A kinetic investigation of the thermal rearrangement of allyloxytetrazoles to *N*-allyltetrazolones

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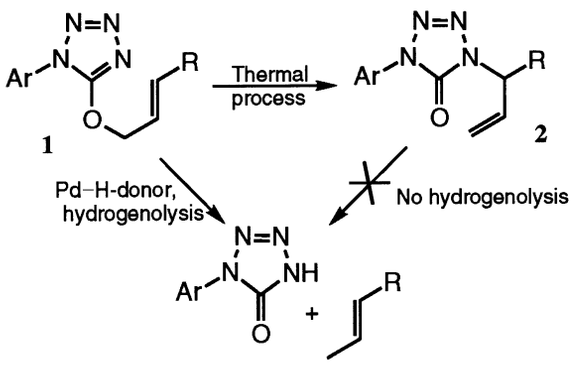
The mechanism of the thermal rearrangement of 1-aryl-5-allyloxytetrazoles 1 to give 1-aryl-4-allyltetrazolones 2 in very high yield has been investigated through kinetic studies in one polar and one less polar solvent. The results suggest mainly a concerted [3,3] sigmatropic process, in which a partially positively charged allyl group migrates from oxygen to nitrogen, similar to the polar transition state found in the Claisen rearrangement.

Introduction

Catalysed phase transfer hydrogenolysis[1] of allyloxytetrazoles **1** by palladium occurs quickly in heterogeneous systems but more slowly in homogeneous ones (Scheme 1).[2] The rapidity of



Scheme 1

this hydrogenolysis proved to be important because of competing migration of the allyl group from *O*-to-*N*, giving *N*-allyltetrazolones **2** (Scheme 1). The rearranged *N*-allyl compounds **2** are stable under the hydrogenolytic conditions that lead to rapid cleavage of their *O*-allyl isomers **1**. Thus, if *O*-to-*N* migration is faster than hydrogenolysis, it leads to reduced yields in the latter reaction. This competition is exacerbated because the allyl migration from *O*-to-*N* is much faster in the presence of palladium than it is without,[2] just as the similar Claisen rearrangement is accelerated by metals.[3] In addition to this metal effect on the migration, the shift of an allyl group from *O*-to-*N* (Scheme 1) is of potential importance for the synthesis of urea-like compounds that are of importance in herbicidal and pharmaceutical research[4] but which would be difficult to prepare by other means. The analogous Claisen rearrangement has found significant use in synthesis for similar reasons.[5] These factors led to the present examination of the mechanism of the rearrangement shown in Scheme 1.

Because the tetrazolyl ring system in compounds **1** can be considered as a classical 6π-aromatic system, the *O*-to-*N* allyl migration appears to be similar to the Claisen rearrangement of *O*-allylphenols[6] or allylic enol ethers.[7] The migration of allyl in a small number of allyloxytetrazoles has been reported[8] and some kinetic measurements were made, but only with neat liquids. Formally similar *O*-to-*N* rearrangements are known for allyloxypyridines,[9] allyloxypyrimidines,[10] *N*-formylamidates,[11] and pseudo-saccharyl ethers.[12] Unlike the thermal Claisen *O*-to-*C* rearrangement, little mechanistic detail is available for the notionally similar *O*-to-*N* migrations.

Table 1 Allyloxytetrazoles **1** and *N*-allyltetrazolones **2** and the ^{1}H NMR signals used to estimate their concentrations

Structure **1** or **2**	Ar	R	δ(**A**)[a]	δ(**B**)
a	C_6H_5	H	7.80	8.0
b	C_6H_5	CH_3	7.75	7.95
c	C_6H_5	C_6H_5	7.75	7.95
d	C_6H_5	4-$NO_2C_6H_4$	7.85	8.05
e	4-$NO_2C_6H_4$	C_6H_5	8.05	8.30
f	4-$NH_2C_6H_4$	C_6H_5	7.25	7.40

[a] *A* refers to the allyoxytetrazoles **1a–f** and **B** to their respective rearrangement products **2a–f** (and see Experimental section).

Results and discussion

Synthesis of allyloxytetrazoles and *N*-allyltetrazolones

For kinetic studies, two series of allyloxytetrazoles **1** were made (Table 1). In the first, 1-phenyl-5-chlorotetrazole was reacted with a number of allylic alcohols under alkaline conditions to give 1-phenyl-5-allyloxytetrazoles **1a–d** (Ar = Ph; R = H, CH_3, Ph, 4-$NO_2C_6H_4$) and, in the second, 1-aryl-5-chlorotetrazoles were reacted with (*E*)-3-phenylprop-2-enol (cinnamyl alcohol) to give allyloxytetrazoles **1e,f** (Ar = 4-$NO_2C_6H_4$, 4-$NH_2C_6H_4$; R = Ph). All reactions were carried out at room temperature to minimise inadvertent rearrangement of the *O*-allyl to *N*-allyl isomers. The corresponding *N*-allyl isomers **2a–f** (Table 1) were prepared by intentional thermal rearrangement of the corresponding allyloxytetrazoles.

