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Metal-assisted reactions. Part 25.[1] Heterogeneous and homogeneous catalytic transfer hydrogenolysis of allyloxytetrazoles to yield alkenes or alkanes

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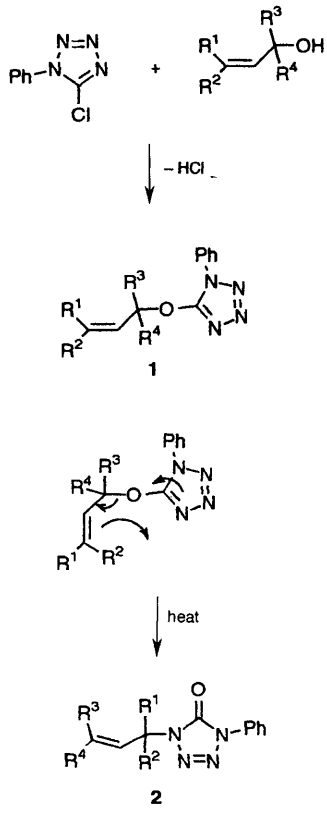
Transfer hydrogenolysis of 5-allyloxy-1-phenyltetrazoles using either a heterogeneous or a homogeneous palladium catalyst and a hydrogen donor leads to cleavage of the allyloxy C–O bond to yield an alkane or an alkene and 1-phenyltetrazolone, depending on the catalyst used.

Introduction

Heterogeneous catalytic transfer reduction has been reviewed[2] and is being used increasingly as an alternative to direct catalytic reduction with hydrogen.[3] One such use has been for the highly specific, fast *ipso* replacement of the hydroxy group of a phenol after first converting it into a 1-phenyltetrazole[4] or *pseudo*-saccharyl derivative.[5] This hydrogenolysis of phenols into arenes appears to be confined to cleavage of aromatic C–O bonds in that alkoxy or benzyloxy derivatives of tetrazoles are very stable under the same reaction conditions. This difference in reactivity provides a means of differential protection of aliphatic as against aromatic hydroxy compounds.[1,4,5] Because this difference is so marked, particularly for the often very reactive benzylic species, it was of interest to examine the behaviour of allylic compounds, which are known to be active in many homogeneous organometallic cross-coupling reactions[6] and in C–O bond cleavages of allylic esters and allylic phenyl ethers.[7] Accordingly, transfer hydrogenolysis of several allyloxytetrazoles was attempted. The reaction was successful under either heterogeneous or homogeneous conditions and was particularly fast in the heterogeneous systems. It was necessary to utilize this speed of cleavage of the allylic C–O bond for some allyloxytetrazoles so as to hydrogenolyse them before there was time for a competing O-to-N migration of the allyl group, analogous to a Claisen reaction, to take place; the resulting rearranged *N*-allylic compounds are not susceptible to hydrogenolysis. Heterogeneous transfer reduction could be conducted so as to give an alkane or an alkene from cleavage of the allyl group, depending on the type of catalyst used. Homogeneous transfer reduction was considerably slower but gave only alkene and no alkane from cleavage of the allyl group.

Results and discussion

5-Allyloxy-1-phenyltetrazoles **1a–h** [reaction (1)] were prepared simply by reaction of the requisite allylic alcohol with 5-chloro-1-phenyltetrazole in the presence of base (Table 1). On heating, these allyloxytetrazoles rearranged with inversion of the allyl group to give *N*-allylic isomers **2a–h** [reaction (2)] in very high yield (Table 2); in a few cases, the rearrangement even proceeded significantly at room temperature. In the hydrogenolyses of allyloxytetrazoles described below, the production of the isomers **2**, which cannot be hydrogenolysed under the same conditions, would lead to decreased yields of cleavage products. Therefore, all reaction mixtures were examined by TLC for evidence of any formation of these Claisen-type rearrangement products **2**. Transfer reduction of the allyloxytetrazoles **1a–h** under heterogeneous conditions was very fast but, in some hydrogenolyses, there were traces of the *N*-allyl isomers although not in sufficient quantity to merit estimation of their yields. The mechanism and rates of formation of isomers **2** from a range of allyloxytetrazoles **1** have been measured[8] and will be reported in another publication.



For the unsubstituted allyloxytetrazole **1a** hydrogenolysis was very fast, most of the starting material having disappeared after five minutes when using palladium-on-charcoal (Pd/C) as catalyst and aqueous formic acid as hydrogen donor. The sole isolated product was 1-phenyltetrazolone **6**; the other product of hydrogenolysis, which could have been propene or propane (both gases), was not recovered [reaction (3)]. Simple hydrolysis of the allylic C–O linkage to 1-phenyltetrazolone could be ruled out because the hydrogenolysis still occurred under non-aqueous conditions. For example, refluxing 5-allyloxy-1-phenyltetrazole **1a** in cyclohexene with Pd/C catalyst again gave only 1-phenyltetrazolone **6**, albeit somewhat more slowly. To determine the other product of hydrogenolysis more

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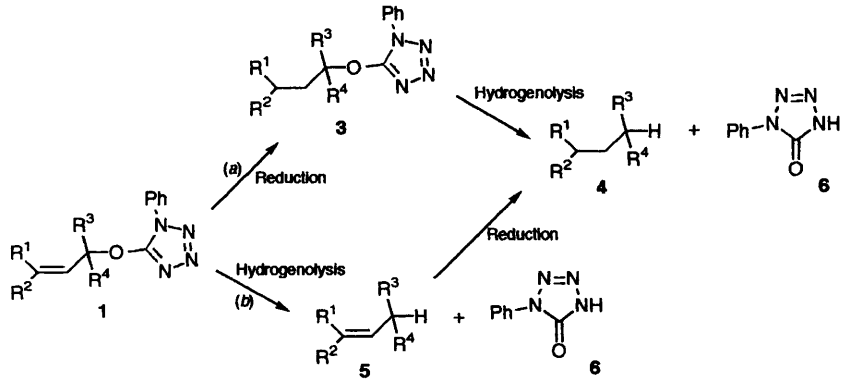
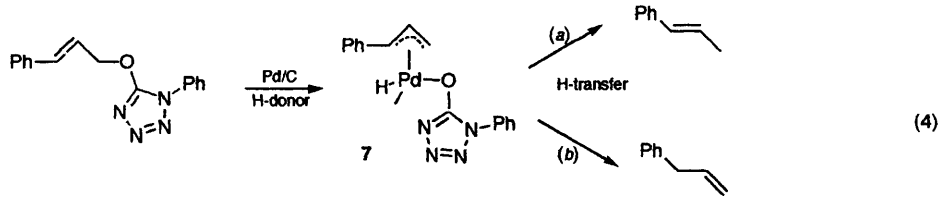
Table 1 5-Allyloxy-1-phenyltetrazoles **1a–h** hydrogenolysed to alkane or alkene

