Thermolysis of Polyazapentadienes. Part 6.[1] Gas-phase Cyclisation of 1,5-Diaryl-1,5-diazapentadienes: Mechanistic Aspects and some Synthetic Applications

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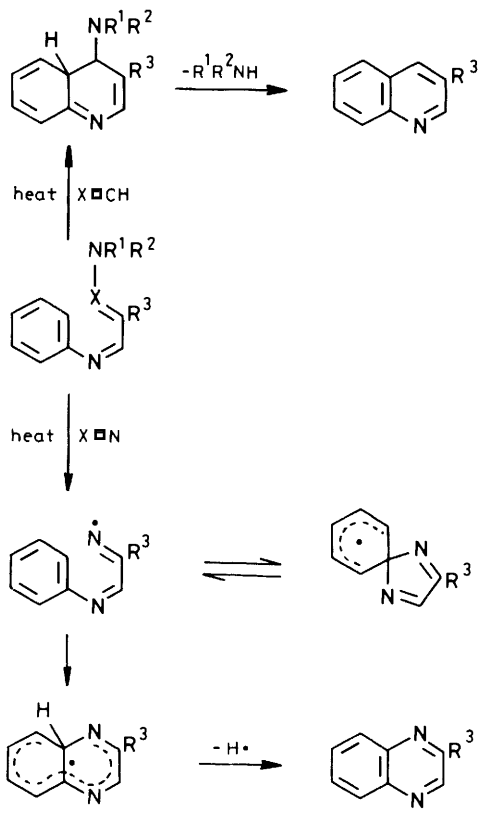
The mode of formation of quinolines by gas-phase pyrolysis of 1,5-diaryl-1,5-diazapentadienes is contrasted with the thermal behaviour of 1,2,5-triazapentadienes. The mechanism involves concerted ring closure followed by a rapid 1,5-hydrogen shift to give a 3,4-dihydroquinoline intermediate, *e.g.* (**19**) or (**21**). Subsequent aromatisation takes place by a stepwise, free-radical process. Methylquinolines (**9**), (**10**), (**12**), and (**13**) were obtained on a preparative scale by this method.

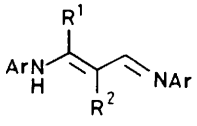
The formation of quinolines by Lewis-acid-catalysed cyclisation of 1-aryl-1,5-diazapentadienes has been known since 1923.[2] More recently, the method has been developed into a useful synthesis by means of Brønsted acid,[3] or base[4] catalysis, and the mechanism under these conditions has been rationalised[4] as an 'electrocyclic ring-closure with elimination' (Scheme 1). Our extension of this work to 5-aryl-1,2,5-triazapentadienes in the gas phase duly leads to quinoxalines, but by an iminyl radical mechanism[5] (Scheme 1). These reactions proceed under relatively mild flash vacuum pyrolysis conditions (600—650 °C) but the yield of quinoxalines is moderate and many by-products are formed. As a consequence of the iminyl mechanism, the reactions are characterised by the effects of methyl groups at certain positions of the starting material. For example (i) a single *o*-methyl group in the 5-aryl ring is ejected;[6] (ii) cyclisation takes place predominantly *ortho* to a *m*-methyl group;[6] (iii) methyl groups in the side-chain are incorporated into the product, though disubstitution (in side-chain and aryl group) gives a mixture of quinoxalines due to scrambling *via* the spirodienyl radical[7] (Scheme 1). Accordingly, we have now studied the reactions of 1,5-diaryl-1,5-diazapentadienes under flash vacuum pyrolysis conditions, with emphasis on the behaviour of methyl substituents as a diagnostic test of the concerted mechanism. In addition, these experiments have provided an authentic source of certain methylquinolines, which were required in connection with another investigation.[8]

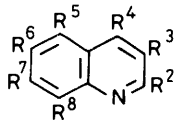
The substrates (**1**)—(**7**) were prepared as perchlorate salts by the action of the appropriate aniline on the acetal (or diacetal) of the 1,3-dicarbonyl compound, in ethanolic perchloric acid,[9] and the free bases were liberated by standard methods. The deuterium atoms of the [$^2H_{10}$] derivative (**7**) did not exchange with the medium, or scramble to other sites of the molecule under these conditions, as shown by mass spectroscopy (M^+ 232) and ^2H n.m.r. [δ 7.22 and 6.98 (ratio 2:3)]. The monodeuteriated derivative (**8**) was obtained specifically from (**1**) by exchange in [^2H]trifluoroacetic acid.

