# The Thermolysis of Polyazapentadienes. Part 4.[1,2] Formation of Indoles and Quinoxalines from 5-(2,6-Disubstituted phenyl)-1,2,5-triazapentadienes and Related Compounds

**Hamish McNab**
*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ*

7-Methylindole and 5-substituted quinoxalines are the principal cyclised products from the gas-phase thermolyses of the hydrazones (2) and (5) and of the oxime ether (7). Both heterocyclic systems arise by competitive decomposition of the spirodienyl radical, *e.g.* (18), the indole by loss of MeCN and a hydrogen atom, and the quinoxalines by loss of a methyl radical.

In earlier parts of this series, we have shown that arylimino-iminyl radicals, generated from 1,2,5-triazapentadienes or from 2,5-diaza-1-oxapentadienes, cyclise to give quinoxalines:[3] the reaction proceeds in part by direct cyclisation, and in part *via* the spirodienyl radical (1) (Scheme 1).[1,4,5] A further complication arises with *o*-substituted aryliminoiminyl radicals, which give mixtures of the 5-substituted quinoxaline and quinoxaline itself, owing to competitive ejection of a hydrogen atom and the substituent.[6] In the present work we sought to remove this ambiguity by the use of *two ortho* blocking groups, and also by this means to gain further information on the role of the spirodienyl radical intermediate.

With these objectives in mind, the radical precursors (2)—(5) and (7) were chosen, (*cf.* refs. 1 and 6). All were prepared by standard methods,[1,3,6] though longer reaction times in the formation of the imine functions were sometimes required in the present examples because of the additional steric requirements. For example, the formation of the imine (6) in reasonable yield from 2,6-dimethylaniline and pyruvaldehyde monoxime required 20 days at room temperature, whereas the anil (6; $R^1 = R^2 = H$) is formed in a few hours under these conditions. Attempts to prepare the corresponding hydrazone (9) failed completely, for similar reasons.

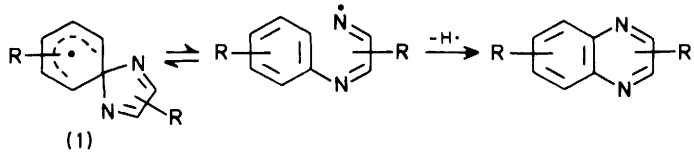
The derivatives (2)—(8) had characteristic spectra.[1,3] For example, the $^1H$ n.m.r. spectra of the 4-methyl oxime (6) and the oxime ether (7) showed the presence of two isomers [1] in the ratio 1 : 5 and 1 : 6 respectively, whereas the 3-methyl hydrazone (5) was formed as a single isomer.

As expected, 5-methylquinoxaline (10) (40%) was the only quinoxaline obtained by the gas-phase pyrolysis of the 5-(2,6-dimethylphenyl)-1,2,5-triazapentadiene (2) (Scheme 2). By analogy with earlier work,[3,6] the quinoxaline must arise by generation of the iminyl radical, followed by cyclisation with loss of a methyl radical (*cf.* Scheme 1). The presence of methyl radicals in the gas phase was substantiated by the isolation of *N*-methylaniline (21%), formed by coupling with the predominant phenylaminyl radicals. These also give rise to the aniline (40%) detected in the pyrolysate. An additional product (32%), whose formation could not have been predicted on the basis of earlier Schemes, was 7-methylindole (11) (see below). Confirmation of the identity of this material was complicated by the fact that the chemical shifts and the pattern of the aromatic signals in its $^1H$ n.m.r. spectrum are strongly concentration dependent. However the $^{13}C$ n.m.r. signals [7] of its non-quaternary carbon atoms were identical with those of an authentic sample.

Pyrolysis of the 5-(2,6-dimethoxyphenyl) and 5-(2,6-dichlorophenyl) derivatives (3) and (4) was less successful. At most, only traces of the expected 5-substituted quinoxalines were detected in the complex pyrolysates. The precursors (3) and (4) decomposed to a significant extent in the inlet to give quantities of the appropriate 2,6-disubstituted aniline,[6] and a considerable amount of involatile residue.

