The Thermolysis of Polyazapentadienes. Part 2.[1] Formation of Quinoxalines from 5-Aryl-1-phenyl-1,2,5-triazapentadienes

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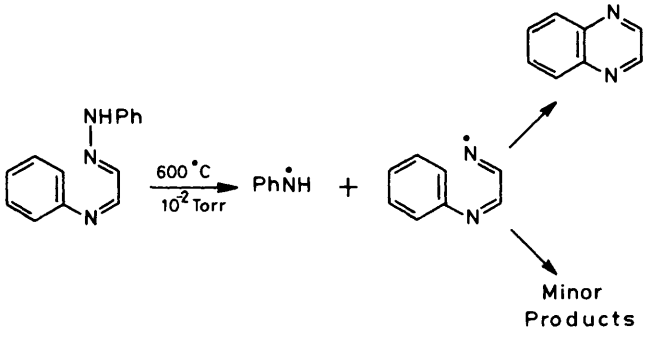
Thermolysis in the gas phase of 5-(*p*-substituted phenyl)-1-phenyl-1,2,5-triazapentadienes at 600 °C and 10^{-2} Torr gives 6-substituted quinoxalines. The yield is *ca.* 30%, and is independent of the electronic nature of the substituent. The corresponding 5-(*o*-substituted) derivatives give 5-substituted quinoxalines, though the yield is lower, and quinoxaline itself is a major contaminant, due to *ipso* attack and ejection of the substituent. 5-(*m*-Substituted) derivatives give mixtures of 5- and 6-substituted quinoxalines on pyrolysis. The 5-isomer is dominant for compounds with *m*-alkyl substituents, while the 6-isomer is the major product for those with electron-withdrawing or electron-donating *m*-substituents.

GAS-PHASE thermolysis of 1,5-diphenyl-1,2,5-triazapentadiene has been shown to give quinoxaline and aniline, together with a variety of minor products, whose formation was explained by a mechanism involving the phenyliminoiminyl radical (Scheme 1).[1] Later results



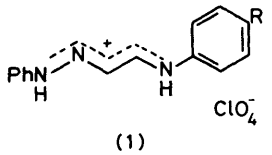
SCHEME 1

demonstrated that the cyclisation itself also proceeds *via* the iminyl,[2] rather than by the electrocyclic process found for thermolyses of related compounds.[3] This paper extends the earlier work to study the effect of substituents in the 5-aryl ring on the radical cyclisation reaction. A range of derivatives was chosen to reflect *o*-, *m*-, and *p*-substitution by inductive and conjugative electron-donating groups (methyl and methoxy respectively), by a halogen substituent (chloro) and by an electron-withdrawing group (acetyl).

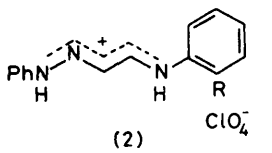
Other intramolecular substitution reactions of iminyls on aromatic [4] and heteroaromatic [5] systems have been reported. However, the intermolecular substitution reactions of diphenylmethaniminyl with benzene derivatives (for which partial rate factors are known) are now thought to proceed by an indirect mechanism.[6]

The bases (4)—(6) were synthesised in two steps by the general method given in Part 1.[1] Reaction of glyoxal monophenylhydrazone with the appropriate arylammonium perchlorate in ethanol gave the salts (1)—(3) in yields of 80—90%. The salts were, in general, characterised by their n.m.r. spectra though some members of the series were too hydrolytically unstable in solvents of sufficient polarity for their solubility, for reasonable spectra to be obtained. The free bases (4)—(6) were liberated from the salts, either by the sodium carbonate method,[1] or under non-aqueous conditions, which were particularly convenient for compounds with low solubility in ether or methylene chloride (see Experimental section). However, the *o*-acetyl derivative (5; R = Ac) could not be isolated despite a number of attempts under a variety of different conditions.

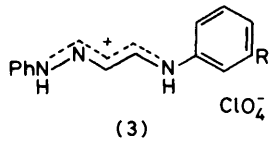
As found for the parent compound,[1] the bases (4)—(6) show well-resolved n.m.r. spectra, characteristic of the *trans*-s-*trans* configuration, in [$^2H_6$]dimethyl sulphoxide.