Flash vacuum pyrolysis of 1,5-diazapentadienes requires much more vigorous conditions than the corresponding 1,2,5-triaza compound and total conversion into quinolines needs furnace temperatures of 800—850 °C. Nevertheless, these reactions give better yields of cyclised products, and analyses of the pyrolysates by g.l.c.–mass spectrometry generally show no significant volatile minor products. Pyrolysis of the di-*p*-tolyl derivative (**2**) gives 6-methylquinoline (**10**) exclusively, as shown by ^1H and ^{13}C n.m.r. spectra of an isolated sample. A free-radical cyclisation might have given some 7-methylquinoline (**12**) *via* a spirodienyl radical (Scheme 1) and preferential C–N migration.[10] Cyclisation of the di-*m*-tolyl compound (**3**) gives 7-and 5-methylquinoline (**12**) and (**11**) in a 2:1 ratio: a free-radical mechanism should generate the latter isomer in greater amount.[6] In further contrast to the results for iminyl cyclisation,[6] pyrolysis of the di-*o*-tolyl derivative (**4**) gives 8-methylquinoline (**13**) (40%) with only a trace of quinoline (**9**) (see later) and a small amount of 4-methylquinoline (**15**) (4%).



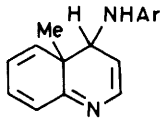
Scheme 1.



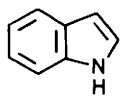


(**1**) Ar = Ph, $R^1 = R^2 = H$
(**2**) Ar = *p*-tolyl, $R^1 = R^2 = H$
(**3**) Ar = *m*-tolyl, $R^1 = R^2 = H$
(**4**) Ar = *o*-tolyl, $R^1 = R^2 = H$
(**5**) Ar = Ph, R^1 = Me, $R^2 = H$
(**6**) Ar = Ph, $R^1 = H$, R^2 = Me
(**7**) Ar = [$^2H_5$]Ph, $R^1 = R^2 = H$
(**8**) Ar = Ph, $R^1 = H$, $R^2 = {}^2H$

(**9**) $R^n = H$
(**10**) R^6 = Me, $R^{n\neq 6} = H$
(**11**) R^5 = Me, $R^{n\neq 5} = H$
(**12**) R^7 = Me, $R^{n\neq 7} = H$
(**13**) R^8 = Me, $R^{n\neq 8} = H$
(**14**) R^2 = Me, $R^{n\neq 2} = H$
(**15**) R^4 = Me, $R^{n\neq 4} = H$
(**16**) R^3 = Me, $R^{n\neq 3} = H$



(17)



(18)

The occurrence of the latter quinoline is unusual, but it may be formed by a 1,2-methyl shift during decomposition of the intermediate (**17**). Unexpectedly, some indole (**18**) was also formed in this reaction: we have previously encountered indoles in iminyl cyclisations with *two ortho*-methyl groups[11] and it seems likely that the aromatic substituent is again involved, though the details of the mechanism remain unclear.

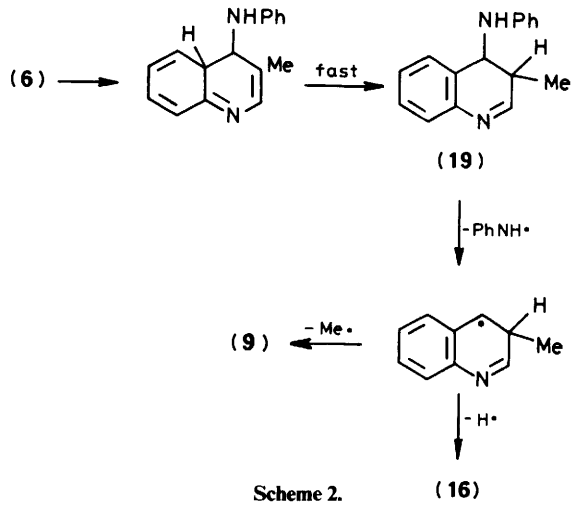
Large scale pyrolyses of (**1**)—(**4**), followed by Hinsberg separation of the aniline or toluidine,[3] and purification *via* the picrate salt if necessary[12] has given pure samples of quinolines (**9**), (**10**), (**12**), and (**13**). Uncontrolled decomposition in the inlet contributes to the lower yields obtained in these preparative reactions. The use of a low molecular weight aliphatic amine as the leaving group,[4] which would have increased the volatility of the base and also obviated the need for the Hinsberg separation, is inappropriate, because of the competitive formation of pyrroles by cyclisation on the alkyl group.[13]

The presence of a substituent on C(2) of the 1,5-diazapentadiene chain destroys the symmetry of the system and indeed both 2- and 4-methylquinolines (**14**) and (**15**) are produced, in a 4.5:1 ratio, by pyrolysis of the 2-methyl derivative (**5**). The major product is formed *via* the less crowded transition state.

