The Thermolysis of Polyazapentadienes. Part 3.[1,2] Cyclisation of *C*-Methyl-1,2,5-triazapentadienes and Related Compounds: The Role of an Intermediate Spirodienyl Radical

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

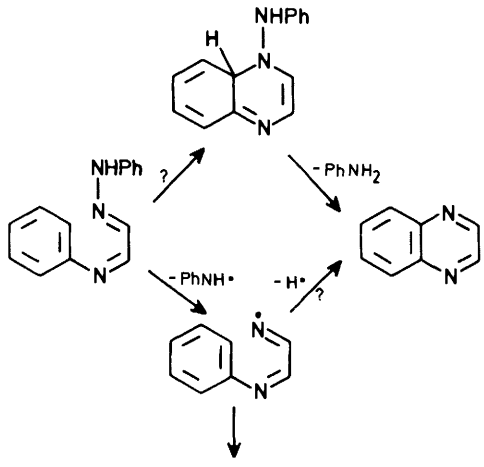
A series of *C*-methyl-1,2,5-triazapentadienes and 2,5-diaza-1-oxapentadienes are prepared from pyruvaldehyde phenylhydrazones and oxime anils respectively. The 4-methyl derivatives show *E*/*Z* isomerism about the 4,5-double bond. Pyrolysis of the 5-phenyl derivatives (1), (3), (5), (7), and (10) causes cyclisation to 2-methylquinoxaline, though 2-phenyliminopropanonitrile is obtained from the oxime ester (9). Pyrolysis of the 5-*p*-tolyl derivatives (2), (4), (6), (8), and (11) gives mixtures of 2,6- and 2,7-dimethylquinoxaline. These are formed predominantly by a rearrangement reaction which involves the spirodienyl radical (19), but also by direct cyclisation of the iminyl radicals (17) and (18).

The thermal reactions of 1,2,5-triazapentadienes are dominated by cyclisation to give quinoxalines and fragmentation to give a variety of minor products.[1,3] We have shown that the fragmentation reactions involve aryliminoiminyl radicals, but there was no direct evidence to distinguish between a radical or a concerted mechanism for the cyclisation process (Scheme 1). At the outset of the present work, we anticipated that *C*-substitution of the pentadiene chain and of the 5-aryl ring would lead to an unambiguous synthesis of quinoxalines with substituents in both rings. In the event, the unexpected rearrangement reactions which took place allowed a solution of the mechanistic dichotomy of Scheme 1.

The 1,2,5-triazapentadiene substrates (1)—(6) were made, *via* their perchlorate salts, by the action of the appropriate aryl ammonium perchlorate on the pyruvaldehyde phenyl-[4,5] or dimethyl-[6] hydrazone. The perchlorates of the 'aldehyde' derivatives (1)—(2) are formed in a few minutes at room temperature, and the product salts and bases exist in solution as single isomers. The perchlorates of the 'ketone' derivatives (3)—(6) require slightly more vigorous conditions for their formation, and both salts and bases are mixtures of two isomers. For example, the ^{1}H n.m.r. spectrum of the 1,5-diphenyl-4-methyl base (3) shows two methyl singlets at δ 2.34 and 2.00 (ratio 1 : 2.4). The methine proton H(3) corresponding to the major isomer resonates at δ 7.60, while that of the minor isomer is confused with the aromatic signals at lower frequency. These data are consistent with *E*/*Z* isomerism about the C(4)=N(5) double bond. The methyl group of isomer (A) would be expected to lie in the shielding zone of the out-of-plane aryl group, and so this structure probably represents the major isomer. The spectra of the salts are more complex, and show evidence of exchange phenomena in addition to isomerism.

As alternative substrates for the pyrolyses, the pyruvaldehyde oxime[7] derivatives (7)—(11) were synthesised. The oxime imines (7)[8,9] and (8) were readily prepared from the parent oxime by the action of the appropriate amine in ethanolic solution. Although the anil (7) was *O*-acetylated in high yield by standard methods[10] to give the ester (9), *O*-alkylation was more troublesome. However, the ethers (10) and (11) could be cleanly obtained from the imines (7) and (8) by the use of iodomethane in dimethylformamide, in the presence of potassium carbonate.[11] No *N*-alkylation was observed under these conditions.

As expected, in view of their close similarity to the hydrazones (3)—(6), the oxime derivatives (7)—(11) show *E*/*Z* isomerism about the C(4)=N(5) bond, with the (*E*)-isomer (A) again dominant. For example the *C*-methyl group of the ether

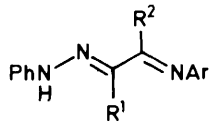


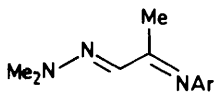
Scheme 1.

(10) resonates at δ 2.37 and 2.00 (ratio 1 : 4.2) with the corresponding H(3) methine signals at δ 7.57 and 7.80, in agreement with this interpretation.