	Compound **1**	Allyl group	R^1	R^2	R^3	R^4
	a	prop-2-enyl	H	H	H	H
	b	3-phenylprop-2-enyl	H	C_6H_5	H	H
	c	3-phenyl[1,1-$^2H_2$]prop-2-enyl	H	C_6H_5	^2H	^2H
	d	but-3-en-2-yl	H	H	H	CH_3
	e	but-2-enyl	H	CH_3	H	H
	f	3,7-dimethylocta-2,6-dienyl	CH_3	C_6H_{11}	H	H
	g	cyclohex-2-enyl		$-CH_2CH_2CH_2-$	H	H
	h	3-(4-nitrophenyl)prop-2-enyl	H	4-$NO_2C_6H_4$	H	H

Table 2 4-Allyl-1-phenyltetrazolones **2a–h** prepared by rearrangement of 5-allyloxy-1-phenyltetrazoles **1a–h**

	Compound **2**	Allyl group	R^1	R^2	R^3	R^4
	a	prop-2-enyl	H	H	H	H
	b	1-phenylprop-2-enyl	H	C_6H_5	H	H
	c	not prepared				
	d	but-2-enyl	H	H	H	CH_3
	e	but-3-en-2-yl	H	CH_3	H	H
	f	3,7-dimethylocta-1,6-dien-3-yl	CH_3	C_6H_{11}	H	H
	g	cyclohex-2-enyl		$-CH_2CH_2CH_2-$	H	H
	h	1-(4-nitrophenyl)prop-2-enyl	H	4-$C_6H_4NO_2$	H	H





conveniently than trying to trap a gas such as propene or propane, 5-cinnamyloxy-1-phenyltetrazole **1b** was prepared and examined.

Treatment of 5-cinnamyloxy-1-phenyltetrazole with formic acid and Pd/C in a two-phase benzene–water solvent system quickly gave the fully reduced 1-phenylpropane **4** ($R^1 = R^3 = R^4 = H$, $R^2 = Ph$) in high yield, together with the expected 1-phenyltetrazolone. This hydrogenolysis can be visualised as taking place either through initial reduction of the 5-cinnamyloxy-1-phenyltetrazole to 5-(3-phenylpropanyloxy)-1-phenyltetrazole **3** [$R^1 = R^3 = R^4 = H$, $R^2 = Ph$; route (*a*) of reaction (3)] followed by hydrogenolysis to 1-phenylpropane or by initial hydrogenolysis to 1-phenylpropene [**5**, $R^1 = R^3 = R^4 = H$, $R^2 = Ph$; route (*b*) of reaction (3)] followed by its reduction to 1-phenylpropane. Previous experience of the lack of reactivity towards hydrogenolysis of alkyloxytetrazoles[4] suggested route (*b*) as the more likely and in keeping with the generally mixed results found on attempted hydrogenolysis of allylic oxygen compounds with a heterogeneous catalyst and hydrogen.[9a] Secondary reduction of initially liberated alkene was confirmed by attempted hydrogenolysis of 5-(3-phenylpropanyloxy)-1-phenyltetrazole **3** ($R^1 = R^3 = R^4 = H$, $R^2 = Ph$), which remained unchanged even after reaction times considerably longer than those used for the cleavage of the cinnamyloxytetrazole **1b**. Reduction of the initially cleaved 1-phenylpropene must also be fast, again in keeping with earlier experience of the rapid reduction of alkenes by transfer methods. The result is also in accord with the need to form a π-allyl complex on the palladium [structure **7**; reaction (4)] before hydrogenolysis can occur.[6,7] Benzylic compounds are frequently more reactive at any carbon attached directly to the aromatic ring than are simple alkyl carbon atoms and benzylic C–O bond hydrogenolysis is easy.[9b] In marked contrast, no C–O bond cleavage was observed on attempted hydrogenolysis of 5-benzyloxy-1-phenyltetrazole. These results show that hydrogenolysis of an allyloxy C–O linkage to a tetrazole must precede reduction of the double bond of the allyl group, probably through a mechanism involving a π-allyl complex on palladium [reaction (4)]. Reduction of the alkene released by hydrogenolysis must occur separately as a second step.

The possibility that the cinnamyloxytetrazole **1b** might first rearrange to its *N*-allyl isomer **2b** before hydrogenolysis was

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also examined because it is known that many Claisen-like rearrangements are accelerated by polar solvents such as those used here and by metals such as palladium.[10] Indeed, some of the allyloxytetrazoles investigated in this work rearranged to their *N*-allyl isomers **2** on standing for a few days at room temperature. However, hydrogenolysis was shown to be highly specific to the allyloxytetrazole C–O bond. On being subjected to the usual conditions for hydrogenolysis, the *N*-allyl isomer **2b** was recovered unchanged, showing that the C–N bond was inert to hydrogenolysis, again indicating a mechanism in which hydrogenolysis involves only the original allyloxytetrazole.

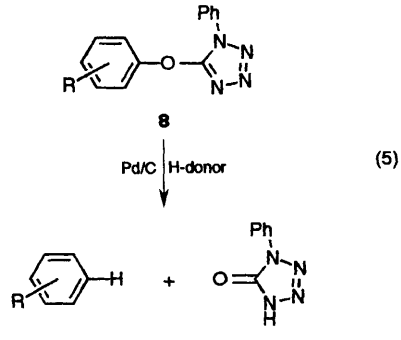
The specificity of addition of hydrogen to the allyl group during hydrogenolysis was revealed by an experiment with a deuterium analogue. The dideuterio compound **1c** was prepared and hydrogenolysed, using non-deuterio formic acid. The resulting 1-phenylpropane was isolated and subjected to ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The 1-phenylpropane was found to retain most of its initial deuterium. From the total amount of deuterium in the molecule (mass spectrum), the ^1H signal peak areas for hydrogen at the three propyl carbon atoms and from observed ^{13}C–^2H coupling only at the terminal carbon, it was clear that the deuterium in the product was confined to the carbon to which it had been originally attached. Whilst a small amount of the original deuterium had been replaced by hydrogen, as might be expected from a mechanism such as that shown in reaction (4), the terminal carbon was still attached to the deuterium it started with. This result shows that, just as with the hydrogenolysis of phenoxytetrazoles, in which deuterium is incorporated specifically into the *ipso* position of the cleaved aromatic C–O bond, hydrogenolysis of 5-cinnamyloxy-1-phenyltetrazole places hydrogen specifically at the carbon atom from which the oxygen of the original C–O bond leaves; there is no scrambling of hydrogens through the rest of 1-phenylpropane during hydrogenolysis. This implies that a π-allyl complex such as **7** in reaction (4) must also remain unrearranged during hydrogenolysis.

