

Rearrangement of substituted azido-1,2,3-triazolides to (α -diazoalkyl)-tetrazolides

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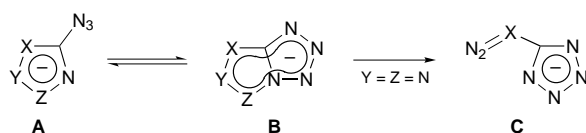
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The scope of the title process has been studied, showing that anions **4'** having R = H, (substituted) Ph and CO₂Me react cleanly (and still satisfactorily in the case R = Me), while with R = COMe, COAr and CN extensive decomposition occurs. The experimental findings (rate constants, activation parameters) have been elucidated through PM3 calculations.

Introduction

Azidoazolide ions (**A**) generated in suitable media are known to equilibrate with their cyclic valence isomers, *viz.* the azapentalenic species **B** (Scheme 1); pertinent examples are pro-



Scheme 1

vided by the azides of pyrazole (X = Y = CH/CR, Z = N), imidazole (X = N, Y = Z = CH) and 1,2,4-triazole† (X = Z = N, Y = CH/CR).¹ The behaviour of the azido-1,2,3-triazolide ion (**A**; Y = Z = N, X = CH), however, was found to be an exception in that the bicycle **B** was not observed, whilst **A** irreversibly disappeared from the reaction mixture.² We have shown that in this case the (diazomethyl)tetrazolide ion (**C**; X = CH) was formed as the final product,³ apparently by a process related to the degenerate rearrangement of azidotetrazolide [(**A**; X = Y = Z = N) → (**C**; X = N)].⁴ Since ligands on the 1,2,3-triazole ring carbon atom are expected to affect the ease of this conversion—a rare type of 1,2,3-triazole ring transformation⁵—we launched a study of its scope.

Starting materials

As candidates we chose the new azides **4b–j**. These compounds, like the previously reported **4a**,² were made routinely by successive diazotisation of the appropriate amines **3** and treatment with sodium azide. Access to **3** was effected as follows. Literature procedures were applied for the synthesis of **3b**,^{5a,b} **3c**,^{7a,b} **3e,f**,^{5a} **3g**⁸ and **3j**,⁹ an attempt to replace the laborious method for **3g**⁸ with a more convenient one, *i.e.* by submitting **3j** to the



- 1** X = NHCOPh **3** X = NH₂
2 X = NHTos **4** X = N₃

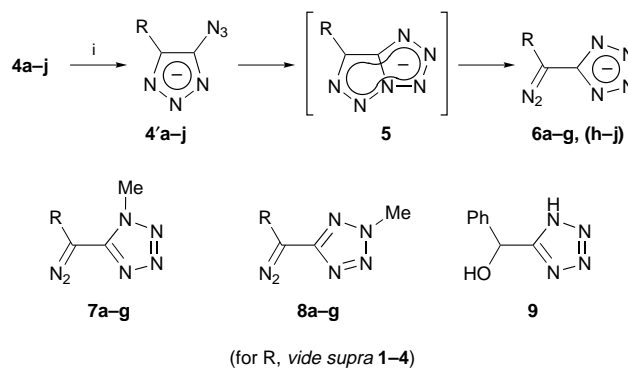
- a** R = H **f** R = C₆H₄CO₂Me-*p*
b R = Me **g** R = CO₂Me
c R = Ph **h** R = Ac
d R = C₆H₄Me-*p* **i** R = COC₆H₄Me-*p*
e R = C₆H₄OMe-*p* **j** R = CN

† 1,2,3- and 1,2,4-triazoles were formerly known as *v*- and *s*-triazole, respectively.

Pinner reaction in methanol, failed because the methyl imidate hydrochloride salt on hydrolysis lost some methyl chloride, thereby producing the respective amide (R = CONH₂) which could not be separated from the target compound **3g**. Regarding the previously unknown derivatives **3d,h,i**, preparation proved effective in the manner detailed below: for **3d**, the two-step entry method to the congeners **3c**^{7a,b} and **3e**^{5a} was adopted; for the ketone **3h**, we hydrolysed the benzamide function in the known triazole **1h**,¹⁰ and for **3i**, the nitrile **2j**¹¹ was reacted with *p*-tolylmagnesium bromide (*cf.* ref. 9) followed by imine hydrolysis and detosylation (employment of **3j** in place of **2j** turned out to be unsatisfactory).

Results

When the azides **4b–j** were dissolved in dimethyl sulfoxide [Me₂SO or (CD₃)₂SO], which contained about 3 equiv. of sodium hydride, and then allowed to stand at room temperature (*cf.* refs. 2, 3), we observed the following (Scheme 2).



Scheme 2 Reagents and conditions: i, NaH (3 equiv.)–Me₂SO or (CD₃)₂SO; rt or 32 °C

(i) In the case of the anions **4'c–f** a smooth reaction proceeded to afford clean solutions of the products **6c–f** (see Table 1; peaks pertaining to impurities were negligible and action of dilute mineral acid on—for example—**6c** gave the expected substituted methanol **9**¹² in fair yield). This finding is comparable to our experience with the parent **4'a**,³ also to the extent that the bicycle **5** remained unobservable throughout. Regarding **4'g→6g**, this transformation worked equally well if one ignores an insignificant ester hydrolysis by traces of moisture.