In order to study the involvement of the spirodienyl radicals [*cf.* (1)] in these reactions, the isomeric *C*-methyl iminyl radicals (12) and (13) were generated from the hydrazone (5) and the oxime ether (7) respectively (Scheme 3). Co-products from the hydrazone (5) included aniline and *N*-methylaniline, while the nitrile (14) (4%) was obtained from the oxime ether. The nitrile (14) was identical with an authentic sample obtained by pyrolysis of the oxime ester (8) (*cf.* ref. 1).

The heterocyclic products obtained from the hydrazone (5) and the oxime (7) are of particular interest (Scheme 3). In *both* cases, 7-methylindole (10) is the major product (62 and 55% respectively) together with only a trace of 2,7-dimethylindole (11) (3 and 5% respectively). The quinoxalines form a much smaller proportion of the total products in these examples. Problems in $^1H$ n.m.r. spectroscopic analysis of the crude pyrolysates were caused by the presence of 7-methylindole, which acts as a shift reagent. For example, the 2-protons and methyl protons of an authentic mixture of 2,5- and 2,8-dimethylquinoxaline resonate at 8.70 (2 s) and 2.76 (s) p.p.m. respectively, but in the presence of an excess of 7-methylindole, these are shifted to 8.65 (2 s), and 2.77 (s) and 2.71 (s) respectively. However, samples of the quinoxaline fractions from (5) and (7), isolated by preparative g.l.c., were identical by $^1H$ n.m.r. with an authentic mixture of 2,5- and 2,8-dimethylquinoxaline (16) and (17), and in both cases the isomer whose 3-proton resonates at lower frequency is present in greater amounts. This isomer has previously [8] been identified by $^{13}C$ n.m.r. as 2,8-dimethylquinoxaline (17). Conclusive proof for the presence only of isomers (16) and (17) was obtained from the $^{13}C$ n.m.r. spectrum of the quinoxaline fraction isolated from the pyrolysis of the oxime (7). Major (*i.e.* non-quaternary) peaks in the $sp^2$ region were shown at δ 145.34, 129.74, 128.36 and 126.94 p.p.m. [δ (2,8-dimethyl-

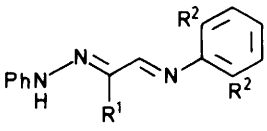



**Scheme 1.**

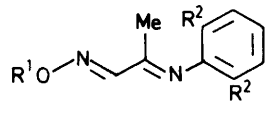
quinoxaline)[8] 144.95, 129.34, 127.98 and 126.55 p.p.m.], with minor peaks occurring at δ 144.53, 129.59, 128.86, and 126.52 p.p.m. [δ (2,5-dimethylquinoxaline)[8] 144.13, 129.20, 128.46, and 126.12 p.p.m.]. Allowing for a consistent systematic difference of 0.4 p.p.m., the two sets of data are identical.

The formation of (17) as the major quinoxaline from (5) is a significant result. This can arise from the iminyl (12) only *via* the spirodienyl (18) (Scheme 4). Earlier assumptions[1,4] that the nitrogen atoms in spirodienyl radicals (1) [or (18)] would have equal migration tendencies are now shown to be invalid, since on this basis the total involvement of (18) would give an amount of the quinoxaline (17) which could, at most, only equal that of (16). No quantitative information on the relative involvement of spirodienyl and direct cyclisation pathways can therefore be obtained in this case, though it is clear from the overall similarity in product distribution from the precursors (5) and (7) that the reactions proceed to a great extent *via* the common intermediate (18). The production of the quinoxaline (17) from (18) involves migration of the nitrogen atom furthest from the five-membered ring substituent, which presumably takes place for steric reasons.