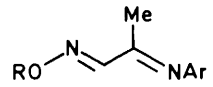
The mass spectra of the dimethylhydrazones (5)—(6) and of the oxime derivatives (7)—(11) show cleavage of the 1,2-bond followed by successive ejection of HCN and of MeCN (Scheme 2). In addition, the spectrum of the oxime ester (9) shows a significant peak at *m*/*z* 144 due to elimination of HOAc from the molecular ion. The behaviour of the phenylhydrazones (1)—(4) under electron impact is quite different. Cleavage of the 1-phenyl group is followed by loss of N_2 and of the methyl substituent (Scheme 3). This corresponds to one of the processes which has been considered in the interpretation of mass spectra obtained from related salts.[12]

Gas-phase pyrolysis of the phenylhydrazones (1) and (3) takes the expected course, with aniline (*ca.* 60%) and 2-methylquinoxaline (12) (*ca.* 25%) as major products (*cf.* Scheme 1). No trace of quinoxaline itself was detected, though quinoline was formed as the major product from the related 1,5-diazapentadiene (13).[13] This provides further circumstantial evidence that the cyclisation mechanisms of 1,5-di- and 1,2,5-tri-azapentadienes are quite distinct. The alternative precursors (5), (7), and (10), under identical conditions, all gave lower yields of 2-methylquinoxaline (12), owing in part to the recovery of significant amounts of starting material. In





(1) R^1 = Me, R^2 = H, Ar = Ph
(2) R^1 = Me, R^2 = H, Ar = *p*-tolyl
(3) R^1 = H, R^2 = Me, Ar = Ph
(4) R^1 = H, R^2 = Me, Ar = *p*-tolyl
(5) Ar = Ph
(6) Ar = *p*-tolyl

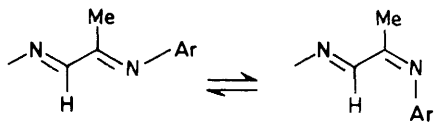


(7) R = H, Ar = Ph
(8) R = H, Ar = *p*-tolyl
(9) R = MeCO, Ar = Ph
(10) R = Me, Ar = Ph
(11) R = Me, Ar = *p*-tolyl

addition, the nitrile (14) is formed in small amounts from the oxime derivatives (7) and (10) and indeed it is the major product (82% yield) from the oxime ester (9). This latter reaction presumably takes place *via* the standard cyclic transition state for *cis*-eliminations,[14] and represents the simplest available preparative method for such iminonitriles.[15,16] These compounds are known also to show *E*/*Z* isomerism about the imine double bond [15] (*cf.* above).

The substituents of the *p*-tolyl derivatives (2) and (4) are arranged such that direct cyclisation would give only 2,7-dimethylquinoxaline and 2,6-dimethylquinoxaline, respectively. However, it was clear from the ^{1}H n.m.r. spectrum of the crude pyrolysates that *two* quinoxalines were formed in both cases, though in different relative amounts. The ^{1}H n.m.r. spectra of samples isolated by preparative g.l.c. of the two pyrolyses were similar to the spectrum of the mixture of 2,6- and 2,7-dimethylquinoxaline obtained by condensation of 3,4-diaminotoluene with pyruvaldehyde.[17] This assignment was confirmed by ^{13}C n.m.r. of the non-quaternary carbon atoms [from (2), major isomer δ ($CDCl_3$) 144.99, 131.00, 128.70, 127.64, 22.37, and 21.63 p.p.m.; minor isomer δ ($CDCl_3$) 145.78, 132.07, 128.23, 128.07, 22.27, and 21.44 p.p.m. The spectrum of an authentic mixture of 2,6- and 2,7-dimethylquinoxaline shows peaks corresponding to these isomers as follows: δ ($CDCl_3$) 144.43, 130.41, 128.05, 127.01, 21.88, and 21.17 p.p.m.; 145.22, 131.48, 127.58, 127.46, 21.82, and 21.02 p.p.m. The sets of data are closely similar, if allowance is made for a systematic difference of *ca.* 0.5 p.p.m.]. It is significant that no other dimethylquinoxalines were detected, and so any mechanism must account for this specificity.

The analysis of components of isomeric mixtures of fused ring compounds is possible by consideration of the multiplicities of ring-junction quaternary carbon atoms in ^{1}H-coupled ^{13}C n.m.r. spectra.[17] In the present case, the major isomer from (2) was confirmed as 2,7-dimethylquinoxaline (15) by comparison with the ^{13}C n.m.r. spectrum of an authentic sample, prepared by an unambiguous route [18] which was developed while the present work was in progress. Similarly, the major product from (4) was 2,6-dimethylquinoxaline (16) (Scheme 4).*



(A) (B)

A number of trivial sources of the rearrangements (Scheme 4) have been eliminated by control reactions. First, direct interconversion of compounds (2) and (4) was discounted by a low-temperature (500 °C) pyrolysis of (2) which gave *both* quinoxalines, though (2) was the only recovered 1,2,5-triazapentadiene. Second, a fragmentation–recombination mechanism was ruled out by co-pyrolysis of (2) and 1,5-diphenyl-1,2,5-triazapentadiene itself. No trace of monomethylquinoxalines could be detected (g.c./mass spectra) in the pyrolysate. The third control experiment was inevitably less clear cut. Interconversion of *products* is always difficult to eliminate as a valid mechanism in gas-phase pyrolysis studies, since they may be generated in a vibrationally activated state which cannot be reproduced by re-pyrolysis. Indeed, in the present example, reasonable interconversion *via* a benzvalene intermediate is possible (Scheme 5), and related examples are known.[19] However, re-pyrolysis of a 2,6- and 2,7-dimethylquinoxaline mixture at 850 °C (*i.e.* 250 °C above their formation temperature) showed no significant change in their ratio, and so it seems *highly likely* that the rearrangement must take place at an intermediate stage of the cyclisation reaction.

