Thermolysis of Polyazapentadienes. Part 8.[1,2] The Formation of Pyrroles from 1,1-Dialkyl-5-aryl-1,5-diazapentadienes

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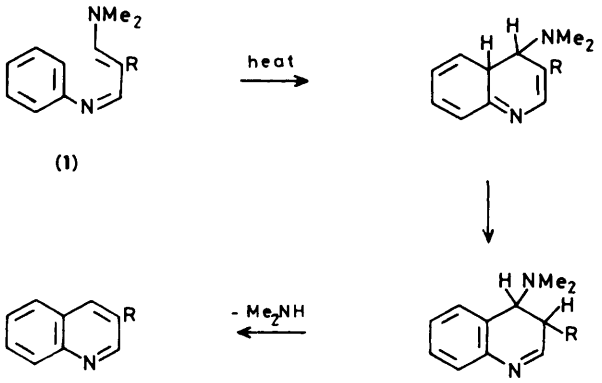
Flash vacuum pyrolysis of the 1,5-diazapentadienes (**4**)—(**10**) gave moderate yields of pyrroles together with quinolines, formed by electrocyclic ring closure with elimination. The pyrroles were formed by hydrogen transfer from an *N*-alkyl group, followed by cyclisation and final aromatisation of the resulting dihydropyrrole intermediate [*e.g.* (**19**)] by free-radical cleavage. The mechanism of the hydrogen transfer and cyclisation is not known with certainty, but may involve diradicals or 1,5-dipolar intermediates.

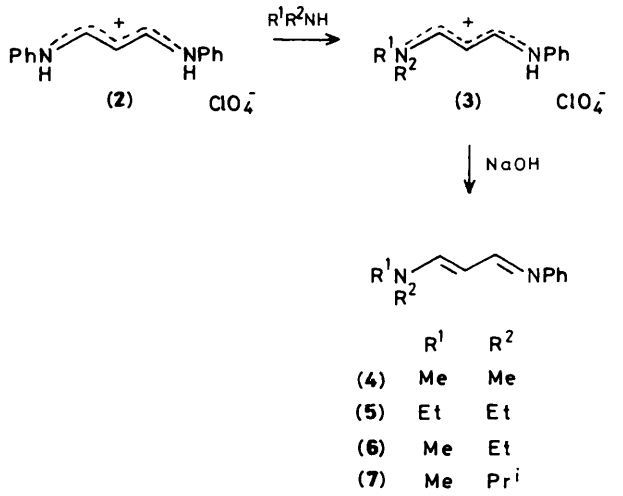
The thermolysis of phenyl-substituted 1,1-dimethyl-1,5-diazapentadienes (**1**) in a high boiling solvent proceeds by electrocyclic ring closure with elimination,[3] and gives an attractive synthetic route to quinolines (Scheme 1). In



Scheme 1.

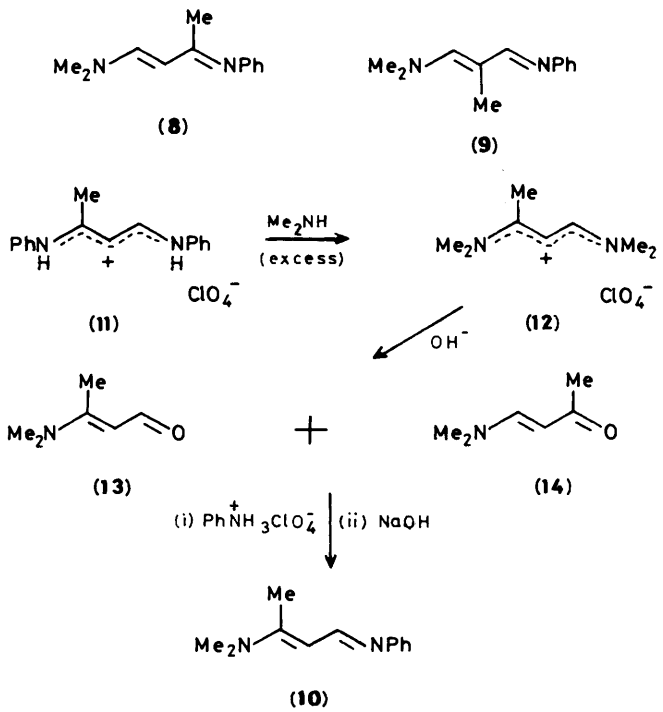
connection with another investigation,[1] we required authentic samples of simple alkylquinolines, and we therefore sought to modify this route by the use of flash vacuum pyrolysis,[4] in order to obviate possible problems in work-up, due to the comparable volatility of the product and the solvent. Surprisingly, quinolines were minor products under these conditions, and instead a new cyclisation–elimination reaction took place to give pyrroles, with incorporation of the carbon atom of one *N*-methyl group from the precursor into the five-membered ring.[2] We now present details of a systematic study of this reaction, in which we report the effect of substituents on the 1-nitrogen atom and at the carbon sites of the diazapentadiene chain. In the following paper, the influence of alternative heteroatoms at the 5-position of the pentadiene chain is investigated.[5]

The required substrates (**4**)—(**7**) were readily made *via* their perchlorate salts (**3**) by utilising the selective monosubstitution[6] of aniline from the dianil (**2**) by an alkylamine[7] (Scheme 2). Conditions had to be separately optimised for each alkylamine, due to competitive formation of the free base of the dianil (**2**) (see Experimental section): for this reason, no substitution products were obtained when di-isopropylamine was used. A similar strategy was employed to synthesize the *C*-methyl derivatives (**8**) and (**9**) from the appropriate dianils.[6,4] The exclusive formation of the derivative (**8**) from the dianil (**11**) by replacement of the anilino group at the unsubstituted terminus is noteworthy, and this methodology was adapted for the preparation of the isomeric compound (**10**) (Scheme 3).



