants ($\vec{k} + \overleftarrow{k}$) and the equilibrium constant (K), the rate constants of the forward ($\vec{k}$) and reverse reactions ($\overleftarrow{k}$) were calculated and the results are summarized in Table I.

Table I. Kinetics of the Rearrangement 8 ⇄ 12 at 50°C

Azide	Solvent	$10^5(\vec{k} + \overleftarrow{k})$ (s^{-1})	$[8]_{eq}$ (%)	K ($\vec{k}/\overleftarrow{k}$)	$10^5\,\vec{k}$ (s^{-1})	$10^5\,\overleftarrow{k}$ (s^{-1})
8a	C_6D_6	22.8	13	6.7	19.8	3.0
	$CDCl_3$ [a]	23.0	11	8.1	20.5	2.5
	CD_3CN	11.7	5.5	17.2	11.06	0.64
	CD_3OD	30.3	6.5	14.4	28.3	2.0
	$(CD_3)_2SO$	7.4	4.5	21.2	7.07	0.33
8d	C_6D_6	36.6	10	9.0	32.9	3.7
	$CDCl_3$ [a]	35.8	12.5	7.0	31.3	4.5
	CD_3CN	13.0	6	15.7	12.2	0.8
	CD_3OD	23.0	7	13.3	21.4	1.6
	$(CD_3)_2SO$	8.62	5	19.0	8.19	0.43

a) This solvent was treated with basic alumina

Both the forward ($\vec{k}$) and reverse reactions ($\overleftarrow{k}$) of the two azides 8a and 8d are accelerated by using less polar solvents in the order: $CDCl_3$ and C_6D_6 > CD_3CN > $(CD_3)_2SO$. Methanol, however, proved to be an exception in the case of 8a and its favourable effect on the rearrangement is probably due to hydrogen bonding with the

pyridine nitrogen, thus increasing the electron-withdrawing capacity of the R^1-substituent.

From Table I, we also conclude that the equilibrium is displaced towards the tetrazole 12 in polar solvents, indicating that this is more polar than 8.

EXPERIMENTAL

4-Azidopyridine. A solution of 4-chloropyridine hydrochloride (6 g, 40 mmol) in water (20 ml) was neutralized with a dilute aqueous solution of NaOH to pH 6-7. Then, ethanol (20 ml) and sodium azide (5.2 g, 80 mmol) were added and the solution was refluxed for 8 h. The solution was concentrated and extracted with ether. The extracts were dried over $MgSO_4$ and evaporated to give 4-azidopyridine as a yellow-orange liquid in 75% yield; IR (neat) 2130 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.0 and 8.6 (two d, Py).

Synthesis of the 5-aminotriazoles 7a-e. Equimolar amounts (24 mmol) of active methylene compound and azide were added dropwise to a methanol solution of sodium methoxide (0.6 g Na in 40 ml of dry MeOH). The mixture was allowed to react at 0°C for 1 h and then at room temperature for 1 day. After removal of the solvent, the residue was treated with water and the resulting semicrystalline material was filtered off, washed with water and dried in vacuo. This yielded 7a in 71% (mp 214°C), 7b in 82% (mp 175.5°C, MeOH), 7c in 73% (mp 169.5°C, MeOH), 7d in 89% (mp 224°C) and 7e in 87% (mp 182.5°C, lit.[7] 182°C). They were all fully characterized by IR, ^1H NMR, ^{13}C NMR and MS.

Synthesis of the 5-azidotriazoles 8a-e by the diazo transfer method.[9] To a suspension of sodium hydride (156 mg, 80%) in dry tetrahydrofuran (20 ml) was added in portions 1 equiv. of 5-aminotriazole (5 mmol) at room temperature. When gas evolution had ceased (ca 30 min), the solution was cooled to -30°C and tosyl azide (0.98 g, 5 mmol) in dry tetrahydrofuran (20 ml) was added dropwise. Then, the reaction mixture was allowed to come to room temperature, filtered and the filtrate was evaporated to give the azides 8a-e.