Kinetics of rearrangement

The small amount of earlier kinetic work reported on the rearrangement of allyloxytetrazoles was carried out with neat liquids and gave orders of reaction varying from 1 for one ether to between 1.5 and 2 for another.[8] Because this may have been due to a 'self-solvation' effect of the neat liquid, the present kinetic work was carried out in dilute solution in either [1,2-$^2H_2$]-1,1,2,2-tetrachloroethane or [$^2H_6$]dimethyl sulfoxide. These deuteriated solvents were used because of the need for ^{1}H NMR monitoring and for high boiling points so that kinetic experiments could be carried out at temperatures up to 140 °C; the solvents are also readily available. The rearrangement was found to follow a simple first-order rate law [eqn. (1)], in which

$$-\ln[\mathbf{A}]/[\mathbf{A}_0] = -\ln[\mathbf{A}]/[\mathbf{A} + \mathbf{B}] = kt \quad (1)$$

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Table 2 Values for rate constants, Arrhenius energies and the enthalpies, entropies and free energies of activation for the rearrangement of tetrazoles **1a–f** in [$^2H_6$]dimethyl sulfoxide

Tetrazole **1**	T^a/K	Rate constant $k/10^{-5}$ s^{-1}	Correlation[b]	Arrhenius energy (E_a)/ kJ mol^{-1}	Correlation[b]	$\Delta H^{\ddagger c}$/ kJ mol^{-1}	$-\Delta S^{\ddagger d}$/ JK^{-1} mol^{-1}	$k(298)^e$ 10^8
a	373	4.4	0.997	91.3	0.999	88.1	93.3	3.03
	383	10.8	0.996					
	409 [391]	60.8	0.990					
b	355	17.6	0.996	93.5	0.999	90.4	64.4	38.2
	373	75.0	0.996					
	383 [369]	181.7	0.992					
c	335	11.0	0.986	82.0	0.978	79.0	91.8	144.7
	358	36.9	0.995					
	383 [359]	443.3	0.986					
d	348	1.9	0.999	79.3	0.993	76.3	120.4	13.9
	364	4.6	0.996					
	390 [369]	34.9	0.995					
e	312	4.7	0.995	95.2	0.998	92.4	33.8	688.0
	328	23.0	0.996					
	345 [328]	156.0	0.999					
f	353	9.5	0.987	93.3	0.989	90.3	71.1	18.4
	373	35.6	0.986					
	391 [372]	213.8	0.993					

[a] The mean temperature is shown in square brackets. [b] Linear correlation coefficient, *r*. See main text for discussion of errors. [c] Based on the mean temperature and $\Delta H^{\ddagger} = E_a - RT$. [d] Based on the mean temperature. [e] Rate constant estimated for 25 °C.

Table 3 Values for rate constants, Arrhenius energies and the enthalpies, entropies and free energies of activation for the rearrangement of tetrazoles **1a–f** in [1,2-$^2H_2$]-1,1,2,2-tetrachloroethane

Tetrazole **1**	T^a/K	Rate constant $k/10^{-5}$ s^{-1}	Correlation[b]	Arrhenius energy (E_a)/ kJ mol^{-1}	Correlation[b]	$\Delta H^{\ddagger c}$/ kJ mol^{-1}	$-\Delta S^{\ddagger d}$/ JK^{-1} mol^{-1}	$k(298)^e$ 10^8
a	363	0.4	0.997	103.2	0.978	100.1	70.7	3.7
	386	4.9	0.999					
	402 [382]	9.1	0.998					
b	363	13.4	0.999	85.3	0.999	82.1	94.6	290.1
	383	59.9	0.998					
	396 [379]	126.3	0.986					
c	363	23.1	0.990	58.7	0.990	55.5	162.2	3951.4
	382	71.7	0.998					
	399 [381]	124.3	0.997					
d	364	0.8	0.992	93.4	0.986	90.2	100.2	5.7
	386	3.0	0.993					
	406 [385]	21.2	0.999					
e	323	3.6	0.997	85.7	0.999	82.9	73.3	2814.4
	344	28.6	0.998					
	362 [342]	118.3	0.988					
f	364	9.9	0.998	107.1	0.999	103.9	37.9	40.5
	382	53.8	0.995					
	396 [380]	168.2	0.993					

[a] The mean temperature is shown in square brackets. [b] Linear correlation coefficient, *r*. See main text for discussion of errors. [c] Based on the mean temperature and $\Delta H^{\ddagger} = E_a - RT$. [d] Based on the mean temperature. [e] Rate constant estimated for 25 °C.

[A] and **[A** + **B]** represent respectively the concentration of the starting allyloxytetrazole (**A**) at time *t* and the concentration of the sum of the starting material plus rearranged compound (equal to the initial concentration **[A$_0$]** of **A**). Since the yield of **B** is close to 100% of that expected from **A**, ^{1}H NMR spectroscopy was found to be convenient for measuring **[A]** and **[A** + **B]** from the integrals for signals corresponding to specific protons in the spectra of **A** and **B**. The *ortho* protons in the aryl ring attached to the nitrogen in the 1-position of the phenyltetrazole **1** or the phenyltetrazolone **2** were convenient for this purpose.

The signals that were monitored are shown in Table 1. As a check on internal consistency, the dimensionless ratio **[A]**/**[A** + **B]** was also evaluated for other proton signals from each of the *O*- and *N*-allyl isomers. The first-order nature of the reaction kinetics was checked by measuring some rates at very different initial concentrations of starting material **A**.

