The Thermolysis of Polyazapentadienes. Part 1. 1,5-Diaryl-1,2,5-triaza-derivatives

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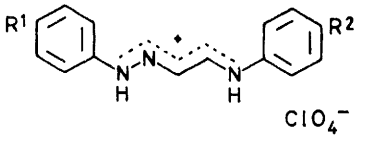
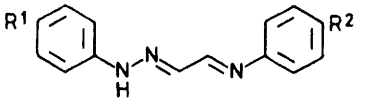
Flash vacuum pyrolysis of the title compounds at 600 °C gives quinoxalines and arylamines, together with small quantities of nitriles, diarylamines, azobenzenes, and formamidines. The mechanism involves homolytic cleavage of the N–N bond to generate a conjugated iminyl radical, which can either cyclise to a quinoxaline, or fragment to simpler radicals which lead to the minor products by coupling reactions.

EARLIER papers have reported the facile preparation of 1,2,5-triazapentadienium salts [1,2] *e.g.* (1). Such compounds are potential sources of the azadimethine structural unit, provided that the terminal nitrogen atoms

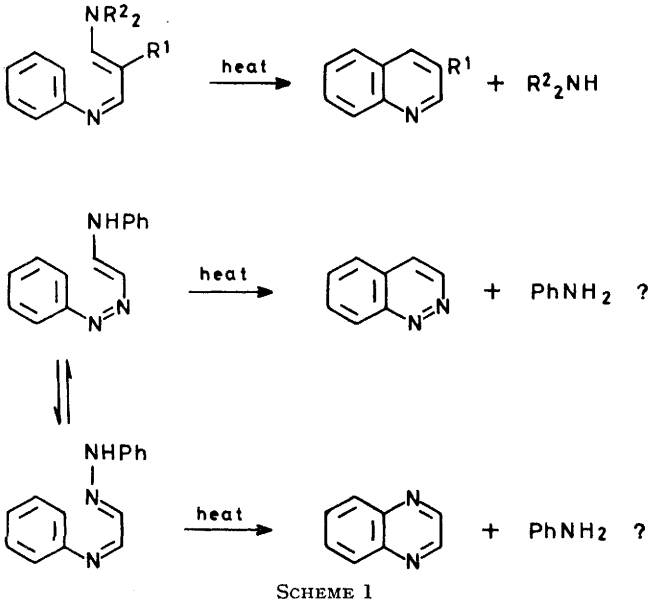


(1) $R^1 = R^2 = H$
(2) $R^1 = H, R^2 = Me$
(3) $R^1 = R^2 = Me$



(4) $R^1 = R^2 = H$
(5) $R^1 = H, R^2 = Me$
(6) $R^1 = R^2 = Me$

(and their substituents) may be utilised as leaving groups or as templates for further reactions. In this context, Jutz and his co-workers have elegantly exploited the thermal cyclisation of 1-aryl-1,5-diazapentadienes to give quinolines [3] and have shown that these are concerted electrocyclic reactions. Similarly, 1,5-diaryl-1,2,5-triazapentadienes might be expected to cyclise either to give cinnolines or quinoxalines depending on the tautomeric form of the base (Scheme 1).

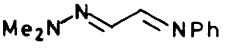


SCHEME 1

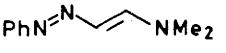
A number of other related reactions are known. For example, the acid-catalysed cyclisation of *o*-anilinoazobenzenes was first reported in 1887 [4] and is known to be electrocyclic,[5] while a similar reaction in the uracil series has been proposed as a useful synthetic method.[6] The cyclisation of 1,5-diarylformazans (1,2,4,5-tetra-azapentadienes) to benzo-1,2,4-triazines under acid conditions has also been extensively studied.[7]

The dark red salts (1)—(3) were prepared in excellent yield by standard methods.[1] The corresponding bases (4)—(6) were obtained as bright yellow crystals by treatment of an ethereal suspension of the salt with an excess of sodium carbonate solution.[8]

In view of the importance of the tautomeric form of the bases on the mode of cyclisation, this aspect of their structure was studied in detail by ^1H n.m.r. spectroscopy. The 3,4-bonds of the two forms have different bond orders and hence different vicinal coupling constants ($^3J_{3,4}$), but the situation is complicated by the possibility of four isomers (or rotamers) of each tautomer.[9] The *NN*-dimethyl derivatives (7) ($^3J_{3,4}$ 7.8 Hz) and (8) ($^3J_{3,4}$ 11.0 Hz) were therefore prepared as models for the 1*H*- and 5*H*-tautomer respectively.