	R^1	R^2
(**4**)	Me	Me
(**5**)	Et	Et
(**6**)	Me	Et
(**7**)	Me	Pr^i

Scheme 2.



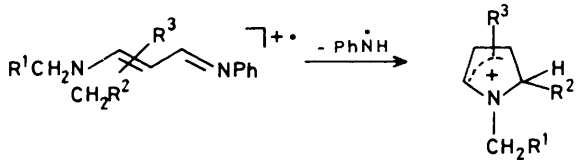
Scheme 3.

Thus replacement of the second anilino group after extended reaction times yielded the pentamethyl derivative (**12**), which could be selectively hydrolysed[8] to give a 2:1 mixture of the aldehyde (**13**) and the ketone (**14**). These were not separated, but were treated with a stoicheiometric amount of anilinium perchlorate based on the amount of aldehyde (**13**). Reaction took place specifically at the aldehyde site to give the perchlorate of compound (**10**) in 70% yield.

The isomers (**8**)—(**10**) were readily distinguished by their n.m.r. spectra, which in addition allowed unambiguous assignment of the spectra of the *C*-unsubstituted pentadienes (**4**)—(**7**). Thus the electron-rich 3-positions give rise to signals at *ca.* δ_H 5.4 and δ_C 99, whereas the electron-deficient 2- and 4-positions resonate to low and high frequency, respectively, of the aromatic signals in the ^1H n.m.r. spectra: their relative positions are maintained in the ^{13}C n.m.r. spectra [δ_C(2-position) *ca.* 152; δ_C(4-position) *ca.* 161]. Vicinal coupling constants $^3J_{H(2),H(3)}$ of *ca.* 13 Hz confirm that the C–C double bonds adopt the *E*-configuration, whereas $^3J_{H(3),H(4)}$ is typically *ca.* 9 Hz. These couplings become equal in the salts (**3**) ($^3J_{HH}$ *ca.* 12 Hz), whereas the chemical shifts of the cations follow similar patterns to those of the bases, although the signals are deshielded by 0.5—1.5 p.p.m.

The *C*-methyl compound (**8**), in which the substituent is located on the carbon atom adjacent to the *N*-phenyl group, exists as a mixture of *E* and *Z* isomers about the C–N double bond, a general feature of such anils.[9,10]

The mass spectra of the 1,1-dialkyl-5-phenyl-1,5-diazapentadienes (**4**)—(**10**) are dominated by loss of an anilino radical to give a species best represented as the pyrrolium cation (**15**) (Scheme 4). This fragmentation route has been proposed



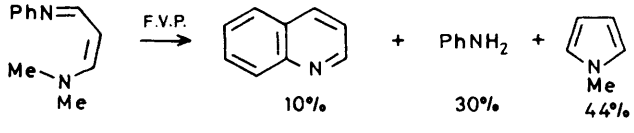
(**15**)

	m/z	%		*m/z*	%
(**4**)	174	15		82	100
(**5**)	202	53	*M**	110	100
(**6**)	188	48		96	100
(**7**)	202	39	*M**	110	100
(**8**)	188	44	*M**	96	100
(**9**)	188	44	*M**	96	100
(**10**)	188	12	*M**	96	35

Scheme 4.

for some 1,2,5-triazapentadienium salts,[11] and is coincidentally parallel to the thermal decomposition pathway discussed below.

Flash vacuum pyrolysis of the 1,1-dimethyl compound (**4**) required a furnace temperature of 800 °C for complete conversion into products, and the same conditions were employed for its analogues (**5**)—(**10**). In contrast to the expected[3] formation of quinoline and dimethylamine (Scheme 1), pyrolysis of compound (**4**) led to *N*-methylpyrrole (**16**) and aniline, with only a small amount of quinoline (Scheme 5). The



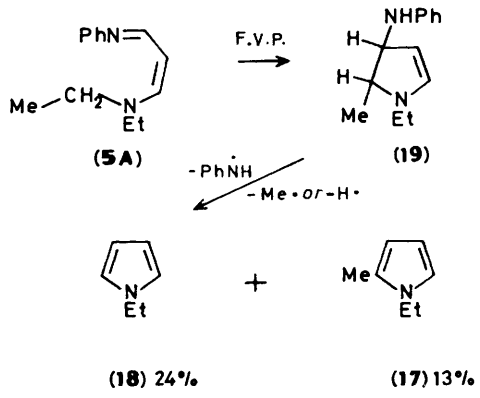
(**4A**) 10% 30% 44%

(**16**)

Scheme 5.

occurrence of the pyrrole (**16**) was particularly surprising, although it could be derived from the starting material (**4**) by elimination of the elements of aniline (the other major product). This requires functionalisation of an unactivated *N*-methyl group of the precursor (**4**) to supply the fourth ring carbon atom of the pyrrole.