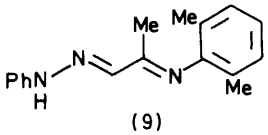
Formation of the indoles (10) and (15) requires loss of a hydrogen atom and MeCN or HCN respectively from the iminyl radicals (12) and (13) and again the similarity in relative yields of these products from both precursors strongly implicates the spirodienyl (18) as the key intermediate in these reactions (Scheme 4). Thus cleavage of the appropriate nitrile from (18) generates the nitrile ylides (19) and (20) which probably lead to the indole skeleton by a 1,3-dipolar cycloaddition. The high selectivity in loss of MeCN *vs.* HCN clearly explains the increase in the yields of indoles in these reactions in comparison with the products from (2), but the effect is difficult to rationalise except by a possible steric buttressing effect in the transition state from (18). It is hoped that work in progress will identify other examples of this selectivity in related systems.



(2) $R^1$ = H, $R^2$ = Me
(3) $R^1$ = H, $R^2$ = OMe
(4) $R^1$ = H, $R^2$ = Cl
(5) $R^1$ = $R^2$ = Me



(6) $R^1$ = H, $R^2$ = Me
(7) $R^1$ = $R^2$ = Me
(8) $R^1$ = MeCO, $R^2$ = Me

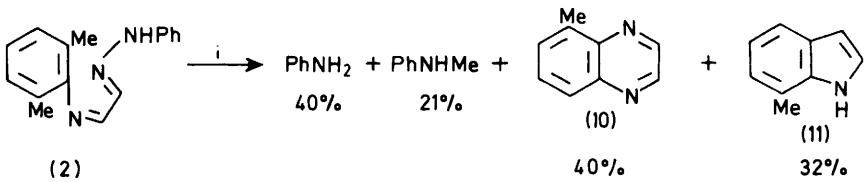


(9)

## Experimental

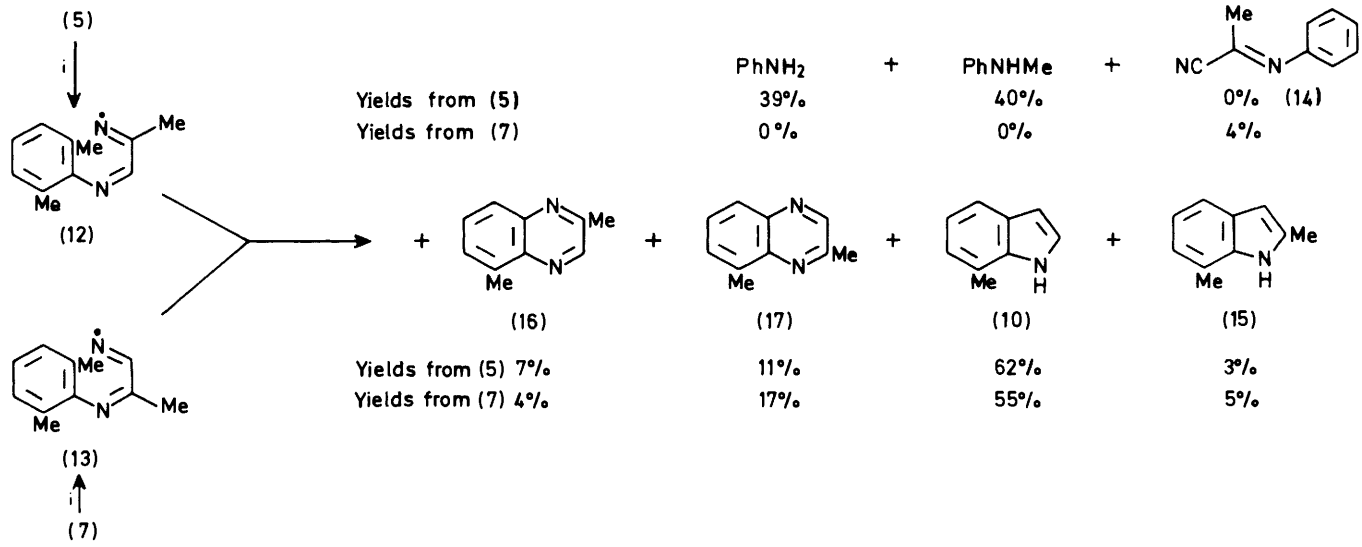
Ether refers to diethyl ether.