Each of the tetrazoles **1a–f** was heated at controlled temperatures in either dideuteriotetrachloroethane or hexadeuteriodimethyl sulfoxide as solvent. Rate constants at different temperatures were evaluated for reaction in each solvent by plotting the expression ln**[A]**/**[A** + **B]** against the time elapsed from the start of reaction (Tables 2 and 3). The resulting straight lines gave the rate constants. Correlation coefficients for each determination of rate constant are also given in Tables 2 and 3. Each rate constant was measured in duplicate from 8 to 12 data points, giving a coefficient of variation between duplicate sets of data of ±0.9–1.2%. During each run, the temperature was held constant to within ±0.5 K. The absolute temperature was verified by comparison with a calibrated thermometer. From plots of the logarithm of the rate constant against the inverse of the absolute temperature, the Arrhenius energy (E_a) was determined and hence the enthalpy of activation ($\Delta H^{\ddagger} = E_a - RT$), where T is the mean temperature of the measurements for each compound. The entropy of activation ($\Delta S^{\ddagger}$) was evaluated from the expression, $\Delta S^{\ddagger} = 8.314 \times \ln(A/T) - 206.0$ and $\ln A = E_a/(8.314\ T) + \ln k$, where k is the rate constant for the mean temperature, T.[13] The resulting mean temperature values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, and estimates for k at 298 K are given

in Tables 2 and 3. The likely error in the determination of $\Delta H^{\ddagger}$ was estimated to be *ca.* ±4% and the error in $\Delta S^{\ddagger}$ *ca.* ±10%.

Search for radical formation during rearrangement

The ^{1}H NMR kinetic experiments were carried out with each sample remaining in the instrument throughout the course of reaction in order to obviate temperature fluctuations that would be caused by transferring the sample from a heating bath to the instrument and *vice versa*. This procedure had the added advantage that the NMR spectra could be observed during a whole experiment. There was no evidence for peak broadening or for signal enhancement or suppression that would have been indicative of the presence of radicals in the system (absence of chemically induced nuclear polarization effects). As a double check, EPR measurements were made on some degassed samples, examined both at room temperature and at the higher temperatures of the kinetic experiments, but there was no evidence for any significant formation of radicals since the EPR spectra were almost identical at the two temperatures. These experiments strongly suggest that the *O*-to-*N* migration is not radical in nature.

Stereochemistry of the migration

Examination of the ^{1}H NMR spectra of the *N*-allyl isomers **2a**–**f** demonstrated that in no case was there any evidence for the allyl group having migrated without concomitant complete inversion of the allylic bond, *viz*., the rearrangement was entirely [3, 3] and not [1, 3] sigmatropic.

Interpretation of the observed values for $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and k

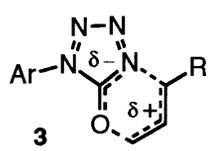
Examination of the results in Tables 2 and 3 reveals that there are significant variations in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ throughout the series in the two solvents. In tetrachloroethane, the enthalpy of activation varies from 58.7 to 103.9 kJ mol^{-1} with the entropy of activation varying from −37.9 to −162.2 J K^{-1} mol^{-1}. In dimethyl sulfoxide, the variation in the enthalpy term is quite small (79.0–92.4 kJ mol^{-1}) but the entropy factor varies from −33.8 to −120.4 J K^{-1} mol^{-1}. An examination of plots showing variations in the rate constants, k, with temperature for compounds **1a**–**f** reveals that the curves cross over a small but different temperature range in each solvent. This suggests there is an isokinetic temperature (or small 'isokinetic' temperature range) for each solvent. With tetrachloroethane, some of the kinetic measurements had been obtained above the isokinetic temperature and some below it. For dimethyl sulfoxide, all rate measurements had been taken above the isokinetic temperature. For each solvent, there is a modest linear correlation of $\Delta H^{\ddagger}$ with $\Delta S^{\ddagger}$ for tetrazoles **1a**–**f**. These plots yield an isokinetic temperature of about 380 K for measurements made in tetrachloroethane and about 240 K for measurements in dimethyl sulfoxide. Such correlations, or lack of them, have been interpreted in four different ways. (*i*) The entropy of activation may be substantially constant throughout the series and changes in rate are caused by changes in the enthalpy of activation. Many reaction series that follow the Hammett relationship fall into this common category.[14] (*ii*) The enthalpy of activation may be substantially constant throughout the series. In this case, changes in rate are due to changes in the entropy of activation, a situation encountered in reactions, in which the rate is highly dependent on solvent.[15] (*iii*) Changes in rate throughout the series may be caused by random changes in enthalpy and entropy of activation. (*iv*) Changes in rate throughout the series may be caused by changes in both enthalpy and entropy of activation and these factors vary in a parallel fashion. In this case, a plot of $\Delta H^{\ddagger}$ *versus* $\Delta S^{\ddagger}$, known as an isokinetic plot, is linear.[16] Items (*i*) and (*ii*) do not apply to the present results but (*iii*) and (*iv*) might. The scope and significance of a linear correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ has been widely discussed but is contentious.[17] For the present work, these isokinetic plots were used simply to extract an isokinetic temperature or range of temperature and the modest correlations of $\Delta H^{\ddagger}$ with $\Delta S^{\ddagger}$ are not interpreted as having any intrinsic significance. To compare results for either solvent within the series of tetrazoles **1a**–**f** rate constants at 220 and 360 K (each *ca.* 20 K below the isokinetic temperatures) and at 298 K were estimated so as to be able to examine the effects of substitution on the rate of allylic *O*-to-*N* migration under comparable conditions. The results are presented in Table 4.