(7)

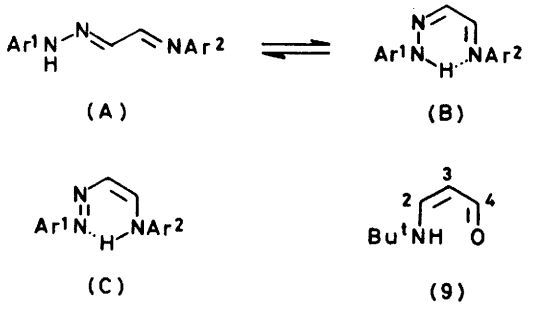


(8)

The ^1H n.m.r. spectra of the bases (4)—(6) in $CDCl_3$ solution were broad and unresolved at room temperature and above. Compound (5) was too insoluble for further study, but at low temperature (−30 to −40 °C) (4) and (6) showed *two* pairs of doublets ($^3J_{3,4}$ 8.0 and 2.0 Hz) for the methine protons, which were present in approximately equal amount. In addition, an NH signal was detected at τ −4.5, which is indicative of a *cis*-s-*cis* hydrogen-bonded chelate structure. The isomer with the larger coupling constant is clearly the 1*H*-tautomer in the same geometric form as the model compound (7). This is thought to be *trans*-s-*trans* (A) by analogy with related systems.[1,9] The second isomer is probably the *cis*-s-*cis* form of the 1*H*-tautomer (B). This is preferred over the 5*H*-tautomer (C) on account of the very small size of the coupling constant, and also by analogy with the corresponding form of the enaminone (9) ($^3J_{3,4}$ 2.3 Hz).[10,11]

In [$^2H_6$]dimethyl sulphoxide, the bases (4)—(6) adopt

the 1*H*-*trans*-s-*trans* form exclusively [$^3J_{3,4}$ 8.2 Hz, τ (NH) −1.5]. Intramolecular hydrogen bonding cannot



(A) (B)

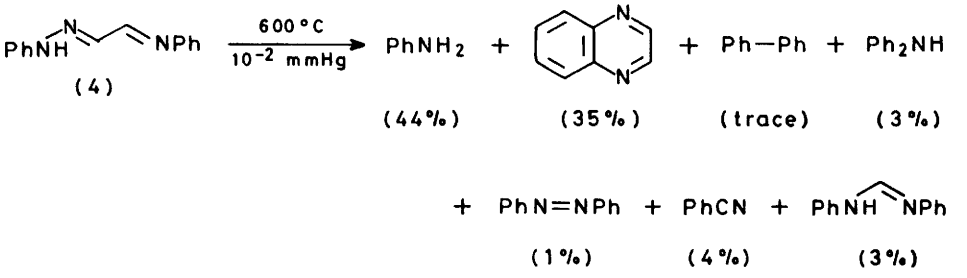
(C) (9)

compete with intermolecular hydrogen bonding to the solvent molecules.