(ii) From the reaction of **4'b** a solution resulted whose spectra still showed the absorptions of Table 1/columns 3–7 as predominant peaks (their assignment to **6b** was confirmed by means of an authentic sample¹³); but here, owing to the reduced stability of the product, some unidentifiable material was also present. For further characterisation methyl iodide

Table 1 Spectroscopic data for the (α -dialkyl)tetrazolide ions **6a–g,i** and the methylation products **7a–g** and **8a–g**

Comp.	$\nu_{\max}(\text{Me}_2\text{SO})/\text{cm}^{-1}(\text{C}=\text{N}_2)$	6					$\delta_{\text{H}}[90 \text{ MHz}; (\text{CD}_3)_2\text{SO}]^a (\text{N}-\text{Me})$	
		$\delta_{\text{H}}[400 \text{ MHz}; (\text{CD}_3)_2\text{SO}]^a$		$\delta_{\text{C}}[100 \text{ MHz}; (\text{CD}_3)_2\text{SO}]^a$			7	8
		(Me)	(other)	(C=N ₂)	(C-5)	(other)		
a ^c	2076		5.58	38.3	150.5		3.87 [45]	4.28 [55]
b	2035	2.15		45.0	153.7		4.03 [35]	4.32 [65]
c	2047		7.08–7.12 (1H, m), 7.38–7.42 (2H, m), 7.73–7.75 (2H, m)	58.2	151.2	10.0 (q)	3.93 [18]	4.33 [82]
d	2047	2.30	7.22, 7.62 (AA'BB', J 8)	57.9	151.4	123.0 [2C], 124.0, 128.8 [2C] (3d); 128.9	3.86 [19]	4.33 [81]
e	2045	3.75	7.02, 7.67 (AA'BB', J 9)	57.4	151.6	20.5 (q); 123.0 [2C] (d); 125.5; 129.5 [2C] (d); 133.2	3.90 [17]	4.43 [83]
f	2049	3.86	7.92, 8.00 (AA'BB', J 9)	59.9	150.4	55.1 (q); 114.9 [2C] (d); 120.1; 124.5 [2C] (d); 156.6	4.03 [12]	4.43 [88]
g	2076	3.78		58.3	147.8	51.9 (q); 122.5 [2C] (d); 124.6; 129.7 [2C] (d); 135.3; 166.1	4.05 [48]	4.38 [52]
i	2075	2.30	7.09, 7.84 (AA'BB', J 8)			52.2 (q); 165.3		

^a Signals are singlets unless otherwise stated. ^b Square brackets: approximate intensity. ^c NMR data in accordance with ref. 3.

Table 2 Kinetic and thermodynamic data for the rearrangement **4'→6** (including range of proton spectrum utilised for determination)^a

Comp.	$10^5 k_{\text{obs}}/\text{s}^{-1}$ (32 °C)	$10^5 k_{\text{obs}}/\text{s}^{-1}$ (23 °C)	t_1/min (32 °C)	$E_a/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	$\delta_{\text{H}}[400 \text{ MHz}; (\text{CD}_3)_2\text{SO}]^b$	
						4'	6
a	7.70 ^c	2.28	149 ^c	101.5	8.9	6.93 ^d	5.58 ^d
b	9.80	3.30	117	90.8	−24.1	1.96	2.15
c	24.0		48			7.25–7.29	7.38–7.42
d	25.5		45			2.26	2.30
e	24.5	7.75	47	96.0	0.5	3.73	3.75
f	26.1		44			3.85	3.86
g	9.90	2.18	116	122.5	79.9	3.68	3.78
i	(3.30)		(348)			2.36	2.30

^a Reaction monitored over 1 (**i**), 2–3 (**a,b,g**) and 3–4 half-lives (**e–f**), respectively; correlation coefficient −0.994 (**i**), otherwise at least −0.997. ^b Signals are singlets except for **c** where area shown denotes a two-proton multiplet each [full spectra of **4'c–f,i** include the following absorptions: **c**, 7.04–7.08 (1H, m), 7.73–7.75 (2H, m); **d**, 7.09, 7.63 (AA'BB', J 8); **e**, 6.89, 7.69 (AA'BB', J 9); **f**, 7.87 (4H); **i**, 7.28, 8.19 (AA'BB', J 8); for full spectra of **6c–f,i** see Table 1]. ^c Ref. 3: $k_{\text{obs}} = 9.2 \times 10^{-5} \text{ s}^{-1}$ and $t_1 = 126 \text{ min}$. ^d In accordance with ref. 3.

was added to the above solution to give a mixture that showed the tetrazoles **7b** and **8b** as main components (see Table 1; the NMR shift values quoted agreed with those of authentic specimens¹³). A similar methylation reaction was also performed with **6c–g**; in these cases purity of **7/8** was accordingly higher (assignments of peaks in Table 1 were based on the assumption that, as with **8a**^{3,14} and **8b**,¹³ the methyl protons of the *2H*-isomer **8** resonate at lower field).