5-Azido-4-methoxycarbonyl-1-(4-pyridyl)-1,2,3-triazole (8a) was purified by column chromatography on silica gel with CCl_4/EtOAc (50:50) as the eluent, yield 35%, mp 84°C (dec.); IR (KBr) 2160 (s), 1710 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 4.05 (s, 3H, OCH_3), 7.8 and 8.9 (two d, 4H, Py β and α-hydrogens); ^{13}C NMR ($CDCl_3$) δ 52.6 (OCH_3), 116.9, 141.4 and 151.4 (β, γ, and α-C-atoms of pyridyl), 129.1 and 140.0 (triazole C-4 and C-5), 160.9 (CO).

5-Azido-4-phenyl-1-(4-pyridyl)-1,2,3-triazole (8b) was crystallized from acetone, yield 38%, mp 101°C (dec.); IR (KBr) 2140 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.4-7.7 (two m, 5H, Ph), 7.8 and 8.8 (two d, 4 H, Py).

5-Azido-4-(4-chlorophenyl)-1-(4-pyridyl)-1,2,3-triazole (8c) was crystallized from acetone, yield 32%, mp 109°C (dec.); IR (KBr) 2140 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.5 and 7.7 (two d, 4H, Ar), 7.8 and 8.8 (two d, 4H, Py).

5-Azido-4-methoxycarbonyl-1-(4-nitrophenyl)-1,2,3-triazole (8d) was purified by column chromatography on silica gel with n-hexane/EtOAc (70:30) as the eluent, yield 39%, mp 102°C (dec.)($CHCl_3$); IR (KBr) 2160 (s), 1730 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 4.07 (s, 3H, OCH_3), 8.0 and 8.5 (two d, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 52.7 (OCH_3), 128.7 and 139.0 (triazole C-4 and C-5), 124.3, 124.8, 138.7 and 147.4 (Ar), 160.8 (CO).

5-Azido-1-(4-nitrophenyl)-4-phenyl-1,2,3-triazole (8e) was crystallized from acetone, yield 32%; IR (KBr) 2140 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.4-7.8 (two m, 5H, Ph), 8.0 and 8.4 (two d, 4H, p-$NO_2C_6H_4$); ^{13}C NMR ($CDCl_3$) δ 123.7, 124.9, 139.8 and 147.5 (p-$NO_2C_6H_4$), 127.8, 128.3, 128.8 and 129.1 (Ph), 130.0 and 138.3 (triazole C-5 and C-4).

Synthesis of 8a by Scheme II. The aminotriazole 9 (mp 192°C) used in this procedure was prepared analogous to 7 from methyl cyanoacetate and 4-azidopyridine-N-oxide[10] (yield 72%).

An aqueous solution of sodium nitrite (1.36 g, 20 mmol) was added to a suspension of 9 (1 g, 4.3 mmol) in 40 ml of dilute hydrochloric acid (20%) at -5°C. The whole was stirred at room temperature for several hours, and then neutralized with sodium carbonate. The precipitate (10) was filtered

off and dried, yield 59%, mp 154°C ($CHCl_3$); IR (KBr) 1750 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 4.05 (s, 3H, OCH_3), 7.7 and 8.9 (two d, 4H, Py); ^{13}C NMR ($CDCl_3$) δ 52.6 (OCH_3), 118.2, 141.2 and 151.6 (Py), 129.9 and 135.7 (triazole C-5 and C-4), 159.6 (CO). Anal. Calcd for $C_9H_7ClN_4O_2$ (mol wt 238): C, 45.37; H, 2.96. Found: C, 45.41; H, 3.05.

An aqueous solution (8 ml) of sodium azide (0.5 g, 7.7 mmol) was added dropwise to an ice-cooled solution of 10 (1.67 g, 7 mmol) in acetone (80 ml). The mixture was allowed to react for several hours at 0°C, and then extracted with chloroform. The extracts were dried over Na_2SO_4 and evaporated to give 8a which was crystallized from ether/petr. ether, yield 20%, mp 83°C (dec.).