No intermediate rearrangement is possible by the concerted mechanism (Scheme 1). Alternatively, *ipso* attack by the iminyl radical (17) or (18) generates a spirodienyl radical (19) which can give both quinoxalines through cleavage and migration of either C–N single bond (Scheme 6). Since equal quantities of the two quinoxalines are not found from the two precursors (2) and (4), it is clear that a direct cyclisation mechanism must compete with the rearrangement. If it is assumed [20] that cleavage and migration of bonds *a* and *b* from (19) have equal probability, then it follows that an equal amount of (15) and (16) must arise from either precursor *via* the spirodienyl pathway. Hence:

$$\text{Spirodienyl component of total reaction pathway} = \frac{2 \times (\text{yield of minor quinoxaline})}{\text{total yield of quinoxalines}} \times 100\%$$

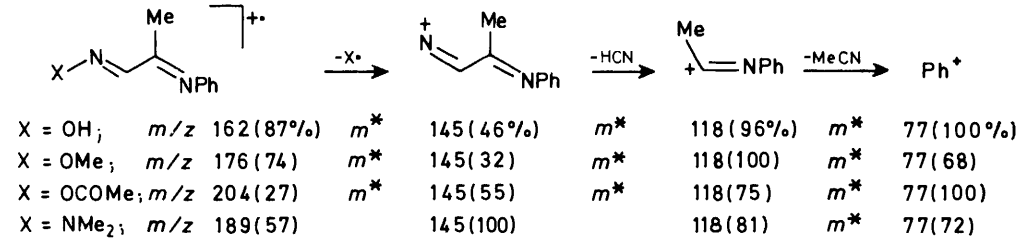
The spirodienyl component from (2) and (4) is therefore 57 and 72% respectively of the overall cyclisation mechanism.

One further ambiguity must be resolved. The remaining direct cyclisation component might occur by either the concerted or the radical processes of Scheme 1. However, the concerted cyclisation would be expected to be independent of the free-radical leaving group, and so an increased proportion of direct ring-closure might be expected if the radical cleavage is inefficient. In practice, thermolysis of compounds (6), (8), and (11) (radical leaving groups $Me_2N^{\cdot}$, $HO^{\cdot}$, and $MeO^{\cdot}$) at 600 °C led to the recovery of the starting material in all cases, but the quinoxalines are formed in unchanged ratio (Table). This result confirms that the iminyl radical pathway is responsible for direct and spiro-cyclisation processes, as well as for the minor products [3] of 1,2,5-triazapentadiene pyrolyses.

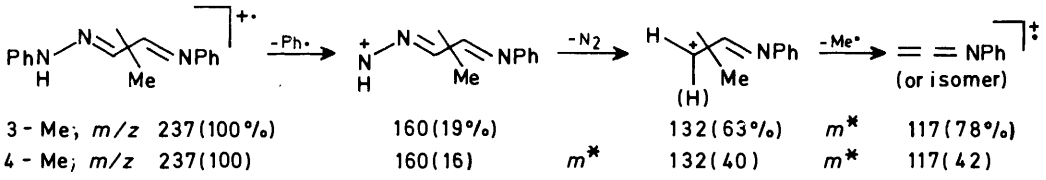
Experimental

Unless otherwise stated, ^{1}H n.m.r. spectra were recorded at 100 MHz for solutions in [$^2H_6$]dimethyl sulphoxide. Ether refers to diethyl ether.

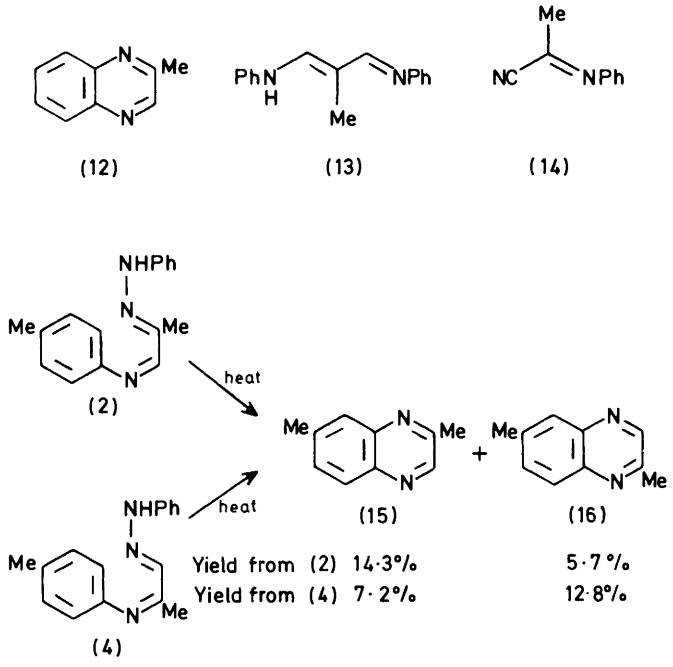
* I am grateful to Dr. D. M. Smith for samples of the quinoxalines (15) and (16) and for his helpful comments throughout the course of the present work.