Hydrogenolyses of other allyloxytetrazoles **1d–h** are listed in Table 1. In all cases, these compounds were separately thermally isomerized to their *N*-allyl isomers **2d–h** but, on hydrogenolysis of the allyloxy compounds **1d–h**, only products from cleavage of the allyl group were significant; TLC of the crude reaction products before work-up sometimes indicated a very small quantity of *N*-allyl isomer had been formed. Because palladium is known to accelerate this[8] and other types of Claisen rearrangement,[10] the cinnamyloxytetrazole **1b** was refluxed in benzene with Pd/C. The migration of the cinnamyl group from oxygen to nitrogen [reaction (2)] was about three times faster in the presence of palladium than in its absence but the total elapsed time for the isomerization (hours) was still much longer than the time needed for hydrogenolysis (minutes).

That alkanes were isolated after hydrogenolysis rather than the initially formed alkenes is not surprising given the rapidity with which alkenes can be reduced to alkanes under phase-transfer conditions.[11] The intermediate formation of an alkene as the initial product of hydrogenolysis was confirmed in the case of 5-3-(4-nitrophenyl)prop-2-enyloxy]-1-phenyltetrazole **1h**. During the course of hydrogenolysis of this compound, monitoring of reaction samples at intervals by gas chromatography–mass spectrometry revealed the intermediate formation of 1-(4-nitrophenyl)prop-1-ene **5** ($R^1 = R^3 = R^4 = H$, $R^2 = 4\text{-}NO_2C_6H_4$) and its subsequent reduction to 1-(4-nitrophenyl)propane. This case was also notable in that there was no preliminary reduction of the nitro group to amine, again a reaction that is known to occur rather easily under phase-transfer conditions.[1]

It has been demonstrated for catalysed phase-transfer hydrogenation that commercial Pd/C catalysts may be selectively deactivated by reaction with controlled quantities of lead or mercury salts.[11] Such modified catalysts are able to differentiate between reduction of alkynes and alkenes so that it is possible to reduce an alkyne to an alkene without further hydrogenation to the alkane stage. If such modified catalysts were sufficiently active as to effect hydrogenolysis of allyloxytetrazoles **1** to the corresponding alkene and tetrazolone [reaction (3*b*)], then the initially produced alkene should not be hydrogenated to alkane. In fact, treatment of cinnamyloxytetrazole **1b** with a lead-modified Pd/C catalyst afforded a mixture (approximately 8:1) of *trans*-1-phenylpropene (β-methylstyrene) and allylbenzene in a total yield of about 90%, with less than 1% of the alkane, 1-phenylpropane, resulting from hydrogenation of the first formed alkene; there was also about 1% of *cis*-1-phenylpropene. Varying the proportion of lead to palladium from 0.5:1 to 0.7:1 to 1:1 had little effect on the combined yield of *trans*-1-phenylpropene and allylbenzene but did change their proportions from 81:8 to 84:13 to 73:12 respectively. Isomerization of allylbenzenes to styrenes is well known with homogeneous transition metal catalysts.[12] Hydrogenolysis of cinnamyloxytetrazole with lead-modified palladium catalyst (Pd/Pb/C) was about three times slower than when unmodified Pd/C was used, indicating that, not only was the catalyst less active for reducing alkenes, it was also less active in the initial hydrogenolysis step. Although this hydrogenolysis with Pd/Pb/C was still fast enough that thermal isomerization to *N*-allyltetrazole isomers was not a problem, a measure of its reduced activity was revealed when it was found that phenoxytetrazoles **8** [reaction (5)] could not be hydrogenolysed to arenes when using the Pd/Pb/C catalyst whereas Pd/C readily effects this cleavage of an aromatic C–O bond [reaction (5)].[4] Similar hydrogenolysis of allyloxytetrazole **1a** using the Pd/Pb/C catalyst was effected at a slightly slower rate than for the cinnamyloxy compound.

Transfer reduction of allylacetates and allyl phenyl ethers has been effected by use of the homogeneous catalysts based on Pd^{II} salts and it was of interest to determine whether or not the same sort of catalyst could effect hydrogenolysis of allyloxytetrazoles **1**. Reaction (4) indicates a mechanism for this reaction similar to the one that has been advanced for the hydrogenolysis of allylic acetates.[7,13] Thus, formation of a π-allyl palladium complex **7** could be expected to be followed by transfer of hydrogen from palladium[6] or directly from a hydrogen donor[13,14] to one of the β-positions of the allyl group with elimination of allylbenzene (3-phenylpropene), *viz.*, with a shift of the double bond. Treatment of cinnamyloxytetrazole **1b** in dioxane with ammonium formate and $Pd(PPh_3)_2Cl_2$ as catalyst gave a 90% yield of *trans*-1-phenylpropene, together with an additional 5% of allylbenzene. During this reaction, it was observed that some decomposition of the catalyst had occurred as shown by a small quantity of black particulate matter. As this was probably freshly precipitated palladium that could serve as an effective catalyst in its own right, there is the possibility that this slow hydrogenolysis might simply have been due to the presence of metallic palladium and not to $Pd(PPh_3)_2Cl_2$. A second reaction was carried out but with addition of extra triphenylphosphine; this time there was no precipitation of metallic palladium and the reaction proceeded somewhat more



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slowly to give the same products, *trans*-1-phenylpropene and allylbenzene. Surprisingly, the observed ratio of the two alkenes changed from the 90:5 ratio of the first experiment without extra triphenylphosphine to 35:55 with added triphenylphosphine. In accord with earlier reports on allylic oxygen hydrogenolysis with palladium catalysts, the result suggests that allylbenzene is the first product,[7,13] followed by its isomerization into 1-phenylpropene.[12] The reaction conditions using excess of triphenylphosphine to stabilize the $PdCl_2$ were homogeneous and showed that the latter catalyst can be used to hydrogenolyse allyloxytetrazoles, as with the hydrogenolysis of allyl acetates. The hydrogenolysis was also carried out successfully with allyloxytetrazole **1a** in about the same reaction time.