Table 4 Rate constants for rearrangement of allyloxytetrazoles **1a**–**f**, compared at temperatures below the isokinetic temperatures for the two solvents

Tetrazole **1**	$k(220)/10^{-14}$ s^{-1} [a]	$k(360)/10^{-6}$ s^{-1} [b]
a	3.6	4.8
b	82.8	108.5
c	1088.7	232.3
d	116.1	3.71
e	846.5	1082.9
f	31.9	40.5

[a] Rate constants k, extrapolated to 220 K in dimethyl sulfoxide, *ca.* 20 K below the isokinetic temperature. [b] Rate constants k, extrapolated to 360 K in tetrachloroethane, *ca.* 20 K below the isokinetic temperature.

For the two solvents, the measured rate constants at *ca.* 350–400 K show that, at equivalent temperatures, rearrangement in the polar dimethyl sulfoxide is faster than in the much less polar tetrachloroethane (Tables 2 and 3). The ranges of rate constants estimated for 298 K in the two solvents are similar to each other, with larger values sometimes occurring in tetrachloroethane rather than in dimethyl sulfoxide (Tables 2 and 3). However, for each solvent, the effects of substitution on the rate constant for migration are quite marked and qualitatively parallel. The simple allyl compound **1a** may be used as a starting point for comparison. In either solvent, insertion of methyl into the allyl group (compound **1b**) leads to a marked increase in the rate constant for rearrangement (Tables 2 and 3). This result would be expected for a charged transition state of the sort shown in structure **3**, in which the electron-donating methyl



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group stabilizes a positively charged migrating allylic species. For the next tetrazole **1c**, the rate constant increases again and is in keeping with there being a phenyl group attached to the migrating allyl portion, which can delocalise the positive charge. This interpretation is confirmed by the behaviour of the 4-nitrophenyl substituent in the allyl group of compound **1d**, which leads to a large fall in the rate constant for rearrangement. Again, this result is in keeping with the expected effect of an electron-withdrawing substituent on a positively charged migrating species.

The results from the tetrazoles **1e,f** may be compared with that for **1c** (Tables 2 and 3). In all three cases, the migrating group is the same (3-phenylallyl) but there is a variation in the substituent in the 4-position of the aryl group attached to N^1 of the tetrazole ring (Scheme 1). Tetrazole **1e** has an electron-withdrawing nitro group, **1f** has an electron-donating amino group and **1c** has the intermediate (free-energy relation) hydrogen atom. If the allyl group migrates as a positively charged species, it implies that the tetrazole unit should be negative, as would be expected of the known electron-withdrawing nature of a tetrazole ring system.[18] Compared with a hydrogen substituent, the 4-nitro group would be expected to stabilize a developing negative charge and lead to faster reaction. In contrast, the amino group should afford a reduction in the rate of rearrangement because of the resulting destabilization of

negative charge in the tetrazolyl ring by the electron-donating nature of the amino substituent. These are exactly the results observed.

A temperature of 298 K corresponds to a position above the isokinetic temperature (240 K) in dimethyl sulfoxide and below the isokinetic temperature (380 K) in tetrachloroethane (Tables 2, 3 and 4). When both sets of rate constants are examined below their isokinetic temperatures (Table 4), where $\Delta H^{\ddagger}$ is more important than $T\Delta S^{\ddagger}$, the same parallel trends as are seen for $k(298)$ are obvious. Thus, for either solvent at 298 K, or for dimethyl sulfoxide at 240 K, or for tetrachloroethane at 380 K, the effects of substitution on the rate constant run qualitatively parallel to each other and follow the trends outlined above. The effects of entropy change with increasing temperature are more significant in the more polar solvent and support the suggestion of a charged transition state.

Rearrangement in a highly polar medium

Very polar reaction media consisting of mixtures of lithium perchlorate in diethyl ether have been employed to accelerate rearrangements proceeding through polar transition states.[19] The effect of such a solvent system on the Claisen rearrangement has been examined for several allyl vinyl ethers,[20] some of which were known to rearrange only very slowly to their [3,3] isomers in solvents of low polarity, even at very high temperatures.[21] For such cases, the allyl vinyl ethers were stirred in a mixture of 3 M $LiClO_4$ in diethyl ether at room temperature and were found to rearrange quickly but to afford [1,3] migration products and not the expected [3,3] isomers.[21] A cross-over experiment on this rearrangement of allyl vinyl ethers under the above special conditions afforded crossed products, indicating that the observed [1,3] rearrangement passes through a transition state, in which there is complete dissociation into ions during rearrangement.[21] Kinetic studies indicated that the rate for the [1,3] rearrangement was dependent on the concentration of lithium ion.[21] It was decided to examine the effect of a similar mixture of 3 M $LiClO_4$ in diethyl ether on the rearrangement of 5-allyloxy-1-phenyltetrazole **1a** because, like the allyl ethers, this particular compound was slow to rearrange in tetrachloroethane or dimethyl sulfoxide. The products of either a [3,3] or a [1,3] shift would be identical, so there should be no major steric effects in comparing [1,3] and [3,3] migrations. If the above special solvent conditions had a similar effect on (*E*)-1-phenyl-5-(prop-2-enyloxy)tetrazole **1a** as they had on the allyl vinyl ethers, then compound **1a** should be converted readily into 1-phenyl-4-(prop-2-enyl)-tetrazol-5-one **2a** at room temperature. Accordingly, a solution of (*E*)-1-phenyl-5-(prop-2-enyloxy)tetrazole **1a** in diethyl ether containing lithium perchlorate was stirred at room temperature. Even after several days, only starting material could be detected in the reaction medium. This result suggests that, unlike the migration of the notionally similar allyl vinyl ethers, the charged transition state for the allyloxytetrazoles must be one in which the migrating entities are not completely separated into ions.

