Synthesis and Properties of 4*H*-Imidazoles[1]

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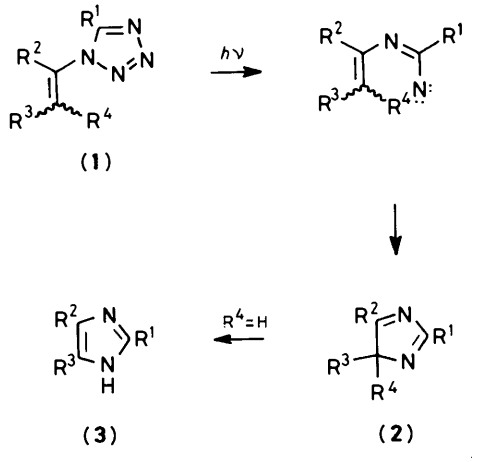
The photolysis of 1-vinyltetrazoles to give 1*H*-imidazoles is extended to the synthesis of isolable non-aromatic 4*H*-imidazoles when the vinyl group is terminally disubstituted. Thus photolysis of the 2-phenyltetrazole (**7a**), prepared from isobutyraldehyde, at 254 nm in light petroleum gives the 4,4-dimethylimidazole (**12a**). Similarly the cyclohexenyltetrazole (**10**) gives the tetrahydro-3a*H*-benzimidazole (**13**). Photolysis of the 2-methyltetrazole (**7b**) in dilute light petroleum solution at 0 °C gives 2,4,4-trimethylimidazole (**12b**) and photolysis of (**7b**) and (**7c**) in methanol gives methanol adducts (**15**) of the corresponding 4*H*-imidazoles. 5-Unsubstituted 4*H*-imidazoles are susceptible to nucleophilic attack at C-5; thus (**12a**) gives the hydrate (**16**) on adsorption on alumina, and the dihydroimidazoles (**15a**) and (**17**) respectively with methanol and methylmagnesium iodide. On heating, the 4,4-dimethylimidazole (**12a**) rearranges quantitatively to the 4,5-dimethylisomer (**19**) by successive [1,5] methyl and hydrogen shifts.

In contrast to the extensive studies on the biologically and pharmacologically important 1*H*-imidazoles,[2] very little attention has been paid to their non-aromatic 4*H*-isomers, because of the difficulties associated with their preparation.[3] Indeed, nearly all the 4*H*-imidazoles reported so far contain at least one heteroatom linked substituent, since the major synthetic approach is based on imidazolones.[3] However, 4*H*-imidazoles are of interest because of their unusual and potentially reactive 1,3-diazabutadiene structure, and because they afford an opportunity to study the isomerisation processes which give rise to the aromatic 1*H*-isomers. We now report in detail on a new route to 4*H*-imidazoles, which makes relatively simple derivatives available for the first time.

Results and Discussion

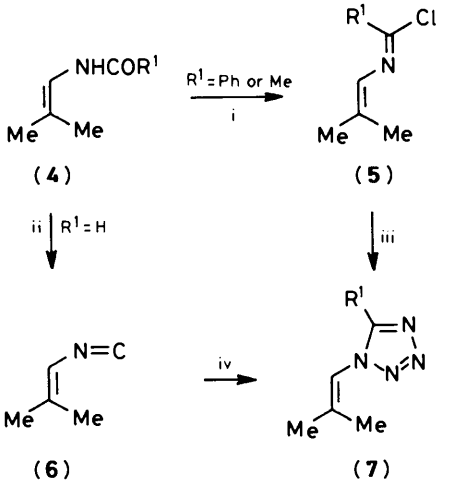
The method is based on our recently reported new synthesis of 1*H*-imidazoles by the photolysis of 1-alkenyltetrazoles (**1**; R^4 = H).[4,5] The imidazoles are presumably formed by cyclisation of the intermediate imidoylnitrene to give the 4*H*-imidazole (**2**; R^4 = H) (Scheme 1), which rapidly aromatises by [1,5] hydrogen shift to the 1*H*-isomer (**3**). It was therefore expected that if R^4 were a group other than hydrogen, for example methyl, then the intermediate 4*H*-imidazole (**2**; R^4 = Me) might be isolated and its properties studied.



(1) (2) (3)

Scheme 1.

The 1-alkenyltetrazole starting materials (**7**) were prepared from the primary amides R^1CONH_2 by condensation with isobutyraldehyde in refluxing benzene containing a catalytic amount of toluene-*p*-sulphonic acid to give the enamides (**4**). Subsequent conversion of these enamides into the imidoyl chlorides (**5**) [or isonitrile (**6**) in the case where R^1 = H] followed by reaction with azide gave the tetrazoles (**7**) (Scheme 2). This method, although a simple extension of the well known conversion of secondary amides into 1,5-disubstituted tetrazoles,[6] has apparently not been applied to enamides before, but would appear to have considerable generality.