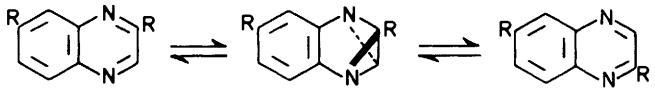
Scheme 2.



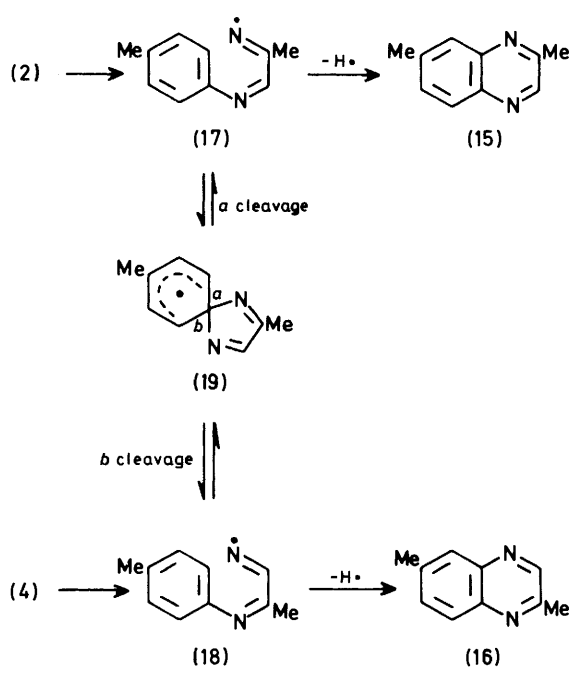
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

C-Methyl-1,2,5-triazapentadiene Salts and Bases.—The salts were made from pyruvaldehyde 1-phenylhydrazone[5] or pyruvaldehyde 2-phenylhydrazone[4] and the appropriate arylammonium perchlorate in ethanol as described in Part 1.[3] The 4-methyl derivatives generally required *ca.* 10 min under reflux for complete reaction to take place, though the 3-methyl derivatives were formed after a few minutes at room temperature. The bases were made from the salts by treatment with aqueous sodium carbonate,[3] or, more conveniently on a large scale, by reaction with methanolic potassium hydroxide.[1]

The following 1-phenyl-1,2,5-triazapentadienes were so obtained: 3-*methyl-5-phenyl perchlorate* (92%), m.p. 189—190 °C (decomp.) (from ethanol); δ 10.7 (br s), 8.82 (1 H, s), 7.1—7.9 (10 H, complex), and 2.32 (3 H, s) (Found: C, 53.6; H, 4.85; N, 12.45. $C_{15}H_{16}ClN_3O_4$ requires C, 53.35; H, 4.75; N, 12.45%), and the *base* (1) (86%), m.p. 81—83 °C (from cyclohexane); δ 9.97 (br s), 8.15 (1 H, s), 6.8—7.5 (10 H, com-

Table. Ratio of quinoxalines (15) : (16) obtained from the pyrolyses of (4), (6), (8), and (11) at 600 °C

Substrate	Leaving group	(15) : (16)
(4)	PhNH	36 : 64
(6)	Me_2N	33 : 67
(8)	HO	35 : 65
(11)	MeO	35 : 65

plex), and 2.20 (3 H, s); *m/z* 237 (M^+, 100%), 160(19), 132(63), 130(34), 117(78), 104(43), 103(40), 93(81), 92(41), 77(100), 65(62), 51(59), and 39(29) (Found: C, 76.2; H, 6.45; N, 17.9. $C_{15}H_{15}N_3$ requires C, 75.95; H, 6.35; N, 17.7%).

3-*Methyl*-5-p-*tolyl perchlorate* (93%), m.p. 202—203 °C (decomp.) (from ethanol); δ 10.95 (br s), 8.79 (1 H, s), 7.1—7.8 (9 H, complex), and 2.34 and 2.31 (6 H, 2 s) (Found: C, 54.75; H, 5.2; N, 11.95. $C_{16}H_{18}ClN_3O_4$ requires C, 54.6; H, 5.1; N, 11.95%), and the *base* (2) (88%), m.p. 123—124 °C (from cyclohexane); δ 9.93 (br s), 8.16 (1 H, s), 6.8—7.4 (9 H, complex), 2.39 (3 H, s), and 2.18 (3 H, s); *m/z* 251 (M^+, 100%), 174(13), 146(25), 131(41), 118(24), 117(25), 107(16), 93(29), 91(47), 77(26), 65(43), and 39(15) (Found: C, 76.55; H, 6.85; N, 16.7. $C_{16}H_{17}N_3$ requires C, 76.5; H, 6.75; N, 16.75%).