Conclusions

Determination of rate constants for a small but strategic range of allyloxytetrazoles has shown that their highly specific and high yielding rearrangement to *N*-allyl isomers is first order and passes through an electronically charged transition state, which appears to have no radical character. The migrating allyl group is positively charged, and is completely inverted during reaction, showing that the process is a [3,3] sigmatropic rearrangement; the corresponding negative charge resides in the tetrazole system. Although the overall free energy of activation for the rearrangements does not differ greatly, there are significant variations in the individual values of the enthalpies and entropies of activation. As the temperature of the reaction is increased, entropy effects become much more important. The increasing and variable effect of changes in the entropy of activation from one allyloxytetrazole to another leads to comparative rates of reaction that cross over at moderate temperatures, of *ca*. 240 K in dimethylsulfoxide and 380 K in tetrachloroethane.

Experimental

Compounds were identified by three or more of the following techniques: melting point, mass spectrometry, IR spectroscopy and ^{1}H NMR spectroscopy. For known compounds only selected spectroscopic data and/or melting points are quoted, sufficient to verify identification. Melting points were recorded on a Reichert microscopic melting point apparatus and are uncorrected. Mass spectra were obtained on a VG 7070E mass spectrometer by electron ionization at 70 eV. IR spectra were recorded on a Perkin-Elmer 1720X FTIR spectrometer, liquids as films and solids as KBr disks. NMR spectra were recorded on either a Bruker WM 250 MHz FT or a Bruker AC 200 FT spectrometer, using $SiMe_4$ as internal standard. *J* values are given in Hz. UV–VIS spectra were recorded on a Hewlett Packard diode array FT spectrophotometer. The solvents, diethyl ether and tetrahydrofuran (THF) were freshly dried by refluxing them over sodium–benzophenone, prior to use. Other chemicals were used as purchased.

Preparation of 1-phenyl-5-allyloxytetrazoles 1a–d

In a typical reaction, (*E*)-but-2-en-1-ol (crotyl alcohol; 1.0 g, 13.9 mmol) in dry THF (20 ml) was added to a slurry of sodium hydride (80% in mineral oil; 0.6 g; 14.6 mmol) in dry THF (20 ml). The mixture was stirred at room temp. under an inert atmosphere until effervescence had ceased (30 min). 5-Chloro-1-phenyltetrazole [2.5 g, 13.9 mmol, prepared by the reaction of *N*-phenyl(dichloromethylene)imine with sodium azide[22]] in dry THF (10 ml) was added and the mixture was stirred at room temp. for 2 h, after which ice–water (30 ml) was added and the organic product was extracted with diethyl ether (3 × 30 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated to dryness to give the required product as a light-yellow oil (3 g), which crystallised on cooling; recrystallization from light petroleum (bp 40–60 °C) gave light-yellow crystals of 5-[(*E*)-but-2-enyloxy-1-phenyltetrazole **1b** (1.8 g; 61% yield), mp 36–37 °C (lit.,[8] 32–33 °C). Found: C, 61.1; H, 5.6; N, 26.0. Calc. $C_{11}H_{12}N_4O$: C, 61.1; H, 5.6; N, 25.9%. $\delta_H(CDCl_3)$: 1.75 (3 H, d, *J* 8.7), 5.05 (2 H, d, *J* 7.9), 5.7–5.9 (1 H, m), 7.4–7.6 (3 H, m) 7.75 (2 H,d, *J* 8.3); ν_{max}/cm^{-1} 1597, 1560, 1505, 1448 and 761; M^+, 216. Similarly, the allyloxytetrazoles **1a,c,d** were prepared: 1-phenyl-5-(prop-2-enyloxy)tetrazole **1a**: from prop-2-en-1-ol (allyl alcohol), light yellow oil (85% yield). Found: C, 59.2; H, 5.1; N, 28.2. Calc. $C_{10}H_{10}N_4O$: C, 59.4; H, 5.0; N, 27.7%. $\delta_H(CDCl_3)$: 5.1 (2 H, d, *J* 5.7), 5.3–5.6 (2 H, m), 6.0–6.2 (1 H, m), 7.4–7.6 (3 H, m), 7.8 (2 H, d, *J* 6.9); ν_{max}/cm^{-1} 1592, 1556, 1500, 1456 and 760; M^+, 202. 1-Phenyl-5-[(*E*)-3-phenylprop-2-enyloxy]tetrazole **1c**: from (*E*)-3-phenylprop-2-en-1-ol (cinnamyl alcohol), colourless needles (ethanol, 51% yield), mp 73–74 °C (lit.,[2] 70–71 °C). Found: C, 68.8; H, 5.0; N, 20.4. Calc. $C_{16}H_{14}N_4O$: C, 69.0; H, 5.1; N, 20.2%. $\delta_H(CDCl_3)$: 5.25 (2 H, d, *J* 7.0), 6.60 (1 H, m), 6.85 (1 H, d, *J* 15.6), 7.2–7.8 (10 H, m); ν_{max}/cm^{-1} 1596, 1559, 1505, 1368 and 757; M^+, 278. 5-[(*E*)-3-(4-Nitrophenyl)prop-2-enyloxy]-1-phenyltetrazole **1d**: from (*E*)-3-(4-nitrophenyl)prop-2-en-1-ol (4-nitrocinnamyl alcohol), yellow crystals (ethyl acetate, 22.5% yield), mp 143–145 °C. Found: C, 59.2; H, 4.1; N, 21.8. $C_{16}H_{13}N_5O_3$ requires: C, 59.4; H, 4.1; N, 21.7%. $\delta_H(CDCl_3)$: 5.3 (2 H, d, *J* 7.9), 6.7–6.9 (1 H, m), 7.0 (1 H, d, *J* 16.6), 7.6–8.0 (7 H, m), 8.2 (2 H, d, *J* 10.8); M^+, 323.