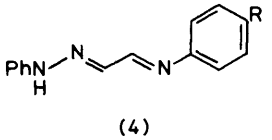
(1)
(a) R = OMe
(b) R = Cl
(c) R = Ac



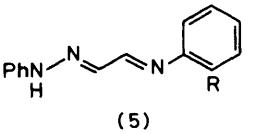
(2)
(a) R = Me
(b) R = OMe
(c) R = Cl
(d) R = Ac



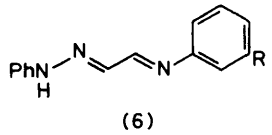
(3)
(a) R = Me
(b) R = OMe
(c) R = Cl
(d) R = Ac
(e) R = Et



(4)
(a) R = Me
(b) R = OMe
(c) R = Cl
(d) R = Ac



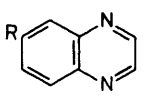
(5)
(a) R = Me
(b) R = OMe
(c) R = Cl



(6)
(a) R = Me
(b) R = OMe
(c) R = Cl
(d) R = Ac
(e) R = Et

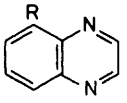
Similarly, broad spectra are generally obtained when [^{2}H]chloroform is used as solvent, due to exchange between *trans*-s-*trans* and *cis*-s-*cis* configurations.[1] Only the chlorophenyl derivatives (4c), (5c), and (6c) show sharp signals, characteristic of a mixture of both rotamers, under these conditions, though the reason for their reduction in exchange rate is not clear at this stage.

Pyrolysis of the bases (4)—(6) at 600 °C and 10^{-2}—10^{-3} Torr gave quinoxaline(s) as the only heterocyclic product, together with aniline and the expected [1] range of minor products which were detected by gas chromatography–mass spectrometry (g.c./m.s.) (Table 1). The presence of the minor products confirms that the iminyl pathway (Scheme 1) is dominant: no significant unexplained components were found by g.c./m.s.



(7)

(a) R = Me
(b) R = OMe
(c) R = Cl
(d) R = Ac
(e) R = Et



(8)

(a) R = Me
(b) R = OMe
(c) R = Cl
(d) R = Ac
(e) R = Et

6-Substituted quinoxalines (7) were obtained exclusively from the *p*-substituted derivatives (4). The yield of the quinoxaline was 29—37% (Table 1 and ref. 1), and was independent of the electronic nature of the substituent. This result is not unexpected, since the radical attack was necessarily at a position *meta* to the substituent. Samples of 6-methyl-, 6-methoxy-, and 6-chloroquinoxaline (7a—c) were readily obtained from (4a—c) by preparative g.l.c. of the pyrolysate from large-scale experiments. However, no 6-acetylquinoxaline (7d) could be isolated from a preparative pyrolysis of (4d). Instead, extensive solid-state decomposition in the inlet took place to give an intractable residue (46% by weight) and *p*-aminoacetophenone (92% molar yield). Large yields of the arylamine (derived from the 5-substituent) are invariably associated with prior decomposition in the inlet (Table 1). This problem could perhaps be avoided by use of a vertical furnace assembly [7] or by a 'fluidized-bed' inlet system.[8]

Pyrolysis of the *o*-substituted derivatives (5) was of particular interest from a synthetic point of view since the expected 5-substituted quinoxalines (8) are normally obtained from 3-substituted *o*-phenylenediamines, whose preparation is often tedious. Although the appropriate quinoxaline (8a—c) was indeed generated by pyrolysis of the triazapentadiene (5a—c), the yield was low, and quinoxaline itself (8; R = H) was a major contaminant (Table 2). The two products arise by competitive attack of the iminyl on the two positions *ortho* to the radical side-chain, followed by ejection of the ring-junction substituent (Scheme 2). In view of the high heat of formation of the hydrogen atom [9] it is perhaps surprising that the parent quinoxaline is not the major

TABLE 1

Products from the pyrolysis of 5-aryl-1-phenyl-1,2,5-triazapentadienes [a]

