Pyrolysis of 1-substituted pyrazoles and chloroform at 550 °C: formation of α-carboline from 1-benzylpyrazoles

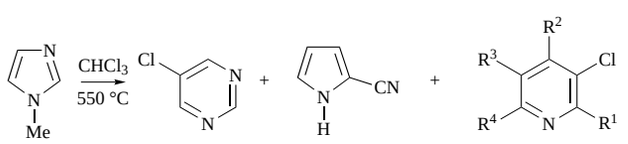
Inayat A. Bhatti, Reginald E. Busby,* Murtedza bin Mohamed, John Parrick * and C. J. Granville Shaw

Chemistry Department, Brunel University, Uxbridge, Middlesex, UK UB8 3PH

Pyrolysis of $^{13}CH_3$ labelled 1-methylpyrazole 8 with chloroform at 550 °C in a continuous flow reactor yields unlabelled 2-chloropyrimidine 9 and 2-cyanopyrrole 10 labelled at the cyano group. However, pyrolysis of 1-benzylpyrazole 14 with chloroform under similar conditions gives 9, 2-phenylpyrimidine 13 and, as the major product, α-carboline 15. Pyrolysis of several substituted 1-(arylmethyl)pyrazoles and the use of ^{13}C and ^{15}N labelled compounds provides direct evidence by which the positions of 7 atoms of 1-benzylpyrazole can be located in the α-carboline. These data support the mechanisms suggested for the formation of 9, 10, and 15.

At 550 °C, chloroform is known to give hydrogen chloride and dichlorocarbene.[1] When a mixture of chloroform and an *N*-unsubstituted azole is passed through a flow reactor at 550 °C a ring expansion reaction occurs by incorporation of the carbon atom of chloroform to form the six-membered ring. Thus, when a solution of pyrrole in chloroform is vapourised into a pyrolysis tube the products are chloropyridines.[2] In a similar way, imidazole gives both 5-chloropyrimidine and 2-chloropyrazine.[3]

Liquid phase processes giving dichlorocarbene in the presence of pyrrole and imidazole heterocycles may give the same products but in lower overall yield and in a different molar ratio.[4] However, *N*-methylimidazole **1** and chloroform in the flow reactor yields 5-chloro-2-methylpyrimidine and 2-chloro-3-methylpyrimidine (in trace quantities) but the major products are 5-chloropyrimidine **2**, 2-cyanopyrrole **3** and the four isomers of cyano-3-chloropyridine **4**–**7** (Scheme 1). The significant



1 **2** **3** **4** R^1 = CN, R^2 = R^3 = R^4 = H; **5** R^1 = R^3 = R^4 = H, R^2 = CN; **6** R^1 = R^2 = R^4 = H, R^3 = CN; **7** R^1 = R^2 = R^3 = H, R^4 = CN

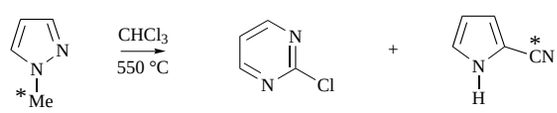
Scheme 1

products are **6** (39%), **2** (24%), **5** (20%) and **3** (10%).[5] It seems likely that these four products are formed directly by the reaction of chloroform (or dichlorocarbene) with **1**. There is evidence that 2-cyanopyrrole **3** in the presence of chloroform at 550 °C affords small quantities of **4** and **7**, so these products found in trace quantities in the pyrolysis of **1** probably arise from a secondary reaction of the pyrrole **3** in the reactor.[5] Also, it is known[6] that 1-methylimidazole **1** rearranges to 2-methylimidazole at 600 °C and this may account for the trace quantity of 5-chloro-2-methylpyrimidine. However, it is noteworthy that in total our investigations have involved the pyrolysis with chloroform of 73 unsubstituted and substituted 5-membered heterocycles and identification of 234 products. Although starting materials (33 examples) and desubstitution (usually *N*-desubstitution) products have been identified in certain pyrolysates, in no case has a product been identified where only migration of substituents to give a positional isomer of the starting material occurred.

The primary products of the reaction of 1-methylimidazole **1** with chloroform at 550 °C can be classified as arising from (i) a ring expansion process giving a chlorinated pyrimidine by a reaction involving incorporation of the carbon atom from chloroform in the ring (**1**→**2**), (ii) a ring expansion in which a six-membered ring is formed and a nitrogen atom becomes part of a nitrile group, *i.e.* two carbon atoms are required to form the new ring (**1**→**4**–**7**), and (iii) a reaction in which the ring size is retained but the heterocycle type changes because a nitrogen atom becomes part of a cyanide substituent (**1**→**3**).