Synthesis of 4-ethoxycarbonyl-5-hydroxy-1-(4-pyridyl)-1,2,3-triazole (11). This compound was prepared analogous to 7. After removal of the solvent, the residue was dissolved in water and treated with one equiv. of acetic acid. This furnished a precipitate of 11 in the triazole form, yield 75%. After crystallization from chloroform/ether, the diazo isomer of 11 was obtained in 64% yield, mp 108.5°C; IR (KBr) 2140 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.32 (t, 3H, CH_3), 4.31 (q, 2H, CH_2), 7.4 and 8.5 (two d, 4H, Py), 9.8 (br, NH); ^{13}C NMR ($CDCl_3$) δ 14.3 and 62.4 (Et), 68.9 (CN_2), 113.6, 144.7 and 150.6 (β, γ, and α-C-atoms of pyridyl), 159.3 (CONH), 164.2 (COO). Anal. Calcd for $C_{10}H_{10}N_4O_3$ (mol wt 234): C, 51.28; H, 4.30. Found: C, 51.17; H, 4.14.

Thermolysis of 8a,d. A. In chloroform. A solution of 8a,d (1 g) in 40 ml of chloroform was heated at 50°C for 4 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel with EtOAc/CCl_4 (for 12a) or EtOAc/n-hexane (for 12d) as the eluent.

5-(α-methoxycarbonyl)diazomethyl-1-(4-pyridyl)tetrazole (12a) was obtained in 75% yield, mp 113°C (dec.)(ether/petr. ether); IR (KBr) 2150 (s), 1710 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.62 (s, 3H, OCH_3), 7.5 and 8.8 (two d, 4H, Py); ^{13}C NMR ($CDCl_3$) δ 52.8 (OCH_3), 56.4 (CN_2), 117.4, 141.9 and 151.4 (β, γ and α-C-atoms of pyridyl), 144.5 (tetrazole C-5), 161.2 (CO); mass spectrum, $M^{+\cdot}$ at m/z 245 (13%). Anal. Calcd for $C_9H_7N_7O_2$ (mol wt 245): C, 44.07; H, 2.88. Found: C, 43.94; H, 2.91.

5-(α-methoxycarbonyl)diazomethyl-1-(4-nitrophenyl)tetrazole (12d) was obtained in 72% yield, mp 110°C (dec.)($CHCl_3$); IR (KBr) 2140 (s), 1715 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.62 (s, 3H, OCH_3), 7.8 and 8.4 (two d, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 52.9 (OCH_3), 56.6 (CN_2), 124.7, 124.9, 139.8 and 148.2 (p-$NO_2C_6H_4$), 145.0 (tetrazole C-5), 161.2 (CO); mass spectrum, $M^{+\cdot}$ at m/z 289 (16%). Anal. Calcd for $C_{10}H_7N_7O_4$ (mol wt 289): C, 41.51; H, 2.44. Found: C, 41.60; H, 2.40.

B. In benzene. A solution of 8a,d (1 g) in benzene (10 ml) was heated at 70°C (80 h for 8a and 5 days for 8d). After removal of the solvent, the residue was crystallized from methanol.

7-Methoxycarbonyl-7-[1-(4-pyridyl)tetrazol-5-yl]norcaradiene (13a) was obtained in 54% yield, mp 159°C; IR (KBr) 1730 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.3 (br, 2H, H-1 and H-6), 3.83 (s, 3H, OCH_3), 5.8 (br s, 4 vinyl H), 7.5 and 8.9 (two d, 4H, Py); ^{13}C NMR ($CDCl_3$) δ 14.6 (C-7), 38.4 (C-1 and C-6), 53.8 (OCH_3), 117.0, 141.5 and 151.6 (β, γ and α-C-atoms of pyridyl), 122.8 and 125.6 (vinyl C), 147.9 (tetrazole C-5, $^3J_{C5,H}$ = 1.7 Hz), 172.7 (CO, $^3J_{CO,H}$ = 4.2 Hz); mass spectrum, $M^{+\cdot}$ at m/z 295 (12%). Anal. Calcd for $C_{15}H_{13}N_5O_2$ (mol wt 295): C, 60.99; H, 4.44. Found: C, 61.03; H, 4.48.

