Synthesis and Properties of 4*H*-Imidazoles. Part 2.[1]

Christopher J. Moody, Charles W. Rees and Richard G. Young
Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

The 1-(2,2-disubstituted alk-1-enyl)-5-phenyltetrazoles **2** and **4** are prepared from 1-methyl-5-phenyltetrazole and 5-phenyl-1-trimethylsilylmethyltetrazole by formation and appropriate interception of the α-lithioalkyl derivatives. Photolysis of the tetrazoles **2a** and **4** gives the stable 4*H*-imidazoles **9** and **5**, respectively. Similar photolysis of the tetrazole **2b** gives the tetrazolophenanthrene **12** by an oxidative photocyclisation which is faster than nitrogen extrusion from the tetrazole ring. However, on further irradiation the tetrazolophenanthrene **12** can be transformed into the polycyclic 4*H*-imidazole **13**. The 4*H*-imidazoles all undergo [1,5] alkyl or aryl shifts to carbon when heated, **5**, **7**, **9** and **13** giving **6**, **8**, **10** and **14** respectively.

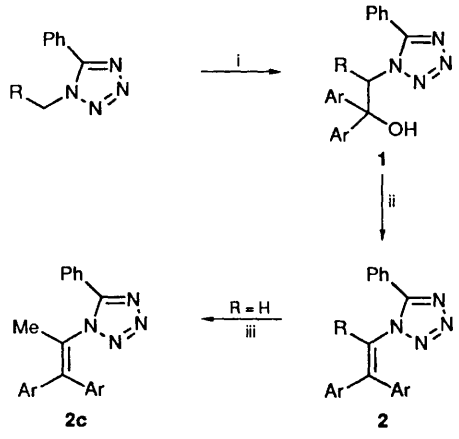
We recently reported a new route to 4*H*-imidazoles,[1] non-aromatic isomers of the well known and important 1*H*-imidazoles. The route was based on the photochemical decomposition of 1-(2,2-disubstituted alk-1-enyl) tetrazoles, and presumably proceeds by electrocyclisation of the intermediate imidoylnitrene (Scheme 1). We now report some

Scheme 1

further results involving the preparation and thermal rearrangement of new 4*H*-imidazoles.

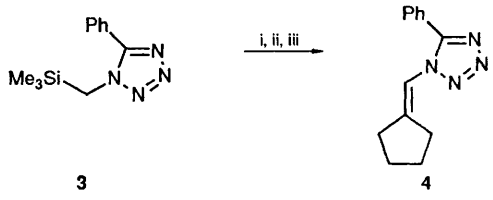
Results and Discussion

Preparation of 1-*Alkenyltetrazoles.*—Two routes to the desired 1-(2,2-disubstituted alk-1-enyl)tetrazoles were investigated. Both are based on our recently described lithiation of 1-alkyltetrazoles.[2] In the first, the tertiary alcohols **1**, prepared by quenching the appropriate lithioalkyltetrazole with 4,4′-dimethylbenzophenone, were readily dehydrated under acidic conditions to give the alkenyltetrazoles **2** in good yield (Scheme 2). In an extension of our lithiation studies, it was found that the alkenyltetrazole **2a** could be metallated further at the sp^2 alkenyl carbon, and the resulting lithio species methylated in quantitative yield to give the tetrazole **2c**.



Scheme 2 [Ar = 4-MeC_6H_4; **a**, R = H; **b**, R = Ar] *Reagents:* i, ref. 2; ii, 4-$MeC_6H_4SO_3H$, benzene, reflux; iii, Bu^{t}Li, THF, then MeI

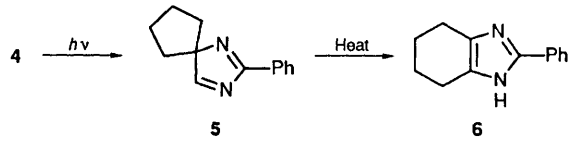
The second route to 1-alkenyltetrazoles was based on the Peterson reaction of 5-phenyl-1-trimethylsilylmethyltetrazole **3**, a reaction which parallels the successful olefinations of the corresponding 2-trimethylsilylalkyltetrazoles.[3] Thus reaction of the tetrazole **3** with t-butyllithium at −78 °C in tetrahydrofuran (THF) followed by quenching with cyclopentanone and work-up gave the desired alkenyltetrazole **4** (57%) together with returned starting material **3** (41%), and a trace of 1-methyl-5-phenyltetrazole (Scheme 3). Since the tetrazoles **3** and **4** were



Scheme 3 *Reagents:* i, Bu^{t}Li, ether, −78 °C; ii, cyclopentanone; iii, NaOMe, MeOH then chromatography