4-*Methyl*-5-*phenyl perchlorate* (68%), m.p. 177—179 °C (decomp.) (from ethanol–ether); δ ([$^2H_6$]acetone) 8.02 and 7.84 (1 H, 2 s), 7.2—7.6 (10 H, complex), and 2.90 and 2.75 (3 H, 2 s) (Found: C, 53.55; H, 4.9; N, 12.35. $C_{15}H_{16}ClN_3O_4$ requires C, 53.35; H, 4.75; N, 12.45%), and the *base* (3) (77%), m.p. 190—192 °C (from cyclohexane); δ 10.85 and 10.80 (2 br s), 7.60 (1 H of one isomer, s), 6.7—7.4 (10 H, complex), and 2.34 and 2.00 (3 H, 2 s); *m/z* 237 (M^+, 100%), 160(16), 132(40), 118(32), 117(42), 93(17), 77(52), 65(12), and 51(16) (Found: C, 75.75; H, 6.45; N, 17.6. $C_{15}H_{15}N_3$ requires C, 75.95; H, 6.35; N, 17.7%).

4-*Methyl*-5-p-*tolyl perchlorate* (86%), m.p. 175—176 °C (decomp.) (from ethanol); δ ([$^2H_6$]acetone) 7.96 and 7.81 (1 H, 2 s), 7.2—7.6 (9 H, complex), 2.84 and 2.70 (3 H, 2 s) and 2.38 and 2.36 (3 H, 2 s) (Found: C, 54.7; H, 5.25; N, 11.8. $C_{16}H_{18}ClN_3O_4$ requires C, 54.6; H, 5.1; N, 11.95%), and the *base* (4) (97%), m.p. 219—221 °C (from cyclohexane–ethanol); δ 10.8 (br s) 7.60 (1 H of one isomer, s), 6.6—7.4 (9 H, complex), 2.28 (3 H, s), and 2.32 and 2.02 (3 H, 2 s); *m/z* 251 (M^+, 100%), 174(17), 146(48), 132(48), 131(65), 93(17), 91(57), 77(22), and 65(39) (Found: C, 76.55; H, 6.95; N, 16.7. $C_{16}H_{17}N_3$ requires C, 76.5; H, 6.75; N, 16.75%).

Similarly, the following 1,1-dimethyl-1,2,5-triazapentadienes were prepared from pyruvaldehyde 1-dimethylhydrazone:[6] 4-*methyl*-5-*phenyl perchlorate* (71% crude yield; 28% after recrystallisation from methanol with low recovery to ensure isomeric purity), m.p. 127—128 °C (from methanol); δ 7.4—7.6 (5 H, complex), 7.19 and 6.90 (1 H, 2 s), 3.48 and 3.40 (6 H, 2 s), and 2.61 and 2.47 (3 H, 2 s) (Found: C, 45.5; H, 5.65; N, 14.55. $C_{11}H_{16}ClN_3O_4$ requires C, 45.6; H, 5.55; N, 14.5%), and the *base* (5) (97%), b.p. 117—120 °C (0.1 Torr); δ ($CDCl_3$) 6.6—7.4 (6 H, complex), 3.02 and 2.87 (6 H, 2 s), and 2.32 and 1.98 (3 H, 2 s); *m/z* 189 (M^+, 57%), 145(100), 118(81), 104(28), 77(72), and 51(24) (Found: C, 69.9; H, 8.0; N, 22.45. $C_{11}H_{15}N_3$ requires C, 69.85; H, 7.95; N, 22.2%).

4-*Methyl*-5-p-*tolyl perchlorate* (52% crude yield; 24% after recrystallisation from methanol with low recovery to ensure isomeric purity), m.p. 118—120 °C (from methanol); δ ([$^2H_6$]acetone) 7.35 (>4 H, s), 7.05 (1 H of one isomer, s), 3.52 (6 H, 2 br s), 2.68 and 2.54 (3 H, 2 s), and 2.37 and 2.36 (3 H, 2 s) (Found: C, 47.7; H, 6.1; N, 13.9. $C_{12}H_{18}ClN_3O_4$ requires C, 47.45; H, 5.95; N, 13.85%), and the *base* (6) (98%), b.p. 129—131 °C (0.1 Torr); δ ($CDCl_3$) 7.08 (2 H, d), 6.99 (1 H, s), 6.65 (2 H, d), 3.00 (6 H, s), 2.31 (3 H, s), and 1.99 (3 H, s); *m/z* 203 (M^+, 57%), 159(38), 156(33), 145(81), 132(95), 118(52), 107(86), 106(100), 91(81), 71(29), 65(38), and 42(57) (Found: C, 71.05; H, 8.35; N, 20.7. $C_{12}H_{17}N_3$ requires C, 70.95; H, 8.35; N, 20.7%).