In order to test this assumption, the *N*,*N*-diethyl compound (**5**) was pyrolysed, and the 2-methylpyrrole (**17**) (13%) was indeed formed (Scheme 6), in addition to aniline, *N*-methyl-



(**5A**) (**19**)

(**18**) 24% (**17**) 13%

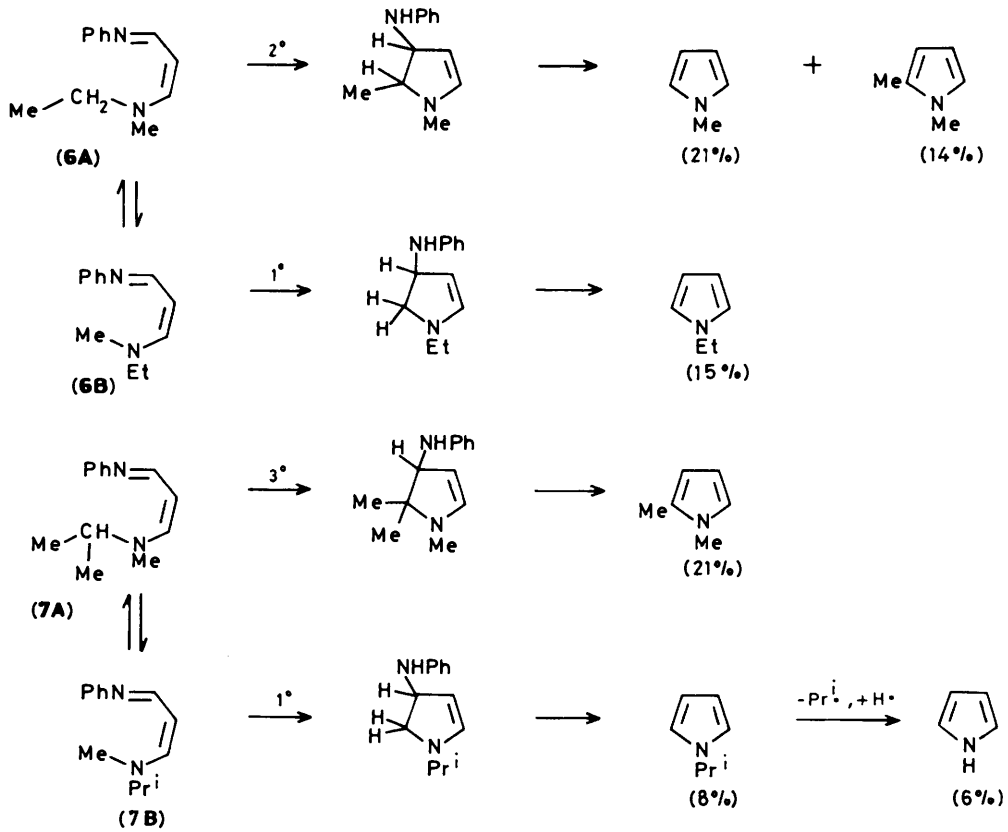
Scheme 6.

aniline, and a trace of quinoline. However, the major 5-membered ring product was *N*-ethylpyrrole (**18**) (24%),* in which the group at the 2-position has been lost in the aromatisation. Competitive loss of alkyl groups rather than hydrogen atoms by free-radical cleavage from dihydro intermediates is a common aromatisation process in pyrolysis chemistry,[4,13] and this suggests that the reaction passes through the intermediate (**19**). The order of cleavage of the methyl and anilino radicals is not known, although there is evidence for initial anilino-group cleavage in related cases[4] (*cf.* ref. 5). As expected, both aniline and *N*-methylaniline are formed from the anilino radical, by capture of a hydrogen atom and methyl group, respectively.

These experiments have given no information as to the mechanism of the formation of the dihydro intermediate [*e.g.* (**19**)] for which activation of the *N*-alkyl group is required at the site adjacent to the nitrogen atom, by some form of hydrogen-transfer process. Although the subsequent aromatisation precludes direct experimental verification, this transfer is almost certainly intramolecular, both by analogy with a related reaction[14,15] and because there is no precedent for specific loss of hydrogen atoms from *N*-alkyl groups under thermal conditions.[16] The molecules can adopt the necessary configuration for intramolecular transfer [*e.g.* (**4A**) and (**5A**)] by *E*/*Z* isomerisation about the 2,3-double bond, which is a general reaction of alkenes under flash pyrolysis conditions.[17]

Some information about the hydrogen transfer may be obtained from the selectivity (primary *versus* secondary *versus* tertiary) of the abstraction in competitive experiments. For comparison, the corresponding selectivity to arylcarbene insertions at 500 °C is 1:4:9.[18] Pyrolysis of the *N*-ethyl-*N*-methyl derivative (**6**) gave all three pyrroles expected for reaction at both possible sites (Scheme 7) with a primary:secondary product ratio of 15%:35%, which corres-

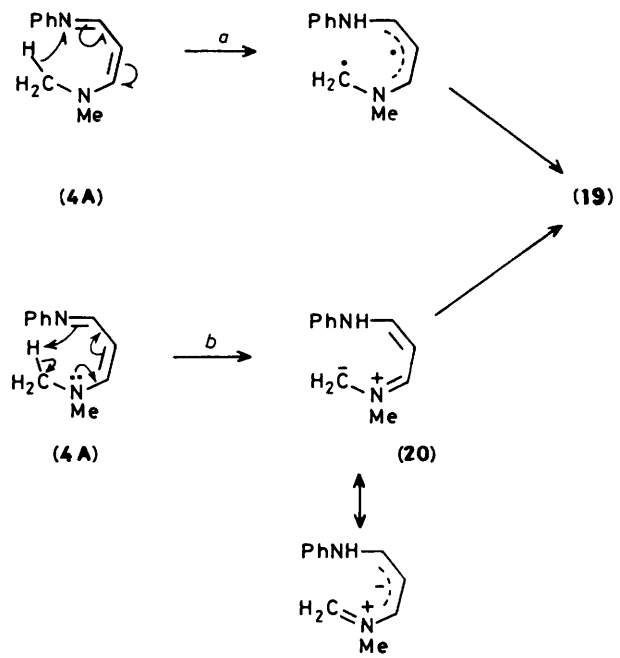
* Thermal rearrangement of *N*- to *C*-substituted pyrroles is a well known reaction[12] but was not observed to any significant extent (*i.e.* less than 10% of the level of the reported products) in the present series of experiments (*cf.* ref 5).