Changes in the ratio of the hydrogenolysis products, *trans*-1-phenylpropene and allylbenzene, with change in reaction conditions suggested that the catalyst might be able to effect bond migration in these alkenes *after* hydrogenolysis had occurred.[12] Accordingly, allylbenzene was heated with $Pd(PPh_3)_2Cl_2$ in dioxane together with ammonium formate. After two hours, double bond migration had produced a maximum yield of 55% of *trans*-1-phenylpropene and 45% of allylbenzene. In the absence of the hydrogen donor (ammonium formate), no migration was observed. When the same experiment was attempted with *trans*-1-phenylpropene as the starting alkene in place of allylbenzene, none of the latter was formed, indicating that the formation of allylbenzene was not favoured, in keeping with reported palladium-induced transformations of safrole and isosafrole.[12] Formation of allylbenzene during hydrogenolysis of 5-cinnamyloxy-1-phenyltetrazole must be due to its initial release from the allyl/catalyst complex **7**; equilibration to give *trans*-1-phenylpropene occurs after release of allylbenzene during hydrogenolysis.

Conclusions

Reaction of 5-allyloxy-1-phenyltetrazoles with the heterogeneous catalyst, Pd/C, and a hydrogen donor leads to rapid hydrogenolysis of the allyloxy C–O bond with formation of a high yield of the alkane derived from the original allyl group. The formation of alkane results from hydrogenation of initially produced alkene and is not due to prior reduction of the starting allyloxytetrazole. By deuterium labelling, the hydrogenolysis was shown to be highly specific to the allyloxy C–O bond. The hydrogenolysis could also be effected through use of a Pd/Pb/C catalyst, which is easily made from commercial Pd/C catalyst. Whilst hydrogenolysis with Pd/Pb/C catalyst is slightly slower than that observed with unmodified Pd/C, use of the modified catalyst has the advantage of not causing reduction of the allyl group either before or after hydrogenolysis, allowing alkenes to be formed in high yield. Thus, allyloxytetrazoles are cleaved by use of heterogeneous catalysts to give either alkanes or alkenes, depending on which catalyst is used. The hydrogenolysis of allyloxytetrazoles to alkenes can be effected also by use of a homogeneous catalyst, $Pd(PPh_3)_2Cl_2$. This reaction is considerably slower than the heterogeneous one but, as with the use of Pd/Pb/C catalyst, only alkenes and not alkanes are formed. A possible competing reaction to hydrogenolysis of the allyloxytetrazoles is their thermal transformation to *N*-allylic isomers, which cannot be hydrogenolysed at the C–N bond. Normally, hydrogenolysis of allyloxytetrazoles is so fast that the thermal rearrangement to the *N*-allyl isomers does not proceed to an extent sufficient to reduce the yields of alkanes or alkenes significantly.

Experimental

All new compounds were characterized by mp or bp, elemental analysis, and mass and ^1H NMR spectrometry. Known compounds were identified by gas chromatographic retention time, mass spectrometry and ^1H NMR spectroscopy and by direct comparison with authentic specimens.

Gas chromatography was carried out on a Dani 3800 instrument fitted with an OV 351 capillary column (25 m × 0.26 mm) and using an internal standard (hexamethylbenzene) for measurement of relative retention times and for quantification of product yields; significant yields based on gas chromatographic peak areas were checked by carrying out the reaction on a larger scale and isolating the product(s) in the normal way. Mass spectra were obtained on an AEI MS12 or a VG 7070 mass spectrometer, using electron ionization at 70 eV or fast atom bombardment ionization by xenon ions with 3-nitrobenzyl alcohol as matrix. NMR spectra were measured in $CDCl_3$ on a Perkin-Elmer R34 (220 MHz) or Bruker (250 MHz) instrument. Infrared spectra were recorded on a Perkin-Elmer or Pye Unicam SP200 spectrometer.

Preparation of allyloxytetrazoles 1a–h

5-(Prop-2-enyloxy)-1-phenyltetrazole 1a. In a typical reaction, potassium *tert*-butoxide (2.0 g, 18 mmol) was added to a stirred solution of allyl alcohol (1.04 g, 18 mmol) in dry THF (25 cm^3). After 5 min when effervescence had ceased, 5-chloro-1-phenyltetrazole (2.0 g, 11 mmol) was added and the reaction mixture was stirred for 1 h at 60 °C and then cooled to room temperature. The resulting mixture was poured into an excess of water and extracted with diethyl ether to give, after work-up, an oil,[15] which slowly crystallized to give the required allyloxytetrazole (1.9 g, 86% yield), mp 29–30 °C (Found: C, 59.1; H, 5.3; N, 27.5. Calc. for $C_{10}H_{10}N_4O$: C, 59.4; H, 5.0; N, 27.7%); *m/z* 202 (M^+); δ_H 5.1 (2 H, d), 5.3–5.6 (2 H, m), 6.0–6.2 (1 H, m), 7.4–7.8 (5 H, m); ν_{max} 1592, 1556, 1500, 1456, 760 cm^{-1}.

5-Cinnamyloxy-1-phenyltetrazole 1b. As for **1a**, except reaction carried out with cinnamyl alcohol at room temperature, to give colourless needles (50%), mp 70–71 °C (from aq. ethanol) (Found: C, 68.6; H, 5.4; N, 20.2. $C_{16}H_{14}N_4O$ requires C, 69.1; H, 5.4; N, 20.1%; *m/z* 278 (M^+); δ_H 5.25 (2 H, d), 6.6 (1 H, m), 6.85 (1 H, d), 7.2–7.8 (10 H, m); ν_{max} 1590, 1567, 1501, 1363, 769 cm^{-1}.

5-(3-Phenyl[1,1-$^2H_2$]prop-2-enyloxy)-1-phenyltetrazole 1c. Prepared from 3-phenyl[1,1-$^2H_2$]prop-2-en-1-ol by a similar reaction to **1b** (61%), mp 79–81 °C (Found: C, 68.4; H/D, 5.2; N, 20.3. $C_{16}H_{12}D_2N_4O$ requires C, 68.6; H/D, 5.8; N, 20.0%); *m/z* 280 (M^+); δ_H 6.44 (1 H, d), 6.82 (1 H, d), 7.15–7.8 (10 H, m); ν_{max} 1558, 1461, 1043, 989, 768 cm^{-1}.