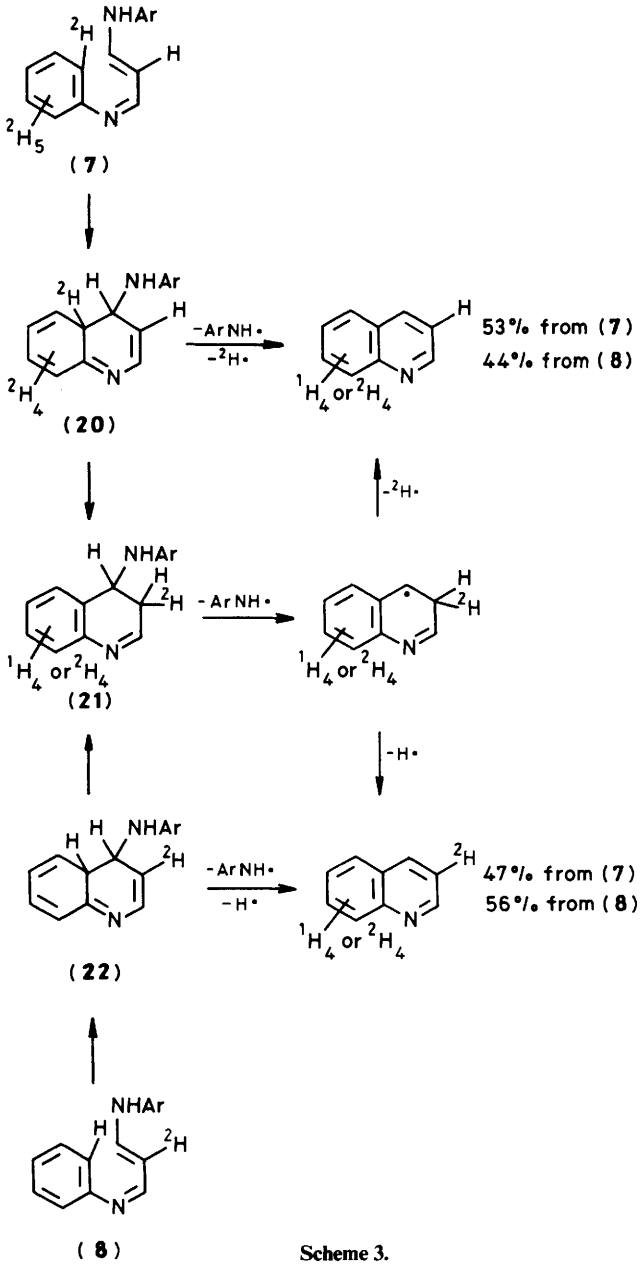
A major distinction between the iminyl and concerted mechanisms lies in the pyrolysis behaviour of 3-methyl derivatives. Whereas 1,5-diaryl-3-methyl-1,2,5-triazapentadienes unexceptionally give 2-methylquinoxalines, the 3-methyl-1,5-diaza analogue (**6**) undergoes cyclisation with concomitant demethylation to give quinoline (**9**) (55%) with only a trace of 3-methylquinoline (**16**) (4%). This result suggests that Scheme 1 presents an incomplete picture of the concerted mechanism, and that the initial cyclisation is followed by a 1,5-hydrogen shift (for which the driving force is regeneration of the benzenoid system) prior to aromatisation of the heterocycle (Scheme 2). Other cases of 1,5-hydrogen shift are known in closely related cyclisations.[14]