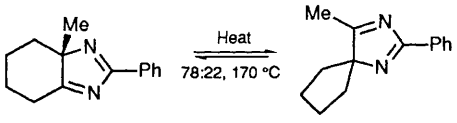
inseparable by chromatography, a higher conversion of **3** into **4** was desirable. Although addition of hexamethylphosphoramide in the lithiation step did not improve the yield, simply carrying out the reaction in ether rather than THF increased the yield of Peterson product **4** to 72%. The remaining starting material **3** (25%) was desilylated by treatment with sodium methoxide in methanol to give 1-methyl-5-phenyltetrazole, which was readily separated from the alkenyltetrazole **4**.

Photolysis of 1-*Alkenyltetrazoles: Preparation and Rearrangement of* 4H-*Imidazoles.*—Irradiation of a light petroleum solution of the alkenyltetrazole **4** at 254 nm for 2 h resulted in the complete disappearance of starting material and the formation of a single product (TLC). Evaporation of the solvent and careful sublimation of the resulting oily solid gave the 4*H*-imidazole **5** as colourless crystals (69%). In contrast to 4,4-dimethyl-2-phenyl-4*H*-imidazole,[1] the 5-unsubstituted 4*H*-imidazole **5** showed no tendency to undergo facile nucleophilic attack by water during chromatography on silica gel. Although compound **5** could be sublimed with high recovery at 50–55 °C, it rearranged cleanly and quantitatively in [$^2H_6$]-DMSO during the acquisition of its ^{13}C NMR spectrum to



give the known 2-phenyl-4,5,6,7-tetrahydrobenzimidazole **6**.[4] Examination of the spectra taken at intervals during the accumulation and applying the first-order rate equation gave a $t_{\frac{1}{2}}$ of 5.2 h at 35 °C for the 1,5-alkyl shift. Even allowing for the less accurate determination of the half life, this is apparently a more rapid rearrangement than that of the 4-methyl group in 4,4-dimethyl-2-phenyl-4*H*-imidazole which has a $t_{\frac{1}{2}}$ of 30 min at 120 °C in [$^2H_6$]-DMSO.

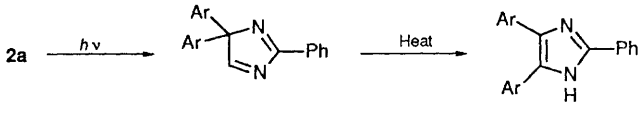
We also investigated the thermal rearrangement of the 4*H*-imidazole **7**, since it would be expected to undergo sigmatropic rearrangement to another 4*H*-imidazole **8**, the methyl substituted version of **5**, and it was of interest to see where the equilibrium between these two non-aromatic heterocycles lay.



7 **8**

The effect of heat on compound **7**, prepared as previously described,[1] was examined by means of variable temperature NMR. Whilst the methylene region of the spectrum was relatively complex, it contained a sharp singlet at δ 1.25 for the 4-methyl group. The first sign of any change in the spectrum on heating (in steps of 25 °C; total time for heating to and equilibration at the new temperature = 15 min) was at 75 °C when a new singlet appeared at δ 2.35. As the temperature was increased to 170 °C the relative size of the new peak increased to 22% of the total methyl peaks. Given the chemical shift of this peak and the concomitant appearance of a methylene multiplet at δ 1.95, it seemed clear that **7** was rearranging to the isomeric **8** as expected. The process is an equilibrium one, as no increase in the proportion of **8** was observed after the first few minutes. The rearrangement was again very clean, there being no evidence of other products, *e.g.* from migration to nitrogen, nor of any intermediate. The proportion of **8** remained at roughly 20% on cooling to room temperature.

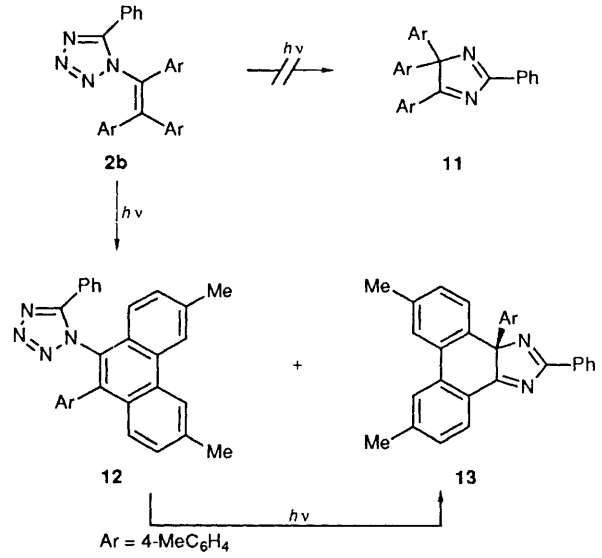
Irradiation of the tetrazole **2a** in cyclohexane for 3 h gave, after evaporation, a yellowish oil, the NMR spectrum of which confirmed the presence of the 4*H*-imidazole **9** (*ca.* 70%). However, attempted purification of the imidazole **9** by sublimation resulted in its conversion into the known[5] triarylimidazole **10**, isolated in 68% yield overall.