5-(But-3-en-2-yloxy)-1-phenyltetrazole 1d. As for **1a**, except reaction carried out with but-3-en-2-ol at room temperature for 1.5 h, to give a colourless oil[15] that solidified on standing (56%), mp 31–33 °C (Found: C, 61.3; H, 5.6; N, 25.9. Calc. for $C_{11}H_{12}N_4O$: C, 61.1; H, 5.6; N, 25.9%); *m/z* 216 (M^+); δ_H 1.52 (3 H, d), 5.2–5.3 (1 H, d), 5.35–5.4 (1 H, d), 5.5–5.7 (1 H, m), 5.85–6.1 (1 H, m), 7.35–7.6 (3 H, m), 7.8 (2 H, d); ν_{max} 1594, 1551, 1501, 762 cm^{-1}.

5-(But-2-en-1-yloxy)-1-phenyltetrazole 1e. As for **1a**, except reaction carried out with *trans*-but-2-en-1-ol at room temperature for 2 h (61%), mp 35–37 °C (lit.,[15] 32–33 °C, from light petroleum, bp 30–35 °C); *m/z* 216 (M^+); δ_H 1.7–1.8 (3 H, d), 5.0–5.8 (2 H, d), 5.65–5.9 (1 H, d), 5.5–5.7 (1 H, m), 5.9–6.1 (1 H, m), 7.35–7.56 (3 H, m), 7.56–7.8 (2 H, d); ν_{max} 1594, 1560, 1501, 1457, 1445, 761 cm^{-1}.

5-(3,7-Dimethylocta-2,6-dien-1-yloxy)-1-phenyltetrazole 1f. As for **1a**, except reaction carried out with geraniol at room temperature for 18 h, to give a colourless solid (53%), mp 47–49 °C (Found: C, 68.3; H, 7.5; N, 19.0. $C_{17}H_{22}N_4O$ requires C, 68.4; H, 7.5; N, 18.8%); *m/z* 298 (M^+); δ_H 1.59 (3 H, s), 1.66 (3 H, s), 1.8 (3 H, s), 2.1 (4 H, s), 5.0–5.1 (1 H, m), 5.1–5.2 (2 H, m), 5.5–5.65 (1 H, m), 7.4–7.6 (3 H, m), 7.6–7.7 (2 H, d); ν_{max} 1588, 1566, 1500, 1458, 768 cm^{-1}.

5-(Cyclohex-2-en-1-yloxy)-1-phenyltetrazole 1g. As for **1a**, except reaction carried out with cyclohex-2-enol at room temperature for 2 h, to give a colourless oil that solidified on

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standing (41%), mp 54–55 °C (Found: M^+ 242.1171. $C_{13}H_{14}N_4O$ requires *M*, 242.1168); δ_H 1.9–2.25 (4 H, m), 5.55 (1 H, m), 5.9–6.2 (2 H, m), 7.35–7.65 (3 H, m), 7.73 (2 H, d); ν_{max} 1591, 1549, 1504, 1457, 910 cm^{-1}.

5-[(*E*)-3-(4-Nitrophenyl)prop-2-en-1-yloxy]-1-phenyltetrazole 1h. 3-(4-Nitrophenyl)prop-2-en-1-ol (0.5 g, 2.79 mmol) in dry THF (25 cm^3) was reacted with sodium hydride (0.16 g, 3 mmol) until there was no further effervescence. To the resulting mixture was added 5-chloro-1-phenyltetrazole (0.5 g, 2.79 mmol) in dry THF (5 cm^3). After 2 h, the reaction mixture was poured into an excess of water and was worked up as above to give the required tetrazole as yellow needles (0.203 g, 22.5%), mp 143–145 °C (from ethyl acetate) (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%); *m*/*z* 323 (M^+); δ_H 5.3 (2 H, d, *J* 7.9 Hz), 6.7–6.9 (1 H, m), 7.0 (1 H, d, *J* 16.6 Hz), 7.6–8.0 (7 H, m), 8.2 (2 H, d, *J* 10.8 Hz).

Preparation of 3-phenyl[1,1-$^2H_2$]prop-2-en-1-ol

Ethyl cinnamate (6.9 g; 40 mmol) in dry diethyl ether (30 cm^3) was added dropwise over a period of 30 min to a slurry of lithium tetradeuterioaluminate (1.0 g, 24 mmol) in dry diethyl ether (80 cm^3), cooled to −10 °C and under nitrogen. The reaction mixture was stirred for 2 h, with the temperature maintained just below 0 °C. Excess of the lithium tetradeuterioaluminate was destroyed by careful addition of water and then sufficient conc. HCl was added to dissolve the resulting precipitate. The organic layer was separated, washed with water and dried ($MgSO_4$). Evaporation of the solvent gave a colourless oil, which solidified on standing. This solid was distilled (bp 110 °C at 0.5 mmHg) to give the required dideuterio alcohol (5.2 g, 95% yield) as a colourless crystalline solid; *m*/*z* 136 (M^+); δ_H 6.24 (1 H, d, *J* 15.7 Hz), 6.55 (1 H, d, *J* 15.7 Hz), 7.05–7.4 (5 H, m); ν_{max} 3500–3050 (broad), 2160 (C–D), 2064 (C–D), 1490, 1443, 1079, 770 cm^{-1}.

Preparation of ethyl (*E*)-3-(4-nitrophenyl)prop-2-enoate

Cinnamic acid (10 g, 51 mmol) was added in small amounts over a period of 1.5 h to well-stirred conc. HNO_3 (specific gravity 1.48; 50 g, 33.7 cm^3) held at 0 °C. The mixture was then diluted with ice–water (50 cm^3) and the crude (*E*)-3-(4-nitrophenyl)prop-2-enoic acid that formed was filtered off and air-dried (20.9 g yield). This crude acid was added to ethanol (165 cm^3) containing conc. H_2SO_4 (specific gravity 1.84; 0.84 g, 0.46 cm^3) and heated under reflux until all the solid had gone into solution. On cooling the mixture to room temperature, ethyl (*E*)-3-(4-nitrophenyl)prop-2-enoate crystallised out and was filtered off. The residue was recrystallised from ethanol to give the required ester as yellow needles, mp 137–138 °C (lit.,[16] 138 °C) (Found: C, 59.6; H, 5.0; N, 6.3. Calc. for $C_{11}H_{11}NO_4$: C, 59.7; H, 5.0; N, 6.3%); *m*/*z* 221 (M^+); δ_H 1.35 (3 H, t), 4.38 (2 H, q), 6.56 (1 H, d, *J* 18.9 Hz), 7.63 (2 H, d, *J* 10.3 Hz), 7.68 (1 H, d, *J* 18.9 Hz), 8.23 (2 H, d, *J* 10.3 Hz); ν_{max} 1713 (C=O), 1595, 1519, 1346, 1193, 759 cm^{-1}.