Scheme 7.

ponds to a selectivity of 1:3.5, after statistical correction. The products from pyrolysis of the *N*-isopropyl-*N*-methyl compound (**7**) were complicated by dealkylation of the *N*-isopropylpyrrole to give pyrrole itself (Scheme 7). This reaction was confirmed by independent pyrolysis of *N*-isopropylpyrrole under the same conditions. The total primary:tertiary product ratio is therefore 14%:21%, corresponding to a selectivity of 1:4.5 after statistical correction. Taken together, these experiments display a consistent trend in selectivity, with the tertiary site most reactive and the primary site least reactive, but the effects are small and are open to large errors in the event of unidentified side-reactions. The results therefore remain consistent with our original[2] suggestion of a diradical mechanism (Scheme 8, route *a*) for which the driving force lies in the stability of the allyl and α-aminoalkyl radical[19–21] fragments. However, an alternative mechanism (Scheme 8, route *b*), in which an 8-electron 1,6-sigmatropic hydrogen shift gives the extended dipole (**20**) cannot be excluded, and indeed the required antarafacial transition state is favoured by a spiral configuration of the starting material [*e.g.* (**4A**)] (see also the following paper). A third possible mechanism, in which N–H and C–C bond formation are concerted, is less likely, since it might be expected to be very sensitive to steric effects in the vicinity of the reaction site.

As expected, pyrolysis of the *C*-methyl 1,5-diazapentadienes (**8**) and (**9**) gave moderate yields of 1,3-dimethylpyrrole by formation of the 2,3- and 4,5-bonds, respectively, whereas 1,2-dimethylpyrrole was obtained in low yield from the isomeric compound (**10**). Surprisingly, the level of quinolines, formed by electrocyclisation (Scheme 1) was much increased in these examples (40—50%). This may be due to the acceleration of 1,3,5-triene ring closure, even though effects in model systems are rather small.[22] Alternatively, this may provide circumstantial evidence for the dipolar mechanism for the hydrogen transfer (Scheme 8, route *b*), which would be relatively disfavoured by electron-releasing substituents on the carbon



Scheme 8.

chain. Whatever the explanation, it serves to illustrate the complexity of the energy surface in which such minor structural changes can severely distort the reaction profile. As found previously for the cyclisation of 3-methyl-1,5-diphenyl-1,5-diazapentadiene,[4] both 3-methylquinoline and quinoline itself were identified in the pyrolysate from the 3-methyl derivative (**9**), due to alkyl cleavage in the 3,4-dihydro intermediate (Scheme 1) during aromatisation.

In conclusion, we have shown that pyrroles are obtained from thermolysis of 1,1-dialkyl-1,5-diazapentadienes (**1**) by a hydrogen-transfer–cyclisation–aromatisation sequence. Mechanistically, the reaction is of interest as one of a growing number of examples in which simple thermal functionalisation of *N*-alkyl groups leads to heterocyclic products.[14,15,23–25] Synthetically, the procedure suffers from the low specificity of the aromatisation step: base-induced cyclisation of 1-ethoxycarbonylmethylene derivatives[26] is probably a better preparative route from 1,5-diazapentadienes to pyrroles.

Experimental

^{1}H N.m.r. spectra were recorded either at 80 or 100 MHz. ^{13}C N.m.r. spectra were recorded at 20 MHz. Unless otherwise stated, all n.m.r. spectra were recorded for solutions in [^{2}H]chloroform.

1,1-*Dialkyl-5-phenyl*-1H-1,5-*diazapentadienium Perchlorates*.—The appropriate 1,5-diphenyl-1*H*-1,5-diazapentadienium perchlorate[4,6,7] (20 mmol) was suspended in methanol (10 ml) and the appropriate dialkylamine (40 mmol) added; the perchlorate salt dissolved as the flask was swirled. The solution was set aside for 5 min after which time the product usually crystallised. Ether (100 ml) was added and the product was filtered off and washed with dilute hydrochloric acid (1M; 2 × 25 ml) and then with water (25 ml). The following compounds were prepared by this method.

1,1-*Dimethyl-5-phenyl*-1H-1,5-*diazapentadienium perchlorate* (62%), m.p. 155—157 °C (from aqueous ethanol) (Found: C, 48.0; H, 5.5; N, 10.1. $C_{11}H_{15}ClN_2O_4$ requires C, 48.1; H, 5.45; N, 10.2%); δ_H([$^2H_6$]acetone) 8.55 (1 H, dd), 8.08 (1 H, d), 7.5—7.1 (5 H, m), 5.98 (1 H, t), 3.40 (3 H, s), and 3.18 (3 H, s).

1,1-*Diethyl-5-phenyl*-1H-1,5-*diazapentadienium perchlorate*. This compound precipitated on the addition of ether after the solution had been set aside overnight (73%), m.p. 142—144 °C (from aqueous ethanol) (Found: C, 51.3; H, 6.4; N, 9.25. $C_{13}H_{19}ClN_2O_4$ requires C, 51.55; H, 6.3; N, 9.25%); δ_H([$^2H_6$]acetone) 8.54 (1 H, d), 8.18 (1 H, d), 7.5—7.2 (5 H, m), 6.14 (1 H, t), 3.67 (4 H, t), and 1.32 (6 H, q).