9 **10**

Ar = 4-MeC$_6$H$_4$

In contrast with these results, irradiation of the methyl substituted tetrazole **2c** gave a mixture of several compounds. Despite extensive chromatography, no pure compounds could be isolated, although the NMR spectrum suggested that a small amount (< 10%) of the desired 4*H*-imidazole was present. The lack of success with this reaction is possibly due to steric effects of the heavily substituted alkene and, in line with this, the alkenyltetrazole **2b** also failed to give the expected 4*H*-imidazole **11** on irradiation in methanol (since photolysis in cyclohexane was extremely slow) (Scheme 4). However, in this case, three discrete compounds were isolated, together with two minor components. We were able to identify two of the three products, the major of which was assigned the phenanthrene structure **12** on the basis of its spectroscopic properties. In particular, the mass spectrum showed a molecular ion at *m*/*z* 440



Scheme 4 Ar = 4-MeC$_6$H$_4$

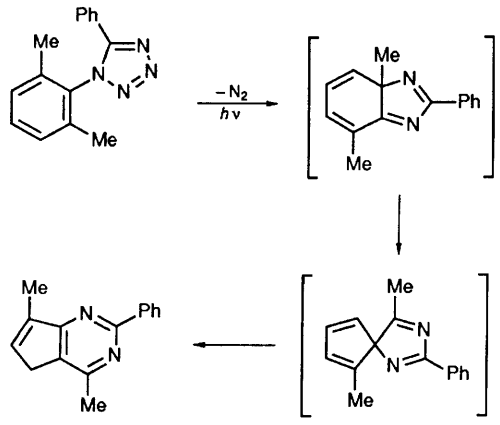
indicating the loss of 2 hydrogens from the starting material, and the ^{1}H NMR spectrum suggested the presence of a condensed aromatic ring system. Structure **12** was eventually confirmed by X-ray crystallography,[6] which also showed that the aryl and tetrazole rings at the 9 and 10 positions were almost orthogonal to the phenanthrene system.[7] Given the steric crowding around the phenanthrene 9 and 10 positions it was of interest to examine the temperature variable NMR of **12**. From the spectra, together with computer simulated lineshape analysis, using the program 'DNMR 3H', the activation energy for racemisation of **12** by rotation about the C-10 to tetrazole N-1 bond is calculated as 91 ± 5 kJ mol^{-1}, a reasonable value for hindered rotation in a system of such rigidity.[7]

Since the formation of phenanthrene **12** required an oxidative photocyclisation, which must have been faster than decomposition of the tetrazole ring, the tetrazole **2b** was irradiated in the presence of air and a trace of iodine. Under these oxidative conditions, the phenanthrene **12** could be isolated in yields of up to 97%.

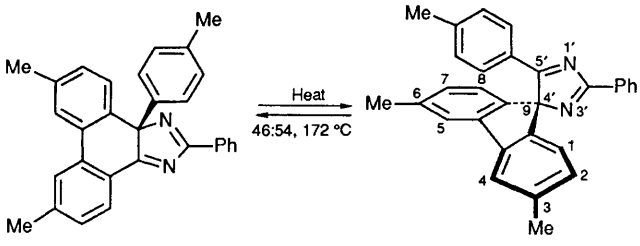
The structure of the second major product form the photolysis of tetrazole **2b** was not immediately obvious from its spectroscopic properties, but the molecular ion at *m*/*z* 412 suggested that it might have been formed from **12** by loss of nitrogen. This was established in a separate experiment by prolonged irradiation of **12** which gave the unknown product in 62% yield. On this basis, the product was assigned the 4*H*-imidazole structure **13**, which is a 3a*H*-phenanthro-[9,10-*d*]imidazole formed by nitrogen extrusion and electrocyclisation of the resulting imidoylnitrene.

Although the photolysis of alkenyltetrazole **2b** did not give the expected 4*H*-imidazole **11**, one of the products **13** is a 4*H*-imidazole derivative. Alternatively, it can be considered as a 3a*H*-benzimidazole stabilised by benzannelation. We have previously proposed 3a*H*-benzimidazoles as intermediates in the conversion of *ortho*-blocked *N*-aryltetrazoles into cyclopentapyrimidines (Scheme 5),[8] and therefore we were interested to see if the 3a*H*-benzimidazole **13** could be induced to undergo further rearrangement.