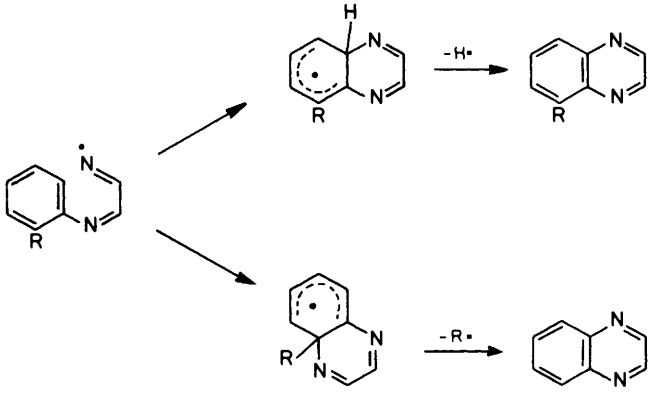
Starting material	ArH	$PhNH_2$	$ArNH_2$	ArCN	Total quinoxalines	PhNHAr	PhN_2Ph
(4b)	9	53	2	3	32 [b]	1	
(4c)	1	30	5	2	37 [b]	1	2
(4d)	10	36	6		31 [b]		
(5a)		29	14	5	37 [c]		1
(5b)	4	13	12		13 [c]		
(5c)	3	24	31	7	27 [c]		
(6a)		23	13		38 [d]	3	2
(6b)	7	38	6		30 [d]		
(6c)	5	37	21		27 [d]		2
(6d)	4	14	52		6.8 [d]		
(6e)	4	17	9		18 [d]	2	1

[a] The quantities given are g.l.c. areas, quoted relative to the actual yield (n.m.r., using cyclohexane as a calibrant) of the quinoxaline fraction. [b] 6-Substituted quinoxaline only. [c] Mixture of quinoxaline and 5-substituted quinoxaline (see Table 2). [d] Mixture of 5- and 6-substituted quinoxaline (see Table 3).

TABLE 2

Percentage yields of quinoxalines from triazapentadienes (5)

Starting material	Quinoxaline (%)	5-Substituted quinoxaline (%)
(5a)	12	25
(5b)	11	2
(5c)	9	18



SCHEME 2

product in all these cases, though the steric requirements for this *ipso*-attack are probably unfavourable. An approach to 5-substituted quinoxalines *via* 5-(2,6-disubstituted phenyl)triazapentadienes which involves mandatory *ipso*-attack and cleavage of the substituent, was only partially successful due to an unexpected competing reaction. These results will be reported in a later Part of this series.

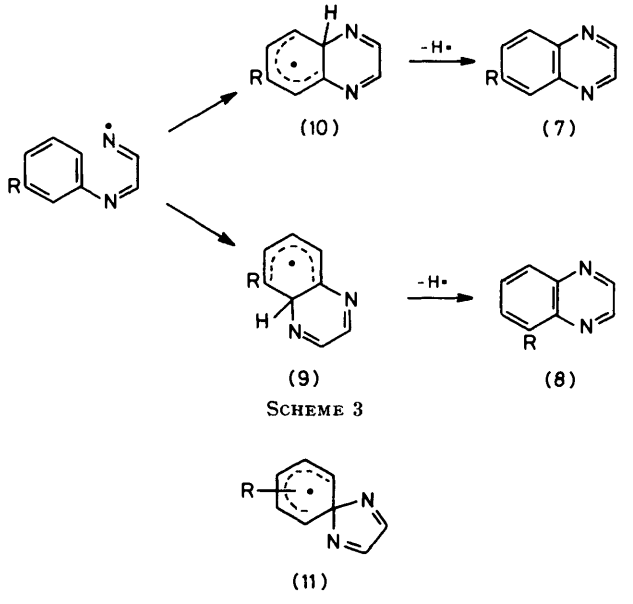
TABLE 3

Percentage yields of quinoxalines from triazapentadienes (6)

Starting material	5-Substituted quinoxaline (8) (%)	6-Substituted quinoxaline (7) (%)	Ratio (8)/(7)
(6a)	23	15	1.53
(6b)	4	26	0.15
(6c)	6	21	0.29
(6d)	≤1.4 [a]	≥5.4	0.26
(6e)	11	7	1.57

[a] Tentative assignment (see Experimental section).