(iii) In marked contrast to the foregoing, attempts to rearrange the anions **4'h–j** led to extensive decomposition and no clear-cut NMR spectra could be obtained. The reason might be, *inter alia*, partial addition of the dimsyl (methylsulfinyl-methanide) anion to the carbonyl function in **4'h,i** and/or **6h,i** (*cf.* ref. 15) and in the case of **6j** the occurrence of secondary reactions typical of base-exposed α -diazonitriles.¹⁶ Yet, the formation of **6h–j** could be made visible by IR monitoring. Besides the original azide absorptions at 2116 (**4'h**) and 2128 cm^{-1} (**4'j**), respectively, new peaks at 2080 (**6h**) and 2112 cm^{-1} (**6j**) developed, in the latter instance extremely slowly (equal intensity of the peaks at 2128 and 2112 cm^{-1} was reached only after 10 days); to observe **6i**, sodium hydroxide (in place of sodium hydride) had to be employed (shift from 2120 to 2075 cm^{-1}).

These qualitative findings led us to investigate the rearrangements mentioned in (i) and (ii) kinetically. The results collected in Table 2 demonstrate that rate constants k are largely independent from electronic effects exerted by the substituents R: the anions **4'c–f** all rearrange at the same rate and, even more conspicuously, **4'g** despite its strong CO_2Me acceptor reacts as fast as the methyl derivative **4'b**. We believe that this latter process is entropy-controlled (see the value found for ΔS^\ddagger). The same deductions have already been reached for the unusual shift of the azido–tetrazole equilibrium towards

the bicycle in the case of 2-azido-1-pivaloylimidazole.¹⁷ A remarkably rapid ring closure was also observed with CO_2Et -substituted azidopyrazolide ions.¹⁸ With these derivatives (including analogues that have Ph or H in place of CO_2Et) the reaction was studied in protic media (ethanol–sodium ethanolate); under comparable conditions (methanol–sodium methanolate) our anions **4'** however reacted exceedingly slowly: *e.g.* the half-life of the conversion **4'c→6c** amounted to about 3 weeks, whereas a mere 7.2 h sufficed for the pyrazolide congener.¹⁸ In spite of the qualitative shortcomings mentioned in paragraph (iii) we tentatively looked at the process **4'i→6i**. The observed rate constant, however, is only an estimate, because monitoring was limited to one half-life and alien peaks could not be distinguished as arising from decomposition of the reagent or product.

Theoretical investigation

To elucidate the experimental findings we performed PM3 calculations.[‡] First we fully optimised **4'**, **5** and **6** and the transition states **TS₁** and **TS₂**; Table 3 shows the geometrical

[‡] Concerning the choice of a suitable semiempirical method we refer to MNDO calculations of the anions of 5-azidotetrazole (Scheme 1: **A**; X = Y = Z = N) and tetrazolotetrazole (**B**; X = Y = Z = N), which might serve as an adequate reference system.⁴ These calculations show that MNDO heats of formation are systematically too low and have to be corrected. We therefore tried AM1 and PM3, finding the PM3 values, though obviously too positive, in best accordance with the reported corrected MNDO, *ab initio* and experimental results. The reported values for the heats of formation of the above ions **A** and **B** are as follows (energy differences in brackets): MNDO: 275.3 and 223.8 (−51.5); corrected MNDO: 401.7 and 393.3 (−8.4); *ab initio* energy difference: 27.6 kJ mol^{-1} .⁴ We found with AM1: 600.4 and 729.7 (129.3); with PM3: 438.5 and 497.1 (58.6) kJ mol^{-1} .

parameters for the unsubstituted species **a**. The calculated non-linear structure for the azido group of **4'a** and the length of the forming N(1)–N(8) bond in the transition state **TS₁a** are in good agreement with the values reported for 2-azidoimidazole–imidazo[1,2-*d*]tetrazole equilibria.²⁰ The N(1)–N(2) bond of **5a** (1.370 Å), widening up to 2.103 Å in **TS₂a**, becomes notably longer if R is an electron withdrawing substituent: we found 1.388 Å for **5j**, 1.389 Å for **5g** and 1.392 Å for **5i**.

To explore the electronic effects of the substituents R we calculated the atomic charges for **4'** and the corresponding transition state **TS₁**. The results summarised in Table 4 show that N(1) is the ring atom with the largest negative charge and, in agreement with the experimental results obtained with **4'a–g**, is only slightly affected by the nature of the substituent R. Major effects are observable for N(3) and C(5). The electron acceptors R = CN, CO₂Me and COC₆H₄Me-*p* as well as the phenyl moiety diminish the atomic charge at these positions. Passing from **4'** to the transition state **TS₁** we notice a change in electron density at N(7) and N(8) of the azido group with a remarkable decrease of negative charge at N(8)—alterations that facilitate ring closure.