Compound **13** when heated in [$^2H_6$]-DMSO showed little change in its ^{1}H NMR spectrum until 112 °C. Above this temperature the formation of a new product was observed, and this was assigned the symmetrical spiro structure **14** on the basis of its spectroscopic properties. The thermal equilibrium of **13** and **14** was analysed by temperature variable ^{1}H NMR, exactly as for compounds **7** and **8** above. Spectra were obtained at



Scheme 5



13 14

10 min intervals over 1 h from the time the sample reached 112 °C. Each interval also corresponded to a rise in temperature of 10 °C to a maximum at 172 °C. A plot of the proportion of **14** in the mixture against time/temperature showed an initially exponential increase which rapidly levelled off to a constant proportion at *ca.* 165 °C. This proportion (58% by peak heights, 54% by peak areas) remained constant over time, and on cooling, and represents the attainment of equilibrium.

Experimental

All solvents were distilled before use. Petroleum refers to light petroleum, b.p. 40–60 °C, and ether refers to diethyl ether. THF and ether were distilled from potassium–benzophenone and sodium–potassium–benzophenone respectively, immediately prior to use. Lithiations were undertaken in magnetically stirred, oven-dried flasks closed with a rubber septum. The flasks were flushed with dry nitrogen before use and experiments were carried out under positive pressure of nitrogen. Additions and transfers were carried out with oven-dried glass syringes and stainless steel needles as required. Pressure equilibration with dry nitrogen was maintained at all times.

Photolyses were carried out in a Rayonet photochemical reactor using lamps emitting at 254 nm in quartz vessels. Unless otherwise stated solutions were purged with nitrogen for 0.5 h prior to irradiation, which was carried out under nitrogen purge. No cooling was employed, so that the typical temperature for photolyses was 35 °C. Thin layer chromatography (TLC) on commercial plates of silica gel 60 F_{254} on aluminium was used to monitor the progress of reactions. Column chromatography was carried out using silica gel 60H (E. Merck). IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer in the range 600–4000 cm^{-1} and calibrated against polystyrene. The spectra of solids were recorded as Nujol mulls and of oils as thin films between sodium chloride plates.

UV spectra were recorded in the range 200–450 nm on a Pye Unicam SP800 spectrophotometer in quartz cells of 0.5 cm path length. Unless otherwise stated the solvent was methanol.

^1H NMR spectra were recorded on one of three instruments as follows: Varian Associates EM-360 (60 MHz), Perkin-Elmer R32 (90 MHz), and Bruker WM 250 (250 MHz) according to the frequency specified. Tetramethylsilane (TMS) was used as an internal reference. Carbon-13 spectra were recorded on the Bruker instrument operating at 62.9 MHz. Mass spectra were recorded on a VG Micromass 7070B mass spectrometer. An ionising potential of 70 or 12 eV was employed using a direct insertion probe or septum inlet.

Acid Catalysed Dehydrations

Tetrazole **1** (R = H).—To a solution of the tetrazole **1** (R = H) (100 mg, 0.27 mmol) in dry benzene (5 ml) was added toluene-*p*-sulphonic acid (100 mg) and the mixture stirred for 12 h at 80 °C. Work-up and removal of the solvent by evaporation gave 1,1-*bis*(p-*tolyl*)-2-(5-*phenyltetrazol*-1-*yl*)-*ethene* **2a** (94.6 mg, 99%), m.p. 110–113 °C (ethanol) (Found: C, 78.2; H, 5.8; N, 15.9. $C_{23}H_{20}N_4$ requires C, 78.4; H, 5.7; N, 15.9%); $\nu_{max}(CCl_4)/cm^{-1}$ 3040, 2930, 1612s, 1510, 1460s, 1415, 1290, 1185, 1115 and 690vs; λ_{max}/nm 209 (log ε 4.31), 241 (4.26) and 290sh; δ(250 MHz, $CDCl_3$) 2.26 (3 H, s), 2.39 (3 H, s), 6.53 (2 H, br d, *J*/Hz 8), 6.87 (2 H, br d, *J*/Hz 8), 7.15–7.27 (5 H, m), 7.32–7.48 (3 H, m) and 7.57–7.63 (2 H, m); *m/z* 352 (M^+), 325, 323, 221, 191, 179, 115, 103, 77 and 57.