1-*Acetyl*-4-*methyl*-5-*phenyl*-2,5-*diaza*-1-*oxapentadiene* (9) (cf. *Ref.* 10).—A solution of 4-methyl-5-phenyl-2,5-diaza-1-oxapentadiene[8] (1.62 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in benzene (25 ml) was cooled to 10 °C. A solution of acetyl chloride (0.78 g, 10 mmol) in benzene was then added dropwise, with stirring, to the mixture, and the stirring was continued at room temperature for 30 min. The precipitated salts were filtered off, washed with ether, and the filtrate was concentrated to give a yellow oil. Bulb-to-bulb distillation gave the required *oxime ester* (9) (1.88 g, 92%), b.p. 110 °C (0.1 Torr); δ ($CDCl_3$) 8.06 (1 H, s), 6.7—7.4 (5 H, complex), 2.23 (3 H, s), and 2.13 (3 H, s); *m/z* 204 (M^+, 27%), 162(15), 145(55), 144(45), 129(20), 118(75), 77(100), 51(35), and 43(50) (Found: C, 64.7; H, 5.8; N, 13.5. $C_{11}H_{12}N_2O_2$ requires C, 64.7; H, 5.9; N, 13.75%).

4-*Methyl*-5-p-*tolyl*-2,5-*diaza*-1-*oxapentadiene* (8).—A solution of pyruvaldehyde mono-oxime[7] (4.35 g, 50 mmol) and *p*-toluidine (5.35 g, 50 mmol) in ethanol (10 ml) was set aside overnight. The resulting *anil* (6.45 g, 73%) was filtered off and washed with ether. It had m.p. 204—205 °C (decomp.) (from methanol); δ 11.91 (br s), 7.73 (1 H, s), 7.13 (2 H, d), 6.65 (2 H, d), 2.27 (3 H, s), and 1.94 (3 H, s); *m/z* 176 (M^+, 100%), 161(17), 159(43), 132(91), 118 (11), 91(69), and 65(31) (Found: C, 68.3; H, 7.05; N, 15.85. $C_{10}H_{12}N_2O$ requires C,68.2; H, 6.8; N, 15.9%).

Methylation of 5-*Aryl*-4-*methyl*-2,5-*diaza*-1-*oxapentadienes* (*General Method*).—A solution of the oxime anil (10 mmol) in dimethylformamide (10 ml) was treated with anhydrous potassium carbonate (2.76 g, 20 mmol) and methyl iodide (1.50 g, slight excess), and the resulting suspension was stirred at room temperature overnight. The solid was filtered off, and the filtrate was concentrated at 10^{-1} Torr. Water (10 ml) was added to the residue, which was extracted with ether (3 × 20 ml). The organic extracts were dried (Na_2SO_4) and concentrated. Bulb-to-bulb distillation of the residue gave the required oxime ether as a yellow oil.

The following 1,4-dimethyl-2,5-diaza-1-oxapentadienes were made in this way: 5-*phenyl* (10) (67%), b.p. 77—79 °C (0.1 Torr); δ ($CDCl_3$) 7.80 and 7.57 (1 H, 2 s), 6.6—7.4 (5 H, complex), 3.98 and 3.92 (3 H, 2 s), and 2.37 and 2.00 (3 H, 2 s); *m/z* 176 (M^+, 74%), 145(32), 118(100), 77(68), and 51(26) (Found: C, 67.95; H, 6.9; N, 15.95. $C_{10}H_{12}N_2O$ requires C, 68.2; H, 6.8; N, 15.9%).

5-p-*Tolyl* (11) (79%), b.p. 85—87 °C (0.1 Torr); δ ($CDCl_3$) 7.79 and 7.60 (1 H, 2 s), 7.13 (2 H, d), 6.64 (2 H, d), 3.98 and 3.92 (3 H, 2 s), 2.33 and 2.32 (3 H, 2 s) and 2.36 and 2.01 (3 H, 2 s); *m/z* 190 (M^+, 88%), 159(29), 132(100), 91(54), and 65(25) (Found: C, 69.7; H, 7.35; N, 14.8. $C_{11}H_{14}N_2O$ requires C, 69.45; H, 7.35; N, 14.75%).

Pyrolysis Experiments.—Small scale (0.5 mmol) pyrolyses were carried out as described previously[3] and results are quoted as follows: precursor, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time, and yields and molecular ions (g.c.-mass spectra) of major products. The expected[3] minor products were also obtained, but are not reported unless they have particular mechanistic significance. Similarly, acetonitrile was almost invariably present [singlet at δ ($CDCl_3$) 1.95] but yields are unreliable because of its volatility and are therefore not quoted. Quinoxalines were separated by preparative g.l.c. using a column of 10% SE30 on Chromosorb (40—60 mesh).

3-Methyl-1,5-diphenyl-1,2,5-triazapentadiene (117.4 mg, 0.5 mmol), 130 °C, 600 °C, 1—2 × 10^{-3} Torr, 20 min: aniline (*ca.* 64%), *m/z* 93; 2-methylquinoxaline (28%), *m/z* 144; residue in inlet 0%. On a larger scale, the base (1.19 g, 5 mmol) was sublimed at 140—160 °C and 10^{-2} Torr during 2½ h into the furnace tube, which was maintained at 650 °C. Preparative g.l.c. of the pyrolysate (0.85 g) at 150 °C gave 2-methylquinoxaline,[17] δ ($CDCl_3$) 8.73 (1 H, s), 7.9—8.1 (2 H, com-

plex), 7.6—7.8 (2 H, complex), and 2.76 (3 H, s). The residue in the inlet was 5%.