Next we tried to establish the energy profile of the reaction pathway by calculating the heats of formation for representative examples of **4'**, **5** and **6** and the corresponding transition states **TS₁** and **TS₂**. The results summarised in Table 5 show that in all cases the bicyclic anions **5** are less stable than their open-

chain isomers **4'** and **6**, and that, comparing the latter, the anions **6** are less stable than the anions **6** (with just one exception: **4'j**). As expected the cyclisation step **4'→5** requires the highest activation energy. Table 6 shows that the predicted barriers between **4'** and **5**, *i.e.* ΔE_{I} , surpass the barriers between **5** and **6**, *i.e.* ΔE_{II} , by *ca.* 50–70 kJ mol⁻¹, whereas the energy barriers for the reverse reaction **5→4'**, *i.e.* ΔE_{III} , are by *ca.* 29–41 kJ mol⁻¹ lower than ΔE_{I} .

These data suggest that the rearrangement **4'→5→6** should be treated as a consecutive reaction of the type **A→B→C** with k_2 and $k_{-1} \gg k_1$, which follows first order kinetics assuming the steady-state approximation given in eqn. (1).^{21,22}

$$\frac{d[\text{C}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [\text{A}] = k[\text{A}] \quad (1)$$

Accepting this premise, it can be stated that (i) it is reasonable to expect the intermediate **5** to be present in concentrations below the limit of detectability in the NMR experiment and (ii) the experimentally found E_a value is equivalent to the activation energy of the overall reaction **4'→5→6**, which is not solely determined by the reaction barrier of the first step of the reaction (therefore E_a may not be directly compared with the calculated reaction barrier ΔE_{I} which seems very high). The reaction barriers ΔE_{I} turn out to be quite uniform (with the exception of **4'c,e/5c,e**) and are not markedly influenced by the substituent R. The calculated lower reaction barriers between **4'c,e** and **5c,e**, which are in good agreement with the experimentally observed fast reactions of the anions **4'c,e**, might be due to conjugative interaction of the phenyl group and the heterocycle adopting a coplanar orientation in **TS₁** and **5**. For **4'c,e** we found two equally stable minima (483.92/325.34 *vs.* 483.88/325.30 kJ mol⁻¹) with a coplanar and a 14.1° out of plane orientation of the phenyl ring.

The second reaction barrier ΔE_{II} is lowered significantly in the case of the **4'g→6g** isomerisation, which on the other hand exhibits the highest ΔE_{I} barrier. Since within the rearrangement process **4'→6** the conversion rate for **5→6** is determined by the relative heights of the reaction barriers ΔE_{II} and ΔE_{III} , we calculated the ratios $\Delta E_{\text{II}}/\Delta E_{\text{III}}$. The values presented in Table 6 indicate that the step from **5g** to **6g** should be accelerated with respect to the congeners. In this case the activation barrier ΔE_{II} is lowered by conformational changes of the side chain as depicted in Scheme 3, which shows the most likely reaction pathway. The reacting system passes from the initial state **4'g** (which represents the global minimum on the potential energy surface of the azidotriazole conformers) through **TS₁g** to the corresponding bicyclic anion **5g-1**. At this stage rotation of the C–C single bond overcomes a low energy barrier of 0.88 kJ mol⁻¹ and leads to **5g-2**, which is the global minimum and by 4.6 kJ mol⁻¹ more stable than **5g-1**. Transition state **TS₂g-2** connects the rotamer **5g-2** with the diazo derivative **6g-2**. The attempt to find a pathway from **5g-1** over **TS₂g-1** to **6g-1** failed: the latter species are apparently not stationary points on the potential energy surface. The results of Table 6 make plain that the extraordinarily slow conversions **4'i→6i** and **4'j→6j** are not due to high reaction barriers for the ring closing step caused by electronic effects of the strong acceptor substituents R.

Table 3 Optimised geometries for **4'a**, **5a**, **6a** and the transition states **TS₁a**, **TS₂a**

	4'a	TS₁a	5a	TS₂a	6a
<i>r</i> /Å					
N(1)–N(2)	1.312	1.312	1.318	1.370	2.103
N(2)–N(3)	1.315	1.315	1.309	1.309	1.184
N(3)–C(4)	1.386	1.386	1.396	1.378	1.331
C(4)–C(5)	1.395	1.395	1.385	1.404	1.443
C(5)–N(1)	1.397	1.397	1.403	1.404	1.392
C(5)–N(6)	1.427	1.427	1.438	1.391	1.363
N(6)–N(7)	1.249	1.249	1.286	1.309	1.329
N(7)–N(8)	1.137	1.137	1.164	1.302	1.304
N(1)–N(8)			2.106	1.377	1.320
<i>θ</i> /°					
N(1)–N(2)–N(3)	110.9	110.9	110.1	105.3	
N(2)–N(3)–C(4)	109.5	109.5	110.2	113.6	134.0
N(3)–C(4)–C(5)	104.9	104.9	104.7	105.7	106.5
N(1)–C(5)–N(6)	124.2	124.2	114.3	104.2	106.7
C(5)–N(6)–N(7)	120.2	120.2	104.3	107.1	106.4
N(6)–N(7)–N(8)	167.6	167.6	140.8	114.7	110.8
C(4)–C(5)–N(1)	107.2	107.2	107.1	104.6	114.8
C(5)–N(1)–N(2)	107.5	107.5	107.9	110.9	
N(7)–N(8)–N(1)				109.3	109.8
N(8)–N(1)–C(5)				106.9	107.0