We report now the results obtained in the pyrolysis of 1-substituted pyrazoles with chloroform and disclose a further example of the reaction type (iii) and more interestingly, two novel reaction processes. In the first of the two reaction processes (reaction type iv) the carbon atom of an *N*-substituent is included in the ring to give a product, and in the second process (reaction type v) a fused tricyclic system is formed from an *N*-(arylmethyl)pyrazole. Evidence is presented which provides an insight into the reaction mechanisms. Pyrolysis reactions were performed under standard conditions and no attempt has been made to optimise the formation of a particular product by variation of those conditions.

The reaction of 1-methylpyrazole **8** with chloroform at 550–555 °C gave a product (42% conversion) containing 2-chloropyrimidine **9** (53% of the total product) and 2-cyanopyrrole **10** (47%) (Scheme 2). In all the pyrolyses a deposit



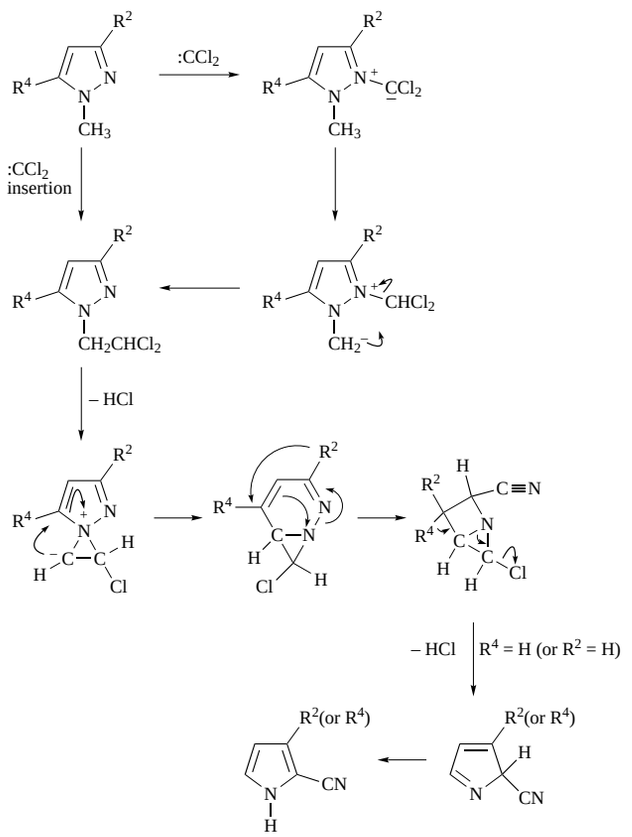
8 **9** **10**

Scheme 2

of carbon was formed in the reaction tube. This deposit was often a shiny, brittle film but did vary in its apppearance with the heterocycle being pyrolysed. Since two or more products were formed by the processes already identified and requiring different stoichiometry, the percentage conversions recorded is the ratio of the weight of isolated basic pyrolysate [mixture free from carbon (char)] to the weight of heterocycle introduced into the reactor. In order to establish the origins of the additional carbon atom in the ring of the pyrimidine **9** and of the carbon atom of the cyanide group in **10**, 1-methylpyrazole was prepared from ^{13}C enriched methyl iodide. Pyrolysis of the labelled compound with chloroform, separation of the products

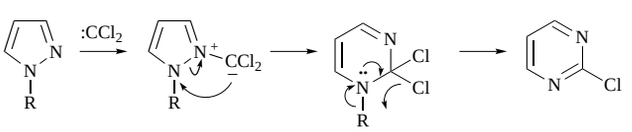
by preparative GLC and comparison of their ^{13}C NMR spectra with those available from pyrolysis of unlabelled methylpyrazole showed that the cyanopyrrole contained the labelled atom in the nitrile function and that no labelling had occurred in the pyrimidine (Scheme 2).

At this stage we had the working hypothesis that the cyanopyrrole was formed by the mechanism in Scheme 3, which



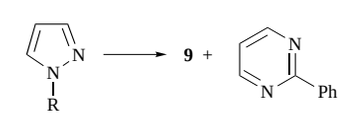
Scheme 3

involves a Stevens type rearrangement, and that the 2-chloropyrimidine was produced by the mechanism in Scheme 4.