Mixtures of quinoxalines were also obtained from the pyrolyses of the *m*-substituted compounds (6) (Table 3), again due to attack at the two positions *ortho* to the side-chain (Scheme 3). In this case the ring formation is at positions *ortho* and *para* to the substituent, and leads to 5- and 6-substituted quinoxalines respectively. It is clear from Table 3 that the ratio of these products is



SCHEME 3

(11)

strongly dependent on the substituent: *ortho*-attack is favoured by alkyl groups, while *para*-attack is preferred by both electron-donating and electron-withdrawing substituents. Steric factors are apparently not important, since the ethyl group [in compound (6e)] and the methoxy-group [in compound (6b)] should have similar steric requirements, yet give rise to quite different ratios of products. Literature data on free-radical aromatic cyclisations is scarce (*cf.* refs. 4 and 5) though it is well known that intermolecular free-radical aromatic substitution reactions are rather unselective with the *ortho*-substituted product often dominant.[10] On this basis it is the results for (6b—d) which are anomalous.

It is also known that free-radicals can be stabilised both by electron-donating and by electron-withdrawing groups, and that this can be rationalised by resonance-type interactions.[11] The stereochemical requirements of the sp^3 carbon atom at the ring junction of the intermediate (9) are such that the group R is twisted out of the plane of the ring, and so any resonance stabilisation will be reduced relative to (10), where full interaction is possible. This factor may explain why 6-substituted quinoxalines (7) are the dominant products when the substituent R can conjugate with the ring.

In conclusion, the cyclisation of aryliminoiminyl radicals has been shown to give quinoxalines. In its present form, the route is unlikely to be preparatively important because of low yields, involatility of precursors, and inconvenient work-up procedure. However, the results are consistent with a radical cyclisation mechanism, though in this context the role of the spirodienyl radical (11) [2] remains unknown. Experiments are in progress to clarify this point using ^{15}N-labelled radical precursors.

EXPERIMENTAL

Unless otherwise stated, n.m.r. spectra were recorded at 100 MHz.

Arylammonium Perchlorates.—These salts were prepared in 50—90% yield from the arylamine and perchloric acid (70%) in ethanol, following earlier procedures.[1]

5-Aryl-1-phenyl-1H-1,2,5-triazapentadienium Perchlorates.—The following perchlorates were obtained by the general method reported in Part 1:[1] 5-p-*methoxyphenyl* (1a) (84%), m.p. 191—192 °C (from ethanol), δ([$^2H_6$]acetone) 8.93 (1 H, d), 8.00 (1 H, d), 7.67 (2 H, d), 7.2—7.5 (5 H, complex), 7.07 (2 H, d), and 3.83 (3 H, s) (Found: C, 50.85; H, 4.5; N, 11.85. $C_{15}H_{16}ClN_3O_5$ requires C, 50.9; H, 4.55; N, 11.9%); 5-p-*chlorophenyl* (1b) (84%), m.p. 180—181 °C (decomp.) (from ethanol), δ([$^2H_6$]acetone) 9.05 (1 H, d), 8.03 (1 H, d), and 7.2—7.8 (9 H, complex) (Found: C, 46.95; H, 3.8; N, 11.4. $C_{14}H_{13}Cl_2N_3O_4$ requires C, 46.95; H, 3.65; N, 11.75%); 5-p-*acetylphenyl* (1c) (82%), m.p. *ca* 195 °C (extensive decomp.) (from ethanol), n.m.r. spectrum could not be recorded, because sample hydrolysed rapidly in polar solvents (Found: C, 52.7; H, 4.5; N, 11.55. $C_{16}H_{16}ClN_3O_5$ requires C, 52.55; H, 4.4; N, 11.5%); 5-o-*tolyl* (2a) (89%), m.p. 156—157 °C (decomp.) (from ethanol), δ([$^2H_6$]acetone) 8.91 (1 H, d), 8.16 (1 H, d), 7.2—7.8 (9 H, complex), and 2.50 (3 H, s) (Found: C, 53.05; H, 5.0; N, 12.0. $C_{15}H_{16}ClN_3O_4$ requires C, 53.35; H, 4.75; N, 12.45%); 5-o-*methoxyphenyl* (2b) (82%), m.p. 169—171 °C (decomp.) (from ethanol), δ([$^2H_6$]acetone) 9.05 (1 H, d), 8.17 (1 H, d), 7.80 (1 H, dd), 7.0—7.6 (8 H, complex), and 3.96 (3 H, s) (Found: C, 49.7; H, 4.6; N, 11.5. $C_{15}H_{16}ClN_3O_5 \cdot \frac{1}{2}H_2O$ requires C, 49.65; H, 4.7; N, 11.6%); 5-o-*chlorophenyl* (2c) (81%), m.p. 143—145 °C (decomp.) (from ethanol), n.m.r. spectrum could not be recorded because of low solubility and hydrolytic instability in solution (Found: C, 45.5; H, 3.7; N, 11.1. $C_{14}H_{13}Cl_2N_3O_4 \cdot \frac{1}{2}H_2O$ requires C, 45.8; H, 3.8; N, 11.45%); 5-o-*acetylphenyl* (2d) (75%), m.p. 160—162 °C (from ethanol), sample