Table 4 Atomic charges for selected examples of **4'** and the respective transition state **TS₁**

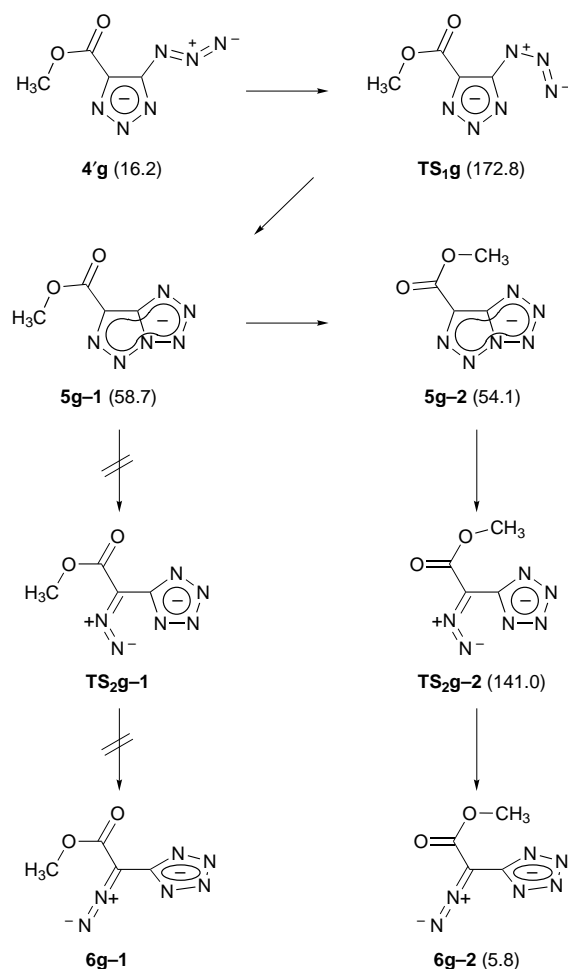
	4'a	TS₁a	4'b	TS₁b	4'c	TS₁c	4'e	TS₁e	4'g	TS₁g	4'i	TS₁i	4'j	TS₁j
N(1)	-0.268	-0.256	-0.273	-0.259	-0.289	-0.279	-0.288	-0.277	-0.278	-0.271	-0.299	-0.297	-0.279	-0.276
N(2)	-0.120	-0.109	-0.116	-0.106	-0.099	-0.088	-0.098	-0.087	-0.095	-0.087	-0.094	-0.080	-0.095	-0.079
N(3)	-0.229	-0.225	-0.216	-0.211	-0.185	-0.179	-0.188	-0.182	-0.172	-0.146	-0.150	-0.148	-0.156	-0.154
C(4)	-0.221	-0.213	-0.206	-0.198	-0.202	-0.192	-0.196	-0.186	-0.296	-0.283	-0.326	-0.313	-0.160	-0.148
C(5)	-0.194	-0.213	-0.179	-0.200	-0.114	-0.141	-0.118	-0.146	-0.083	-0.129	-0.050	-0.073	-0.039	-0.116
N(6)	-0.348	-0.333	-0.346	-0.331	-0.362	-0.343	-0.363	-0.344	-0.355	-0.345	-0.344	-0.325	-0.360	-0.336
N(7)	0.750	0.429	0.750	0.429	0.758	0.443	0.758	0.443	0.757	0.445	0.754	0.441	0.757	0.442
N(8)	-0.448	-0.199	-0.486	-0.198	-0.460	-0.178	-0.460	-0.178	-0.453	-0.169	-0.455	-0.172	-0.464	-0.167

Table 5 Heats of formation (kJ mol^{-1}) for selected examples of **4'**–**6** and the respective transition states **TS₁**, **TS₂**

	$\Delta H_f/\text{kJ mol}^{-1}$				
	4'	TS₁	5	TS₂	6
a	396.1	551.6	427.7	528.2	375.3
b	358.7	515.1	389.6	489.8	344.6
c	484.1	635.5	513.1	610.5	475.7
e	325.4	477.0	354.9	453.8	318.3
g	16.2	172.8	54.1	141.0	5.8
i	299.2	455.3	335.6	436.0	280.1
j	498.2	653.7	539.2	638.9	506.1