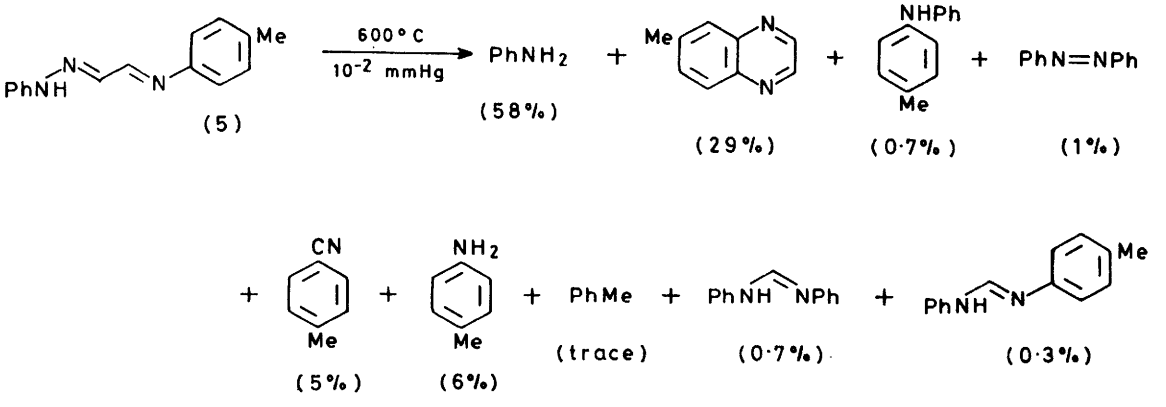
Preliminary studies of the thermolysis of the diphenyl compound (4) in solution and in a sealed tube were unpromising, and so a gas-phase flow pyrolysis system was used [12] (see Experimental section). Under these conditions, the base was recovered unchanged at a furnace temperature of 500 °C, but the decomposition was complete at 600 °C. These conditions were used for all subsequent pyrolyses.

As expected on the basis of the tautomerism studies, examination of the crude pyrolysate by ^{1}H n.m.r. spectroscopy showed that quinoxaline (35%) was the heterocyclic base present. The 3-proton of cinnoline resonates at a characteristic low field, and so this compound could readily have been detected. In addition to quinoxaline and aniline, a number of minor products were identified (Scheme 2), whose total yields amount to nearly one third that of the quinoxaline. This result is clearly unexpected on the basis of a concerted reaction, and so the source of these minor products was investigated by two cross-over experiments.

Thus pyrolysis of the *p*-tolyl derivative (5) gave the expected aniline and 6-methylquinoxaline (Scheme 3). However, the only nitrile present was the *p*-tolyl derivative, which confirms the source of this product as the 5-aryl group. Similarly, no substituted azobenzene could be detected, and so the azobenzene itself must arise *via* intermolecular coupling processes. That two formamidines are formed is of no mechanistic significance, since aniline (present in vast excess) reacts with formamidines under these conditions (see Experimental section). The presence of only the mixed diarylamine suggests either that intramolecular pathways may operate, or that anilino and *p*-tolyl radicals (or *p*-tolylamino and phenyl radicals) are formed exclusively.