too insoluble or hydrolytically unstable for a meaningful n.m.r. spectrum (Found: C, 52.75; H, 4.6; N, 11.05. $C_{16}H_{16}ClN_3O_5$ requires C, 52.55; H, 4.4; N, 11.5%); 5-m-*tolyl* (3a) (75%), m.p. 175—176 °C (decomp.) (from ethanol), δ([$^2H_6$]acetone) 9.02 (1 H, d), 8.03 (1 H, d), 7.2—7.6 (9 H, complex), and 2.38 (3 H, s) (Found: C, 53.55; H, 4.85; N, 12.5. $C_{15}H_{16}ClN_3O_4$ requires C, 53.35; H, 4.75; N, 12.45%); 5-m-*methoxyphenyl* (3b) (53%), m.p. 163—164 °C (from ethanol), δ([$^2H_6$]acetone) 9.08 (1 H, d), 8.02 (1 H, d), 6.9—7.6 (9 H, complex), and 3.94 (3 H, s) (Found: C, 51.05; H, 4.5; N, 11.85. $C_{15}H_{16}ClN_3O_5$ requires C, 50.9; H, 4.55; N, 11.9%); 5-m-*chlorophenyl* (3c) (81%), m.p. 165—167 °C (decomp.) (from ethanol), δ([$^2H_6$]acetone) 9.14 (1 H, d), 8.06 (1 H, d), and 7.2—7.8 (9 H, complex) (Found: C, 46.95; H, 3.6; N, 11.8. $C_{14}H_{13}Cl_2N_3O_4$ requires C, 46.95; H, 3.65; N, 11.75%); 5-m-*acetylphenyl* (3d) (95%), m.p. 163—165 °C (decomp.) (from ethanol–ether), n.m.r. spectrum invariably contaminated with spectra of hydrolysis products (Found: C, 52.6; H, 4.35; N, 11.55. $C_{16}H_{16}ClN_3O_5$ requires C, 52.55; H, 4.4; N, 11.5%); 5-m-*ethylphenyl* (3e) (60%), m.p. 166—168 °C (from ethanol–ether) δ([$^2H_6$]acetone) 9.06 (1 H, d), 8.02 (1 H, d), 7.2—7.6 (9 H, complex), 2.70 (2 H, q), and 1.23 (3 H, t) (Found: C, 54.85; H, 5.1; N, 12.05. $C_{16}H_{18}ClN_3O_4$ requires C, 54.6; H, 5.1; N, 11.95%).