Table 6 Calculated activation energies and energy ratios

	$\Delta E_I/\text{kJ mol}^{-1}$	$\Delta E_{II}/\text{kJ mol}^{-1}$	$\Delta E_{III}/\text{kJ mol}^{-1}$	Ratio $\Delta E_{II}/\Delta E_{III}$
a	155.5	100.5	123.9	0.81
b	156.4	100.2	125.5	0.80
c	151.4	97.4	122.4	0.79
e	151.6	98.9	122.1	0.81
g	156.6	86.9	118.7	0.73
i	156.1	100.4	119.7	0.84
j	155.5	99.7	114.5	0.87



Scheme 3 Heats of formation (kJ mol^{-1}) in parentheses

Although the calculated $\Delta E_{III}/\Delta E_{II}$ ratios suggest a lower rate for the second half of the rearrangement process, the exceptional course with **4'i** should mainly be attributed to the above mentioned side reaction which might consume **4'** and/or **5** and thus reduce the overall rate constant. As for **4'j**, it is interesting to note that also in L'abbé's 1,2,3-triazole \rightarrow tetrazole transformation (which differs in type from ours)

azidotriazoles that have a cyano group react extremely sluggishly compared to their ester-functionalised analogues.²³

Experimental

Mps were determined on a Linström apparatus and are uncorrected. IR spectra were taken on Pye-Unicam SP 3200 and Philips PU-9800 instruments. ^1H and ^{13}C NMR spectra, unless otherwise indicated, were recorded at 400 and 100 MHz, respectively (Bruker AM 400 instrument, tetramethylsilane as internal standard; J values in Hz). Starting amines **3b**,^{5a,6} **3c**,^{7a,b} **3e,f**,^{5a} **3g**⁸ and **3j**⁹ and the azide **4a**² were made according to literature procedures.

PM3 calculations were performed on an IBM 100 MHz Pentium PC using version 4.5 of the HyperChem program (Hypercube, Inc., 419 Philip Street, Waterloo N2L 3X2, Canada). The geometries of **4'**, **5** and **6** were fully optimised (Polak-Ribiere optimiser, RMS gradient $\leq 10^{-2}$ kcal Å^{-1} mol^{-1} , convergence limit $\leq 10^{-5}$ kcal mol^{-1}) and are true energy minima as the vibrational analysis yielded no imaginary frequencies. The transition states **TS₁** and **TS₂** were calculated by using the transition state routine of MOPAC 7.0²⁴ (MOPAC keywords: „TS“ „PRECISE“). The MOPAC output files were submitted to HyperChem for vibrational analysis providing only one imaginary frequency. Animation of the respective normal mode confirmed the connection of products and reactants on the reaction coordinate.

4-(*p*-Tolyl)-1*H*-1,2,3-triazol-5-amine **3d**

Potassium *tert*-butoxide^{§7c} (24.7 g, 220 mmol) was dissolved in dry THF (300 cm^3) and added over 2 h to a solution of (*p*-tolyl)acetonitrile (26.2 g, 200 mmol) and benzyl azide (26.6 g, 200 mmol) in the same solvent (300 cm^3). The mixture was stirred overnight at ambient temperature, poured into ice-water (3 l), and 1 h later the precipitate was collected by filtration. Air-drying and recrystallisation from benzene gave 1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazol-5-amine (39.1 g, 74%), mp 152–154 °C (Found: C, 72.71; H, 6.16; N, 21.17. $\text{C}_{16}\text{H}_{16}\text{N}_4$ requires C, 72.70; H, 6.10; N, 21.20%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3320, 3200 and 1645. This material (37.0 g, 140 mmol) was suspended in liquid ammonia (400–500 cm^3) at -70 °C and treated with small pieces of sodium until the blue colour persisted (required: *ca.* 7.0 g, *ca.* 300 mmol). 30 min later ammonium chloride (29.9 g, *ca.* 560 mmol) was added portionwise; the mixture was left stirring for a further 30 min, whereupon the ammonia was allowed to evaporate. The residue was taken up in warm water (**CAUTION**: unreacted sodium) followed by addition of aqueous sodium hydroxide (14 M, 50 cm^3) and, after removal of insoluble material and neutralisation, the clear solution was extracted with ethyl acetate to give the product **3d** (17.1 g, 70%), mp 131–133 °C (from methanol) (Found: C, 62.09; H, 5.82; N, 32.14. $\text{C}_9\text{H}_{10}\text{N}_4$ requires C, 62.05; H, 5.79; N, 32.16%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3405, 3320, 3260 and 1625; $\delta_{\text{H}}[90 \text{ MHz}; (\text{CD}_3)_2\text{SO}]$ 2.33 (3H, s), 4.65–5.1 (2H, br s), 7.20/7.60 (4H, AA'BB', J 8) and 13.45–13.75 (1H, br).