Tetrazole **1** (R = 4-MeC_6H_4).—To a solution of the tetrazole **1** (R = 4-MeC_6H_4) (324 mg, 0.703 mmol) in dry benzene (10 ml) was added PTSA (*ca.* 50 mg) and the mixture stirred 0.5 h at 80 °C. Work-up and crystallisation from chloroform–ether gave 1,1,2-*tris*(p-*tolyl*)-2-(5-*phenyltetrazol*-1-*yl*)*ethane* **2b** (217 mg, 70%), m.p. 237–240 °C (Found: C, 81.3; H, 6.0; N, 12.6. $C_{30}H_{26}N_4$ requires C, 81.4; H, 5.9; N, 12.7%); ν_{max}/cm^{-1} 3020, 1610, 1510, 1455, 1400, 1375, 815 and 695; λ_{max}/nm 209 (log ε 5.34), 240 (5.31) and 321 (4.99); δ(250 MHz, $CDCl_3$) 2.20 (3 H, s), 2.29 (3 H, s), 2.31 (3 H, s), 6.29 (2 H, ≃d, *J*/Hz 8), 6.72 (2 H, ≃d, *J*/Hz 8), 6.93–7.06 (8 H, m), 7.29–7.46 (3 H, m) and 7.54–7.60 (2 H, m); *m/z* 442 (M^+), 414, 399, 386, 311, 297, 282, 267, 252, 195, 179(base), 119 and 105.

An improved yield (estimated at 85% by NMR) was obtained when the isolation of tetrazolyl alcohol **1** (R = 4-MeC_6H_4) was omitted. A comparable reaction at 25 °C using TFA gave the tetrazole **2b** in only *ca.* 50% yield together with a number of side-products (TLC).

Reaction of the Tetrazole **2b** *with Methyl Iodide.*—To a solution of the tetrazole **2b** (200 mg, 0.568 mmol) in THF (10 ml) were added t-butyllithium in pentane (0.681 mmol, 1.2 equiv.) and after 0.75 h methyl iodide (0.043 ml, 0.681 mmol, 1.2 equiv.). The mixture was stirred for 2 h at −78 °C and allowed to warm to 20 °C over 16 h. Work-up and crystallisation from ether gave 1,1-*bis*(p-*tolyl*)-2-(5-*phenyltetrazol*-1-*yl*)*prop*-1-*ene* **2c** (207 mg, 99%), m.p. 153–154 °C (Found: C, 78.5; H, 6.1; N, 15.3. $C_{24}H_{22}N_4$ requires C, 78.7; H, 6.05; N, 15.3%); ν_{max}/cm^{-1} 3030, 1610, 1505, 1450, 1400, 1180, 820, 780, 750 and 700; δ(250 MHz, $CDCl_3$) 2.18 (3 H, s), 2.37 (3 H, s), 2.48 (3 H, s), 6.20 (2 H, m), 6.70 (2 H, m), 7.06 (2 H, m), 7.17 (2 H, m) and 7.34–7.43 (5 H, m); *m/z* 366 (M^+), 338, 323, 308, 297, 282, 235, 220, 205, 194, 179(base), 165, 152, 139, 129, 115, 105, 89 and 77.

Reaction of the Tetrazole **3** *with Cyclopentanone.*—To a solution of the tetrazole **3** (111 mg, 0.48 mmol) in ether (20 ml) was added t-butyllithium in pentane (0.49 mmol, 1.02 equiv.) and after 0.1 h a fine orange–red solid was precipitated. The mixture was stirred 0.5 h and cyclopentanone (0.085 ml, 0.96 mmol, 2.0 equiv.) was added. The mixture was quenched after 0.2 h and work-up gave an inseparable mixture of starting material **3** (27.8 mg, 25%) and the alkene **4** (78.1 mg, 72%) by NMR. The

product residue was desilylated (see below) to enable isolation of the alkene **4**. Similar reactions in THF and THF–HMPA gave the above products together with 5-phenyltetrazol-1-ylmethane.