5-*Aryl*-1-*phenyl*-1H-1,2,5-*triazapentadienes*.—The general method of Part 1 was used to prepare the following bases from the corresponding perchlorate salts:[1] 5-p-*methoxyphenyl* (4b) (95%), m.p. 156—157 °C (from cyclohexane), δ([$^2H_6$]DMSO) 11.02 (1 H, s), 8.27 (1 H, d), 7.70 (1 H, d), 6.7—7.4 (9 H, complex), and 3.74 (3 H, s) (Found: C, 71.35; H, 6.1; N, 16.5. $C_{15}H_{15}N_3O$ requires C, 71.15; H, 5.95; N, 16.6%); 5-*chlorophenyl* (4c) (74%), m.p. 176—177 °C (decomp.) (from cyclohexane), δ([$^2H_6$]DMSO) 11.17 (1 H, s), 8.25 (1 H, d), 7.70 (1 H, d), and 6.8—7.5 (9 H, complex) (Found: C, 65.25; H, 4.8; N, 16.1. $C_{14}H_{12}ClN_3$ requires C, 65.25; H, 4.65; N, 16.3%); 5-p *acetylphenyl* (4d) (53%) (methylene chloride used for the extraction), m.p. 196—197 °C (from ethanol), δ([$^2H_6$]DMSO) 8.28 (1 H, d), 7.95 (2 H, d), 7.73 (1 H, d), 6.9—7.5 (7 H, complex), and 2.56 (3 H, s) (Found: C, 72.5; H, 5.7; N, 15.7. $C_{16}H_{15}N_3O$ requires C, 72.45; H, 5.65; N, 15.85%); 5-o-*tolyl* (5a) (76%), m.p. 112—113 °C (from cyclohexane), δ([$^2H_6$]-DMSO) 11.09 (1 H, s), 8.11 (1 H, d), 7.74 (1 H, d), 6.8—7.4 (9 H, complex), and 2.26 (3 H, s) (Found: C, 75.9; H, 6.45; N, 17.5. $C_{15}H_{15}N_3$ requires C, 75.95; H, 6.35; N, 17.7%); 5-o-*methoxyphenyl* (5b) (71%), m.p. 140—141 °C (decomp.) (from cyclohexane), δ([$^2H_6$]DMSO) 11.09 (1 H, s), 8.18 (1 H, d), 7.72 (1 H, d), 6.8—7.5 (9 H, complex), and 3.77 (3 H, s) (Found: C, 71.3; H, 6.15; N, 16.55. $C_{15}H_{15}N_3O$ requires C, 71.15; H, 5.95; N, 16.6%); 5-o-*chlorophenyl* (5c) (74%), m.p. 132—133 °C (decomp.) (from cyclohexane), δ([$^2H_6$]DMSO) 11.24 (1 H, s), 8.16 (1 H, d), 7.74 (1 H, d), and 6.8—7.6 (9 H, complex) (Found: C, 65.5; H, 5.05; N, 15.75. $C_{14}H_{12}ClN_3$ requires C, 65.25; H, 4.65; N, 15.3%); 5-m-*tolyl* (6a) (76%), m.p. 128—129 °C (from cyclohexane), δ([$^2H_6$]DMSO) 11.11 (1 H, s), 8.24 (1 H, s), 7.72 (1 H, s), 6.8—7.4 (9 H, complex), and 2.32 (3 H, s) (Found: C, 76.15; H, 6.15; N, 17.9. $C_{15}H_{15}N_3$ requires C, 75.95; H, 6.35; N, 17.7%); 5-m-*methoxyphenyl* (6b) (79%), m.p. 172—173 °C (decomp.) (from cyclohexane), δ([$^2H_6$]-DMSO) 11.13 (1 H, s), 8.24 (1 H, d), 7.70 (1 H, d), 6.7—7.4 (9 H, complex), and 3.76 (3 H, s) (Found: C, 71.15; H, 6.05; N, 16.65. $C_{15}H_{15}N_3O$ requires C, 71.15; H, 5.95; N, 16.6%); 5-m-*chlorophenyl* (6c) (66%), m.p. 140—142 °C (from cyclohexane), δ([$^2H_6$]DMSO) 11.10 (1 H, s), 8.23 (1 H, d), 7.79 (1 H, d), and 6.8—7.5 (9 H, complex) (Found: C, 65.2; H, 4.8; N, 16.25. $C_{14}H_{12}ClN_3$ requires C, 65.25; H, 4.65; N, 16.3%); 5-m-*acetylphenyl* (6d) (53%) (methylene chloride used for the extraction), m.p. 155—156 °C [from cyclohexane–light petroleum (b.p. 40—60 °C)], δ([$^2H_6$]-DMSO) 11.18 (1 H, s), 8.30 (1 H, d), 6.8—7.8 (10 H, complex), and 2.60 (3 H, s) (Found: C, 72.45; H, 5.6; N, 15.9. $C_{16}H_{15}N_3O$ requires C, 72.45; H, 5.65; N, 15.85%); 5-m-*ethylphenyl* (6e) (84%), m.p. 133—134 °C (from cyclohexane), δ([$^2H_6$]DMSO) 11.11 (1 H, s), 8.24 (1 H, d), 7.71 (1 H, d), 6.8—7.4 (9 H, complex), 2.60 (2 H, q), and 1.18 (3 H, t) (Found: C, 76.95; H, 6.95; N, 16.9. $C_{16}H_{17}N_3$ requires C, 76.5; H, 6.75; N, 16.75%).