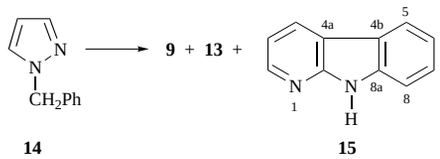
Scheme 4

In an attempt to prevent the formation of the cyanopyrrole and increase the yield of the chloropyrimidine we investigated the reactions of pyrazoles carrying trityl **11**, benzhydryl **12** and benzyl **14** groups as their *N*-substituents. 2-Cyanopyrrole was absent from the products formed in the reactions of **11**, **12** and **14** (Scheme 5 and 6). Compound **12** gave a higher yield of **9**



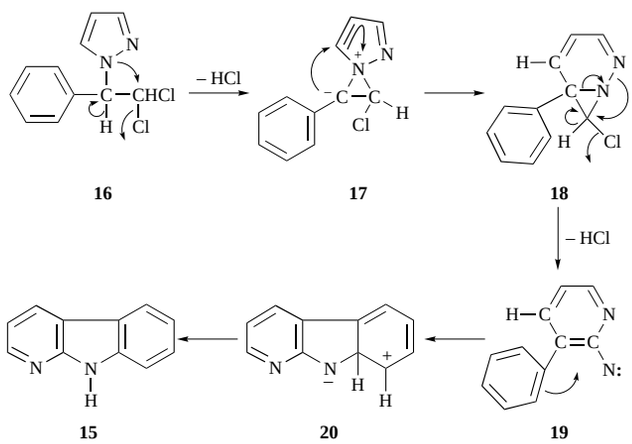
Scheme 5

than was obtained from **8** but 2-phenylpyrimidine **13** was obtained in each case. However, the pyrolysis of 1-benzylpyrazole **14** gave an unexpected result. The yield of **9** was small (*ca*. 3%) and the major products were **13** and α-carboline (9*H*-pyrido[2,3-*b*]indole) **15** (Scheme 6). Replacement of



Scheme 6

chloroform by carbon tetrachloride (known to produce trichloromethyl radicals on pyrolysis[7]) gave no α-carboline. The production of **15**, while initially unexpected, was consistent with the proposed mechanism (Scheme 3) and requires the formation of the dichlorocarbene C–H bond insertion product **16** (Scheme 7), intramolecular reaction to give the spiro intermedi-

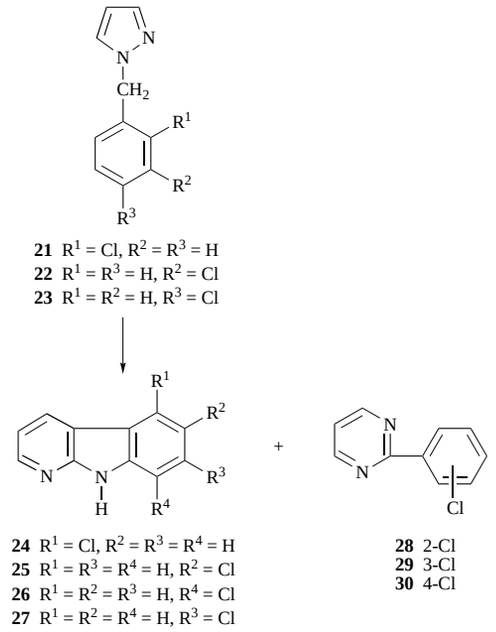


Scheme 7

ate **17** followed by its Stevens-type rearrangement to give **18.** These processes are analogous to the proposed steps in the formation of **3** (Scheme 3). The pathways diverge at the elimination of hydrogen chloride from the 1,2-diazabicyclo-[4.1.0]heptane **18** in Scheme 7 to give the pyridylnitrene **19** which then leads *via* **20** to α-carboline **15**.

Since (i) the pyrolytic breakdown of chloroform alone is catalysed by the carbon deposited on the surface of the combustion tube[8] and (ii) the pyrolysis of chloroform with 2,5-dimethylpyrrole is first order with respect to chloroform and 2,5-dimethylpyrrole is involved in a Langmuir–Hinshelwood mechanism,[4] it is highly likely that the reactions discussed here similarly take place at a surface. The feasibility of a five or six stage series of elimination and rearrangement reactions (Schemes 3 and 7) is more likely if the reaction occurs at the surface of the tube rather than in the vapour phase. Since the elimination steps are largely driven by hydrogen chloride formation, the intermediates would be relatively high energy species. The activation energies of the rearrangement stages would probably, therefore, be relatively low. If it was possible for a surface functionality or a carbon structure to be included in the mechanism it is possible that sequences of some stages could be combined into fewer steps. The possibility that pyrolytic reactions with chloroform involve a radical mechanism has been ruled out.[4]