4-Methyl-1,5-diphenyl-1,2,5-triazapentadiene (137.4 mg, 0.58 mmol), 130 °C, 600 °C, 5—10 × 10^{-3} Torr, 50 min: aniline (*ca.* 62%), 93; 2-methylquinoxaline (22%), *m/z* 144; residue in inlet 0%. Sublimation of the base (1.19 g, 5 mmol) at 170—180 °C and 10^{-2} Torr into the furnace tube (650 °C) gave a volatile pyrolysate (0.78 g) and a residue (0.13 g, 11%). Preparative g.l.c. of the volatiles at 150 °C gave 2-methylquinoxaline,[17] δ ($CDCl_3$) 8.73 (1 H, s), 7.9—8.1 (2 H, complex), 7.6—7.8 (2 H, complex), and 2.77 (3 H, s).

5-Phenyl-1,1,4-trimethyl-1,2,5-triazapentadiene (65.3 mg, 0.35 mmol), 90 °C, 600 °C, 5—10 × 10^{-3} Torr, 15 min: 2-methylquinoxaline (9%), *m/z* 144; recovered starting material (30%), *m/z* 189; residue in inlet 0%.

4-Methyl-5-phenyl-2,5-diaza-1-oxapentadiene (107.0 mg, 0.66 mmol), 140 °C, 600 °C, 3 × 10^{-3} Torr, 10 min: 2-phenyliminopropanonitrile (10%), *m/z* 144; 2-methylquinoxaline (5.5%), *m/z* 144; residue in inlet 0%. A substantial portion of the pyrolysate was recovered starting material: this was not quantified becase of its low solubility in $CDCl_3$.

1-Acetyl-4-methyl-5-phenyl-2,5-diaza-1-oxapentadiene. The ester (1.02 g, 5 mmol) was distilled at 90—100 °C and 10^{-2} Torr during 1.5 h into the furnace tube, which was at a temperature of 650 °C. The total pyrolysate was dissolved in methylene dichloride (10 ml), and was shaken with sodium hydroxide solution (2M; 10 ml) to remove acetic acid. The organic layer was separated, dried (Na_2SO_4), and concentrated. Bulb-to-bulb distillation of the residue gave pure 2-phenyliminopropanonitrile (0.58 g, 82%), b.p. 59—62 °C (0.1 Torr) [lit.,[16] 45—50 °C (10^{-3} Torr)] as a mixture of two isomers in the ratio 4.5 : 1; δ ($CDCl_3$) 6.6—7.5 (5 H, complex,) and 2.42 and 2.10 (3 H, 2 s) (major isomer at δ 2.42); *m/z* 144 (M^+, 94%), 129(49), 118(44), 77(100), and 51(34). (The ^1H n.m.r. spectrum of the crude pyrolysate showed that the other isomer was present in a greater amount at that stage.)

1,4-Dimethyl-5-phenyl-2,5-diaza-1-oxapentadiene (79.3 mg, 0.45 mmol), 40 °C, 600 °C, 5 × 10^{-3} Torr, 20 min: 2- phenyliminopropanonitrile (2%), *m/z* 144; 2-methylquinoxaline (25%), *m/z* 144; recovered starting material (6%), *m/z* 176; residue in inlet 0%. Distillation of the oxime ether (0.88 g, 5 mmol) at 60—80 °C and 5—25 × 10^{-3} Torr during 3 h through the furnace tube (650 °C) gave a yellow liquid pyrolysate (0.52 g). There was no significant involatile residue in the inlet. Preparative g.l.c. at 160 °C gave 2-methylquinoxaline,[17] δ ($CDCl_3$) 8.72 (1 H, s), 7.9—8.1 (2 H, complex), 7.6—7.8 (2 H, complex), and 2.78 (3 H, s).

3-Methyl-1-phenyl-5-*p*-tolyl-1,2,5-triazapentadiene (142.5 mg, 0.57 mmol), 120—130 °C, 600 °C, 5 × 10^{-3} Torr, 30 min: aniline (*ca.* 59%), *m/z* 93; 2,6-dimethylquinoxaline (5.7%) and 2,7-dimethylquinoxaline (14.3%), *m/z* 158; residue in inlet 0%. On a larger scale, sublimation of the base (1.26 g, 5 mmol) at 160—170 °C and 10—15 × 10^{-3} Torr during *ca.* 1 h into the furnace tube at 650 °C gave a pyrolysate (0.76 g), while a residue of some 26% remained in the inlet. Preparative g.l.c. at 160 °C gave 2,6- and 2,7-dimethylquinoxaline,[17] δ ($CDCl_3$) 8.64 and 8.67 (1 H, 2 s), 7.93 and 7.88 (1 H, 2 d), 7.76 and 7.80 (1 H, 2 br s), 7.51 and 7.55 (1 H, 2 dd), 2.73 (3 H, s), and 2.57 (3 H, s) [the chemical shift of the major isomer (2,7-dimethylquinoxaline) is quoted first].