1,2,5-*Triazapentadienium Salts*.—The following 5-aryl-1-phenyl-1*H*-1,2,5-triazapentadienium perchlorates were made by the general method given in Part 1:[3] 5-(2,6-*dimethylphenyl*) (71%), m.p. 198—199 °C (from ethanol–ether), δ ([$^2H_6$]-acetone) 8.87 (1 H, d), 7.2—7.5 (9 H, complex), and 2.30 (6 H, s) (Found: C, 54.85; H, 5.2; N, 11.85. $C_{16}H_{18}ClN_3O_4$ requires C, 54.6; H, 5.1; N, 11.95%); 5-(2,6-*dimethoxyphenyl*) (70%), m.p. 170—171 °C (from ethanol), δ ([$^2H_6$]acetone) 9.09 (1 H, d), 8.13 (1 H, d), 6.8—7.6 (8 H, complex), and

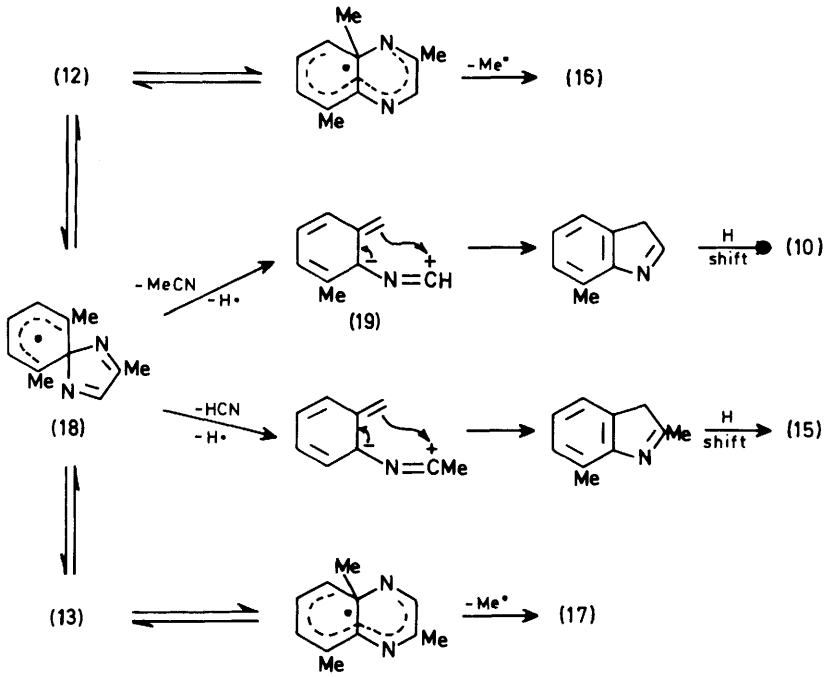



(2) (10) (11)

**Scheme 2.** *Conditions:* i, 600 °C, $10^{-2}$ Torr




**Scheme 3.** *Conditions:* i, 600 °C, $10^{-2}$ Torr



Scheme 4.

3.98 (6 H, s) (Found: C, 49.9; H, 5.3; N, 10.25. $C_{16}H_{18}ClN_3O_6 \cdot \frac{1}{2}EtOH$ requires C, 50.2; H, 5.15; N, 10.35%) and 5-(2,6-*dichlorophenyl*) (61%), m.p. 185—186 °C (second crop from preparation: compound could not be satisfactorily recrystallised), δ ([$^2H_6$]acetone) 8.87 (1 H, d), 8.25 (1 H, d), and 7.2—7.7 (8 H, complex) (Found: C, 43.05; H, 3.2; N, 10.7. $C_{14}H_{12}Cl_3N_3O_4$ requires C, 42.8; H, 3.05; N, 10.7%); and 3-*methyl*-5-(2,6-*dimethylphenyl*) (82%), m.p. 191—192 °C (decomp.) (from ethanol), δ ([$^2H_6$]dimethyl sulphoxide) 10.60 (br s), 8.42 (1 H, s), 7.1—7.7 (8 H, complex), and 2.35 and 2.25 (9 H, 2 s) (Found: C, 55.75; H, 5.65; N, 11.35. $C_{17}H_{20}ClN_3O_4$ requires C, 55.8; H, 5.45; N, 11.5%). Attempts to prepare the corresponding 4-methyl derivative by a variety of methods were without success.