5-Amino-1*H*-1,2,3-triazol-4-yl methyl ketone **3h**

N-(4-Acetyl-1*H*-1,2,3-triazol-5-yl)benzamide **1h**¹⁰ (50.0 g, 217 mmol) was heated with aqueous sodium hydroxide (3 M, 70 cm^3) at 80 °C for 4 h. The cooled solution was acidified to pH 1 with 12 M hydrochloric acid and kept overnight at 0–5 °C. Then the solid was collected, thoroughly dried and, for removal of benzoic acid, extracted with diethyl ether (3 \times 100 cm^3) to afford the crude product **3h** (28.9 g; containing some sodium chloride). Of this material, 5.00 g were dissolved in the minimum amount of cold absolute ethanol followed by filtration and evaporation of the solvent to give, after repetition of the

[§] Employment of sodium methoxide, which was used in ref. 7a for making the benzyl precursor to **3c**, gave lower yields.

Table 7 Yields, physical and analytical data for the azides **4b–j**

Comp. (Formula)	Yield (%)	Mp/°C (decomp.)	$\nu_{\max}(\text{KBr})/$ $\text{cm}^{-1}(\text{N}_3)^a$	Elemental analysis (%)		
				Found (required)	C	H
4b (C ₃ H ₄ N ₆)	83	133–136 ^b	2149, 2114 [2119]	28.92 (29.03)	3.14 (3.25)	67.86 (67.72)
4c (C ₈ H ₆ N ₆)	71	131–133 ^c	2135 [2114]	51.68 (51.61)	3.27 (3.25)	44.97 (45.14)
4d (C ₉ H ₈ N ₆)	68	119–120 ^c	2134 [2112]	53.97 (53.99)	4.10 (4.03)	41.87 (41.98)
4e (C ₉ H ₈ N ₆ O)	84	114–115 ^c	2139 [2113]	49.98 (50.00)	3.75 (3.73)	38.90 (38.87)
4f (C ₁₀ H ₈ N ₆ O ₂)	89	146–147 ^c	2134 [2114]	48.78 (49.18)	3.34 (3.30)	34.52 (34.41)
4g (C ₄ H ₄ N ₆ O ₂)	39	148–150 ^d	2141 [2118]	28.66 (28.58)	2.41 (2.40)	50.05 (49.99)
4h (C ₄ H ₄ N ₆ O)	76	136–137 ^c	2134 [2116]	31.57 (31.58)	2.54 (2.65)	55.28 (55.25)
4i (C ₁₀ H ₈ N ₆ O)	86	156–157 ^c	2143 [2115]	52.60 (52.63)	3.65 (3.53)	36.73 (36.83)
4j (C ₃ HN ₇)	45	129–131 ^e	2153 [2128]	26.67 (26.67)	0.57 (0.75)	72.56 (72.58)

^a Square brackets: anion **4'** (Me₂SO–NaH). ^b From chloroform (**CAUTION**: compound shock-sensitive). ^c From methanol–water. ^d From ethyl acetate–light petroleum. ^e From diethyl ether–light petroleum.

procedure, pure **3h** (3.42 g, 72%), mp 184–185 °C (Found: C, 38.03; H, 4.81; N, 44.47. C₄H₆N₄O requires C, 38.09; H, 4.80; N, 44.42%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3430, 3320, 3130 (br), 1660, 1630 and 1565; $\delta_{\text{H}}[90 \text{ MHz}; (\text{CD}_3)_2\text{SO}]$ 2.45 (3H, s), 6.55 (2H, br s) and 14.0–14.4 (1H, br).

5-Amino-1*H*-1,2,3-triazol-4-yl *p*-tolyl ketone **3i**

A solution of *p*-tolylmagnesium bromide (46.9 g, 240 mmol) in dry diethyl ether (*ca.* 100 cm³) was added dropwise to a vigorously stirred solution of *N*-(4-cyano-1*H*-1,2,3-triazol-5-yl)-toluene-*p*-sulfonamide **2j**¹¹ (7.92 g, 30 mmol) in the same solvent (*ca.* 700 cm³), whereupon the mixture was heated under reflux for 2 h. Work-up by cautious addition of ice, acidification with 75% sulfuric acid and evaporation of the organic solvent gave an aqueous phase which was extracted with ethyl acetate (3 × 100 cm³). Removal of the solvent after drying over sodium sulfate afforded a solid which was dissolved in the minimum amount of ethyl acetate. Careful addition of light petroleum precipitated *N*-[4-(*α*-imino-4-methylbenzyl)-1*H*-1,2,3-triazol-5-yl]toluene-*p*-sulfonamide (9.60 g, 90%), mp 193–196 °C (from methanol–water) (Found: C, 56.72; H, 5.00; N, 19.23. C₁₇H₁₇N₅O₂S requires C, 57.45; H, 4.82; N, 19.71%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3400, 3330, 1640 and 1560. This material was heated with stirring in 6 M hydrochloric acid (350 cm³) under reflux for 1 h; after cooling to 20 °C, the solid was collected by filtration. Recrystallisation from methanol–water gave *N*-[4-(*p*-toluoyl)-1*H*-1,2,3-triazol-5-yl]toluene-*p*-sulfonamide **2i** (8.44 g, 79% relative to **2j**), mp 199 °C (Found: C, 57.49; H, 4.59; N, 15.57. C₁₇H₁₆N₄O₃S requires C, 57.29; H, 4.53; N, 15.72%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3270, 1635, 1610, 1520 and 1160; $\delta_{\text{H}}[400 \text{ MHz}; (\text{CD}_3)_2\text{SO}]$ 2.37 (3H, s), 2.45 (3H, s), 7.36/7.40/7.80/8.01 (8H, 2 AA'BB', *J* 8), 10.4 (1H, br) and 15.2–15.5 (1H, br). The sulfonamide **2i** was portionwise dissolved in conc. sulfuric acid (*ca.* 230 cm³) and, after stirring for 1 h at 15 °C, the mixture was slowly poured onto ice (*ca.* 750 g). After another 30 min of stirring at 0 °C the solid formed was filtered off and recrystallised from methanol to give the product **3i** (3.87 g, 64% relative to **2j**), mp 216–217 °C (Found: C, 59.47; H, 4.94; N, 27.68. C₁₀H₁₀N₄O requires C, 59.40; H, 4.98; N, 27.71%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3440, 3290, 1650, 1610 and 1550; $\delta_{\text{H}}[400 \text{ MHz}; (\text{CD}_3)_2\text{SO}]$ 2.40 (3H, s), 6.7–7.0 (2H, br), 7.35/8.29 (4H, AA'BB', *J* 8) and 14.2–14.5 (1H, br).