Attention now turned to a more detailed examination of the pyrolysis of 1-(arylmethyl)pyrazoles in the presence of chloroform in order to get information about the preparative usefulness of the reaction and to obtain more information in support of a mechanism. All the monochloro-α-carbolines are known and characterised[9] and evidence concerning the origin of certain atoms in the α-carboline was obtained by using 1-(chlorobenzyl)pyrazoles as substrates in the pyrolysis reactions (Scheme 8). Pyrolysis of 1-(2-chlorobenzyl)pyrazole **21** in chloroform yielded 5-chloro-α-carboline **24**, but 1-(3-chlorobenzyl)pyrazole **22** gave both 6-chloro- **25** and 8-chloro-α-carboline **26**, and 1-(4-chlorobenzyl)pyrazole **23** afforded



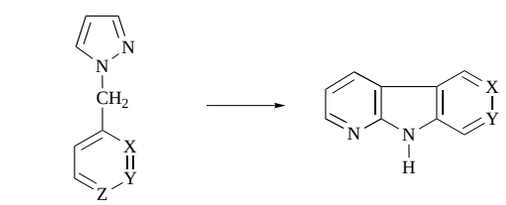
21 R^1 = Cl, R^2 = R^3 = H
22 R^1 = R^3 = H, R^2 = Cl
23 R^1 = R^2 = H, R^3 = Cl

24 R^1 = Cl, R^2 = R^3 = R^4 = H
25 R^1 = R^3 = R^4 = H, R^2 = Cl
26 R^1 = R^2 = R^3 = H, R^4 = Cl
27 R^1 = R^2 = R^4 = H, R^3 = Cl

28 2-Cl
29 3-Cl
30 4-Cl

Scheme 8

7-chloro-α-carboline **27**. In each case the second major product was the 2-(chlorophenyl)pyrimidine **28**–**30** which was expected if the methylene carbon atom provided the C-2 atom of the pyrimidine nucleus. The chlorinated carbolines obtained provide evidence that the 5-, 6-, 7- and 8-carbon atoms of the carboline nucleus are provided by the 2-, 3-, 4- and 5-atoms of the phenyl nucleus, respectively, and indicate that a step in the reaction pathway involves an electrophilic attack on the 2- (or 6-) position of the phenyl group. These ideas were supported when pyrazoles having a *N*-pyridylmethyl substituent were pyrolysed with chloroform. 1,6-Diazacarbazole **34** and 1,7-diazacarbazole **35** (Scheme 9) were isolated as only 2 and 10%

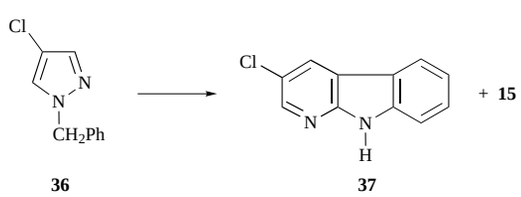


31 X = N, Y = Z = CH
32 X = Z = CH, Y = N
33 X = Y = CH, Z = N

34 X = N, Y = CH
35 X = CH, Y = N

Scheme 9

of the total product from 1-(3-pyridylmethyl)- **32** and 1-(4-pyridylmethyl)-pyrazole **33**, respectively, but no identified basic tricyclic product was obtained from 1-(2-pyridylmethyl)-pyrazole **31** though five unidentified products were formed but none had a mass spectrum expected for a diazacarbazole. Pyrolysis of 1-benzyl-4-chloropyrazole **36** gave mainly 3-chloro-α-carboline **37** but with some α-carboline **15** (Scheme 10). Apart

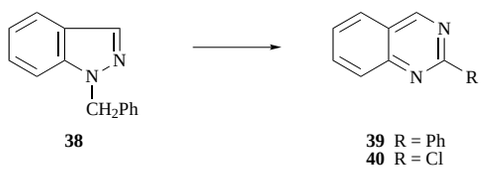


36 **37**

Scheme 10

from the formation of **15** from **36**, these results are in agreement with the reaction mechanism given in Scheme 7 for the formation of the carboline nucleus.