We have established that the slower decomposition of (**19**) to give the fully conjugated species (**9**) or (**16**) takes place by a stepwise free radical mechanism (Scheme 2), since a cross-over experiment shows the existence of both arylamino and methyl radicals in the gas phase during these experiments. Thus the amine fraction obtained by co-pyrolysis of (**2**) and (**6**) consists of *N*-methyl-*p*-toluidine in addition to aniline, *N*-methylaniline, and *p*-toluidine: a separate cross-over experiment has confirmed that *N*-methylaniline and *p*-toluidine are stable under the reaction conditions. The order of arylamino and alkyl radical (or hydrogen) cleavage from (**19**) remains ambiguous, though the sequence of Scheme 2 is preferred for consistency with the behaviour of the parent compound (see later). The preponderance of alkyl radical over hydrogen atom cleavage is typical of a free-radical mechanism.[15]

We have proved that the 1,5-hydrogen shift mechanism is general, by examination of the pyrolyses of the complementary deuterium-labelled precursors (**7**) and (**8**) (Scheme 3). In both cases, the amount of migrating species ultimately incorporated at position 3 is 45 ± 2%. The results are best explained by a common mechanism *via* (**21**), superimposed upon a 5—10% leakage by direct cleavage from (**19**) or (**22**). Since a deuterium isotope effect of *ca.* 1.4 is expected at high temperatures,[16] and



Scheme 2.



Scheme 3.

none is observed,* C–H bond breaking cannot be involved in any slow step of the sequence. This is consistent with initial arylamino radical cleavage from (**21**), followed by rapid statistical loss of the protium or deuterium atom (Scheme 3).

This interpretation of the results suggests that the rate constants for direct cleavage from (**20**) or (**22**) are smaller by only a factor of 10—20 than that for 1,5-hydrogen shift to give (**21**). The formation of quinoline from the *o*-tolyl compound (**4**) is therefore best rationalised as a direct cleavage from (**17**), since sigmatropic shifts of alkyl groups are known to be very slow.[18]

Experimental

Unless otherwise stated, n.m.r. spectra were recorded at 100 MHz for solutions in [^{2}H]chloroform.

1,5-Diaryl-1,5-diazapentadiene Salts and Bases.—The perchlorate salts were prepared by the action of the appropriate aniline on the 1,3-dicarbonyl compound, protected as its mono- or di-acetal, in the presence of perchloric acid.[9] The bases were best obtained from the salts by the action of 1 mol equiv. of potassium hydroxide in methanol, as previously described for 1,2,5-triaza-derivatives.[6]

The following derivatives were prepared by these methods: 1,5-diphenyl perchlorate[9] and base, m.p. 112—113 °C (lit.,[19] 114—115 °C); *m/z* 222 (M^+, 100%), 221 (91), 130 (23), and 77 (40); 1,5-di-*p*-tolyl perchlorate, m.p. 232—234 °C (lit.,[19] 231—232 °C), and base, m.p. 160—162 °C (lit.,[19] 164 °C), *m/z* 250 (M^+,100%), 249 (72), 144 (23), and 91 (28); *1,5-di-m-tolyl perchlorate* (70%), m.p. 215—216 °C (from ethanol) (Found: C, 58.05; H, 5.35; N, 7.75. $C_{17}H_{19}ClN_2O_4$ requires C, 58.2; H, 5.4; N, 8.0%); δ_H ([$^2H_6$]acetone) 10.92 (br, d), 8.76 (2 H, dd), 7.0—7.4 (8 H, complex), 6.30 (1 H, t), and 2.32 (6 H, s), and base, m.p. 78—81 °C (^{1}H n.m.r. identical with literature spectrum[20]); *m/z* 250 (M^+, 100%), 249 (78), 144 (24), 91 (41), and 65 (24); *1,5-di-o-tolyl perchlorate* (84%), m.p. 209—211 °C (from ethanol) (Found: C, 58.65; H, 5.4; N, 7.75. $C_{17}H_{19}ClN_2O_4$ requires C, 58.2; H, 5.4; N, 8.0%), δ_H ([$^2H_6$]acetone) 10.7 (br), 8.3—8.9 (2 H, complex), 7.2—7.6 (8 H, complex), 6.59 and 6.01 (1 H, 2 t), and 2.40, 2.36 and 2.32 (3 H, 3 s) (two isomers were present in 6:4 ratio), and base, b.p. 127—132 °C (0.2 Torr) (^{1}H n.m.r. identical with literature spectrum[20]), *m/z* 250 (M^+, 100%), 144 (90), 107 (46), and 91 (29); 2-methyl-1,5-diphenyl perchlorate[21] and *base* (84%), b.p. 140—144 °C (0.1 Torr) which slowly crystallised (Found: C, 81.2; H, 6.55; N, 12.05. $C_{16}H_{16}N_2$ requires C, 81.3; H, 6.8; N, 11.85%), δ_H 11.67 (1 H, br, s), 6.8—7.5 (11 H, complex), 5.02 (1 H, d) and 1.97 (3 H, s), δ_C 165.79 (q), 149.58 (q), 142.78 (q), 139.05, 129.24, 128.61, 122.87, 121.81, 121.14, 115.76, 97.65, and 20.79, *m/z* 236 (M^+, 100%), 235 (53), 221 (37), 145 (97), 118 (30), 93 (27), and 77 (53); *3-methyl-1,5-diphenyl perchlorate* (67%; from the diethyl acetal[22]), m.p. 250—252 °C (from aqueous ethanol–acetone) (Found: C, 56.9; H, 5.0; N, 8.35. $C_{16}H_{17}ClN_2O_4$ requires C, 57.05; H, 5.1; N, 8.3%), δ_H ([$^2H_6$]DMSO) 11.12 (2 H, d), 8.58 (2 H, d), 7.1—7.6 (10 H, complex), and 2.09 (3 H, s), and base, m.p. 139—140 °C (lit.,[23] 140—141.5 °C), δ_C 149.94 (br, q), 146.87 (q), 129.14, 122.89, 117.72, and *ca.* 13 (vbr) (broad peaks are apparently associated with an exchange process, which is not apparent in the spectrum of the 2-methyl isomer), *m/z* 236 (M^+, 100%), 235 (76), 218 (21), 144 (29), and 77 (64); 1,5-di([$^2H_5$]phenyl) perchlorate (93%, from [$^2H_5$]aniline), and base, (63%), ^{2}H n.m.r. δ($CHCl_3$) 7.22 (4 ^{2}H, s) and 6.98 (6 ^{2}H, s), *m/z* 232 (M^+, 100%), 231 (49), 230 (95), and 82 (43).