1-*Ethyl*-1-*methyl-5-phenyl*-1H-1,5-*diazapentadienium perchlorate* (79%), m.p. 128—130 °C (from isopropyl alcohol) (Found: C, 50.15, H, 5.9; N, 9.9. $C_{12}H_{17}ClN_2O_4$ requires C, 49.9; H, 5.9; N, 9.7%). ^{1}H N.m.r. showed two isomers to be present, the major isomer is recorded first; δ_H([$^2H_6$]acetone) 8.50 (1 H, br d), 8.24, 8.12 (1 H, d), 7.5—7.2 (5 H, m), 6.03, 6.14 (1 H, t), 3.71, 3.63 (2 H, q), 3.23, 3.45 (3 H, s, and 1.35, 1.28 (3 H, t).

1-*Isopropyl*-1-*methyl-5-phenyl*-1H-1,5-*diazapentadienium perchlorate* (75%), m.p. 112—114 °C (from ethanol) (Found: C, 51.4; H, 6.3; N, 9.3. $C_{13}H_{19}ClN_2O_4$ requires C, 51.55; H, 6.3; N, 9.25%). The aliphatic resonances in the ^{1}H n.m.r. spectrum suggested that two isomers were present in a 7:3 ratio and where appropriate the signal of the major isomer is recorded first; δ_H([$^2H_6$]acetone) 8.56 (1 H, d), 8.29 (1 H, d), 7.4—7.2 (5 H, m), 6.05 (1 H, t), 5.74 (1 H, br s), 4.05, 3.51 (1 H, septet), 3.19, 2.88 (3 H, s,), and 1.38, 1.42 (6 H, d).

1,1,4-*Trimethyl-5-phenyl*-1H-1,5-*diazapentadienium perchlorate* (81%), m.p. 165—167 °C (from ethanol) (Found: C, 50.0; H, 6.0; N, 9.85. $C_{12}H_{17}ClN_2O_4$ requires C, 49.9; H, 5.9; N, 9.7%); δ_H([$^2H_6$]acetone) 8.21 (1 H, d), 7.6—7.2 (5 H, m), 5.35 (1 H, d), 3.32 (6 H, br s), and 2.94 (3 H, s).

1,1,3-*Trimethyl-5-phenyl*-1H-1,5-*diazapentadienium perchlorate* (60%), m.p. 204—206 °C (from aqueous ethanol) (Found: C, 50.15; H, 5.8; N, 9.45. $C_{12}H_{17}ClN_2O_4$ requires C, 49.9; H, 5.9; N, 9.7%); δ_H([$^2H_6$]DMSO) 8.38 (1 H, s), 8.15 (1 H, s), 7.3—6.9 (5 H, m), 4.05 br (1 H, s), 3.23 (6 H, s), and 1.90 (3 H, s).

Attempted Preparation of 1,1-*Di-isopropyl-5-phenyl*-1H-1,5-*diazapentadienium Perchlorate*.—The general method used for the preparation of 1,1-dialkyl-5-phenyl-1*H*-1,5-diazapentadienium perchlorates was tried but did not give the required product even after the mixture was heated under reflux for 6 h.

1,1,2-*Trimethyl-5-phenyl*-1H-1,5-*diazapentadienium Perchlorate*.—(*a*) 1,1,2,5,5-*Pentamethyl*-1H-1,5-*diazapentadienium perchlorate* (**12**). 2-Methyl-1,5-diphenyl-1*H*-1,5-diazapentadienium perchlorate (**11**) (6.73 g, 20 mmol) was suspended in methanol (10 ml), an excess of dimethylamine (6.8 g, 10 ml, 150 mmol) added and the resulting mixture stirred overnight. Ether (150 ml) was added and the *pentadienium perchlorate* precipitated as a pink solid (4.29 g, 90%), m.p. 162—163 °C (from aqueous ethanol) (lit.,[27] m.p. 154—155 °C) (Found: C, 39.9; H, 7.1; N, 11.65. $C_8H_{17}ClN_2O_4$ requires C, 40.15; H, 7.15; N, 11.55%); δ_H([$^2H_6$]DMSO) 8.05 (1 H, d), 5.19 (1 H, d), 3.29 (3 H, s), 3.27 (3 H, s), 3.20 (3 H, s), 3.05 (3 H, s), and 2.29 (3 H, s).

(*b*) 3-*Dimethylamino*-3-*methylacrylaldehyde* (**13**). 1,1,2,5,5-Pentamethyl-1*H*-1,5-diazapentadienium perchlorate (**12**) was hydrolysed using the general method of Arnold.[8] The above perchlorate salt (18.0 g, 75 mmol) was suspended in water (200 ml) and treated with a solution of potassium hydroxide (21.0 g, 375 mmol) in water (200 ml). The mixture was stirred for 2 h at room temperature. The precipitated potassium perchlorate was then filtered off and solid potassium carbonate was added to the filtrate. The resulting solution was extracted with methylene dichloride (6 × 75 ml) and the combined organic extracts were dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was then purified by bulb-to-bulb distillation [b.p. 80—82 °C (0.1 Torr)] to give a yellow solid which became liquid with time (6.8 g, 80%). This liquid was shown by ^{1}H n.m.r. spectroscopy to be a mixture of the required aldehyde and its 1-methyl isomer in a 2:1 ratio. The major product is reported first δ_H 9.48 (1 H, d), 5.15 (1 H, d), 3.02 (6 H, s), and 2.28 (3 H, s); δ_H 7.44 (1 H, d), 5.00 (1 H, d), 2.96 (6 H, s), and 2.08 (3 H, s).