Reaction of the Tetrazoles **3** *and* **4** *with Sodium Methoxide.*—To a solution of the tetrazole **3** (125 mg, 0.538 mmol) and the tetrazole **4** (104 mg, 0.460 mmol) in dry methanol (2 ml) at 0 °C was added a solution of sodium methoxide (0.8 mmol) in methanol (2 ml) [prepared by adding sodium metal (20 mg) to dry methanol (2 ml) and stirring]. The mixture was stirred for 0.25 h when work-up and chromatography gave (i) 5-*phenyltetrazol*-1-*ylmethylenecyclopentane* **4** (102 mg, 98%) as an oil [Found: $(M^+ + 1) = 227.1296$. $C_{13}H_{15}N_4 = 227.1297$]; ν_{max}/cm^{-1} 3070, 2960, 2870, 1605w, 1525w, 1455s, 1400, 1275, 1090, 780 and 730; δ(250 MHz, $CDCl_3$) 1.70–1.80 (4 H, m), 2.39–2.49 (2 H, m), 2.50–2.59 (2 H, m), 6.74 (1 H, ≃quintet, *J*/Hz 2.2), 7.48–7.58 (3 H, m) and 7.77–7.86 (2 H, m); *m*/*z* (14 eV) 227 ($M^+ + 1$), 198, 197, 171(base), 157, 143, 132, 118, 104, 93 and 81 and (ii) 5-phenyltetrazol-1-ylmethane (84 mg, 97%) identical (TLC, NMR) with an authentic sample.[2]

Photolysis of 1-*Alken*-1-*yltetrazoles*

A solution of the tetrazole in the solvent specified was irradiated under a stream of nitrogen. The irradiation was continued until no tetrazole remained (TLC) or for *ca.* 24 h. The products were respectively isolated by: (i) short-path sublimation onto a cold-finger from a round-bottomed vessel heated in an oil bath; (ii) crystallisation; (iii) chromatography.

Tetrazole **4**.—A solution of the tetrazole **4** (63 mg, 0.278 mmol) in petroleum (120 ml) (distilled twice from calcium hydride) was irradiated for 2 h. The solvent was removed by evaporation at 0–10 °C to leave a partly crystalline residue which was sublimed (0.45 Torr, bath temp. 45–60 °C) to give 2-*phenyl*-1,3-*diazaspiro*[4.4]*nona*-2,9-*diene* **5** (38.0 mg, 69%), m.p. 65–68 °C; δ(90 MHz, $CDCl_3$) 2.10 (8 H, m), 7.49 (3 H, m), 8.30 (2 H, m) and 8.80 (1 H, s); δ_C 17.1, 22.7, 83.2, 124.1, 126.8, 128.2, 140.0, 176.5 and 198.9. During the acquisition of the carbon-13 spectrum 4*H*-imidazole **5** underwent thermal rearrangement to 2-phenyl-4,5,6,7-tetrahydrobenzimidazole **6**, m.p. 297–298 °C (methanol) (lit.,[4] 298 °C). The first-order[1,9] rate equation was solved to give a half-life for the rearrangement of 5.2 h at 35 °C.

Tetrazole **2a**.—A solution of the tetrazole **2a** (103 mg, 0.292 mmol) in cyclohexane (120 ml) was irradiated for 3 h. The solvent was removed by evaporation to give 4,4-bis(*p*-tolyl)-2-phenyl-4-*H*-imidazole **9** (*ca.* 70% by NMR); δ(90 MHz, $CDCl_3$) 2.30 (6 H, s), 7.02–7.35 (8 H, m), 7.35–7.51 (3 H, m), 8.05–8.15 (2 H, m) and 9.12 (1 H, s) in a mixture and it was attempted to sublime the residue (0.02 Torr, bath temp. 45–100 °C). Since only a trace quantity of sublimate was apparent after 0.33 h the apparatus was allowed to cool, when the residue crystallised. Recrystallisation from chloroform–petroleum gave 4,5-bis(*p*-tolyl)-2-phenylimidazole **10** (65 mg, 68%), m.p. 273–274 °C (lit.,[5] 269–271 °C).