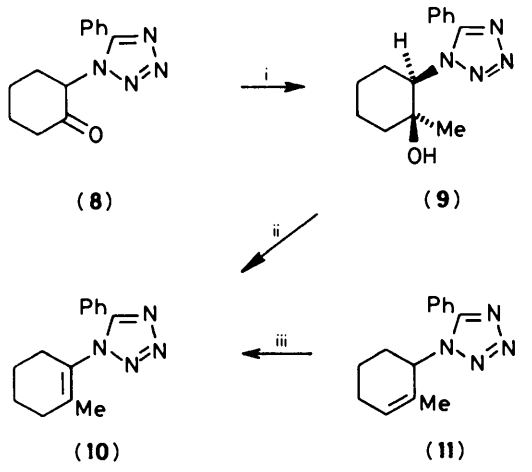
(4) (5) (6) (7)

a, R^1=Ph; b, R^1=Me; c, R^1=H

Scheme 2. *Reagents:* i, PCl_5 or $SOCl_2$; ii, TsCl, pyridine; iii, NaN_3, DMF; iv, HN_3, ether

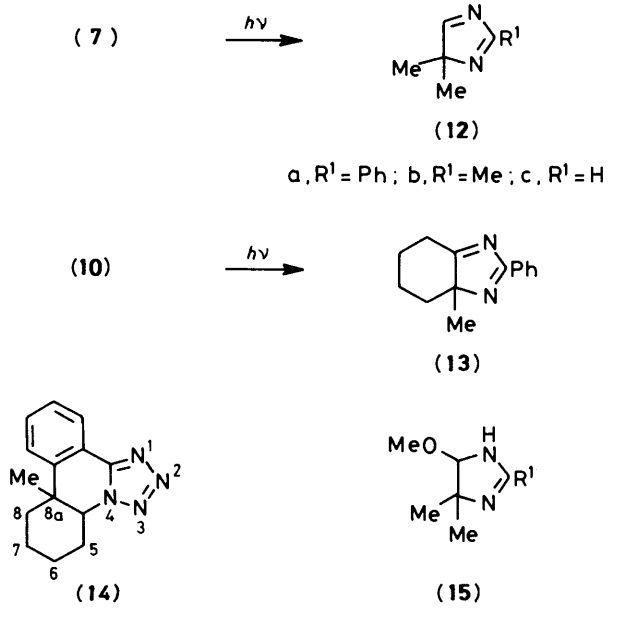
The tetrazole (**10**) was prepared from 1-(2-hydroxycyclohexyl)-5-phenyltetrazole[4] by oxidation to the corresponding ketone (**8**) with Jones' reagent, followed by addition of methylmagnesium iodide to give the alcohol (**9**) as the major product (77%) (Scheme 3). The isomeric alcohol, in which the tetrazole and methyl groups are *cis* on the cyclohexyl ring was also formed as a minor (10%) product. Dehydration of the alcohol (**9**) with phosphorus oxychloride in pyridine gave a mixture of the required vinyltetrazole (**10**) (19%) and the

allyltetrazole (**11**) (49%) together with a trace of the exomethylene isomer. In contrast, dehydration of the minor isomeric alcohol in which a *trans*-elimination of water to give (**10**) is not possible gave only a 2:1 mixture of the exomethylene and allyl (**11**) isomers in poor yield. Although the required vinyltetrazole (**10**) was only a minor product in the dehydration of (**9**), the unwanted allyl isomer (**11**) could be isomerised to (**10**) by treatment with potassium amide on alumina.[7]



Scheme 3. *Reagents:* i, MeMgI, ether; ii, $POCl_3$, pyridine; iii, KNH_2, alumina, ether

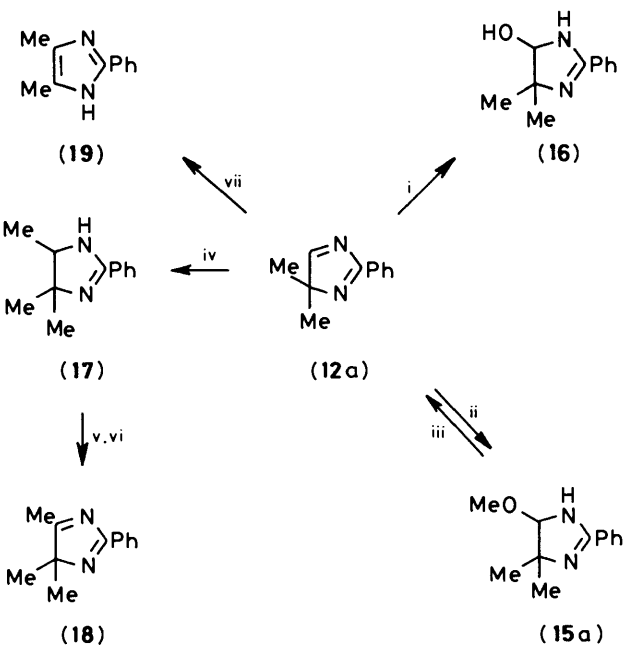
Photolysis of the alkenyltetrazoles (**7a**) and (**10**) in light petroleum (b.p. 60—80 °C) at 254 nm gave the corresponding 4*H*-imidazoles (**12a**) and (**13**) both in 55% yield, although in the case of (**10**), the photocyclisation product (**14**) was also formed in 6% yield. The amount of the photocyclisation product was greater (35%) when the tetrazole (**10**) was irradiated in the more polar solvent acetonitrile (*cf.* ref. 4). There was no indication of