Preparation of 1-aryl-5-allyloxytetrazoles 1e,f

5-Chloro-1-(4-nitrophenyl)tetrazole (1 g, 4.4 mmol) in THF (10 ml) was added to a mixture of (*E*)-3-phenylprop-2-en-1-ol

(cinnamyl alcohol; 0.66 g, 4.4 mmol) and sodium hydride (0.2 g, 5 mmol) in THF (30 ml). Work-up as above gave 1-(4-nitrophenyl)-5-[(*E*)-3-phenylprop-2-enyloxy]tetrazole **1e** as yellow crystals (0.9 g; 63.6% yield), mp 131–132 °C (from ethanol). Found: C, 59.6; H, 4.1 N, 21.7. $C_{16}H_{13}N_5O_3$ requires C, 59.5; H, 4.1; N, 21.6%. $\delta_H(CDCl_3)$: 5.35 (2 H, d, *J* 5.7), 6.4–6.6 (1 H, m), 6.95 (1 H, d, *J* 16), 7.3–7.5 (5 H, m), 8.05 (2 H, d, *J* 9.1), 8.45 (2 H, d, *J* 9.1); ν_{max}/cm^{-1} 1731, 1598, 1526, 1502, 1346, 856 and 750; M^+, 323. 5-Chloro-1-(4-aminophenyl)tetrazole (0.7 g, 3.6 mmol) in THF (5 ml) and (*E*)-3-phenylprop-2-en-1-ol (cinnamyl alcohol; 0.56 g, 3.7 mmol) in the presence of NaH (0.2 g, 5 mmol) in THF (20 ml) gave the required 1-(4-aminophenyl)-5-[(*E*)-3-phenyl-prop-2-enyloxy]tetrazole **1f** as a yellow solid (0.87 g; 83% yield), mp 30–32 °C. Found: C, 65.3; H, 5.2; N, 23.9. $C_{16}H_{15}N_5O$ requires C, 65.5; H, 5.2; N, 23.9%. $\delta_H(CDCl_3)$: 5.15 (2 H, d, *J* 5.7), 6.4–6.6 (1 H, m), 6.7–6.9 (3 H, m), 7.1–7.3 (7 H, m); ν_{max}/cm^{-1} 3027, 2361, 1722, 1612, 1520, 1494 and 735; M^+, 293 (accurate mass for $C_{16}H_{15}N_5O$ = 293.1270, error = −2.2 ppm).

Preparation of intermediate compounds

(*E*)-3-(4-Nitrophenyl)prop-2-enol. Ethyl (*E*)-3-(4-nitrophenyl)propenoate (ethyl cinnamate) was prepared from 4-nitrocinnamic acid and ethanol in the presence of conc. H_2SO_4 by standard methods.[23] Ethyl-(*E*)-3-(4-nitrophenyl)prop-2-enoate (1.0 g, 4.2 mmol) dissolved in dry diethyl ether (10 ml) was added dropwise, over a period of 30 min to a slurry of lithium tetrahydroaluminate (0.11 g, 2.5 mmol) in dry diethyl ether (20 ml) at room temp., under an inert atmosphere. The reaction mixture was stirred for another 2 h. Excess of reducing agent was destroyed by careful addiction of ice–water and the resulting precipitate was dissolved by addition of a little conc. HCl. The organic layer was separated, washed twice with water, dried over sodium sulfate and evaporated to dryness to give (*E*)-3-(4-nitrophenyl)prop-2-enol as a yellow solid (0.32 g; 30% yield), mp 122–123 °C. Found: C, 60.4; H, 5.1; N, 7.8. $C_9H_9NO_3$ requires C, 60.3; H, 5.1; N, 7.8%. $\delta_H(CDCl_3)$: 4.40 (2 H, d, *J* 4.6), 6.4–6.6 (1 H, m), 6.75 (1 H, d, *J* 16.6, 7.55 (2 H, d, *J* 10.3), 8.15 (2 H, d, *J* 10.3); ν_{max}/cm^{-1} 3543, 1598, 1504, 1347, 1101 and 737; M^+, 179.

5-Chloro-1-(4-nitrophenyl)tetrazole. 5-Chloro-1-phenyltetrazole (5 g, 28 mmol) was added gradually in small amounts to fuming nitric acid (sg 1.42; 15 ml), with stirring at room temp. The reaction mixture was then heated to 100 °C for 5 min and poured onto a large excess of ice. After allowing the mixture to stand until the ice had melted, the thick yellow precipitate which formed was filtered off, washed with water and air dried at room temp. to give the required 5-chloro-1-(4-nitrophenyl)-tetrazole as yellow plates (4.65 g; 79% yield), mp 95–96 °C (lit.,[24] 98–99 °C). Found: C, 37.4; H, 1.8; N, 31.2. Calc. $C_7H_4N_5O_2Cl$: C, 37.3; H, 1.8; N, 31%. $\delta_H(CDCl_3)$: 7.85 (2 H, d, *J* 9.0), 8.55 (2 H, d, *J* 9.0); ν_{max}/cm^{-1} 1612, 1599, 1520, 1500, 1357, 1252 and 751; M^+, 225, 227 (3:1; chlorine isotopes).