1,5-Diphenyl-1,5-diaza[3-^{2}H]*pentadiene* (*Base*).—The corresponding unlabelled perchlorate (0.64 g, 2 mmol) was dissolved in [^{2}H]trifluoroacetic acid (5 ml). This solution was neutralised with a solution of sodium deuterioxide and extracted thrice with ether. The organic extracts were dried (Na_2SO_4) and concentrated to give the [3-^{2}H] base (0.18 g, 43%); ^{1}H n.m.r. showed a broad singlet at δ 8.27 and no peaks at δ < 6; *m/z* 223 (M^+, 100%) and 222 (95) (there was no significant peak corresponding to [$^2H_2$] species).

Pyrolysis Experiments.—Small-scale (0.5 mmol) pyrolyses were carried out as previously described;[5] conditions are quoted as follows: diazapentadiene, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time, and yields of products [calculated from ^{1}H n.m.r. and confirmed by g.l.c.–mass spectrometry (5% SE30)]. Isolation of the quinoline(s) from preparative pyrolyses (10—15 mmol) was accomplished by the Hinsberg method[3] since attempted chromatographic separation of the aniline was unsatisfactory. Thus, the volatile fraction from a 15 mmol pyrolysis was suspended in a solution of sodium hydroxide (2.3 g) in water (50 ml) and toluene-*p*-sulphonyl chloride (6.0 g, *ca.* two-fold excess) was added. The mixture was stirred at room temperature for 3 h and was then steam distilled. The distillate was saturated with sodium chloride and extracted with methylene chloride (3 × 30 ml), and the organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by bulb-to-bulb distillation at reduced pressure to give the pure quinoline. Yields are often much lower than found in the trial experiments because of significant decomposition in the inlet, and because of losses in work-up.

1,5-Diphenyl, 82.1 mg (0.37 mmol), 100—120 °C, 800 °C, 3—5 × 10^{-3} Torr, 20 min, aniline (*ca.* 73%), *m/z* 93; quinoline (46%), *m/z* 129; unchanged 1,5-diphenyl-1,5-diazapentadiene (*m/z* 222) was also present and so most subsequent pyrolyses were carried out at 850 °C; residue in inlet 7%. Pyrolysis of the base (3.33 g, 15 mmol) at 850 °C and 10^{-2} Torr (inlet temperature 110—120 °C) over 2.5 h gave a volatile fraction (2.08 g), a tarry involatile fraction at the exit point of the furnace (0.43 g) and a residue in the inlet (0.78 g, 23%). Hinsberg separation of the volatile fraction as before gave quinoline (0.76 g, 39%), b.p. 98—101 °C (16 Torr) (lit.,[24] 238 °C), δ_H (200 MHz) 8.61 (1 H, dd), 7.88 (1 H, d), 7.70 (1 H, d), 7.3—7.5 (2 H, complex), 7.17 (1 H, t of d), and 6.96 (1 H, dd); δ_C[25] 149.86, 147.83 (q), 135.45, 128.93, 127.79 (q), 127.30, 125.99, and 120.53.