six-membered ring formation by insertion of the intermediate nitrene into the methyl group, and this is in accord with other reports that imidoylnitrenes do not undergo C–H insertion reactions.[8] When the tetrazoles (**7b**) and (**7c**) were irradiated under similar conditions complex mixtures containing only traces of the required 4*H*-imidazoles were formed. However, when the photolyses were carried in methanol, n.m.r. spectroscopy indicated that the corresponding methanol adducts (**15b**) and (**15c**) were formed, showing that the 4*H*-imidazoles (**12b**) and (**12c**) were generated but had reacted rapidly with the solvent. Several attempts were made to regenerate the 2-methyl 4*H*-imidazole (**12b**) from the adduct (**15b**) by removal of methanol under various conditions, but these were unsuccessful. The 4*H*-imidazole (**12b**) was finally isolated as a volatile liquid by carrying out the photolysis in dilute light petroleum (b.p. 30—40 °C) solution at 0 °C, although it could not be obtained completely pure, being contaminated with another compound tentatively assigned as *N*-isobutenyl-*N'*-methylcarbodi-imide. Unfortunately, when the tetrazole (**7c**) was irradiated under identical conditions only a trace of the 4*H*-imidazole (**12c**) was formed as evidenced by the characteristic signals in the n.m.r. spectrum of the photolysate.

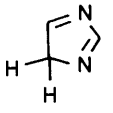
It is clear that the preparation of simple, lightly substituted 4*H*-imidazoles presents considerable problems because of their reactivity and volatility. The mildness of the photochemical procedure is crucial in overcoming these problems, and it thus provides a route to the 4*H*-imidazole ring system, making 2,4,4-trisubstituted derivatives available for the first time.

Since 5-unsubstituted 4*H*-imidazoles have not previously been isolated, the properties of (**12a**) were briefly studied. The 5-proton resonates at δ 8.77 in the ^1H n.m.r. spectrum, typical of an imine type proton, and the corresponding carbon (C-5) at δ 193.1 in the ^{13}C n.m.r. spectrum. In the mass spectrum, a strong loss of methyl ($M - 15$) and of HCN ($M - 27$) is observed, but no loss of PhCN ($M - 103$). The 5-unsubstituted 4*H*-imidazole (**12a**) is very reactive towards nucleophiles. Thus it was rapidly hydrated on attempted chromatography on alumina to give the hydrate (**16**). Similarly, addition of methanol gave the adduct (**15a**) from which the 4*H*-imidazole (**12a**) could be regenerated in good yield by heating in benzene with azeotropic removal of methanol. Addition of methylmagnesium iodide to (**12a**) was very rapid and gave the expected dihydroimidazole (**17**) in high yield. Dehydrogenation of this

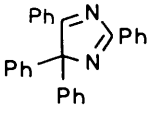


Scheme 4. *Reagents:* i, Chromatography on alumina; ii, MeOH; iii, heat in benzene with azeotropic removal of MeOH; iv, MeMgI, ether; v, Bu^{t}OCl; vi, DBU; vii, heat

dihydroimidazole by *N*-chlorination followed by treatment with base (Scheme 4) gave the 5-methyl-4*H*-imidazole (**18**) albeit in low yield. As expected this 5-substituted 4*H*-imidazole is much less susceptible to nucleophilic attack and can be readily purified by chromatography on alumina. Thus these simple 5-unsubstituted 4*H*-imidazoles are highly electrophilic species, and react readily with nucleophiles at the 5-position in accord with MNDO calculations on the parent 4*H*-imidazole ring system (**20**) which suggest that C-5 should be considerably more electrophilic than C-2 by virtue of its higher orbital coefficient of the LUMO (0.62 *vs.* 0.42 for C-2).[9]



(**20**)



(**21**)

When heated in diphenyl ether at 180 °C, the 4*H*-imidazole (**12a**) rearranged to 4,5-dimethyl-2-phenylimidazole (**19**) (93%). The reaction could conveniently be followed by n.m.r. spectroscopy. Thus on heating to 120 °C in [$^2H_6$]dimethyl sulphoxide, the 4*H*-imidazole (**12a**) rearranged to the aromatic imidazole (**19**) in quantitative yield. The reaction had first order kinetics with a half life of 30 min, and no intermediates were detectable by n.m.r. spectroscopy. This is consistent with a rate-determining [1,5] methyl migration to C-5, followed by a rapid aromatising hydrogen shift. Although only one example of an aromatising rearrangement in a 4*H*-imidazole has been reported,[10] the tetraphenyl 4*H*-imidazole (**21**) rearranging to 1,2,4,5-tetraphenyl-1*H*-imidazole at the (remarkably) high temperature of 300 °C, relatively facile alkyl shifts in other non-aromatic azoles such as 3*H*-pyrazoles are known.[11] The fact that the methyl group in the 4*H*-imidazole (**12a**) migrates exclusively to carbon to give another non-aromatic 4*H*-imidazole intermediate which subsequently aromatises by a hydrogen shift, rather than to nitrogen to give aromatic 1*H*-imidazole directly, is also consistent with other work.[11–13] The preference for migration to carbon rather than nitrogen is well documented, and is ascribed to better orbital overlap in the transition state.[12]

Experimental

For general points see ref. 4.