5-Chloro-1-(4-aminophenyl)tetrazole. A solution of 1-(4-nitrophenyl)-5-chlorotetrazole (2.0 g, 8.9 mmol) in ethanol (100 ml) containing hydrochloric acid (9 M; 2 ml) and PtO_2 (0.6 g) was hydrogenated at 100 psi‡ for 2 h. The resulting mixture was filtered through Celite to remove catalyst and the Celite was washed with ethanol; the combined filtrates were evaporated to give a residue, which was dissolved in water (20 ml) and the aqueous solution was brought to pH 9 by addition of aqueous NaOH. The thick precipitate that formed was filtered off, washed with water, dried in air at room temp. and recrystallised from ethyl acetate–light petroleum (bp 60–80 °C) (3:1 v/v) to give 5-chloro-1-(4-aminophenyl)tetrazole (0.8 g; 49% yield) as pale-yellow plates, mp 141–143 °C (lit.,[24] 142–144 °C); $\delta_H(CDCl_3)$: 4.10 (2 H, br s), 6.85 (2 H, d, *J* 8.9), 7.25 (2 H, d, *J* 8.9); ν_{max}/cm^{-1} 3485, 3370, 3300, 1628, 1540, 1512, 1430, 1241 and 832; $(M + H)^+$, FAB, 196/198 (3:1; chlorine isotopes) and $M + NH_4)^+$, 213, 215 (3:1). In an attempt to selectively reduce the nitro group by heterogeneous transfer reduction, it was found that the chloro group was hydrogenolysed off also. Thus, a solution of sodium phosphinate (1.44 g, 16.4 mmol) in water (5 ml) was added to a mixture of palladium-on-charcoal catalyst (10%; 0.08 g) and a solution of 5-chloro-1-(4-nitrophenyl)tetrazole (0.31 g, 1.3 mmol) in toluene (20 ml). The mixture was stirred under the reflux for 2 h. After filtration from catalyst, the toluene layer afforded 1-(4-aminophenyl)tetrazole (0.15 g); $\delta_H(CDCl_3)$: 6.80 (2 H, d, *J* 8.9), 7.50 (2 H, d, *J* 8.9), 8.90 (1 H, s); M^+, 161.

‡ 1 psi = 6.895 Pa.