(*c*) 1,1,2-*Trimethyl-5-phenyl*-1H-1,5-*diazapentadienium perchlorate* (**10**). Anilinium perchlorate[28] (1.28 g, 6.7 mmol) was dissolved in ethanol (4 ml) and added to a solution of the above aldehyde–ketone mixture [1.13 g, 6.7 mmol (aldehyde), 3.3 mmol (ketone)] in ethanol (2 ml). A yellow solid precipitated immediately (1.34 g, 70%, based on amount of aldehyde), m.p. 216—218 °C (from aqueous ethanol) (Found: C, 49.7; H, 5.8; N, 9.45. $C_{12}H_{17}ClN_2O_4$ requires C, 49.9; H, 5.9; N, 9.7); δ_H([$^2H_6$]DMSO) 8.79 (1 H, t), 7.8—7.6 (5 H, m), 6.18 (1 H, d), 3.67 (3 H, s), 3.58 (3 H, s), and 2.78 (3 H, s).

1,5-*Diazapentadienes*.—The corresponding perchlorate salt (10 mmol) was suspended in a solution of sodium hydroxide (30 mmol) in water (20 ml). The mixture was extracted with ether (3 × 30 ml) and the combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by bulb-to-bulb distillation. The following compounds were made using this general procedure.

1,1-*Dimethyl-5-phenyl*-1,5-*diazapentadiene* (**4**) (84%), b.p. 152—155 °C (0.1 Torr) (lit.,[29] m.p. 62—65 °C); this compound was fully characterised because of the discrepancy with the literature value (Found: C, 75.85; H, 8.05; N, 16.1. $C_{11}H_{14}N_2$ requires C, 75.85; H, 8.25; N, 16.15%); δ_H 7.95 (1 H, d), 7.4—7.0 (5 H, m), 6.75 (1 H, d), 5.35 (1 H, dd), and 2.80 (6 H, s); *m/z* 174

(M^+, 15%), 130 (11), 96 (23), 93 (35), 82 (100), and 77 (27); δ_C 161.18, 153.14 (q), 153.02, 128.61, 123.37, 120.44, 98.72, and 40.31.

1,1-*Diethyl*-5-*phenyl*-1,5-*diazapentadiene* (**5**) (94%), b.p. 156—159 °C (0.1 Torr) (Found: C, 77.1; H, 8.75; N, 13.95. $C_{13}H_{18}N_2$ requires C, 77.2; H, 8.95, N, 13.85%); δ_H 7.95 (1 H, d), 7.4—7.0 (5 H, m), 6.75 (1 H, d), 5.45 (1 H, dd), 3.21 (4 H, q), and 1.16 (6 H, t); *m/z* 202 (M^+, 53%), 173 (23), 157 (18), 145 (25), 130 (47), 110 (100), 104 (30), and 93 (22); δ_C 161.44, 153.06 (q), 151.03, 128.46, 123.04, 120.31, 97.76, 45.73, and 12.77.

1-*Ethyl*-1-*methyl*-5-*phenyl*-1,5-*diazapentadiene* (**6**) (92%), b.p. 130—133 °C (0.1 Torr) (Found: C, 74.7; H, 8.55; N, 13.8. $C_{12}H_{16}N_2$ requires C, 76.55; H, 8.55; N, 14.90%); δ_H 7.93 (1 H, d), 7.4—7.0 (5 H, m), 6.80 (1 H, d), 5.39 (1 H, dd), 3.21 (2 H, q), 2.81 (3 H, s), and 1.14 (3 H, t); *m/z* 188 (M^+, 48%), 159 (18), 96 (100), 93 (40), and 77 (52); δ_C 161.52, 152.88 (q), 152.38, 128.42, 123.13, 120.26, 98.00, 49.32, 24.87, and 23.58.

1-*Isopropyl*-1-*methyl*-5-*phenyl*-1,5-*diazapentadiene* (**7**) (50%), b.p. 171—173 °C (0.1 Torr) (Found: C, 77.25; H, 8.95; N, 13.9. $C_{13}H_{18}N_2$ requires C, 77.25; H, 8.9; N, 13.85%); δ_H 7.94 (1 H, d), 7.4—7.0 (5 H, m), 6.90 (1 H, d), 5.40 (1 H, dd), 3.52 (1 H, septet), 2.73 (3 H, s), and 1.18 (6 H, d); *m/z* 202 (M^+, 39%), 159 (29), 130 (18), 110 (100), and 77 (32); δ_C 161.70, 153.33 (q), 151.21, 128.75, 123.43, 120.59, 98.47, 55.59, 31.82, and 20.44.

1,1,4-*Trimethyl*-5-*phenyl*-1,5-*diazapentadiene* (**8**) (91%), b.p. 104—106 °C (0.1 Torr) (Found: C, 76.4; H, 8.6; N, 14.9. $C_{12}H_{16}N_2$ requires C, 76.55; H, 8.55; N, 14.9%); ^{1}H n.m.r. showed two isomers to be present, the major isomer is reported first δ_H 7.3—6.6 (6 H, m), 4.77, 5.18 (1 H, d), 2.66, 2.83 (6 H, s), and 2.20, 1.83 (3 H, s); *m/z* 188 (M^+, 44%), 173 (28), 144 (18), 96 (100), and 77 (34); δ_C (the minor isomer is recorded in brackets) 164.26 (165.09) (q), 152.13 (q), 148.07 (146.74), 128.31 (128.19), 121.61 (121.66), 120.55 (120.58), 92.33 (100.06), 40.11, and 22.65 (16.16).