1-(2-*Methylprop*-1-*enyl*)-5-*phenyltetrazole* (**7a**).—A mixture of isobutyraldehyde (12.7 ml, 0.14 mol), benzamide (8.40 g, 0.07 mol), and toluene-*p*-sulphonic acid (*ca.* 250 mg) in benzene (300 ml) was heated under reflux with a Dean and Stark trap for 21 h. The mixture was filtered, the filtrate evaporated, and the residue purified by chromatography to give *N*-isobutenylbenzamide (**4a**)[14] (11.1 g, 91%).

A solution of the enamide (**4a**) (2.67 g, 15.2 mmol) and thionyl chloride (2.21 ml, 30.5 mmol) in benzene (10 ml) was heated under reflux for 30 h. The solvent was evaporated, and the crude imidoyl chloride (**5a**) was dissolved in DMF (10 ml) and the solution was added dropwise to a stirred ice-cooled suspension of sodium azide (2.96 g, 45.6 mmol) in DMF (10 ml). The mixture was stirred at room temperature for 4 h, poured into water (200 ml), and extracted with ether (3 × 50 ml). The ether extracts were combined, dried over $MgSO_4$, evaporated, and the residue chromatographed to give the *title compound* (**7a**) (1.36 g, 45%), m.p. 66—67 °C (Found: C, 66.2; H, 6.0; N, 28.2. $C_{11}H_{12}N_4$ requires C, 66.0; H, 6.0; N, 28.0%); $\nu_{max.}$ 1 413, 1 278, 1 107, 814, 809, 775, 729, and 698 cm^{-1}; $\lambda_{max.}$ 238 nm (log ε 4.09); δ (90 MHz; $CDCl_3$) 1.65 (3 H, d, *J* 2 Hz), 1.99 (3 H, d, *J* 2 Hz), 6.69 (1 H, m), 7.40—7.75 (3 H, m), and 7.75—8.05 (2 H, m); *m/z* 201 (M^+ + 1), 172, 145, 130, 104, 103, 85, 83, 77, 76, and 47 (100%).

1-(2-*Methylprop*-1-*enyl*)-5-*methyltetrazole* (**7b**).—Acetamide (2.96 g, 50 mmol) was condensed with isobutyraldehyde (9.19 ml, 100 mmol) as described above to give *N*-isobutenylacetamide (**4b**)[14] (4.45 g, 79%).

Phosphorus pentachloride (6.76 g, 32.5 mmol) was added over 10 min to a stirred solution of the enamide (**4b**) (3.34 g, 29.5 mmol) in benzene (30 ml). The mixture was stirred for a further 30 min and the solvent evaporated. The resulting crude imidoyl chloride (**5b**) was dissolved in DMF (20 ml) and added to a stirred ice-cooled suspension of sodium azide (3.42 g, 52.6 mmol) in DMF (20 ml). The mixture was stirred for 1 h, diluted with water (200 ml), and extracted with chloroform (4 × 50 ml). The extracts were combined, dried, evaporated, and the residue chromatographed to give the *title compound* (**7b**) (2.04 g, 50%), m.p. 41—43 °C (Found: C, 52.0; H, 7.3; N, 41.1. $C_6H_{10}N_4$ requires C, 52.2; H, 7.3; N, 40.55%); $\nu_{max.}$ 1 522, 1 419, 1 343, 1 274, 1 266, 1 124, 1 087, 1 063, 819, 810, 704, and 680 cm^{-1}; $\lambda_{max.}$ 215 nm (log ε 3.53); δ (90 MHz; $CDCl_3$) 1.77 (3 H, d, *J* 2 Hz), 2.08 (3 H, *J* 2 Hz), 2.59 (3 H, s), and 6.65 (1 H, m); *m/z* 139, 138 (M^+), 109, 95, 83, 69, 68, 55, 42 (100%), and 41.