Tetrazole **2b**.—A solution of the tetrazole **2b** (43.3 mg, 0.098 mmol) in methanol (30 ml) was irradiated for 28 h. Analysis of the solution by TLC showed that the starting material had been consumed. The solvent was removed by evaporation and the residue was chromatographed to give: (i) a component (5.4 mg, 13.5%) which had *inter alia* δ(250 MHz, $CDCl_3$) 2.27 (3 H, s), 2.41 (3 H, s), 2.44 (3 H, s) and 2.48 (3 H, s); all other resonances between δ 6.95 and 7.95 (complex). (ii) 7,9-Dimethyl-3a-(*p*-tolyl)-2-phenyl-3a*H*-phenanthro[9,10-*d*]imidazole **13** (2.0 mg, 5%) as an amorphous solid; ν_{max}(Nujol mull)/cm^{-1} 3020, 1610vs, 1575, 1555, 1500, 1315, 1055, 825, 810, 725 and 710 cm^{-1}; $\nu_{max}(CCl_4)/cm^{-1}$ 3030, 2920, 2860, 1610vs, 1500w, 1485w, 1445, 1315, 1280, 1055, 910 and 690; λ_{max}/nm 207 (log ε 4.02), 217sh, 262 (4.09), 270sh and 295sh tailing to 400; δ(250 MHz, $CDCl_3$) 2.18 (3 H, s), 2.44 (6 H, s) [gives 2 × (3 H, s) in [$^2H_6$]-DMSO or [$^2H_6$]-benzene], 6.78 (2 H, m), 6.90 (2 H, m), 7.18 (1 H, ≃d, *J*/Hz 8), 7.21 (1 H, ≃d, *J*/Hz 8), 7.48–7.55 (3 H, m), 7.66 (1 H, ≃s), 7.69 (1 H, ≃s), 7.80 (1 H, d, *J*/Hz 8), 7.84 (1 H, d, *J*/Hz 8) and 8.45–8.52 (2 H, m) (in an n.O.e.d. experiment irradiation of the signal at δ 2.44 caused 10, 12, 10 and 6% enhancements of the signals at δ 7.18, 7.21, 7.66 and 7.69 respectively, irradiation of the signal at δ 6.78 caused 11, 0.8 and 4% enhancements of the signals at δ 6.90, 7.80 and 7.84 respectively, irradiation of the signal at δ 6.90 caused 3 and 14% enhancements of the signals at δ 2.18 and 6.78 respectively, irradiation of the signal at δ 7.69 caused 3 and 20% enhancements of the signals at δ 2.44 and 7.66 respectively, irradiation of the signal at δ 7.80 caused 0.4 and 10% enhancements of the signals at δ 6.78 and 7.18 respectively and irradiation of the signal at δ 7.84 caused 1 and 9% enhancements of the signals at δ 6.78 and 7.21 respectively); δ_C 20.8, 21.4, 22.0, 91.1, 124.5, 125.5, 126.0, 128.4, 129.0, 129.2, 129.5, 131.2, 132.4, 132.9, 134.7, 135.2, 137.2, 137.4, 138.0, 143.3, 174.0 and 200.1; *m*/*z* 413, 412 (M^+)(base), 309, 295, 282, 224, 210, 192, 165, 119, 111, 105, 97, 91, 85, 77, 71 and 57; and (iii) 3,6-*dimethyl*-9-(p-*tolyl*)-10(5-*phenyltetrazol*-1-*yl*)*phenanthrene* **12** (7.7 mg, 18%), m.p. 243–244 °C (chloroform–ether) (Found: C, 81.6; H, 5.6; N, 12.65. $C_{30}H_{24}N_4$ requires C, 81.8; H, 5.5; N, 12.7%); $\nu_{max}(CCl_4)/cm^{-1}$ 3030, 2920, 2865, 1620br, 1510, 1465, 1410, 1095, 910 and 690; λ_{max}/nm 212 (log ε 4.51), 230 (4.52), 253 (4.65), 260 (4.69), 271sh, 300 (4.01) and 312 (4.03), tailing to 360; δ(250 MHz, $CDCl_3$) 2.29 (3 H, s), 2.65 (3 H, s), 2.68 (3 H, s), 6.28 (1 H, dd, *J*/Hz 4.9 and 1.2), 6.81 (1 H, dd, *J*/Hz 4.9 and 0.9), 6.97 (1 H, dd, *J*/Hz 4.9 and 1.2), 7.06 (1 H, dd, *J*/Hz 4.9 and 0.9), 7.11–7.27 (5 H, m), 7.29–7.38 (2 H, m), 7.47 (2 H, d, *J*/Hz 5.2), 8.63 (1 H, br s) and 8.66 (1 H, br s) (in an n.O.e.d. experiment irradiation of the signal at δ 2.29 caused 115 and 92% enhancements of the signals at δ 6.81 and 7.06 respectively, irradiation of the signal at δ 2.65 caused 73 and 76% enhancements of the signals at δ 7.33 and 8.66 respectively, irradiation of the signal at δ 2.68 caused 37 and 72% enhancements of the signals at δ 7.47 and 8.63 respectively, irradiation of the signal at δ 6.28 caused 133 and 33% enhancements of the signals at δ 6.81 and 7.47 respectively, irradiation of the signal at δ 6.81 caused 23 and 162% enhancements of the signals at δ 2.29 and 6.28 respectively and irradiation of the signal at δ 7.47 caused 3, 24, 69, 92 and 66% enhancements of the signals at δ 2.29, 2.68, 6.28, 7.17 and 7.33 respectively); *m*/*z* (10 eV) 440 (M^+), 412(base), 309, 199, 120, 103, 94, 73 and 45.