1,5-Di-p-tolyl, 103.4 mg (0.41 mmol), 110—130 °C, 850 °C, 3—5 × 10^{-3} Torr, 40 min, *p*-toluidine (75%), *m/z* 107; 6-methylquinoline (69%), *m/z* 143; residue in inlet 9%. Pyrolysis of the base (3.75 g, 15 mmol) at 850 °C and 10^{-2} Torr over 3.5 h (inlet temperature 150—170 °C) gave a volatile fraction (2.35 g) and a residue (0.74 g, 20%). Hinsberg separation of the volatiles as before gave 6-methylquinoline (0.84 g, 39%), b.p. 110—112 °C (16 Torr) (lit.,[26] 258 °C), δ_H (200 MHz) 8.68 (1 H, dd), 7.87 (1 H, d), 7.78 (1 H, d), 7.2—7.3 (2 H, complex), 7.09 (1 H, dd), and 2.30 (3 H, s); δ_C[25] 148.86, 146.37 (q), 135.64 (q), 134.64, 131.05, 128.51, 127.71 (q), 126.01, 120.40, and 20.87.

1,5-Di-m-tolyl, 148.4 mg (0.59 mmol), 120 °C, 850 °C, 2 × 10^{-3} Torr, 15 min, *m*-toluidine (79%), *m/z* 107; 5- and 7-methylquinoline (37% total), *m/z* 143 (^{1}H n.m.r. shows that the mixture is 65% 7-methyl- and 35% 5-methylquinoline); residue in inlet > 15%. Pyrolysis of the base (3.75 g, 15 mmol) at 850 °C and 10^{-2} Torr over 1.5 h (inlet temperature 130 °C) gave only a low total yield of volatiles (1.61 g) after extensive decomposition in the inlet (residue 49%). Hinsberg separation of the volatiles gave 5- and 7-methylquinolines (0.24 g, 11% total), in ratio identical with that of the trial pyrolysis. Pure 7-methylquinoline was isolated by fractional crystallisation[12] of the mixed picrates, which were obtained on the addition of a solution of picric acid (0.8 g; wet with ethanol) in acetone to a solution of the crude mixture (0.24 g) in ether. The yellow solid (0.55 g) so

* In another case, we have obtained isotope effects of > 1.5 under flash vacuum pyrolysis conditions at 650 °C.[17]

obtained was recrystallised twice from ethanol (*ca.* 2 × 350 ml) to give 7-methylquinolinium picrate (0.16 g), m.p. 241—243 °C (lit.,[27] 242 °C), δ_H (200 MHz; [$^2H_6$]DMSO) 9.24 (1 H, dd), 9.07 (1 H, d), 8.57 (2 H, s), 8.25 (1 H, d), 7.9—8.1 (2 H, complex), 7.79 (1 H, dd), and 2.64 (3 H, s). Treatment with base and extraction with methylene chloride gave pure 7-methylquinoline (0.05 g), b.p. 138—141 °C (16 Torr) (lit.,[27] 257 °C), δ_H (200 MHz) 8.81 (1 H, dd), 8.01 (1 H, d), 7.85 (1 H, s), 7.62 (1 H, d), 7.30 (1 H, dd), 7.23 (1 H, dd), and 2.50 (3 H, s); δ_C[25] 150.18, 148.38 (q), 139.54 (q), 135.52, 128.63, 128.26, 127.23, 126.20 (q), 120.09, and 21.68.