1,2,5-*Triazapentadienes*.—The following 5-aryl-1-phenyl-1*H*-1,2,5-triazapentadienes were prepared from the corresponding salt, either by the sodium carbonate method,[3] or by the potassium hydroxide method:[6] 5-(2,6-*dimethylphenyl*) (2) (92%), m.p. 152—153 °C (from cyclohexane), δ ([$^2H_6$]dimethyl sulphoxide) 11.10 (1 H, s), 7.88 (1 H, d), 7.75 (1 H, d), 6.8—7.4 (8 H, complex), and 2.05 (6 H, s); *m/z* 251 ($M^+$, 100%), 174 (23), 146 (10), 144 (19), 131 (74), 105 (17), 93 (26), 77 (38), and 65 (16) (Found: C, 76.6; H, 7.05; N, 16.75. $C_{16}H_{17}N_3$ requires C, 76.5; H, 6.75; N, 16.75%); 5-(2,6-*dimethoxyphenyl*) (3) (74%), m.p. 116—118 °C (decomp.) (from cyclohexane), δ ([$^2H_6$]dimethyl sulphoxide) 11.04 (1 H, s), 8.12 (1 H, d), 7.70 (1 H, d), 6.5—7.4 (8 H, complex), and 7.72 (6 H, s); *m/z* 283 ($M^+$, 100%), 178 (11), 163 (52), 153 (22), 148 (20), 138 (19), 93 (20), 92 (18), 77 (30), and 65 (20) (Found: C, 67.6; H, 6.1; N, 14.85. $C_{16}H_{17}N_3O_2$ requires C, 67.85; H, 6.0; N, 14.85%); 3-*methyl*-5-(2,6-*dimethylphenyl*) (5) (87%), m.p. 109—110 °C (from cyclohexane); δ ([$^2H_6$]dimethyl sulphoxide) 9.95 (br s), 7.79 (1 H, s), 6.8—7.4 (8 H, complex), and 2.24 and 2.02 (9 H, 2 s); *m/z* 265 ($M^+$, 100%), 250 (27), 160 (23), 145 (43), 144 (43), 132 (87), 131 (90), 117 (23), 105 (63), 93 (93), 92 (60), 79 (37), 77 (87), and 65 (67) (Found: C, 77.25; H, 7.3; N, 15.85. $C_{17}H_{19}N_3$ requires C, 77.0; H, 7.15; N, 15.85%).

5-(2,6-*Dichlorophenyl*)-1-*phenyl*-1H-1,2,5-*triazapentadiene* (4).—Triethylamine was added dropwise, with shaking, to a suspension of the triazapentadienium perchlorate (0.39 g, 1 mmol) in ether (30 ml), until the red solid had disappeared, and the solution had become bright yellow in colour. The precipitate of triethylammonium perchlorate was filtered off, and the filtrate was concentrated and triturated with hexane. The *triazapentadiene* (0.27 g, 95%) so obtained had m.p. 169—171 °C (decomp.) (from toluene at −30 °C), δ ([$^2H_6$]dimethyl sulphoxide) 11.38 (1 H, s), 8.02 (1 H, d), 7.77 (1 H, d), and 6.8—7.7 (8 H, complex); *m/z* 295 ($M^+$, 11%), 293 (48), 291 (70), 216 (19), 214 (26), 188 (33), 186 (48), 151 (37), 92 (93), 91 (100), 77 (44), and 65 (41) (Found: C, 59.75; H, 4.2; N, 13.8. $C_{14}H_{11}Cl_2N_3 \cdot 1/5C_7H_8$ requires C, 59.55; H, 4.05; N, 13.55%). (The presence of toluene of crystallisation is substantiated by the peaks at *m/z* 92 and 91 in the mass spectrum.)