1-(2-*Methylprop*-1-*enyl*)*tetrazole* (**7c**).—Formamide (1.0 ml, 25 mmol) was condensed with isobutyraldehyde (4.60 ml, 50 mmol) as described above to give *N*-isobutenylformamide (**4c**) as a liquid (Found: M^+, 99.0683. C_5H_9NO requires *M*, 99.0684); $\nu_{max.}$ 3 280, 1 654, 1 416, 1 386, 1 035, and 847 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.67 (6 H, br s), 6.09 (0.17 H, br d, *J* 11 Hz), 6.50 (0.83 H, br d *J* 11 Hz), 8.02 (0.83 H, d, *J* 2 Hz), 8.16 (0.17 H, d, *J* 11 Hz), and 9.05 (1 H, br d, *J* 11 Hz); *m/z* 99 (M^+, 100%), 70, 56, and 43. A solution of toluene-*p*-sulphonyl chloride (3.71 g, 19.5 mmol) in tetrachloromethane (25 ml) was added slowly to a stirred solution of the enamide (**4c**) (1.93 g, 19.5 mmol) and pyridine (3.15 ml, 39 mmol) in tetrachloromethane (25 ml) at 4 °C under nitrogen. The mixture was stirred at 4 °C for 15 h, filtered, and the resulting solution of the isonitrile (**6**) was treated with an ethereal solution of hydrazoic acid [prepared from sodium azide (7.60 g, 117 mmol) and concentrated sulphuric acid (20 ml) in water (75 ml) and ether (150 ml)]. The solution was heated under reflux for 30 h, hydrochloric acid (4M; 30 ml) was added, and the mixture stirred vigorously for 6 h. The layers were separated, and the aqueous layer extracted with chloroform (4 × 30 ml). The organic extracts were dried, evaporated, and the residue chromatographed to give the *title compound* (**7c**) (994 mg, 41%), b.p. 90 °C at 0.4 mmHg (Found: M^+ 124.0749. $C_5H_8N_4$ requires 124.0749); $\nu_{max.}$ 3 135, 1 474, 1 183, 1 092, 1 012, 962, 803, and 663 cm^{-1}; $\lambda_{max.}$ 228 nm (log ε 3.70); δ (90 MHz; CCl_4) 1.82 (3 H, d, *J* 1 Hz), 1.97 (3 H, d, *J* 1 Hz), 6.89 (1 H, m), and 8.93 (1 H, s); *m/z* 124 (M^+), 95, 81, 69, 68, 55, 54, 42 (100%), 41, and 39.

1-(2-*Oxocyclohexyl*)-5-*phenyltetrazole* (**8**).—A solution of chromic acid (1.14M; 5.5 ml) was added dropwise to a stirred solution of 1-(2-hydroxycyclohexyl)-5-phenyltetrazole[4] (1.80 g, 7.37 mmol) in acetone (40 ml). The mixture was stirred for 24 h and then diluted with water (20 ml) and dichloromethane (40 ml). The layers were separated and the aqueous phase was extracted with chloroform. The organic layers were combined, washed with brine (30 ml), dried, and evaporated to give the *title compound* (**8**) (1.77 g, 99%), m.p. 135—138 °C (from chloroform–light petroleum) (Found: C, 64.8; H, 5.8; N, 23.4. $C_{13}H_{14}N_4O$ requires C, 64.45; H, 5.8; N, 23.4%); $\nu_{max.}$ 1 717, 1 069, 788, 773, 740, and 690 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.6—2.9 (8 H, m), 5.16 (1 H, dd, *J* 9, 13 Hz), and 7.54 (5 H, s); *m/z* 242 (M^+), 202, 171, 118, 104 (100%), and 103.

1-(2-*Hydroxy*-2-*methylcyclohexyl*)-5-*phenyltetrazole* (**9**).—A solution of methylmagnesium iodide was made in the standard way from iodomethane (2.10 g, 14.8 mmol) and magnesium (0.30 g, 12.3 mmol) in ether (15 ml). A solution of the ketone (**8**) (1.50 g, 6.19 mmol) in benzene (80 ml) was added dropwise to the stirred Grignard solution, and the resulting mixture was heated under reflux for 3 h. The reaction mixture was poured into water (100 ml), acidified with dilute hydrochloric acid, and the layers separated. The aqueous phase was extracted with dichloromethane (3 × 50 ml), and the organic extracts were combined, washed with water, dried, evaporated, and the residue chromatographed to give (i) 1-[(1RS,2SR)-2-*hydroxy*-2-*methylcyclohexyl*]-5-*phenyltetrazole* (**9**) (1.32 g, 77%), m.p. 99—101 °C (Found: C, 65.0; H, 7.0; N, 21.8. $C_{14}H_{18}N_4O$ requires C, 65.1; H, 7.0; N, 21.7%); $\nu_{max.}$ 3 480, 1 283, 1 176, 1 099, 1 008, 963, 784, 703, and 699 cm^{-1}; δ (90 MHz; $CDCl_3$) 0.84 (3 H, s), 1.1—2.7 (8 H, m), 3.73 (1 H, d, *J* 3 Hz), 4.32 (1 H, dd, *J* 4, 15 Hz), and 7.63 (5 H, s); *m/z* 258 (M^+), 243, 215, 173 (100%), 160, 147, 104, and 43, and (ii) the (1RS,2RS)-*isomeric alcohol* (0.23 g, 10%), m.p. 155—158 °C (Found: C, 64.8; H, 7.0; N, 21.7); $\nu_{max.}$ 3 360, 1 398, 1 168, 936, 883, 783, 741, and 700 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.15—4.43 (8 H, m), 1.55 (3 H, s), 3.76 (1 H, br s), 4.41 (1 H, dd, *J* 3, 12 Hz), 7.31—7.64 (3 H, m), and 7.67—7.95 (2 H, m); *m/z* 258 (M^+), 229, 215, 173 (100%), 160, and 104, and (iii) unreacted ketone (69 mg, 5%).