Preparation of 1-phenyl-4-allyl-5-tetrazolones 2a–f

In a typical reaction, 1-phenyl-5-[(*E*)-3-phenylprop-2-enyloxy]-tetrazole (**1c**; 0.55 g, 2 mmol) in 1,1,2,2-tetrachloroethane (5 ml) was heated at 100 °C for 2 h. The solvent was removed on a rotary evaporator to give 1-phenyl-4-(1-phenylprop-2-enyl)-tetrazol-5-one **2c** as a colourless oil (0.54 g; 98% yield). Found: C, 69.2; H, 5.1; N, 20.2. Calc. $C_{16}H_{14}N_4O$: C, 69.1; H, 5.1; N, 20.1%. $\delta_H(CDCl_3)$: 5.28–5.52 (2 H, m), 6.0 (1 H, d, *J* 5.7), 6.36–6.55 (1 H, m), 7.3–7.5 (7 H, m), 7.95 (2 H, d, *J* 8.6); ν_{max}/cm^{-1} 1729, 1598, 1504, 1382 and 756 cm^{-1}; M^+, 278. Similarly were prepared 1-phenyl-4-(prop-2-enyl)tetrazol-5-one **2a** from 1-phenyl-5-(prop-2-enyloxy)tetrazole **1a**. Found: C, 59.8; H, 5.2; N, 28.1. Calc. $C_{10}H_{10}N_4O$: C, 59.4; H, 5.0; N, 27.7%. $\delta_H(CDCl_3)$: 4.65 (2 H, d, *J* 5.7), 5.3–5.5 (2 H, m), 5.9–6.1 (1 H, m), 7.4–7.6 (3 H, m), 8.0 (2 H, d, *J* 6.86); ν_{max}/cm^{-1} 1729, 1598, 1504, 1388 and 757; M^+, 202. 4-(1-Methylprop-2-enyl)-tetrazol-5-one **2b** from 1-phenyl-5-[(*E*)-but-2-enyloxy]tetrazole **1b**. Found: C, 61.0; H, 5.6; N, 26.1. Calc. $C_{11}H_{12}N_4O$: C, 61.1; H, 5.6; N, 25.9%. $\delta_H(CDCl_3)$: 1.65 (3 H, d, *J* 5.7), 4.9–5.1 (1 H, m), 5.22–5.4 (2 H, m), 6.0–6.2 (1 H, m), 7.3–7.55 (3 H, m) 7.95 (2 H, d, *J* 8.6); ν_{max}/cm^{-1} 1729, 1599, 1504, 1382 and 757; M^+, 216. 4-[1-(4-Nitrophenyprop-2-enyl)-1-phenyltetrazol-5-one **2d** from 1-phenyl-5-[(*E*)-(4-nitrophenyl)prop-2-enyloxy]-tetrazole **1d** as yellow crystals, mp 137–139 °C (from ethyl acetate). Found: C, 59.6; H, 4.1; N, 21.8. $C_{16}H_{13}N_5O_3$ requires C, 59.4; H, 4.1; N, 21.7%. $\delta_H(CDCl_3)$: 5.30–5.55 (2 H, m), 6.15 (1 H, d, *J* 5.8), 6.32–6.51 (1 H, m), 7.30–7.70 (5 H, m), 8.05 (2 H, d, *J* 10.2), 8.25 (2 H, d, *J* 10.8); ν_{max}/cm^{-1} 1733, 1597, 1522, 1500, 1341 and 856; M^+, 323. 1-(4-Nitrophenyl)-4-(1-phenylprop-2-enyl)tetrazol-5-one **2e** from 1-(4-nitrophenyl)-5-[(*E*)-3-phenylprop-2-enyloxy]tetrazole **1e** as yellow crystals, mp 128–129 °C (from ethanol). Found: C, 60.4; H, 4.3; N, 20.9. Calc. $C_{16}H_{13}N_5O_3$: C, 60.0; H, 4.1; N, 21.6%. $\delta_H(CDCl_3)$: 5.30–5.55 (2 H, m), 6.0 (1 H, d, *J* 5.7), 6.35–6.55 (1 H, m, 7.35–7.55 (5 H, m), 8.30 (2 H, d, *J* 10.8), 8.40 (2 H, d, *J* 10.8); ν_{max}/cm^{-1} 1732, 1597, 1523, 1500, 1341 and 856; M^+, 323. 1-(4-Aminophenyl)-4-(1-phenylprop-2-enyl)tetrazol-5-one **2f** from 1-(4-aminophenyl)-5-[(*E*)-3-phenylprop-2-enyloxy]tetrazole **1f** as yellow crystals, mp 169–170 °C (from methanol). Found: C, 65.3; H, 5.2; N, 23.9. $C_{16}H_{15}N_5O$ requires C, 65.5; H, 5.2; N, 23.9%. $\delta_H(CDCl_3)$: 5.1–5.5 (2 H, m), 5.95 (1 H, d, *J* 6.3), 6.3–6.6 (1 H, m), 6.75 (2 H, d, *J* 9.7), 7.20–7.45 (5 H, m), 7.60 (2 H, d, *J* 9.7); ν_{max}/cm^{-1} 1730 cm^{-1}; M^+, 293. Resonances for the rearranged compounds were unambiguously assigned using 2D correlated spectroscopy (COSY).

Rate measurements on the thermal rearrangement of 1-aryl-5-allyloxytetrazoles

Rearrangement of (*E*)-1-phenyl-5-(prop-2-enyloxy)tetrazole 1a in [$^2H_6$]dimethyl sulfoxide. In a typical experiment, 1-phenyl-5-(prop-2-enyloxy)tetrazole (0.02 g, 0.1 mmol) in [$^2H_6$]dimethyl sulfoxide (1 ml) was placed in an NMR tube, which in turn was placed in the pre-heated probe of a Bruker WN250 ^1H NMR instrument.The temperature was noted at the beginning and end of the kinetic run and at intervals during it, to monitor its constancy. Spectra (δ range, 0–10) were acquired, each over a scan period of 40 s, at various time intervals, depending on the

reaction rate. As the rearrangement progressed, the doublet peak representing the initial allyloxy compound (**A**) decreased and a new doublet corresponding to the *N*-allyl isomer (**B**) appeared (Table 1) and gradually increased. Integrals for these doublets were measured and were used to evaluate the relative concentrations of starting material (**A**) and rearranged product (**B**), from which the dimensionless concentration ratio, [**A**]/[**A** + **B**], could be obtained. A reaction rate constant was calculated as described in the Discussion section. The same experiment was repeated at other temperatures and in [1,2-$^2H_2$]-1,1,2,2-tetrachloroethane as solvent at several temperatures. The above kinetic runs in the two solvents at various temperatures were carried out for each of the allyloxytetrazoles **1a**–**f**. Rate constants are provided in Tables 2 and 3. In all cases of these rearrangements, TLC revealed no evidence for the formation of any other product than the expected *N*-allyl compound, giving further confidence in the use of the NMR integrals as a measure of the relative concentrations of **A** and **B**.

First-order nature of the rearrangement. In a typical experiment, two solutions of 1-phenyl-5-[(*E*)-3-phenylprop-2-enyloxy]tetrazole were prepared, one at 10^{-2} M in [$^2H_6$]dimethyl sulfoxide (sample X) and the other similarly at 10^{-1} M (sample Y). The samples X and Y were heated separately at 100 °C for 5 min and the ratio of [**A**]/[**A** + **B**] was measured from the ^{1}H NMR spectra. The ratios found for samples X, Y respectively were 0.52 and 0.51, identical within the limits of experimental error.

Attempted rearrangement in a highly polar medium. A 0.2 M solution of 1-phenyl-5-(prop-2-enyloxy)tetrazole **1a** in diethyl ether containing $LiClO_4$ (3 M) was stirred at *ca.* 20 °C for several days. The solution was examined periodically by TLC but none of the rearrangement product **2a** was observed. On work-up, only starting material was recovered.

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