Scheme 2



Scheme 3

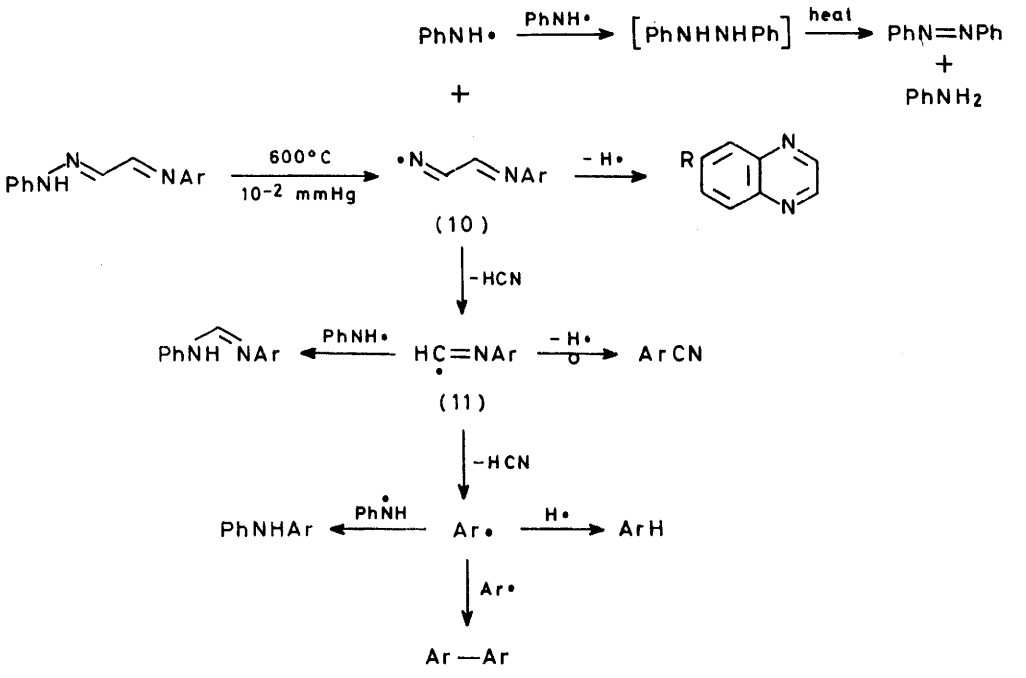
In order to distinguish between these possibilities, the second cross-over experiment was carried out. The 1,5-diphenyl and 1,5-di-*p*-tolyl derivatives (4) and (6) were co-pyrolysed, using a transparent inlet system to confirm simultaneous sublimation. Radical pathways would lead to diphenylamine, di-*p*-tolylamine, and *N*-phenyl-*p*-

toluidine, whereas only the first two compounds could arise by an intramolecular route.* Analysis by g.l.c. on SE30 and on Carbowax allowed unambiguous identification of the three diarylamines, *all* of which were present in the pyrolysate. As expected, azobenzene, *p*,*p*'-dimethylazobenzene, and *p*-methylazobenzene were all detected: the radical pathway for the minor products is thus confirmed.

The mechanism in Scheme 4 is proposed to explain the results. Cleavage of the N–N bond generates the anilino-radical and the conjugated iminyl radical (10). The latter may either cyclise (see below) or fragment by loss of HCN to the radical (11) which is the source of the nitrile (by loss of H· and rearrangement; thermal rearrangement of isocyanides is known [13]) and the amidine (by coupling with anilino-radicals). Further loss of HCN from (11) generates the small amount of aryl radicals, which may couple with the predominant anilino or hydrogen radicals to give the diarylamine and the hydrocarbon respectively. That only traces of biaryls could be detected is thus explained on a statistical basis.

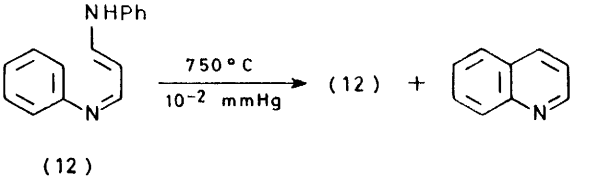
Coupling of the anilino-radicals should give hydrazobenzene. However, this compound is quantitatively decomposed under the conditions of the experiment to azobenzene (1 mol) and aniline (2 mol). This source of the azobenzene is preferred to an alternative route involving dimerisation of phenylnitrene.

The mechanism of Scheme 4 does not explain the presence of *p*-toluidine in the pyrolysate of the *p*-tolyl compound (5), a product which again was not accompanied by any detectable amount of cinnoline. Later experiments [10] have shown that high yields of the arylamine derived from the 5-position are associated with extensive solid-state decomposition in the inlet, which leads to involatile tars.



SCHEME 4

The presence of the iminyl radical (10) offers an alternative to the electrocyclic mechanism for the ring-closure to the quinoxaline. Iminyls are known to effect intramolecular aromatic substitution in solution, and indeed cyclisation of vinyliminyls to quinolines has been observed in favourable cases.[14] In the present case, the mechanisms are difficult to distinguish. For comparison, however, preliminary pyrolyses of 1,5-diphenyl-1,5-diazapentadiene (12) have been carried out in the gas phase, and have shown conversion to quinoline in high yield with the absence of minor products (Scheme 5), consistent with the concerted mechanism proposed



SCHEME 5

for solution-phase work.[3] However, the reaction is only 50% complete at 750 °C. With these more vigorous conditions in mind, it would appear that the 1,2,5-triazapentadienes find a more easy cyclisation pathway *via* the iminyl, though the detailed question of competing mechanisms must await further work.