1-(2-*Methylcyclohex*-1-*enyl*)-5-*phenyltetrazole* (**10**).—(a) Phosphorus oxychloride (5 ml) was added to a well stirred solution of the alcohol (**9**) (741 mg, 2.87 mmol) in pyridine (10 ml), and the resulting mixture was stirred for 1.5 h. The mixture was poured carefully into ice-water (100 ml), extracted with ether (3 × 30 ml), and the extracts were washed with water, dried, evaporated, and the residue chromatographed to give (i) the *title compound* (**10**) (132 mg, 19%), m.p. 81—82.5 °C (Found: C, 70.0; H, 6.7; N, 23.35. $C_{14}H_{16}N_4$ requires C, 70.0; H, 6.7; N, 23.35%); $\nu_{max.}$ 1 400, 1 283, 1 187, 788, 736, and 702 cm^{-1}; $\lambda_{max.}$ 237 nm (log ε 4.08); δ (90 MHz; $CDCl_3$) 1.36 (3 H, s), 1.60—2.15 (8 H, m), 7.48—7.75 (3 H, m), and 7.79—8.05 (2 H, m); *m/z* 240 (M^+), 212, 211, 197, 184, 144 (100%), 118, 117, 104, 97, and 77, and (ii) 1-(2-*methylcyclohex*-2-*enyl*)-5-*phenyltetrazole* (**11**) (337 mg, 49%), m.p. 65—68 °C (Found: C, 69.8; H, 6.7; N, 23.25); $\nu_{max.}$ 1 394, 1 157, 970, 799, 779, 738, and 703 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.37 (3 H, s), 1.50—2.45 (6 H, m), 4.93—5.20 (1 H, m), 5.87 (1 H, m), and 7.65 (5 H, s); *m/z* 241, 240 (M^+), 169, 156, 147, 95, 94 (100%), and 79, together with a trace amount of 1-(2-methylenecyclohexyl)-5-phenyltetrazole.

(b) Ammonia (5 ml) was condensed into a flask containing dried alumina H (600 mg) at −78 °C. Potassium (80 mg) was added with stirring to give deep blue solution. After 5 min, a few crystals of iron(III) nitrate were added, and the suspension became colourless. The ammonia was allowed to evaporate under nitrogen at room temperature, and then a solution of the tetrazole (**11**) (186 mg) in ether (3 ml) was added. The mixture was stirred for 5 h, filtered, and evaporated to give the title compound (**10**) (136 mg, 73%) as a colourless solid.

Photolysis of the Tetrazole (**7a**).—A solution of the tetrazole (**7a**) (980 mg) in light petroleum (800 ml) was irradiated[4] at 254 nm for 6 h. The solvent was evaporated and the residue was sublimed at 50 °C and 5 mmHg to give 4,4-*dimethyl*-2-*phenyl*-4H-*imidazole* (**12a**) (464 mg, 55%), m.p. 40—44 °C (from light petroleum at −78 °C) (Found: M^+ 172.1006. $C_{11}H_{12}N_2$ requires 172.1000); $\nu_{max.}$ 2 980, 1 611, 1 602, 1 574, 1 450, 1 320, 1 281, 1 022, 914, 718, and 677 cm^{-1}; $\lambda_{max.}$ 257 (log ε 3.95), 282 (3.57), and 291 nm (3.38); δ (90 MHz; $CDCl_3$) 1.41 (6 H, s), 7.35—7.65 (3 H, m), 8.20—8.47 (2 H, m), and 8.77 (1 H, s); δ_C 20.7, 83.1, 128.2, 130.8, 131.5, 170.3, and 193.1; *m/z* 172 (M^+, 25%), 157 (6), 145 (100), 104 (79), and 77; m* (172—145) 122.2, (145—104) 74.6, and (104—77) 57.0.