Large-scale Preparation of 5-*Aryl*-1-*phenyl*-1H-1,2,5-*triazapentadienes* (*General Method*).—Due to the low solubility of many of these bases, the earlier extraction method for their preparation is inconvenient when large quantities are required. Thus the pentadienium perchlorate (15 mmol) was suspended in methanol (30 ml) and a solution of potassium hydroxide (0.84 g, 15 mmol) in methanol (20 ml) was added. The resulting yellow suspension which consists of pentadiene and potassium perchlorate, was recrystallised *in situ*, with the addition of more methanol if necessary, and was filtered whilst hot to remove the inorganic salts. The pure base crystallised from the filtrate on cooling and was filtered off. Further product could be obtained by concentration of the filtrate.

By this method, the following 5-aryl-1-phenyl-1*H*-1,2,5-triazapentadienes were obtained (quantity of additional methanol required for the recrystallisation given in parenthesis): 5-*p*-tolyl (4a) (250 ml) (97%), 5-*p*-methoxyphenyl (4b) (60 ml) (89%), and 5-*p*-chlorophenyl (4c) (100 ml) (96%).

This method was not suitable for the preparation of the 5-*p*-acetylphenyl derivative (4d), which is particularly insoluble, and was obtained as follows: a suspension of the corresponding perchlorate (5.48 g, 15 mmol) in methylene chloride (500 ml) was treated with triethylamine (2.02 g, 20 mmol). The suspension was stirred vigorously for 30 min and the pentadiene which had formed was filtered off (2.80 g, 71%).

Pyrolysis Experiments.—Small-scale (0.5 mmol) pyrolyses were carried out as previously described,[1] and results are quoted as follows: 5-*aryl*-1-phenyl-1*H*-1,2,5-triazapentadiene, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time, and yields of quinoxaline products. Details of minor products are given in Table 1. For certain of the triazapentadienes, large-scale pyrolyses (5 mmol) were performed, so that the quinoxaline could be isolated by preparative g.l.c. [10% SE30 on Chromosorb (40—60 mesh)]. In the majority of the other cases the quinoxaline was identified by comparison (n.m.r., g.l.c.) with an authentic sample.

5-p-*Tolyl* (4a). Small-scale pyrolyses of this compound have been previously reported.[1] On a preparative scale, the *base* (1.19 g, 5 mmol) was sublimed at 180—190 °C and 0.5—2 × 10^{-2} Torr over a period of 1 h into the furnace tube which was maintained at 650 °C. The involatile residue in the inlet was 0.15 g (13%). Preparative g.l.c. at 150 °C of the crude pyrolysate (0.90 g) gave 6-methylquinoxaline (7a) (δ($CDCl_3$) 8.77 (2 H, q), 7.99 (1 H, d), 7.86 (1 H, br s), 7.60 (1 H, dd), and 2.60 (3 H, s).

5-p-*Methoxyphenyl* (4b), 137.8 mg (0.54 mmol), 120 °C, 600 °C, 2—15 × 10^{-3} Torr, 45 min, 6-methoxyquinoxaline

(32%), residue in inlet 5%. On a preparative scale, the *base* (1.27 g, 5 mmol) was sublimed at 160—165 °C and 10^{-2} Torr for 75 min into the pyrolysis tube which was heated to 650 °C. Under these conditions, the residue in the inlet was 0.53 g (42%). Preparative g.l.c. of the liquid pyrolysate (0.46 g) at 170 °C gave 6-methoxyquinoxaline (7b), δ($CDCl_3$, 360 MHz), 8.75 (1 H, d), 8.69 (1 H, d), 7.98 (1 H, d), 7.42 (1 H, dd), 7.38 (1 H, d), and 3.97 (6 H, s).

5-p-*Chlorophenyl* (4c), 130.5 mg (0.51 mmol), 130 °C, 600 °C, 2—10 × 10^{-3} Torr, 35 min, 6-chloroquinoxaline (37%), residue in inlet 5%. On a preparative scale, sublimation of the *base* (1.30 g, 5 mmol) at 170 °C and 10^{-2} Torr over 90 min into the pyrolysis tube (650 °C) gave a residue in the inlet of 0.33 g (25%) and a liquid pyrolysate of 0.83 g. Preparative g.l.c. at 160 °C gave 6-chloroquinoxaline (7c) δ($CDCl_3$) 8.80 (2 H, s), 8.10 (1 H, d), 8.04 (1 H, d), and 7.70 (1 H, dd).