7-Methoxycarbonyl-7-[1-(4-nitrophenyl)tetrazol-5-yl]norcaradiene (13d) was obtained in 55% yield, mp 194°C; IR (KBr) 1705 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.3 (br, 2H, H-1 and H-6), 3.79 (s, 3H, OCH_3), 5.7 (br s, 4 vinyl H), 7.7 and 8.5 (two d, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 14.8 (C-7), 38.5 (C-1 and C-6), 53.9 (OCH_3), 122.9 and 125.8 (vinyl C), 124.5, 125.1, 139.3 and 148.1 (Ar), 148.1 (tetrazole C-5), 172.7 (CO, $^3J_{CO,H}$ = 4.5 Hz); mass spectrum, $M^{+\cdot}$ at m/z 339 (12%). Anal. Calcd for $C_{16}H_{13}N_5O_4$ (mol wt 339): C, 56.62; H, 3.86. Found: C, 56.84; H, 3.76.

C. In acetonitrile and benzonitrile. A solution of 8a,d (1 g) in acetonitrile or benzonitrile (20 ml) was heated at 70°C for 5 days. After removal of the solvent, the residue was crystallized from the appropriate solvent.

7-Methoxycarbonyl-5-methyl-1-(4-pyridyl)imidazo[1,5-d]tetrazole (14a) was crystallized from acetone in 65% yield, mp 180°C; IR (KBr) 1695 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.76 (s, 3H, ring CH_3), 3.91 (s, 3H, OCH_3), 7.9 and 8.9 (two d, 4H, Py); ^{13}C NMR ($CDCl_3$) δ 12.2 (ring CH_3), 51.9 (OCH_3), 101.6 (C-7), 116.8, 141.0 and 150.9 (β, γ and α-C-atoms of pyridyl), 127.5 (C-5), 133.3 (C-7a), 161.8 (CO); mass spectrum, $M^{+\cdot}$ at m/z 258 (25%). Anal. Calcd for $C_{11}H_{10}N_6O_2$ (mol wt 258): C, 51.15; H, 3.90.

Found: C, 51.26; H, 3.99.

7-Methoxycarbonyl-5-methyl-1-(4-nitrophenyl)imidazo[1,5-d]tetrazole (14d) was crystallized from acetonitrile in 62% yield, mp 214°C; IR (KBr) 1695 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.78 (s, 3H, ring CH_3), 3.88 (s, 3H, OCH_3), 8.0 and 8.5 (two d, 4H, p-$NO_2C_6H_4$); ^{13}C NMR ($CDCl_3$) δ 12.4 (ring CH_3), 52.1 (OMe), 101.3 (C-7), 124.1, 124.6, 138.4 and 147.2 (Ar), 127.6 (C-5), 133.7 (C-7a), 161.8 (CO); mass spectrum, $M^{+\cdot}$ at m/z 302 (26%). Anal. Calcd for $C_{12}H_{10}N_6O_4$ (mol wt 302): C, 47.67; H, 3.34. Found: C, 47.61; H, 3.20.

7-Methoxycarbonyl-5-phenyl-1-(4-pyridyl)imidazo[1,5-d]tetrazole (15a) was crystallized from acetone in 60% yield, mp 208°C; IR (KBr) 1705 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.90 (s, 3H, OCH_3), 7.4-7.6 (m, 3H, Ph), 8.3 (m, 2H, ortho-H Ph), 7.8 and 8.9 (two d, 4H, Py); ^{13}C NMR ($CDCl_3$) δ 51.9 (OCH_3), 102.9 (C-7), 117.5, 140.8 and 150.8 (β, γ and α-C-atoms of pyridyl), 125.9, 126.7, 128.9 and 129.8 (Ph), 130.0 (C-5), 134.5 (C-7a), 161.7 (CO); mass spectrum, $M^{+\cdot}$ at m/z 320 (6%). Anal. Calcd for $C_{16}H_{12}N_6O_2$ (mol wt 320): C, 59.98; H, 3.78. Found: C, 60.15; H, 3.86.