* Pyrolysis of the 1,5-di-*p*-tolyl derivative alone gave no demethylated products.

EXPERIMENTAL

Unless otherwise stated, n.m.r. spectra were recorded at 100 MHz and mass spectra at 24 eV.

*Glyoxal Mono-*p*-tolylhydrazone*.—A suspension of *p*-tolylhydrazine hydrochloride (1.60 g, 10 mmol) in methanol (15 ml) containing potassium hydroxide (0.56 g, 10 mmol) was added dropwise to a solution of glyoxal (40%; 3 ml) in water (150 ml), with vigorous stirring. The yellow solid which formed was filtered off and washed with water to give the *hydrazone* (1.25 g, 77%), m.p. 126—128 °C (from cyclohexane), $\nu_{max.}$ (Nujol) 3 200, 1 650, 1 600, 1 550, 1 500, 1 270, 1 150, 880, and 820 cm^{-1}, τ ([$^2H_6$]acetone) −0.66br (s), 0.50 (1 H, d, $^3J_{3,4}$ 7.8 Hz), 2.72 (1 H, dd, $^3J_{3,4}$ 7.8, $^4J_{1,3}$ 0.1 Hz), 2.88 (4 H, s), and 7.74 (3 H, s); *m/e* (70 eV) 162 (100%, $M^{+\cdot}$), 107 (38), 106 (96), 91 (67), 79 (42), 77 (46), and 65 (17) (Found: C, 66.7; H, 6.25; N, 17.1. $C_9H_{10}N_2O$ requires C, 66.65; H, 6.15; N, 17.3%).

p-*Tolylammonium Perchlorate* (*see Ref.* 15).—A solution of *p*-toluidine (5.35 g, 50 mmol) in ethanol (3 ml) was cooled in ice, and perchloric acid (70%; 7 ml) was added dropwise. The perchlorate, which crystallised immediately, was filtered off, washed thoroughly with ether, and dried in air, m.p. 252—254 °C (decomp.), 57% yield.

1,5-*Diaryl*-1H-1,2,5-*triazapentadienium Perchlorates* (*General Method*).[1]—Ethanol (10 ml) was added to a mixture of the aryl ammonium perchlorate (15 mmol) and the α-dicarbonyl monoarylhydrazone (15 mmol), and the deep red solution was vigorously shaken until crystallisation occurred (usually < 1 min). The red perchlorate was filtered off, and was washed thoroughly with ether.

By this method were obtained 1-*phenyl*-5-p-*tolyl*-1H-1,2,5-*triazapentadienium perchlorate* (2) (81%), m.p. 191—192 °C (decomp.) (from ethanol), τ ([$^2H_6$]acetone) 0.99 (1 H, d), 1.97 (1 H, d), 2.3—2.9 (9 H, complex), and 7.64 (3 H, s) (Found: C, 53.4; H, 4.75; N, 12.35. $C_{15}H_{16}ClN_3O_4$ requires C, 53.35; H, 4.75; N, 12.45%), and 1,5-*di*-p-*tolyl*-1H-1,2,5-*triazapentadienium perchlorate* (3) (90%), m.p. 185—186 °C (decomp.) (from ethanol–ether), which crystallised reproducably as a partial hydrate, τ([$^2H_6$]acetone) 0.99 (1 H, d), 1.97 (1 H, d), 2.3—2.8 (8 H, two overlapping AA′BB′ systems), 7.63 (3 H, s), and 7.69 (3 H, s) (Found: C, 52.55; H, 5.05; N, 11.2. $C_{16}H_{18}ClN_3O_4 \cdot 0.75H_2O$ requires C, 52.6; H, 5.35; N, 11.5%).