5-p-*Acetylphenyl* (4d), 107.3 mg (0.40 mmol), 160 °C, 600 °C, 2 × 10^{-3} Torr, 30 min, 6-acetylquinoxaline (31%) (identified by g.c./m.s., and by analogy with the other experiments in the series), residue in inlet 10%. Because of the low volatility of the base, no quinolaxine was isolated when this pyrolysis was repeated on a 5-mmol (1.33 g) scale (inlet temperature 170—190 °C, furnace temperature 650 °C, pressure range 5—20 × 10^{-3} Torr, pyrolysis time 2.5 h). Instead, a large inlet residue (0.61 g, 46% by weight) was accompanied by a solid pyrolysate (0.62 g), which was identified as *p*-aminoacetophenone (92% molar yield), m.p. 102—104 °C (from cyclohexane) (lit.,[12] 104—106 °C).

5-o-*Tolyl* (5a), 100.6 mg (0.42 mmol), 110 °C, 600 °C, 2 × 10^{-3} Torr, 20 min, quinoxaline (12%), 5-methylquinoxaline (25%), residue in inlet 5%. (Quinoxalines identical with authentic samples.[13])

5-o-*Methoxyphenyl* (5b), 134.6 mg (0.53 mmol), 120 °C, 600 °C, 1—5 × 10^{-3} Torr, 40 min, quinoxaline (10%), 5-methoxyquinoxaline (3%), residue in inlet (28%). (Quinoxalines identical with authentic samples.[13])

5 o-*Chlorophenyl* (5c), 127.7 mg (0.50 mmol), 110 °C, 600 °C, 10^{-2} Torr, 20 min, quinoxaline (9%), 5-chloroquinoxaline (18%), residue in inlet 20%. (Quinoxalines identical with authentic samples.[13])

5-m-*Tolyl* (6a), 113.5 mg (0.48 mmol), 100 °C, 600 °C, 2—6 × 10^{-3} Torr, 35 min, 5-methylquinoxaline (23%), 6-methylquinoxaline (15%), residue in inlet 5%. (Quinoxalines identified by comparison with n.m.r. spectra of authentic samples.[13])

5-m-*Methoxyphenyl* (6b), 122.0 mg (0.48 mmol), 120 °C, 600 °C, 5 × 10^{-3} Torr, 35 min, 5-methoxyquinoxaline (4%), 6-methoxyquinoxaline (26%), residue in inlet 10%. (Quinoxalines identified by comparison with n.m.r. spectra of authentic samples.[13])

5-m-*Chlorophenyl* (6c), 113.2 mg (0.44 mmol), 110 °C, 600 °C, 2 × 10^{-3} Torr, 30 min, 5-chloroquinoxaline (12%), 6-chloroquinoxaline (15%), residue in inlet 20%. (Quinoxalines identified by comparison with n.m.r. spectra of authentic samples.[13])

5-m-*Acetylphenyl* (6d), 65.3 mg (0.25 mmol), 130 °C, 600 °C, 2—5 × 10^{-3} Torr, 30 min, 5-acetylquinoxaline (tentative) (1.4%), 6-acetylquinoxaline (5.4%), residue in inlet 38%. {6-Acetylquinoxaline was identified by comparison of the n.m.r. spectrum of the crude pyrolysate with that from compound (4d). The region δ > 8.5 p.p.m is particularly informative, since 6-acetylquinoxaline shows two characteristic peaks, *viz.* δ 8.85 [2 H, s, H (2,3)] and δ 8.62 [1 H, d, H (5)]. Only one other peak in this range was observed in the spectrum of the pyrolysate of the *m*-acetyl derivative (singlet at δ 8.79) and this was tentatively assigned as the 2- and 3-protons of the hitherto unknown 5-acetylquinoxaline}.

5-m-*Ethylphenyl* (6e), 124.5 mg (0.5 mmol), 100 °C, 600 °C, 5—10 × 10^{-3} Torr, 30 min, 5-ethylquinoxaline (11%), 6-ethylquinoxaline (7%), residue in inlet 15%. (Quinoxalines assigned by comparison of the n.m.r. spectrum of the pyrolysate with that of the 5-*m*-tolyl analogue.)

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