Preparation of (*E*)-3-(4-nitrophenyl)prop-2-en-1-ol

Ethyl (*E*)-3-(4-nitrophenyl)prop-2-enoate (1.0 g, 4.5 mmol) was dissolved in dry diethyl ether (10 cm^3) and the solution was added dropwise over a period of 30 min to a slurry of lithium tetrahydroaluminate (0.11 g; 2.5 mmol) in diethyl ether (20 cm^3) at room temperature under argon. The reaction mixture was stirred for a further 2 h, after which the excess of reducing agent was destroyed by careful addition of water; the resulting colourless precipitate was dissolved by addition of a little conc. HCl. The organic layer was separated, washed twice with water and dried (Na_2SO_4) to yield the required alcohol as a yellow solid (0.32 g, 30% yield), mp 122–123 °C (lit.,[17] 127.5–8 °C); *m*/*z* 179 (M^+) (Found: C, 60.4; H, 5.1; N, 7.8. Calc. for $C_9H_9NO_3$: C, 60.3; H, 5.1; N, 7.8%); δ_H 4.4 (2 H, d, *J* 4.6 Hz), 6.4–6.6 (1 H, m), 6.75 (1 H, d, *J* 16.6 Hz), 7.55 (2 H, d, *J* 10.3 Hz), 8.15 (2 H, d, *J* 10.3 Hz); ν_{max} 3543 (br, OH), 1598, 1504, 1347, 1101, 737 cm^{-1}.

Preparation of alkyloxytetrazoles

5-Benzyloxy-1-phenyltetrazole. This was prepared in a similar fashion to the allyloxy compounds described above from benzyl alcohol and 5-chloro-1-phenyltetrazole; the reaction mixture was stirred for 1 h at room temperature to give a 74% yield of the required product as colourless needles, mp 149–151 °C (from ethanol) (Found: C, 66.5; H, 4.8; N, 22.4. $C_{14}H_{12}N_4O$ requires C, 66.6; H, 4.8; N, 22.4%); *m*/*z* 252 (M^+); δ_H 5.16 (2 H, s), 7.2–7.6 (8 H, m), 7.9–7.98 (2 H, d); ν_{max} 1580, 1560, 1499, 1452, 1367, 769 cm^{-1}.

5-(3-Phenyl-1-propoxy)-1-phenyltetrazole 3 ($R^1 = R^3 = R^4 = H$; $R^2 = Ph$). This was prepared as for 5-benzyloxy-1-phenyltetrazole, but using 3-phenylpropanol, except that the reaction time was 2.5 h and the crude product was purified by chromatography on silica gel (toluene as eluent) to give the required product as a viscous oil in 62% yield (Found: C, 68.9; H, 5.8; N, 20.0. $C_{16}H_{16}N_4O$ requires C, 68.9; H, 5.8; N, 19.9%); *m*/*z* 280 (M^+); δ_H 2.2 (2 H, q), 2.78 (2 H, t), 4.75 (2 H, t), 7.0–7.8 (10 H, m); ν_{max} 1591, 1560, 1500, 1454, 760 cm^{-1}.

Preparation of *N*-allyltetrazolones 2a–h

The preparation of these tetrazolones followed those described for the allyloxytetrazoles, except that the reaction mixtures were heated at higher temperatures for longer times so as to thermally rearrange the initially formed allyloxytetrazoles to the required tetrazolones (Method A). Alternatively, the initially prepared allyloxytetrazole was subsequently heated alone or in a solvent for some time to effect rearrangement (Method B). All of the rearrangements from pre-prepared tetrazole proceeded in nearly 100% yield. Some of the tetrazoles rearrange so readily that the change occurs slowly even at room temperature. Typical preparations are given here:

Method A

1-Phenyl-4-(but-2-enyl)tetrazol-5(4*H*)-one 2d. Potassium *tert*-butoxide (2.0 g, 18 mmol) was added with stirring to but-3-en-2-ol (25 cm^3) under nitrogen. When all of the base had dissolved (5 min), 5-chloro-1-phenyltetrazole (2.0 g, 11 mmol) was added and the reaction mixture was stirred for 3 h at 60 °C and then cooled to room temperature. The resulting mixture was poured into an excess of ice-water to give an oil, which was extracted into diethyl ether. The organic layer was washed repeatedly with water to remove excess of *trans*-but-2-en-1-ol and then the solvent was removed *in vacuo* to give a light yellow oil which was chromatographed on silica gel to give the required tetrazolone as an oil[15] in 80% yield (Found: C, 61.3; H, 5.8; N, 25.9. Calc. for $C_{11}H_{12}N_4O$: C, 61.1; H, 5.6; N, 25.9%); *m*/*z* 216 (M^+); δ_H 1.7–1.86 (3 H, d), 4.5–4.6 (2 H, d), 5.5–5.75 (1 H, m), 5.5–6.0 (1 H, m), 7.35–7.6 (3 H, m), 7.9–8.0 (2 H, d); ν_{max} 1725, 1593, 1549, 1498, 758 cm^{-1}.

4-[3-(3,7-Dimethylocta-1,6-dienyl)]-1-phenyltetrazol-5(4*H*)-one 2f. From geraniol (1.5 g), after stirring the reaction mixture for 2 h at 40 °C; colourless, viscous oil (0.93 g, 32%) (Found: C, 68.0; H, 7.3; N, 18.9. $C_{17}H_{22}N_4O$ requires C, 68.4; H, 7.4; N, 18.8%); *m*/*z* 298 (M^+); δ_H 1.54 (3 H, s), 1.58 (3 H, s), 1.77 (3 H, s), 1.9–2.45 (4 H, m), 5.0–5.15 (2 H, m), 6.15–6.35 (1 H, m), 7.25–7.65 (3 H, m), 7.9–8.0 (2 H, d); ν_{max} 1720, 1595, 1500, 1377 cm^{-1}.

4-(Cyclohex-2-enyl)-1-phenyltetrazol-5(4*H*)-one 2g. From cyclohex-2-enol (0.99 g, 0.01 mol), after stirring at 40 °C for 4 h; colourless oil (1.5 g, 61%) (Found: C, 64.8; H, 5.9; N, 23.2. $C_{13}H_{14}N_4O$ requires C, 64.4; H, 5.8; N, 23.1%); *m*/*z* 242 (M^+); δ_H 1.5–2.4 (6 H, m), 4.9–5.05 (1 H, m), 7.3–7.6 (3 H, m), 7.9–8.1 (2 H, d); ν_{max}1720, 1593, 1497, 1378, 1114, 749 cm^{-1}.