7-Methoxycarbonyl-1-(4-nitrophenyl)-5-phenylimidazo[1,5-d]tetrazole (15d) was crystallized from chloroform in 61% yield, mp 206°C; IR (KBr) 1720 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.89 (s, 3H, OCH_3), 7.4-7.7 (m, 3H, Ph), 8.3-8.4 (m, ortho-H Ph), 8.0 and 8.5 (two d, 4H, p-$NO_2C_6H_4$); ^{13}C NMR ($CDCl_3$) δ 52.0 (OCH_3), 102.8 (C-7), 124.5, 124.9, 138.4 and 147.8 (p-$NO_2C_6H_4$), 126.0, 126.7, 128.9 and 129.9 (Ph), 130.1 (C-5), 135.0 (C-7a), 161.8 (CO); mass spectrum, $M^{+\cdot}$ at m/z 364 (8%). Anal. Calcd for $C_{17}H_{12}N_6O_4$ (mol wt 364): C, 56.03; H, 3.32. Found: C, 56.22; H, 3.23.

Thermolysis of 8b,c,e. A solution of 8b,c,e (ca 5 mmol) in petr. ether (50 ml) was heated at 50° for 2 h. After cooling, the precipitate was filtered off.

3-(α-Cyano)benzylidene-1-(4-pyridyl)triazene (16b) was crystallized from ether/petr. ether in 88% yield, mp 132°C; IR (KBr) 2220 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 7.5-7.8 (two m, 3H, Ph), 8.2-8.3 (m, 2H, ortho-H Ph), 7.7 and 8.85 (two d, 4H, Py); ^{13}C NMR ($CDCl_3$) δ 109.9 (CN), 117.0, 151.5 and 153.6 (β, γ and α-C-atoms of pyridyl), 129.2, 129.4, 129.7 and 135.2 (Ph), 151.5 (C=N). Anal. Calcd for $C_{13}H_9N_5$ (mol wt 235): C, 66.36; H, 3.86. Found: C, 66.18; H, 4.03.

When 16b was dissolved in dry methanol, nitrogen evolution occurred and the red-brown colour disappeared. The solvent was removed and the residue was crystallized from chloroform/petr. ether to give N-(4-pyridyl)-α,α-dimethoxyphenylacetamidine (17b) in 62% yield as a mixture of syn-anti isomers, mp 148°C; IR (KBr) 1660 cm^{-1} (s); ^1H NMR ($CDCl_3$/-40°C) δ 3.23/3.34 (two s, 6H, two OCH_3), 5.07 and 5.78 (two br s, 2H, NH_2), 6.73 (d, 2H, ortho-H, Ph), 7.69 (m, 3H, Ph), 7.45 and 8.35 (two d, 4H, Py). Anal. Calcd for $C_{15}H_{17}N_3O_2$ (mol wt 271): C, 66.39; H, 6.32. Found: C, 66.57; H, 6.23.

3-(α-Cyano)(p-chloro)benzylidene-1-(4-pyridyl)triazene (16c) was crystallized from ether/petr. ether in 71% yield, mp 172°C; IR (KBr) 2230 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 7.6 and 8.2 (two d, 4H, p-Cl-C_6H_4), 7.75 and 8.9 (two d, 4H, Py); ^{13}C NMR ($CDCl_3$) δ 109.9 (CN), 117.1, 151.8 and 153.7 (β, γ and α-C-atoms of pyridyl), 128.3, 130.0, 130.5 and 142.2 (p-ClC_6H_4), 150.4 (C=N). Anal. Calcd for $C_{13}H_8ClN_5$ (mol wt 269): C, 57.98; H, 3.00. Found: C, 58.36; H, 3.18.