Photolysis of the Tetrazole (**10**).—(a) A solution of the tetrazole (**10**) (303 mg) in light petroleum (200 ml) was irradiated at 254 nm for 3 h. The solution was evaporated and the residue chromatographed on alumina to give (i) 3a-*methyl*-2-*phenyl*-4,5,6,7-*tetrahydro*-3aH-*benzimidazole* (**13**) (147 mg, 55%), m.p. 110—113 °C (Found: C, 79.0; H, 7.6; N, 13.22. $C_{14}H_{16}N_2$ requires C, 79.2; H, 7.6; N, 13.2%); $\nu_{max.}$ 1 614, 1 276, 1 145, 1 046, 1 023, 732, 726, and 699 cm^{-1}; $\lambda_{max.}$ 255 (log ε 3.96), 281 sh, and 290 sh nm; δ (250 MHz; $CDCl_3$) 1.18—1.25 (2 H, m), 1.38 (3 H, s), 1.60—1.86 (2 H, m) 2.20—2.34 (1 H, m), 2.43—2.68 (2 H, m), 3.02—3.12 (1 H, m), 7.43—7.54 (3 H, m), and 8.24—8.34 (2 H, m); δ_C 19.6, 21.9, 29.3, 29.9, 40.8, 82.0, 128.4, 128.8, 130.8, 132.3, 171.0, and 205.8; *m/z* 212 (M^+, 32%), 171 (12), 144 (29), 131 (7), 104 (100), and 77 (15); m* (212—171) 137.9, (212—144) 97.8, (144—104) 75.1, and (104—77) 59.0, and (ii) 8a-*methyl*-4a,5,6,7,8,8a-*hexahydrotetrazolo*[1,5-f]*phenanthridine* (**14**) (17 mg, 6%) as an oil (Found: M^+, 240.1381. $C_{14}H_{16}N_4$ requires *M*, 240.1374); $\nu_{max.}$ 1 484, 1 446, 1 101, 1 037, 778, 765, 733, and 701 cm^{-1}; δ (90 MHz; $CDCl_3$) 0.95 (3 H, s), 1.3—3.0 (8 H, m), 4.14 (1 H, dd, *J* 4, 12 Hz), 7.30—7.67 (3 H, m), and 8.05—8.20 (2 H, m); *m/z* 240 (M^+), 212, 211, 197, 169, 145, 141, 85, 83, 74, and 59.

(b) A solution of the tetrazole (**10**) (131 mg) in acetonitrile (50 ml) was irradiated at 254 nm for 2.5 h. The solvent was evaporated and the residue chromatographed to give (i) the 4*H*-imidazole (**13**) (47 mg, 41%) and the tetrazolophenanthridine (**14**) (46 mg, 35%).

Photolysis of the Tetrazole (**7b**).—(a) A solution of the tetrazole (**7b**) (55 mg) in methanol (40 ml) was irradiated at 254 nm for 1 h. The solvent was evaporated to give 1,5-dihydro-5-methoxy-2,4,4-trimethyl-4*H*-imidazole (**15b**) as the only product, δ (90 MHz; $CDCl_3$) 1.18 (3 H, s), 1.24 (3 H, s), 1.97 (3 H, s), 3.39 (3 H, s), 4.49 (1 H, s), and 5.93 (1 H, br s).

(b) A solution of the tetrazole (**7b**) (241 mg) in light petroleum (b.p. 30—40 °C) (250 ml) was irradiated at 254 nm at 0 °C for 1 h. The solvent was removed at *ca.* 5 °C under vacuum and the residue was distilled at 18 °C and 2 mmHg into a receiver cooled to −78 °C to give 2,4,4-trimethyl-4*H*-imidazole (**12b**) as a colourless oil, δ (90 MHz; $CDCl_3$) 1.33 (6 H, s), 2.43 (3 H, s), and 8.56 (1 H, s); δ_C 18.0, 20.7, 82.8, 171.7, and 193.5, which was contaminated with a minor product tentatively assigned as *N*-isobutenyl-*N'*-methylcarbodi-imide, $\nu_{max.}$ 2 130 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.64 (3 H, m), 1.69 (3 H, m), 3.01 (3 H, s), and 5.96 (1 H, m).

Photolysis of the Tetrazole (**7c**)—(a) A solution of the tetrazole (**7c**) (106 mg) in methanol (40 ml) was irradiated at 254 nm for 1.3 h. The solvent was evaporated to give 1,5-dihydro-5-methoxy-4,4-dimethyl-4*H*-imidazole (**15c**), δ (90 MHz; $CDCl_3$) 1.21 (3 H, s), 1.28 (3 H, s), 3.38 (3 H, s), 4.50 (1 H, s), and 6.85 (1 H, br s) as the major product contaminated with several minor ones.

(b) A solution of the tetrazole (**7c**) (65 mg) in light petroleum (b.p. 30—40 °C) (100 ml) was irradiated at 254 nm at 0 °C for 1 h. The solvent was removed under vacuum at 0 °C to give an oil, the n.m.r. spectrum of which showed it to be a complex mixture with possibly a trace of 4,4-dimethyl-4*H*-imidazole (**12c**) as characterised by small singlets at δ 8.06 and 8.74.

Reactions of the 4H-*Imidazole* (**12a**)

1,5-*Dihydro*-5-*methoxy*-4,4-*dimethyl*-2-*phenyl*-4H-*imidazole* (**15a**).—The 4*H*-imidazole (**12a**) (58 mg) was dissolved in methanol (1 ml), and the mixture was kept at room temperature

for 40 h. The solvent was evaporated to give the title compound (**15a**) as the only product, δ (90 MHz; CCl_4) 1.13 (3 H, s), 1.22 (3 H, s), 3.27 (3 H, s), 4.44 (1 H, s), 6.88 (1 H, br s), 7.01—7.44 (3 H, m) and 7.72—7.98 (2 H, m).