Method B

1-Phenyl-4-(1-phenylprop-2-enyl)tetrazol-5(4*H*)-one 2b. A sample of 5-cinnamyloxy-1-phenyltetrazole (0.55 g, 2 mmol) was heated in 1,1,2,2-tetrachloroethane (5 cm^3) at 100 °C for 2 h. After evaporation of the solvent, the required

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rearranged product was isolated as a colourless oil (0.54 g, 98%) (Found: C, 69.2; H, 5.1; N, 20.2. $C_{16}H_{14}N_4O$ requires C, 69.1; H, 5.1; N, 20.1%); *m/z* 278 (M^+); δ_H 5.28–5.52 (2 H, m), 6.0 (1 H, d, *J* 5.7 Hz), 6.36–6.55 (1 H, m), 7.3–7.5 (7 H, m), 7.95 (2 H, d, *J* 8.6 Hz); ν_{max} 1729 (C=O), 1598, 1504, 1382, 756 cm^{-1}.

1-Phenyl-4-(prop-2-enyl)tetrazol-5(4*H*)-one 2a. From compound **1a** after 15 h reflux; colourless oil[15] (98%) (Found: C, 59.6; H, 5.1; N, 27.8. Calc. for $C_{10}H_{10}N_4O$: C, 59.4; H, 5.0; N, 27.7%); *m/z* 202 (M^+); δ_H 4.65 (2 H, d, *J* 5.7 Hz), 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* 6.9 Hz); ν_{max} 1729 (C=O), 1598, 1504, 1388, 757 cm^{-1}.

4-(But-3-en-2-yl)-1-phenyltetrazol-5(4*H*)-one 2e. From compound **1e** after heating it at 100 °C for 3 h in tetrachloroethane; colourless oil[15] (97%) (Found: C, 61.0; H, 5.6; N, 26.1 Calc. for $C_{11}H_{12}N_4O$: C, 61.1; H, 5.6; N, 25.9%); *m/z* 216 (M^+); δ_H 1.65 (3 H, d, *J* 5.7 Hz), 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 Hz); ν_{max} 1729 (C=O), 1599, 1504, 1382, 757 cm^{-1}.

1-Phenyl-4-[1-(4-nitrophenyl)prop-2-enyl]tetrazol-5(4*H*)-one 2h. From compound **1h** after heating it in tetrachloroethane at 100 °C for 24 h; yellow solid (98%), 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%); *m/z* 323 (M^+); δ_H 5.3–5.55 (2 H, m), 6.15 (1 H, d, *J* 5.8 Hz), 6.32–6.51 (1 H, m), 7.3–7.7 (5 H, m), 8.05 (2 H, d, *J* 10.2 Hz), 8.25 (2 H, d, *J* 10.8 Hz); ν_{max} 1733 (C=O), 1597, 1522, 1500, 1341, 856 cm^{-1}.

Rate of isomerization of 5-cinnamyloxy-1-phenyltetrazole 1b to 1-phenyl-4-1(1-phenylprop-2-enyl)tetrazol-5(4*H*)-one 2b in the presence and absence of Pd/C catalyst

The rates of isomerization in these highly specific rearrangements were easily determined by observation of ^1H NMR spectra at intervals;[8] for the present rearrangement, peak integrals for a doublet at δ 6.85 (from 5-cinnamyloxy-1-phenyltetrazole) and a doublet at δ 6.03 [from 1-phenyl-4-(1-phenylprop-2-enyl)tetrazolone] were used to estimate the relative amounts of the two isomers.

Pd/C catalyst (10% w/w; 150 mg) was added to a solution of 5 cinnamyloxy-1-phenyltetrazole (150 mg) in benzene (10 cm^3) and the mixture was heated under reflux with vigorous stirring for 4 h. The catalyst was filtered off and, after evaporation of the solvent from the filtrate, the residual viscous oil was examined by ^1H NMR spectroscopy, which revealed a 1:1 mixture of the initial cinnamyloxytetrazole and its *N*-allyl isomer. In a similar experiment but without the Pd/C catalyst, the ratio of the two isomers was 3:1 respectively after 4 h, showing that the reaction was significantly faster in the presence of the catalyst.

Hydrogenolysis of allyloxytetrazoles

(a) Using palladium on charcoal (10% w/w) as catalyst. Hydrogenolysis conditions are described for one typical allyloxytetrazole **1**. Other similar tetrazoles were reduced under very similar conditions. All hydrogenolyses were monitored by gas chromatography or gas chromatography–mass spectrometry; retention times and mass spectra of products were compared with those of authentic materials. Reaction yields were based mainly on gas chromatographic peak areas, using an internal standard (usually hexamethylbenzene) for calibration. As a check on these yields, various hydrogenolyses were carried out on a larger scale and the products were weighed after isolation; their ^1H NMR spectra were compared with those from authentic specimens.

(*i*) In a two-phase solvent system.—*5-Cinnamyloxy-1-phenyltetrazole* **1b**. Distilled water (2 cm^3), ethanol (3 cm^3) and Pd/C catalyst (10% w/w; 100 mg) were added to 5-cinnamyloxy-1-phenyltetrazole (100 mg; 36 mmol) and hexamethylbenzene (internal standard; 58 mg, 36 mmol) in benzene (7 cm^3). Formic acid (98%; 1 cm^3) was added and the vigorously stirred solution was heated under reflux. TLC on silica (benzene–acetone, 9:1 v/v as eluent) showed that all of the tetrazole had disappeared in 5 min and that 1-phenyltetrazolone **6** had been formed. Gas chromatography showed that 1-phenylpropane had been formed in 100% yield in the same 5 min. There was no evidence for other products. The other allyloxytetrazoles listed in Table 1 were reduced similarly to give the expected products of alkane and phenyltetrazolone **6**, usually in yields close to 100%. On a larger scale, 1-phenylpropane was isolated as a colourless oil (90%); δ_H 0.94 (3 H, t), 1.63 (2 H, m), 2.58 (2 H, d of d), 7.18 (2 H, d), 7.26 (3 H, t); *m/z* 120 (M^+).