4-*Methyl*-5-(2,6-*dimethylphenyl*)-2,5-*diaza*-1-*oxapentadiene* (6).—Prepared from pyruvaldehyde mono-oxime and 2,6-dimethylaniline in ethanol (*cf.* ref. 1) this *oxime anil* was obtained in 64% yield after 20 days at room temperature, m.p. 169—171 °C (from ethanol); δ($CDCl_3$) (major isomer) 8.09 (1 H, s), 6.9—7.1 (3 H, complex), 1.98 (6 H, s), and 1.83 (3 H, s); *m/z* 190 ($M^+$, 70%), 175 (100), 158 (30), 146 (65), 131 (15), 105 (50), 103 (15), 79 (20), and 77 (30) (Found: C, 69.3; H, 7.3; N, 14.55. $C_{11}H_{14}N_2O$ requires C, 69.45; H, 7.35; N, 14.75%).

1,4-*Dimethyl*-5-(2,6-*dimethylphenyl*)-2,5-*diaza*-1-*oxapentadiene* (7).—Obtained in 75% yield by alkylation of the above oxime using methyl iodide and potassium carbonate in dimethylformamide (DMF) (*cf.* ref. 1) this *ether* had b.p. 88—90 °C (0.1 Torr); δ($CDCl_3$) (major isomer) 7.88 (1 H, s), 6.8—7.1 (3 H, complex), 3.98 (3 H, s), 1.95 (6 H, s), and 1.81 (3 H, s); *m/z* 204 ($M^+$, 100%), 189 (72), 173 (19), 158 (36), 146 (69), 131 (10), 105 (47), 79 (17), 77 (28), and 39 (11) (Found: C, 70.55; H, 7.8; N, 13.9. $C_{12}H_{16}N_2O$ requires C, 70.6; H, 7.85; N, 13.75%).

1-*Acetyl*-4-*methyl*-5-(2,6-*dimethylphenyl*)-2,5-*diaza*-1-*oxapentadiene* (8).—Acetylation of the oxime (6) using acetyl chloride in benzene,[1] gave the *oxime ester*, b.p. 128—130 °C (0.1 Torr) in 97% yield. The product, which was stored at −30 °C, had δ($CDCl_3$) 8.17 (1 H, s), 7.9—8.1 (3 H, complex), 2.20 (3 H, s), and 1.95 and 1.94 (9 H, 2 s); *m/z* 232 ($M^+$, 14%), 217 (5), 175 (38), 173 (25), 157 (57), 146 (100), 105 (88), 103 (34), 79 (39), 77 (66), 51 (23), 43 (54), and 39 (32) (Found: C, 67.25; H, 6.85; N, 11.9. $C_{13}H_{16}N_2O_2$ requires C, 67.25; H, 6.9; N, 12.1%).

2-(2,6-*Dimethylphenylimino*)*propanonitrile* (14).—The oxime ester (8) (1.16 g, 5 mmol) was distilled at 80—100 °C and 5 × $10^{-3}$ Torr during 90 min into the standard horizontal silica furnace, which was held at 650 °C. The pyrolysis was complete in 90 min. The crude pyrolysate was dissolved in methylene dichloride (10 ml) and was extracted once with sodium hydroxide solution (2M; 10 ml). The organic layer was dried ($Na_2SO_4$) and concentrated. The *nitrile* (0.60 g, 70%) was isolated as a mixture of two isomers (*ca.* 2 : 1) by bulb-to-bulb distillation at 70—72 °C (0.1 Torr); $\nu_{max.}$ 2 230, 1 640, 1 210, and 770 $cm^{-1}$; δ($CDCl_3$) (major isomer) 7.0—7.1 (complex), 2.53 (3 H, s), and 2.02 (6 H, s); (minor isomer) 7.0—7.1 (complex), 1.98 (6 H, s), and 1.93 (3 H, s), *m/z* 172 ($M^+$, 76%), 157 (100), 142 (21), 130 (16), 117 (13), 105 (16), 103 (13), 77 (26), 51 (13), and 39 (16) (Found: C, 76.95; H, 6.7; N, 16.05. $C_{11}H_{12}N_2$ requires C, 76.75; H, 7.0; N, 16.3%).