4-Methyl-1-phenyl-5-*p*-tolyl-1,2,5-triazapentadiene (140.2 mg, 0.56 mmol), 130—140 °C, 1—3 × 10^{-3} Torr, 40 min: aniline (*ca.* 54%), *m/z* 93, 2,6-dimethylquinoxaline (12.8%) and 2,7-dimethylquinoxaline (7.2%), *m/z* 158; residue in inlet 1%. Pyrolysis of the base (1.26 g, 5 mmol) at 650 °C (inlet temperature 160—180 °C) and 10^{-2} Torr during 2 h gave a pyrolysate (0.72 g) and an involatile residue of 32%. A mixture of 2,6- and 2,7-dimethylquinoxaline [17] [δ ($CDCl_3$) 8.69 and 8.66 (1 H, 2 s), 7.91 and 7.95 (1 H, 2 d), 7.83 and 7.79 (1 H, 2 br s), 7.56 and 7.53 (1 H, 2 dd), 2.75 (3 H, s) and 2.58 (3 H, s): the chemical shift of the major isomer (2,6-dimethylquinoxaline) is quoted first] was obtained by preparative g.l.c. at 160 °C.

5-*p*-Tolyl-1,1,4-trimethyl-1,2,5-triazapentadiene (72.2 mg, 0.36 mmol), 90—110 °C, 600 °C, 3 × 10^{-3} Torr, 15 min: 2,6-dimethylquinoxaline (5.4%) and 2,7-dimethylquinoxaline (2.6%) *m/z* 158; recovered starting material (30%); residue in inlet 0%.

4-Methyl-5-*p*-tolyl-2,5-diaza-1-oxapentadiene (128.0 mg, 0.73 mmol), 140—150 °C, 600 °C, 10^{-3} Torr, 20 min: 2,6-dimethylquinoxaline (2.8%) and 2,7-dimethylquinoxaline (1.5%), *m/z* 158; residue in inlet 0%. 2-*p*-Tolyliminopropanonitrile was tentatively identified from the g.c. mass spectra (*m/z* 158): a substantial proportion of the pyrolysate was recovered starting material, m.p. 202—203 °C (decomp.).

1,4-Dimethyl-5-*p*-tolyl-2,5-diaza-1-oxapentadiene (99.5 mg, 0.52 mmol), 40 °C, 600 °C, 10^{-3} Torr, 30 min: 2,6-dimethylquinoxaline (13%) and 2,7-dimethylquinoxaline (7%), *m/z* 158; recovered starting material (5%), *m/z* 190; residue in inlet 0%. On a larger scale, the oxime ether (0.95 g, 5 mmol) was distilled at 60—80 °C and 1—2 × 10^{-2} Torr during 1.5 h into the furnace tube at 650 °C. The yield of pyrolysate was 0.48 g, and there was no significant residue in the inlet. Preparative g.l.c. at 160 °C gave 2,6- and 2,7-dimethylquinoxaline [17] [major isomer (2,6-dimethylquinoxaline) quoted first], δ ($CDCl_3$) 8.70 and 8.68 (1 H, 2 s), 7.92 and 7.97 (1 H, 2 d), 7.82 and 7.80 (1 H, 2 br s), 7.57 and 7.53 (1 H, 2 dd), 2.73 (3 H, s), and 2.57 (3 H, s).

3-Methyl-1-phenyl-5-*p*-tolyl-1,2,5-triazapentadiene was pyrolysed at 500 °C (44.3 mg, 0.18 mmol), 130—140 °C, 500 °C, 5 × 10^{-3} Torr, 30 min. The ^1H n.m.r. spectrum of the crude pyrolysate showed 2,6- and 2,7-dimethylquinoxaline (total yield 9%) and recovered starting material (38%). The isomeric 4-methyl derivative was absent.

Co-pyrolysis of 1,5-*diphenyl*-1,2,5-*triazapentadiene and* 3-*methyl*-1-*phenyl*-5-p-*tolyl*-1,2,5-*triazapentadiene*. 1,5-Diphenyl derivative (44.2 mg, 0.2 mmol), 3-methyl derivative (50.1 mg, 0.2 mmol), 140 °C, 600 °C, 10^{-3} Torr, 30 min. The pyrolysis was terminated when the more volatile diphenyl derivative had sublimed completely. G.c.-mass spectrometry of the pyrolysate showed quinoxaline (*m/z* 130) and 2,6- and 2,7-dimethylquinoxalines (*m/z* 158). No monomethylquinoxalines were present.

Pyrolysis of 2,6- *and* 2,7-*dimethylquinoxalines at* 850 °C. A sample of 2,6- and 2,7-dimethylquinoxaline (35.6 mg, 0.23 mmol) (ratio 24 : 76) was distilled at 40 °C and 10^{-3} Torr during *ca.* 30 min into the furnace tube, which was maintained at 850 °C. The 2,6- and 2,7-dimethylquinoxalines which were recovered were present in the ratio 27 : 73, *i.e.* no scrambling had taken place, within experimental error.

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