When 16c was dissolved in dry methanol, nitrogen evolution occurred and the red-brown colour disappeared. The solvent was removed and the residue was crystallized from chloroform/petr. ether to give N-(4-pyridyl)-α,α-dimethoxy(p-chloro)phenylacetamidine (17c) in 60% yield as a mixture of syn-anti isomers, mp 154.5°C; IR (KBr) 1660 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.22/3.32 (two s, 6H, two OCH_3), 5.1-5.3 (br, 2H, NH_2), 6.7 and 7.4-7.7 (two m, 4 aromatic H), 7.4 and 8.4 (two d, 4H, Py). Anal. Calcd for $C_{15}H_{16}ClN_3O_2$ (mol wt 305): C, 58.99; H, 5.28. Found: C, 58.76; H, 5.22.

3-(α-Cyano)benzylidene-1-(4-nitrophenyl)triazene (16e) was crystallized from chloroform/petr. ether in 75% yield, mp 173°C; IR (KBr) 2230 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 7.58-7.78 and 8.26-8.32 (three m, 5H, Ph), 8.10 and 8.41 (two d, 4H, p-$NO_2C_6H_4$); ^{13}C NMR ($CDCl_3$) δ 110.1 (CN), 125.0, 149.7 and 152.2 (p-$NO_2C_6H_4$), 129.4, 129.5, 129.9 and 135.3 (Ph), 151.8 (C=N). Anal. Calcd for $C_{14}H_9N_5O_2$ (mol wt 279): C, 60.20; H, 3.25. Found: C, 60.08; H, 3.38.

Kinetic measurements. Solutions of the azides 8a (0.23 M) and 8d (0.09-0.18 M) were placed in NMR tubes at 50°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 methyl ester singlets in the spectra until constant values were reached. First order rates

were observed for several half-lives (see Fig. 1). The equilibrium positions were checked by further measurements after several more hours. By plotting log ($[8] - [8]_{eq}$)% vs time, linear plots were obtained, all having a correlation coefficient of at least 0.996. The overall first-order rate constants ($\vec{k} + \overleftarrow{k}$) were determined from the slopes of the linear plots. From ($\vec{k} + \overleftarrow{k}$) and the equilibrium constants ($K = \%[12]/[8]$ at equilibrium) the separate values of $\vec{k}$ and $\overleftarrow{k}$ were calculated. The results are summarized in Table I.

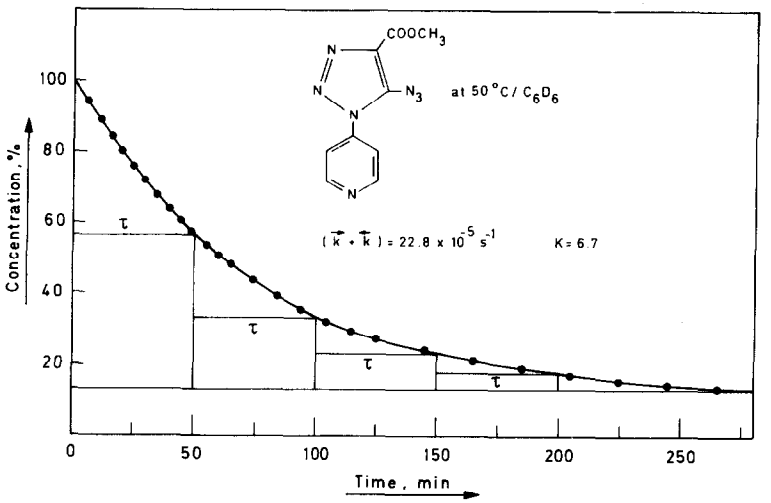


Fig. 1. Thermal decomposition of 8a in C_6D_6 at 50°C

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