*Pyrolysis Experiments.*—Small-scale (0.5 mmol) pyrolyses were carried out as described in Part 1,[3] and the results are quoted as follows: precursor, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time, and major products, with their yields, and parent ions from g.l.c.-mass spectrometry (5%, SE30). In all cases the assigned products were identical by g.l.c. with authentic samples, and showed similar breakdown peaks in their mass spectra. Major products were isolated from large-scale (2—5 mmol) pyrolyses by preparative g.l.c. [10% SE30 on Chromosorb (40—60 mesh), unless otherwise stated].

5-(2,6-Dimethylphenyl)-1-phenyl-1*H*-1,2,5-triazapentadiene (119.6 mg, 0.48 mmol), 120 °C, 600 °C, 2—10 × $10^{-3}$ Torr, 20 min: aniline (40%), *m/z* 93; *N*-methylaniline (21%), *m/z* 107; 5-methylquinoxaline (40%), *m/z* 144; 7-methylindole (32%), *m/z* 131; residue in inlet 1%. On a preparative scale, the *base* (1.27 g, 5 mmol) was sublimed at 140—150 °C during 75 min through the furnace tube which was maintained at 650 °C and $10^{-2}$ Torr. The residue in the inlet was (0.06 g, 5%). The crude pyrolysate (1.14 g) was subjected to preparative g.l.c. at 120 °C to give *N*-methylaniline, δ($CDCl_3$) 7.1—7.3 (2 H, complex), 6.5—6.8 (3 H, complex), 3.65 (1 H, br s), and 2.82 (3 H, s); and to preparative g.l.c. at 150 °C, to give 5-methylquinoxaline,[8] δ($CDCl_3$) 8.81 (2 H, s), 7.6—8.0 (3 H, complex), and 2.80 (3 H, s); and 7-methylindole, δ($CDCl_3$) 7.84 (1 H, br s), 7.47 (1 H, dd), 7.0—7.2 (3 H, complex), 6.51 (1 H, dd, *J* 2.0 and 3.0 Hz), and 2.41 (3 H, s); $\delta_C$ ($CDCl_3$) 123.68, 122.34, 119.87, 118.31, 102.96, and 16.51 p.p.m. (quaternaries not detected) [authentic sample[7] δ($CDCl_3$) 135.25(q), 127.23(q), 123.71, 122.31, 120.04(q), 119.86, 118.29, 102.88, and 16.48 p.p.m.]

5-(2,6-Dimethoxyphenyl)-1-phenyl-1*H*-1,2,5-triazapentadiene (104.6 mg, 0.37 mmol), 100 °C, 600 °C, $10^{-2}$ Torr, 20 min. The major product was 2,6-dimethoxyaniline (51%), *m/z* 153. The possible presence of 5-methoxyquinoxaline could not be confirmed by g.l.c. comparison with an authentic sample[8] (5% SE30 and 5% Carbowax). Other minor products were not investigated. Residue in inlet >50%.

5-(2,6-Dichlorophenyl)-1-phenyl-1*H*-1,2,5-triazapentadiene (125.6 mg, 0.43 mmol), 120 °C, 600 °C, $10^{-2}$ Torr, 25 min. The major product was 2,6-dichloroaniline (37%), *m/z* 161, 163, 165, but 5-chloroquinoxaline[8] (13%), *m/z* 164, 166, was also obtained: the minor products were not investigated. Residue in inlet 19%.