The crude product was dissolved in benzene (4 ml), toluene-*p*-sulphonic acid (5 mg) was added, and the mixture was refluxed with slow distillation for 1 h. The solvent was evaporated to give the 4*H*-imidazole (**12a**) as the only product (n.m.r.).

1,5-*Dihydro*-5-*hydroxy*-4,4-*dimethyl*-2-*phenyl*-4H-*imidazole* (**16**).—A sample of the 4*H*-imidazole (**12a**) was chromatographed on alumina to give the title compound (**16**), δ (90 MHz; $CDCl_3$) 1.16 (3 H, s), 1.27 (3 H, s), 4.96 (1 H, s), 5.0 (2 H, br s), 7.33—7.67 (3 H, m), and 7.69—8.12 (2 H, m); *m/z* 190 (M^+), 172, 145 (100%), 104, and 77.

1,5-*Dihydro*-4,4,5-*trimethyl*-2-*phenyl*-4H-*imidazole* (**17**).—A solution of the 4*H*-imidazole (**12a**) (87 mg, 0.5 mmol) in ether (1 ml) was added dropwise to a solution of methylmagnesium iodide [from iodomethane (0.12 ml, 1.0 mmol) and magnesium (25 mg, 1.0 mmol)] in ether (1 ml), and the resulting mixture was stirred for 30 min. Dilute hydrochloric acid was added, and the ether layer was separated. The aqueous layer was basified with sodium hydroxide solution, extracted with dichloromethane (3 × 5 ml), and the extracts were combined, dried, and evaporated to give the *title compound* (**17**) (85 mg, 89%), m.p. 120—122 °C (from light petroleum) (Found: C, 76.8; H, 8.7; N, 14.9. $C_{12}H_{16}N_2$ requires C, 76.6; H, 8.6; N, 14.9%); $\nu_{max.}$ 3 160, 1 597, 1 567, 1 513, 1 320, 963, 790, and 701 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.19 (3 H, s), 1.26 (3 H, d, *J* 7 Hz), 1.37 (3 H, s), 3.72 (1 H, q, *J* 7 Hz), 4.05 (1 H, br s), 7.25—7.48 (3 H, m), and 7.60—7.86 (2 H, m); *m/z* 188 (M^+), 163, 145 (100%), 131, 104, and 77.

4,4,5-*Trimethyl*-2-*phenyl*-4H-*imidazole* (**18**).—A solution of t-butylhypochlorite (0.28 ml, 2.34 mmol) in ether was added dropwise to a stirred suspension of the imidazoline (**17**) (220 mg, 1.17 mmol) in ether (5 ml). The mixture was stirred for 4 h, and then treated with DBU (0.35 ml, 2.34 mmol). After a further 1 h, the mixture was filtered, and the filtrate cooled to −20 °C whereupon an oil precipitated. The ether was decanted off, evaporated and the residue chromatographed on alumina to give the *title compound* (**18**) (62 mg, 28%), m.p. 57—60 °C (sublimed) (Found: M^+ 186.1157. $C_{12}H_{14}N_2$ requires *M*, 186.1157); $\nu_{max.}$ 2 980, 1 620, 1 581, 1 563, 1 461, 1 327, 1 275, 1 065, 719, and 698 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.36 (6 H, s), 2.35 (3 H, s), 7.30—7.65 (3 H, m), and 8.15—8.45 (2 H, m); δ_C 15.4, 22.7, 82.5, 128.5, 128.9, 130.9, 132.3, 170.3, and 203.4; *m/z* 186 (M^+, 9%), 171 (1), 145 (100), 104 (73), and 77 (16); *m** (186—145) 113.0 and (145—104) 74.6.

Thermal Rearrangement of the 4H-*Imidazole* (**12a**).—(a) A solution of the 4*H*-imidazole (**12a**) (54 mg) in diphenyl ether (1 ml) was heated to 180 °C under nitrogen for 1 h. The mixture was diluted with ether, and extracted with dilute hydrochloric acid (1M; 2 × 5 ml). The aqueous layer was basified, and extracted with dichloromethane (3 × 5 ml). The dichloromethane extracts were combined, dried and evaporated to give 4,5-dimethyl-2-phenylimidazole (**19**) (50 mg, 93%), m.p. 229—235 °C (lit.,[15] 241 °C).

(b) A solution of the 4*H*-imidazole (**12a**) (20 mg) in [$^2H_6$]dimethyl sulphoxide (0.5 ml) was heated to 120 °C in the probe of a Bruker WM250 n.m.r. spectrometer. The rearrangement was monitored by recording spectra at intervals of 100 s. A clean and quantitative rearrangement into 4,5-dimethyl-2-phenyl-1*H*-imidazole (**19**) was observed. A plot of the logarithm of the concentration of (**12a**) against time was linear, and gave a half-life of 30 min for the rearrangement.

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