Tetrazole **2b**: *Dehydrocyclisation under Modified Conditions.*—A solution of tetrazole **2b** (263 mg, 0.594 mmol) and iodine (2 crystals) in 10% (v/v) dichloromethane in cyclohexane (80 ml) was irradiated under air purge for 1 h. The solution was washed with 10% aq. sodium metabisulphite (10 ml), water (5 ml), and satd. brine (10 ml) and dried ($MgSO_4$). The solvent was removed by evaporation and the residue was recrystallised from 50% ethanol in chloroform to give the tetrazolophenanthrene **12** (253.2 mg, 97%) in two crops, m.p. 243–244 and 240–243 °C respectively.

Tetrazole **12**.—A solution of the tetrazole **12** (120.3 mg, 0.273 mmol) in methanol (120 ml) was irradiated for 24 h. The solvent was removed by evaporation and the residue was chromatographed to give (i) the phenanthro[9,10-*d*]imidazole **13** (48 mg, 43%) identical (TLC, IR, NMR) with material isolated from the photolysis of the tetrazole **2b** and (ii) starting material **12** (38 mg, 32%).

Thermal Rearrangements of Non-aromatic Heterocycles: General Procedure.—A solution of the imidazole (*ca.* 20 mg) in [$^2H_6$]-DMSO (0.5 ml) was placed in a 5 mm NMR tube with a tightly fitting cap and placed in the Bruker WM-250 machine arranged for variable temperature (VT) operation. The thermocouple was calibrated prior to insertion (error ±2 °C) and spectra were recorded against [$^2H_5$]-DMSO internal standard (δ 2.49) at standard time intervals which also corresponded to a preset standard temperature rise, to a maximum of 172 °C (445 K). Intervals were chosen such that the instrument had time to equilibrate at the new temperature prior to fine tuning and measurement. At least one spectrum was recorded during the cooling procedure, which was exactly the reverse of that on heating, and on reaching room temperature.

4H-*Imidazole* **7**.—The spectrum showed a new singlet (sharp) at δ 2.37 at 75 °C (348 K) and a plot of the log of the relative height of this peak in the spectrum against temperature/time was linear to *ca.* 125 °C (398 K) and showed no increase thereafter. The simultaneous appearance of a methylene multiplet at δ 1.89–2.04 was also noted, indicating the formation of 9-*methyl*-2-*phenyl*-1,3-*diazaspiro*[4.4]*nona*-2,9-*diene* **8** (*ca.* 22% by peak heights of methyl groups). Spectra obtained during cooling and on reaching 24 °C were identical, apart from minor temperature shift effects, to that obtained at 172 °C.

In a separate experiment a solution of 4*H*-imidazole **7** (39.8 mg, 0.19 mmol) in ODCB (10 ml) was heated under nitrogen at 180 °C for 70 h. Examination by TLC and NMR of the residue on evaporation after 3.5 and 70 h showed that in each case it was identical with that obtained from the VT experiment.

4H-*Imidazole* **13**.—From 112 °C (385 K) the gradual appearance of 3,6-dimethyl-5′-(*p*-tolyl)-2′-phenylspiro[fluorene-9,4′(4*H*)-imidazole **14**, δ 2.23 (3 H, s), 2.43 (6 H, s), 6.73 (2 H, d, *J*/Hz 7.6), 7.02 (4 H, br d, *J*/Hz 8), 7.38 (2 H, ≃d, *J*/Hz 8.3), 7.50–7.60 (3 H, m), 7.78 (2 H, ≃s) and 8.32–8.41 (2 H, m) was observed. A plot of the log of the ratio of **14** to **13** (by peak heights of methyl groups) in the mixture against temperature/time was linear over the range 112–148 °C and showed no increase on further heating or over time. The proportions of the two components (54:46) remained constant during and after cooling to 24 °C.

Acknowledgements

We thank Dr. R. Jones and Dr. D. J. Williams for the X-ray structure determination of compound **12**.

References

1 Part 1, M. Casey, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1389.
2 C. J. Moody, C. W. Rees and R. G. Young, *J. Chem. Soc., Perkin Trans. 1*, 1991, preceding paper.
3 C. J. Moody, C. W. Rees and R. G. Young, *J. Chem. Soc., Perkin Trans. 1*, 1991, 323.
4 R. Weidenhagen and H. Wegner, *Chem. Ber.*, 1938, **71**, 2124.
5 H. Tanino, T. Kondo, K. Okada and T. Goto, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1474.
6 R. Jones and D. J. Williams, Chemistry Department, Imperial College, unpublished results.
7 R. G. Young, Ph.D. Thesis, University of London, 1989.
8 T. L. Gilchrist, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1871.
9 C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.

Paper 0/03362F
Received 24*th July* 1990
Accepted 16*th August* 1990