1,1,3-*Trimethyl*-5-*phenyl*-1,5-*diazapentadiene* (**9**) (74%), b.p. 132—136 °C (0.1 Torr) (Found: C, 76.3; H, 8.4; N, 14.65. $C_{12}H_{16}N_2$ requires C, 76.55; H, 8.55; N, 14.88%); δ_H 7.72 (1 H, s), 7.3—6.9 (5 H, m), 6.28 (1 H, s), 2.96 (6 H, s), and 2.10 (3 H, s); *m/z* 188 (M^+, 44%), 173 (18), 159 (14), 144 (29), 96 (100), and 77 (86); δ_C 165.28, 153.75 (q), 152.26, 128.40, 122.89, 120.53, 105.84 (q), 42.57, and 10.68.

1,1,2-*Trimethyl*-5-*phenyl*-1,5-*diazapentadiene* (**10**) (64%), b.p. 127—130 °C (0.1 Torr) (Found: C, 76.4; H, 8.6; N, 14.75. $C_{12}H_{16}N_2$ requires C, 76.55; H, 8.55; N, 14.9%); δ_H 8.29 (1 H, d), 7.3—7.0 (5 H, m), 5.43 (1 H, d), 2.90 (6 H, s), and 2.10 (3 H, s), *m/z* 188 (M^+, 12%), 173 (9), 163 (6), 113 (100), 98 (23), 96 (35), 93 (35), 82 (11), and 77 (17); δ_C 159.58, 156.73 (q), 153.91 (q), 128.68, 123.34, 120.59, 99.08, 39.63, and 14.96.

Preparation of Authentic 1-*Alkylpyrroles*.[30]—Dry dimethyl sulphoxide (100 ml) was added to potassium hydroxide (11.2 g, 0.2 mol) (crushed pellets) and the mixture was stirred for 5 min. The appropriate pyrrole (0.05 mol) was then added and the mixture was stirred for 45 min. The mixture was cooled briefly and the appropriate alkyl halide (0.1 mol) was added before the mixture was stirred for a further 45 min. Water (100 ml) was added, the mixture extracted with ether (3 × 50 ml), and the extracts were washed with water (3 × 25 ml). The combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure (10 Torr) at low temperature. The crude product was then purified by bulb-to-bulb distillation at atmospheric pressure and with the receiver bulb cooled by solid carbon dioxide. The quoted 'boiling points' are the temperature of the Kugelrohr oven. The following compounds were prepared by this general procedure.

1-Ethylpyrrole (**18**) (65%), b.p. 126—130 °C (lit.,[31] b.p. 129—130 °C) δ_H 6.55 (2 H, m, 2- and 5-H), 6.14 (2 H, m, 3- and 4-H), 3.92 (2 H, q), and 1.41 (3 H, t).

1-Ethyl-2-methylpyrrole (**17**) (72%), from 2-methylpyrrole,[32] b.p. 135—137 °C (lit.,[33] b.p. 157 °C); δ_H 6.56 (1 H, m, 5-H), 6.04 (1 H, m), 5.85 (1 H, br m), (3- and 4-H), 4.83 (2 H, q), 2.20 (3 H, s), and 1.35 (3 H, t).

1,2-Dimethylpyrrole (74%), b.p. 102—104 °C (lit.,[34] b.p. 139—140 °C). δ_H 6.51 (1 H, t, 5-H), 5.99 (1 H, t), 5.86 (1 H, br m), (3- and 4-H), 3.47 (3 H, s), and 2.18 (3 H, s).

1-Isopropylpyrrole (68%), b.p. 135—138 °C [lit.,[31] b.p. 49—51 °C (21 Torr)]. δ_H 6.80 (2 H, m, 2- and 5-H), 6.22 (2 H, m, 3- and 4-H), 2.46 (1 H, septet), and 1.51 (6 H, d).

Pyrolysis Experiments.—These were carried out on a small scale (*ca.* 100 mg) as described previously.[35] Unless otherwise stated, the products were identified by g.l.c. and g.c.–m.s. (5% Carbowax or 5% SE 30) comparison with authentic samples. Yields of major products were obtained from the ^{1}H n.m.r. spectrum of the crude pyrolysate, using cyclohexane (5 µl) as an integral standard. The results are presented as follows: compound pyrolysed; quantity; inlet temperature; furnace temperature; pressure range; pyrolysis time; and products with their yields and parent ions from g.c.–m.s. Major products were generally isolated by preparative g.l.c., and their structures were confirmed by ^{1}H n.m.r. spectroscopy.

1,1-*Dimethyl*-5-*phenyl*-1,5-*diazapentadiene* (**4**). 0.108 g (0.62 mmol); 100 °C; 800 °C; 2 × 10^{-3} Torr; 180 min; 1-methylpyrrole (**16**) (44%), *m/z* 81; aniline (30%), *m/z* 93; quinoline (10%), *m/z* 129; residue in inlet 3%. The pyrolysis was then repeated on a larger scale and, using preparative g.c. (10% Carbowax), the major products were separated: 1-methylpyrrole δ_H 6.58 (2 H, t), 6.13 (2 H, t), and 3.63 (3 H, s); aniline δ_H 7.2—6.3 (5 H, m) and 3.35 (2 H, br s); quinoline δ_H 8.90 (1 H, d) and 8.2—7.2 (6 H, m).