1,2,5-*Triazapentadienes* (*General Method*).[8]—A mixture of the pentadienium perchlorate (1 mmol) and sodium carbonate (3 mmol) was suspended in ether or methylene chloride (20 ml), and water (10 ml) was added. The mixture was shaken, with the addition of more solvent if necessary, until the organic layer was deep yellow, and no solids remained. The aqueous layer was extracted twice more with ether or methylene chloride, the combined organic extracts were dried (Na_2SO_4), and the solvent was evaporated off to leave the base, generally as yellow crystals.

By this method were prepared 1,5-*diphenyl*-1,2,5-*triazapentadiene* (4) (80%), m.p. 155—156 °C (decomp.) (from cyclohexane), τ ([$^2H_6$]DMSO) −1.12br (s), 1.77 (1 H, d, ^3J 8.2 Hz), 2.28 (1 H, d, ^3J 8.2 Hz), and 2.5—3.2 (10 H, complex) (Found: C, 75.55; H, 5.85; N, 18.6. $C_{14}H_{13}N_3$ requires C, 75.35; H, 5.85; N, 18.85%), 5,5-dimethyl-1-phenyl-1,2,5-triazapentadiene (8),[8] τ ([$^2H_6$]DMSO 2.34 (1 H, d, ^3J 11.0 Hz), 2.4—2.9 (5 H, complex), 2.95 (1 H, d, ^3J 11.0 Hz), and 6.97 (6 H, s); 1,1-*dimethyl*-5-*phenyl*-1,2,5-*triazapentadiene* (7) (76%) as a pale yellow oil, b.p. 113—115 °C at 0.3 mmHg, τ ([$^2H_6$]DMSO) 1.89 (1 H, d, ^3J 7.8 Hz), 2.5—3.0 (6 H, complex), and 6.92 (6 H, s) (Found: C, 68.45; H, 7.55; N, 23.95. $C_{10}H_{13}N_3$ requires C, 68.55; H, 7.45; N, 24.0%); 1-*phenyl*-5-p-*tolyl*-1,2,5-*triazapentadiene* (5) (95%), m.p. 192—193 °C (from cyclohexane), τ([$^2H_6$]-DMSO) −1.06br (s), 1.76 (1 H, d, ^3J 8.3 Hz), 2.31 (1 H, d, ^3J 8.3 Hz), 2.6—3.2 (9 H, complex), and 7.71 (3 H, s) (Found: C, 76.1; H, 6.6; N, 17.45. $C_{15}H_{15}N_3$ requires C, 75.95; H, 6.35; N, 17.7%); and 1,5-*di*-p-*tolyl*-1,2,5-*triazapentadiene* (6) (80%), m.p. 154—155 °C (sublimed at 10^{-2} mmHg), τ ([$^2H_6$]DMSO) −1.00br (s), 1.77 (1 H, d, ^3J 8.0 Hz), 2.34 (1 H, d, ^3J 8.0 Hz), 2.7—3.1 (8 H, apparently 2s), 7.72 (3 H, s), and 7.79 (3 H, s) (Found: C, 76.2; H, 6.7; N, 16.45. $C_{16}H_{17}N_3$ requires C, 76.5; H, 6.75; N, 16.75%).