5-(3-phenyl[1,1-$^2H_2$]prop-2-enyloxy)-1-phenyltetrazole **1c**. In a very similar reaction to that for cinnamyloxytetrazole, 5-(3-phenyl[1,1-^2H]$_2$prop-2-enyloxy)-1-phenyltetrazole (0.5 g) in benzene (8 cm^3) was hydrogenolysed fully in less than 10 min with Pd/C (10%; 0.5 g) and formic acid (1 cm^3) in water (2 cm^3) and ethanol (3 cm^3). The catalyst was filtered off and the filtrate was extracted with diethyl ether. The organic layer was washed with aq. NaOH (2 mol dm^{-3}) to remove 1-phenyltetrazolone, then with water and finally dried ($MgSO_4$). The solvent was removed *in vacuo* to give the required 1-phenylpropane as a colourless liquid (92%); δ_H 0.81 (1.5 H, br m), 1.55 (2 H, br m), 2.51 (2 H, t), 7.18 (2 H, d), 7.27 (3 H, t); δ_C(proton decoupled) 128.5 (Ph), 128.2 (Ph), 125.6 (Ph), 38.1 (CH_2), 24.4 (CH_2), 12.6–13.9 (five clearly distinct lines from coupling to $^2H_2$ plus a small triplet from coupling to $^2H_1$; $CH_x{}^2H_y$: $x + y = 3$); mass spectrum *m/z* (M^+) 120 (25%), 121 (40%), 122 (95%), 123 (10%), corrected for ^{13}C isotopes.

(*ii*) *Using a one-phase solvent system.*—A mixture of 5-allyloxy-1-phenyltetrazole **1a** (100 mg, 0.5 mmol), cyclohexene (10 cm^3) and Pd/C catalyst (10% w/w; 100 mg) was vigorously stirred under reflux. TLC showed that all of the starting material had been hydrogenolysed to 1-phenyltetrazolone in 90 min.

(b) Using lead-modified palladium on charcoal as catalyst. Commercial Pd/C (10%; Engelhardt) was modified by reaction with lead chloride to give Pd/Pb/C catalysts with molar ratios of Pd to Pb of 1.0:1.0, 1.0:0.7 and 1.0:0.5.[11] The catalysts are designated as Pd/Pb/C (1:1), Pd/Pb/C (1:0.7) and Pd/Pb/C (1:0.5).

In a typical reaction, distilled water (2 cm^3) ethanol (3 cm^3) and Pd/Pb/C catalyst (1:0.5; 150 mg) were added to a solution of 5-cinnamyloxy-1-phenyltetrazole (100 mg, 36 mmol) and 1,2,4,5-tetramethylbenzene (internal standard; 49 mg, 36 mmol) in benzene (7 cm^3). Formic acid (98%; 1 cm^3) was added and the mixture was stirred vigorously under reflux. After 15 min, TLC showed that reduction was complete by the absence of starting material and the formation of 1-phenyltetrazolone. Gas chromatography showed that *trans*-1-phenylpropene (81%), *cis*-1-phenylpropene (1%), allylbenzene (8%) and 1-phenylpropane (1%) had been formed. The same reaction was carried out with Pd/Pb/C (1:1) and Pd/Pb/C (1:0.7). In these cases the yields of *trans*-1-phenylpropene were 73 and 84% respectively and of allylbenzene were 12 and 13% respectively, with only traces of the fully reduced 1-phenylpropane being observed. In an attempt to speed up the reaction, the experiment with Pd/Pb/C (1:0.7) was repeated with more catalyst (500 mg in place of 150 mg). Hydrogenolysis was complete in less than 15 min but the yields of *trans*-1-phenylpropene and allylbenzene had changed from 84 and 13% respectively to 76 and 13% respectively.

(c) Using bis(triphenylphosphine)palladium(II) chloride, Pd(Ph$_3$P)$_2$Cl$_2$. To a solution of 5-cinnamyloxy-1-phenyltetrazole (100 mg, 0.36 mmol) and hexamethylbenzene (internal standard; 58 mg, 0.36 mmol) in dioxane (15 cm^3) under nitrogen was added bis(triphenylphosphine)palladium(II) chloride (20 mg, 28 μmol), followed by ammonium formate (164 mg, 2.6 mmol). The reaction mixture was heated under reflux for 4 h. Allylbenzene and *trans*-1-phenylpropene were formed in 55 and 35% yield, respectively.

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Attempted hydrogenolysis of alkyloxytetrazoles

To a stirred solution of 5-benzyloxy-1-phenyltetrazole (50 mg, 0.2 mmol) in benzene (7 cm^3) was added distilled water (2 cm^3), ethanol (3 cm^3), Pd/C catalyst (10%; 50 mg) and formic acid (98%; 1 cm^3). The mixture was stirred vigorously and heated under reflux for 1 h. TLC revealed that no reaction had occurred. Similarly, with 5-(3-phenylpropanyloxy)-1-phenyltetrazole, there was no reaction after 2 h.

Attempted hydrogenolysis of 5-phenoxy-1-phenyltetrazole using bis(triphenylphosphine)palladium(II) chloride

To a solution of 5-phenoxy-1-phenyltetrazole (238 mg, 1 mmol) in benzene (7 cm^3) under nitrogen was added distilled water (2 cm^3), ethanol (3 cm^3), triphenylphosphine (39.3 mg, 0.15 mmol), $Pd(Ph_3P)_2Cl_2$ (7 mg, 10 μmol) and formic acid (98%; 1 cm^3). The whole was heated under reflux with vigorous stirring for 2 h, after which time no hydrogenolysis had occurred, in contrast to the observed hydrogenolysis of the allylic 5-cinnamyloxy-1-phenyltetrazole.

Rearrangement of allylbenzene to *trans*-1-phenylpropene

Ammonium formate (164 mg, 2.6 mmol) and $Pd(Ph_3P)_2Cl_2$ (20 mg, 28 μmol) were added to a stirred solution of allylbenzene (43 mg, 0.36 mmol) and hexamethylbenzene (internal standard; 58 mg, 0.35 mmol) in dioxane (15 cm^3) and the mixture was heated under reflux. Samples of the reaction mixture were removed at intervals and examined by GLC. After 30 min, *trans*-1-phenylpropene had formed in 25% yield and, after 2 h the yield was 55%, the remainder of the product being allylbenzene. Some catalyst decomposition was observed from the appearance of a fine black precipitate. Accordingly, the experiment was repeated in the presence of an excess of triphenylphosphine (100 mg, 0.38 mmol). In this case, there was no catalyst decomposition and *trans*-1-phenylpropene was formed in 40% yield after 4 h. In a repeat of this experiment, the ammonium formate and excess of triphenylphosphine were omitted. There was no rearrangement to *trans*-1-phenylpropene and only allylbenzene was recovered. In a reverse of these experiments, ammonium formate and $Pd(Ph_3P)_2Cl_2$ were reacted with *trans*-1-phenylpropene but, after 2 h, there had been no conversion to allylbenzene, indicating that rearrangement from allylbenzene to *trans*-1-phenylpropene was facilitated by the catalyst but not the reverse reaction and that the above yields could not have been due to an equilibrium between the two alkenes.

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