1,1-*Diethyl*-5-*phenyl*-1,5-*diazapentadiene* (**5**). 0.097 g (0.48 mmol); 140 °C; 800 °C; 7 × 10^{-3} Torr; 60 min; aniline (41%), *m/z* 93; 1-ethylpyrrole (24%), *m/z* 95; 1-ethyl-2-methylpyrrole (13%), *m/z* 109; *N*-methylaniline (13%), *m/z* 107; quinoline (5%), *m/z* 129; residue in inlet nil. The products obtained by preparative g.c. (10% Carbowax) were aniline δ_H 7.2—6.5 (5 H, m) and 3.45 (2 H, br s); 1-ethylpyrrole δ_H 6.67 (2 H, t), 6.13 (2 H, t), 3.92 (2 H, q), and 1.42 (3 H, t); 1-ethyl-2-methylpyrrole δ_H 6.57 (2 H, t), 6.03 (1 H, t), 5.84 (1 H, m), 3.83 (2 H, q), 2.21 (3 H, s), and 1.34 (3 H, t); *N*-methylaniline δ_H 7.1—6.5 (5 H, m), 3.50 (1 H, br s), and 2.72 (3 H, s); quinoline δ_H 8.88 (1 H, d) and 8.2—7.2 (6 H, m).

1-*Ethyl*-1-*methyl*-5-*phenyl*-1,5-*diazapentadiene* (**6**). 0.109 g (0.58 mmol); 140 °C; 800 °C; 4 × 10^{-3} Torr; 60 min; aniline (37%), *m/z* 93; 1-methylpyrrole (21%), *m/z* 81% 1,2-dimethylpyrrole (14%), *m/z* 95; 1-ethylpyrrole (13%), *m/z* 95; *N*-methylaniline (7%), *m/z* 107; quinoline (8%), *m/z* 129; residue in inlet 3%.

1-*Isopropyl*-1-*methyl*-5-*phenyl*-1,5-*diazapentadiene* (**7**). 0.038 g, (0.19 mmol); 140—160 °C; 800 °C; 3—5 × 10^{-3} Torr; 40 min; aniline (23%), *m/z* 93; 1,2-dimethylpyrrole (21%), *m/z* 95; *N*-methylaniline (14%), *m/z* 107; pyrrole (8%), *m/z* 67; 1-isopropylpyrrole (6%), *m/z* 109; quinoline (5%) *m/z* 129; residue in inlet 5%.

1,1,4-*Trimethyl*-5-*phenyl*-1,5-*diazapentadiene* (**8**). 0.134 g (0.71 mmol); 100 °C; 800 °C; 4 × 10^{-3} Torr; 60 min; 2-methylquinoline (43%), *m/z* 143; 1,3-dimethylpyrrole (20%), *m/z* 95; (although there was no authentic sample for comparison by g.c., the ^{1}H n.m.r. spectrum of the crude pyrolysate showed signals identical with those of the 1,3-dimethylpyrrole isolated below); aniline (19%), *m/z* 93; residue in inlet 1%. The pyrolysis was then repeated on a larger scale and, using preparative g.c. (10% Carbowax), it was attempted to separate out the products. However, 1,3-dimethylpyrrole could not be isolated in this case. Those products which were isolated had their identity confirmed by ^{1}H n.m.r. spectroscopy: aniline δ_H 7.2—6.5 (5 H, m), and 3.55 (2 H, br s); 2-methylquinoline δ_H 8.03 (1 H, m), 7.94 (1 H, m), 7.8—7.2 (4 H, m), and 2.70 (3 H, s).

1,1,3-*Trimethyl*-5-*phenyl*-1,5-*diazapentadiene* (**9**). 0.076 g (0.41 mmol); 120 °C; 800 °C; 3×10^{-3} Torr; 60 min; aniline (44%), *m/z* 93; 1,3-dimethylpyrrole (49%), *m/z* 95; 3-methylquinoline (25%), *m/z* 143; quinoline (21%), *m/z* 129; *N*-methylaniline (13%), *m/z* 107; residue in inlet 1%. The pyrolysis was then repeated on a larger scale and, using preparative g.c. (10% Carbowax), the following products were separated: aniline δ_H 7.2—6.5 (5 H, m) and 3.50 (2 H, br s); *N*-methylaniline δ_H 7.2—6.5 (5 H, m), 3.50 (1 H, br s), and 2.78 (3 H, s); 1,3-dimethylpyrrole δ_H 6.46 (1 H, t), 6.35 (1 H, br s), 5.93 (1 H, m), 3.54 (3 H, s), and 2.05 (3 H, s); quinoline δ_H 8.90 (1 H, d) and 8.2—7.3 (6 H, m); 3-methylquinoline δ_H 8.75 (1 H, d), 8.2—7.3 (5 H, m), and 2.52 (3 H, s).

1,1,2-*Trimethyl*-5-*phenyl*-1,5-*diazapentadiene* (**10**). 0.116 g (0.62 mmol); 160 °C; 800 °C; 5×10^{-3} Torr; 45 min; aniline (33%), *m/z* 93; 4-methylquinoline (26%), *m/z* 143; 1,2-dimethylpyrrole (10%), *m/z* 95; *N*-methylaniline (trace), *m/z* 107; residue in inlet 3%. After preparative g.c. (10% Carbowax), the following products were identified by ^{1}H n.m.r. spectroscopy: aniline δ_H 7.2—6.5 (5 H, m) and 2.75 (2 H, br s); 4-methylquinoline δ_H 8.73 (1 H, d), 8.2—7.1 (5 H, m), and 2.63 (3 H, s); 1,2-dimethylpyrrole δ_H 6.48 (1 H, t), 5.99 (1 H, t), 5.84 (1 H, m), 3.47 (3 H, s), and 2.17 (3 H, s); *N*-methylaniline δ_H 7.2—6.5 (5 H, m) and 2.78 (3 H, s).

N-*Isopropylpyrrole*. 0.28 g (2.57 mmol); 25 °C; 800 °C; 3×10^{-3} Torr; 90 min. The ^{1}H n.m.r. spectrum of the pyrolysate showed a 3:1 ratio of pyrrole and *N*-isopropylpyrrole.

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