Preparation of Authentic Compounds.—Unless otherwise stated, these were commercial samples used without purification. The following materials were prepared by literature methods: 6-methylquinoxaline,[16] b.p. 118—120 °C at 16 mmHg, τ ($CDCl_3$) 1.31 (2 H, AB system), 2.10 (1 H, d), 2.24br (1 H, s), 2.57 (1 H, dd), and 7.56 (3 H, s), *m/e* 144 (100%), 143 (22), 117 (38), 90 (57), and 89 (23); *p*-methylazobenzene,[17] m.p. 68—70 °C, τ ($CDCl_3$) 2.0—2.8 (9 H, complex) and 7.61 (3 H, s), *m/e* 196 (67%), 119 (24), 91 (100), and 77 (39); *pp*′-dimethylazobenzene,[18] m.p. 142—144 °C, τ ($CDCl_3$) 2.22 (4 H, d), 2.75 (4 H, d), and 7.61 (6 H, s), *m/e* 210 (43%), 119 (20), and 91 (100); *N*-phenyl-*p*-toluidine,[19] m.p. 87—88 °C, τ ($CDCl_3$) 2.8—3.3 (9 H, complex), 4.24br (1 H, s), and 7.75 (3 H, s), *m/e* 183 (100%) and 182 (25); di-*p*-tolylamine,[20] m.p. 77—78 °C, τ ($CDCl_3$) 3.04 (8 H, AA′BB′ system), 4.7vbr (s), and 7.74 (6 H, s), *m/e* 197 (100%), 196 (30), and 91 (20); *NN*′-diphenylformamidine,[21] m.p. 137—138 °C, τ ($CDCl_3$) 0.3vbr (s), 1.83 (1 H, s), and 2.6—3.2 (10 H, complex), *m/e* 196 (34%) 195 (20), 104 (14), 93 (100), and 77 (14); * *N*-phenyl-*N*′-*p*-tolylformamidine,[22] m.p. 95—97 °C [this melting-point is significantly different from those reported,[22,23] but was unchanged after two crystallisations from light petroleum; g.l.c.–mass spectrometry (2½% SE30, 215 °C) on both the crude and recrystallised samples confirmed [23] the presence of *NN*′-diphenylformamidine (*m/e* 196) and *NN*′-di-*p*-tolylformamidine (*m/e* 224) as contaminants], τ ($CDCl_3$) −0.1br (s), 1.86 (1 H, s), 2.6—3.2 (9 H, complex), and 7.73 (3 H, s), *m/e* 210 (58%), 209 (18), 107 (87), and 93 (100); and *NN*′-di-*p*-tolylformamidine,[18] m.p. 139—140 °C (prepared by the action of *p*-toluidine on triethyl orthoformate in the presence of a trace of methanolic hydrogen chloride), τ ($CDCl_3$) 0.90br (s), 1.88 (1 H, s), 2.94 (4 H, d), 3.12 (4 H, d), and 7.72 (6 H, s), *m/e* 224 (47%), 223 (9), and 107 (100).

Reaction of N-*Phenyl*-N′-p-*tolylformamidine with Aniline*.—Aniline (53.2 mg, 0.57 mmol) was added to a solution of the formamidine (32.3 mg, 0.15 mmol) in $CDCl_3$ (0.3 ml). After 22 h at room temperature, the presence of two formamidines was apparent from two peaks in the region τ 1.85—1.95, and that of *p*-toluidine by its characteristic singlet at τ 7.80 in the n.m.r. spectrum of the mixture.

Pyrolysis Experiments (*General Method*).—The triazapentadiene (*ca.* 0.5 mmol) was sublimed at *ca.* 10^{-2} mmHg into a silica tube (30 cm) which was maintained at 600 °C. The products were trapped in a U-tube which was cooled by liquid nitrogen and situated at the exit point of the furnace. The pressure was measured by either a McLeod or a Pirani gauge situated between the trap and the pump.

The crude pyrolysate was dissolved in $CDCl_3$ (0.3 ml) and this solution was analysed directly by n.m.r. [after the

* Benzaldehyde phenylhydrazone, which is isomeric, shows a different breakdown pattern: *m/e* 196 (100%) 195 (33), 93(30), 92 (47), 77 (16), and 66 (21).

addition of cyclohexane (5 μl) as an integral calibrant] and by g.l.c. (2½ SE30 and 2½% Carbowax). Relative yields were calculated from the g.l.c. results by calibration of detector response with authentic samples. Absolute yields were obtained from the n.m.r. spectra by relating the integral of the 2,3-protons of the quinoxaline to that of the added cyclohexane, and are reported as the average of two pyrolyses. This procedure is estimated to be accurate to ±5%. Minor products were identified by g.l.c.–mass spectrometry (2½ SE30, unless otherwise stated) and by comparison (g.l.c.) with authentic samples. Results are quoted as follows: triazapentadiene, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time, and products, with their yields and parent ions in their mass spectra. In all cases, breakdown peaks were consistent with those of authentic samples.