3-Methyl-5-(2,6-dimethylphenyl)-1-phenyl-1*H*-1,2,5-triazapentadiene (110.0 mg, 0.42 mmol), 130 °C, 600 °C, 3—5 × $10^{-3}$ Torr, 40 min: aniline (39%), *m/z* 93; *N*-methylaniline (40%), *m/z* 107; 7-methylindole (62%), *m/z* 131; 2,5-dimethylquinoxaline (7%) and 2,8-dimethylquinoxaline (11%), *m/z* 158; 2,7-dimethylindole (3%), *m/z* 145, identical with an authentic sample by g.l.c. on 5% SE30 and 5% Carbowax: residue in inlet 0%. Pyrolysis of the *base* (2.12 g, 8 mmol) at 650 °C and 5—20 × $10^{-3}$ Torr (inlet temperature 150 °C) during 1 h gave a pyrolysate of 1.47 g (residue in inlet 0.31 g, 15%). Preparative g.l.c. on 10% SE30 at 120 °C gave *N*-methylaniline, δ($CDCl_3$) 7.1—7.3 (2 H, complex), 6.5—6.8 (3 H, complex), 3.58 (1 H, br s), and 2.80 (3 H, s), and on 10% Carbowax at 190 °C gave 2,5- and 2,8-dimethylquinoxaline,[8] δ($CDCl_3$) 8.68 and 8.71 (1 H, 2 s), 7.5—8.0 (3 H, complex), and 2.76 (6 H, 2 s), and 7-methylindole, δ($CDCl_3$) 8.0 (1 H, br), 7.49 (1 H, dd), 7.0—7.2 (3 H, complex), 6.54 (1 H, dd), and 2.46 (3 H, s), m.p. and mixed m.p. 80—81 °C (from hexane) (lit.,[9] 85 °C).

1,4-Dimethyl-5-(2,6-dimethylphenyl)-2,5-diaza-1-oxapentadiene (104.9 mg, 0.51 mmol), 30 °C, 600 °C, 3 × $10^{-3}$ Torr, 30 min: 2-(2,6-dimethylphenylimino)propanonitrile (4%), *m/z* 172; 7-methylindole (55%), *m/z* 131; 2,5-dimethylquinoxaline (4%) and 2,8-dimethylquinoxaline (17%), *m/z* 158; 2,7-dimethylindole (5%), *m/z* 145, identical with an authentic sample by g.l.c. on 5% SE30 and 5% Carbowax: residue in inlet 0%. Pyrolysis of the oxime ether (0.82 g, 4 mmol) at 650 °C and 2 × $10^{-2}$ Torr (inlet temperature 40—50 °C) during 2 h gave a crude pyrolysate (0.69 g) which was purified by preparative g.l.c. on 10% Carbowax at 200 °C to give 2,5- and 2,8-dimethylquinoxaline,[8] δ($CDCl_3$) 8.68 and 8.70 (1 H, 2 s), 7.5—8.0 (3 H, complex), and 2.76 (6 H, s), and 7-methylindole, δ($CDCl_3$) 8.0 (1 H, br), 7.47 (1 H, dd), 7.0—7.2 (3 H, complex), 6.54 (1 H, dd), and 2.45 (3 H, s). In a replicate experiment, the crude pyrolysate was dissolved in methylene dichloride (10 ml) and was extracted with dilute hydrochloric acid (1M; 3 × 5 ml). The organic layer was dried ($Na_2SO_4$) and concentrated to give a brown oil which crystallised from hexane. The white solid so obtained (100 mg) was identified as 7-methylindole (19%), m.p. 78—80 °C, mixed m.p. 79—81 °C (lit.,[9] 85 °C).

## Acknowledgements

I am most grateful to Miss O. Johnson for the g.c.-mass spectrometric results.

## References

1 Part 3, H. McNab, *J. Chem. Soc., Perkin Trans. 1*, preceding paper.
2 Preliminary communication, H. McNab and G. S. Smith, *J. Chem. Soc., Chem. Commun.*, 1982, 996.
3 H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2200.
4 H. McNab, *J. Chem. Soc., Chem. Commun.*, 1980, 422.
5 H. McNab and G. S. Smith, *J. Chem. Soc., Perkin Trans. 1*, following paper.
6 H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1941.
7 *Cf.* R. G. Parker and J. D. Roberts, *J. Org. Chem.*, 1970, **35**, 996.
8 H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1982, 357, and references therein.
9 O. Kruber, *Chem. Ber.*, 1926, **59**, 2752.

*Received 2nd August* 1983; *Paper* 3/1361