1,5-*Di*-o-*tolyl*, 85 mg (0.34 mmol), 120—130 °C, 800 °C, 4 × 10^{-3} Torr, 45 min, aniline (trace), *m/z* 93; *o*-toluidine (40%), *m/z* 107; quinoline (trace), *m/z* 129; 8-methylquinoline (40%), *m/z* 143; 4-methylquinoline (4%), *m/z* 143; recovered starting material (12%); indole (trace), *m/z* 117; residue in inlet 5%. 3-Methylquinoline was unambiguously shown to be absent and 4-methylquinoline unambiguously shown to be present as demonstrated by ^1H n.m.r. 'spiking' experiments with authentic samples. Pyrolysis of the base (3.70 g, 14.8 mmol) at 850 °C and 3 × 10^{-3} Torr (inlet temperature 150 °C) over 3 h gave a liquid pyrolysate (2.65 g). (Residue in inlet 20%). Hinsberg separation gave a mixture of quinolines (0.99 g) from which 8-methylquinoline was obtained by recrystallisation of the picrate salt from ethanol. The picrate had m.p. 199—201 °C (lit.,[28] 200 °C), δ_H (200 MHz; [$^2H_6$]DMSO) 9.19 (1 H, dd), 9.12 (1 H, dd), 8.51 (2 H, s), 8.14 (1 H, d), 8.05 (1 H, dd), 7.93 (1 H, br, d), 7.78 (1 H, t), and 2.77 (3 H, s).

2-*Methyl*-1,5-*diphenyl*, 82 mg (0.35 mmol), 140—150 °C, 800 °C, 5 × 10^{-3} Torr, 45 min, aniline (56%), *m/z* 93; *N*-methylaniline (trace), *m/z* 107; 2-methylquinoline (54%), *m/z* 143; 4-methylquinoline (12%), *m/z* 143; residue in inlet 3%. The quinolines were identified by g.l.c. comparison with authentic samples: the presence of 4-methylquinoline was confirmed by 'spiking' the n.m.r. solution with the authentic sample.

3-*Methyl*-1,5-*diphenyl*, 99.1 mg (0.42 mmol), 140 °C, 800 °C, 4 × 10^{-3} Torr, 45 min, aniline (49%), *m/z* 93; *N*-methylaniline (19%), *m/z* 107; quinoline (55%), *m/z* 129; 3-methylquinoline (4%), *m/z* 143; residue in inlet 4%. The minor and major quinolines were identified as before.

1,5-*Di*([$^2H_5$]*phenyl*), 61.5 mg (0.27 mmol), 100 °C, 800 °C, 3 × 10^{-3} Torr, 45 min, residue in inlet 7%. The entire pyrolysate was dissolved in [^2H]chloroform and analysed by ^1H n.m.r. at 360 MHz, which showed significant peaks at δ 8.92 (1.0 H, complex), 8.15 (1.01 H, complex) and 7.39 (0.53 H, dd), due to the 2-, 4-, and 3-protons of quinoline respectively. Deuterium incorporation at position 3 is 47%.

1,5-*Diphenyl*[3-^2H], 71.2 mg (0.32 mmol), 100 °C, 800 °C, 4 × 10^{-3} Torr, 60 min, residue in inlet 7%. ^1H N.m.r. at 360 MHz showed complex signals due to H(2) and H(4), partially coupled to H(3), at δ 9.19 (1.0 H) and 8.70 (1.0 H). The double doublet due to residual ^1H at position 3 overlapped with a doublet of triplets at δ 7.80 (1.44 H): this chemical shift was confirmed by ^2H n.m.r. δ($CHCl_3$) 7.83. Variation of chemical shift with concentration is well known in quinolines. Protium incorporation at position 3 is therefore 44%.

Co-pyrolysis of 1,5-*di*-p-*tolyl*-1,5-*diazapentadiene and* 3-*methyl*-1,5-*diphenyl*-1,5-*diazapentadiene* (for method, see ref. 5). Di-*p*-tolyl derivative (32.5 mg, 0.13 mmol), diphenyl derivative (33.6 mg, 0.14 mmol), 150 °C, 850 °C, 3 × 10^{-3} Torr, 45 min. Residues in inlet 22% and 4%, respectively. Analysis by g.l.c. (5% Carbowax, 140 °C) showed the presence of *N*-methylaniline (*m/z* 107), aniline (*m/z* 93), *N*-methyl-*p*-toluidine (*m/z* 121), and *p*-toluidine (*m/z* 107). Assignments were confirmed by comparison with authentic samples and by g.l.c.–mass spectrometry.

Co-pyrolysis of N-*methylaniline and* p-*toluidine*. *N*-methylaniline (220 mg, 2.05 mmol), *p*-toluidine (210 mg, 1.95 mmol), 80—100 °C, 850 °C, 5 × 10^{-3} Torr, 60 min. Only starting materials were detected by g.l.c. (5% Carbowax, 130 °C).

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