1,5-*Diphenyl*-1,2,5-*triazapentadiene* (4). 94.5 mg (0.42 mmol), 110 °C, 600 °C, 2—8 × 10^{-3} mmHg, 30 min: aniline (44%), *m/e* 93; benzonitrile (4%), resolved from aniline on Carbowax, *m/e* 103; quinoxaline (35%), *m/e* 130; biphenyl (trace), resolved on Carbowax, *m/e* 154; azobenzene (1%), *m/e* 182; diphenylamine (3%), resolved from azobenzene on Carbowax, *m/e* 169; diphenylformamidine (3%), *m/e* 196; residue in inlet 0%.

1-*Phenyl*-5-p-*tolyl*-1,2,5-*triazapentadiene* (5). 114.2 mg (0.48 mmol), 125 °C, 600 °C, 5—8 × 10^{-3} mmHg, 30 min: toluene (trace), *m/e* 92; aniline (69%), *m/e* 93; *p*-toluidine (7%), *m/e* 107; *p*-toluonitrile (6%), *m/e* 117; 6-methylquinoxaline (35%), *m/e* 144; azobenzene (1%), *m/e* 182; *N*-phenyl-*p*-toluidine (1%), *m/e* 183; *NN'*diphenylformamidine (1%), *m/e* 196; *N*-phenyl-*N'*-*p*-tolylformamidine (0.5%), *m/e* 210; residue in inlet 0%.

1,5-*Di*-p-*tolyl*-1,2,5-*triazapentadiene* (6). 49.7 mg (0.20 mmol), 135 °C, 600 °C, 5—10 × 10^{-3} mmHg, 30 min: toluene (trace), *m/e* 92; *p*-toludine (46%), *m/e* 107; *p*-toluonitrile (4%), *m/e* 117; 6-methylquinoxaline (36%), *m/e* 144; di-*p*-tolylamine (1%), *m/e* 197; *p,p'*-dimethylazobenzene (1%), *m/e* 210 (the pyrolysis was not analysed for formamidines); residue in inlet 5%.

Mixed pyrolysis of 1,5-*diphenyl*- (4) *and* 1,5-*di*-p-*tolyl*-1,2,5-*triazapentadiene* (6). In order to minimise solid-state co-decomposition, both bases were contained in a separate test-tube within the inlet system, with the open end protruding into the heated zone of the furnace. The pyrolysate was analysed only for the azobenzene–diarylamine fraction. SE30 at 170 °C resolved *p*-methylazobenzene, *p,p'*-dimethylazobenzene, *N*-phenyl-*p*-toluidine, and di-*p*-tolylamine. Azobenzene and diphenylamine were indistinguishable; these were resolved on Carbowax at 190 °C, though *p,p'*-dimethylazobenzene and *N*-phenyl-*p*-toluidine could not be separated under these conditions. Diphenyl derivative, 32.0 mg (0.14 mmol); di-*p*-tolyl derivative, 28.9 mg (0.12 mmol), 135 °C, 600 °C, 10^{-2} mmHg, 30 min: azobenzene (19% of fraction) *m/e* 182; *p*-methylazobenzene (15% of fraction), *m/e* 196; *p,p'*-dimethylazobenzene (4% of fraction), *m/e* 210; diphenylamine (27% of fraction), *m/e* 169; *N*-phenyl-*p*-toluidine (18% of fraction), *m/e* 183; di-*p*-tolylamine (17% of fraction), *m/e* 197; residue of diphenyl derivative in inlet 3%; residue of di-*p*-tolyl derivative in inlet 3%.

Hydrazobenzene. 129.7 mg (0.70 mmol), 90 °C, 600 °C, 10^{-2} mmHg, 85 min; aniline (53%) and azobenzene (51%) were identified by n.m.r. and by g.l.c. comparison with authentic samples on Carbowax; traces of minor products were not investigated.

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