4-Substituted 5-azido-1*H*-1,2,3-triazoles **4**. General procedure

(i) **4b,g,h,j**. (**CAUTION**: the azide **4b** proved shock-sensitive;

all experiments with this compound were performed behind a safety screen.) The appropriate amine **3** (10 mmol) was dissolved in 6 M hydrochloric acid (5 cm³) and cooled to <0 °C. Cold aqueous sodium nitrite (1 M, 11 cm³) was added and the mixture was stirred at 0 °C for 30 min. After removal of excess nitrite by adding some urea and cooling to –15 °C, a solution of sodium azide (0.72 g, 11 mmol) in water (minimum amount) was cautiously added and the mixture was stirred at this temperature for a further 30 min. The products **4g,h** and part of **4j** were collected by filtration, while **4b** and a second crop of **4j** were obtained by extraction with diethyl ether. Data are given in Table 7.

(ii) **4c–f,i**. The appropriate amine **3** (5 mmol) was dissolved or suspended in ethanol (25 cm³) and cooled to <0 °C. After addition of 6 M hydrochloric acid (25 cm³) **3** was diazotised with aqueous sodium nitrite (1 M, 5.5 cm³) as above and the mixture was stirred for a further 30 min (1 h in case of **3i**) followed by treatment with a trace of urea. Then sodium azide (0.36 g, 5.5 mmol; for **4i**: 3.6 g, 55 mmol) in water was added at –15 °C and, after stirring for another 30 min (3 h in case of **4i**), the products were filtered off. Data are given in Table 7.

Rearrangement of azido-1,2,3-triazolides **4'** into 5-(*α*-diazoalkyl)tetrazolides **6**. General procedure

Sodium hydride (80% suspension in mineral oil; 0.06–0.07 g, *ca.* 2.1 mmol) was dispersed in (CD₃)₂SO (0.7 cm³) with brief sonication followed by addition of the azide **4** (*ca.* 0.7 mmol). After the mixture was degassed, it was filtered into an NMR tube and kept at room temperature with protection from light; for the derivatives **7** and **8**, freshly distilled methyl iodide (0.05–0.07 cm³) was added when the process **4'**→**6** had reached ≥90% of conversion. For IR spectroscopic monitoring of **4'**→**6**, Me₂SO was employed throughout (in case of **4'i**, sodium hydroxide was used in place of sodium hydride). Data are given in Table 1.

Kinetic measurements. To a suspension of sodium hydride (above material; 0.005 g, *ca.* 0.15 mmol) in (CD₃)₂SO (0.7 cm³) the azide **4** (*ca.* 0.05 mmol) was added and the mixture was kept at 32 ± 1 °C and 23 ± 1 °C, respectively. At several intervals ¹H NMR spectra were taken and the progress of the reaction **4'**→**6** was followed by comparative integration of the signals indicated in Table 2.

Phenyl(1*H*-tetrazol-5-yl)methanol **9**

Sodium hydride (above material; 0.20 g, 7 mmol) was suspended in dry Me₂SO (5 cm³) followed by addition of the azide

4c (0.50 g, 2.7 mmol). The mixture was kept at room temperature for 48 h, then diluted with methanol and water (2 cm³ each) and acidified to pH 1. After stirring at 50 °C for 1 h and pH adjustment to 4 the solvents were evaporated *in vacuo* and the residue extracted with boiling ethyl acetate (2 × 30 cm³; 30 min). Concentration of the extracts left an oil which, after purification by column chromatography on silica gel using ethyl acetate as eluent, slowly crystallised from benzene–ethanol–water. Yield 0.23 g (48%), mp 150–152 °C (lit.,¹² mp 159 °C); material identical with an authentic sample¹² (comparison of IR spectra).

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