Use of pyrazole derivatives that have a 1-benzyl substituent but where the 3 or 5 position is blocked by a fused ring as in 1-benzylindazole **38** or where the hydrogen atoms are replaced as in 1-benzyl-3,5-dimethylpyrazole **41** did not give a carboline on pyrolysis in chloroform. In these examples the yield of basic organic products (excluding carbonaceous polymer) was smaller than usually found in reactions where carbolines were formed. However, 2-phenylquinazoline **39** was produced from **38** together with 2-chloroquinazoline **40** (Scheme 11) and a

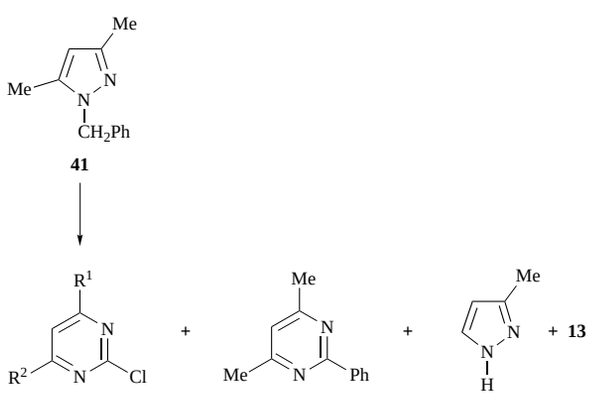


38

39 R = Ph
40 R = Cl

Scheme 11

product we were unable to identify. 1-Benzyl-3,5-dimethylpyrazole **41** afforded 2-chloro-4-methylpyrimidine **42**, 2-chloro-4,6-dimethylpyrimidine **43**, 4,6-dimethyl-2-phenylpyrimidine **44**, 3-methylpyrazole **45** and 2-phenylpyrimidine **13** (Scheme 12).



41

42 R^1 = Me, R^2 = H
43 R^1 = R^2 = Me

44 **45**

Scheme 12

Isotopic labelling with ^{13}C and ^{15}N was also used in attempts to obtain more mechanistically relevant information. Pyrolysis with chloroform of the 1-benzylpyrazole obtained by alkylation of pyrazole with Ph-$^{13}CH_2Cl$ provided a labelled α-carboline and comparison of its ^{13}C NMR spectrum[9,10] with that of unlabelled α-carboline showed the labelled atom to be in the 4a-position (Scheme 6). As expected, the second major reaction product, 2-phenylpyrimidine **13** was labelled at C-2. It was then necessary to determine the origin of the pyridine- and pyrrole-type nitrogen atoms in the carboline. Pyrolysis with chloroform of 1-benzylpyrazole labelled with ^{15}N at position 2[11] afforded α-carboline which showed an enhanced signal at −114.9 ppm in the ^{15}N NMR spectrum and a smaller peak at −258.7 ppm. Pyrrolic nitrogen is known to resonate at lower frequency than a pyridine-type nitrogen atom and the values obtained are in close agreement with published data.[12] Thus, *N*-2 in 1-benzylpyrazole provides the *N*-1 in α-carboline (Scheme 6).

In summary, evidence is provided for the origin (from 1-benzylpyrazole) for six of the ten carbon atoms in α-carboline (a, c, d, e, f and 4 in Fig. 1a) and for one of the two nitrogen atoms. It is very unlikely that C-b and C-g in α-carboline (Fig. 1b) arise from other than the remaining two carbon atoms of the phenyl nucleus of the benzylpyrazole. Unfortunately, the conditions under which the pyrolysis reactions were performed required relatively large quantities of chloroform and financial constraints made it impossible to use ^{13}C labelled chloroform in the reactions. However, it is very likely that the bridgehead atom

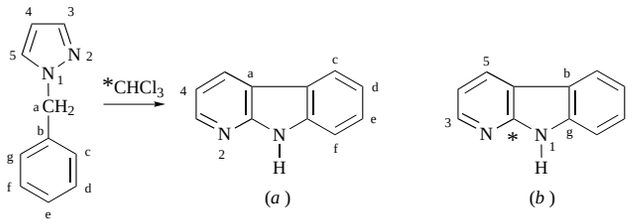


Fig. 1 The (*a*) proven and (*b*) inferred origin of atoms in α-carboline formed by pyrolysis of 1-benzylpyrazole and chloroform

indicated by the asterisk in Fig. 1b arises from chloroform. There remains some doubt about the fate of C-3 and C-5 in the pyrazole. They probably occur in the α-carboline in the positions shown in Fig. 1b but these atoms may be reversed. With that possible exception, the evidence presented is in agreement with the mechanism given in Scheme 7.

Experimental

Melting points were determined using a Gallenkamp melting point apparatus and elemental analyses were carried out by Butterworth Microanalytical Consultancy Ltd. Infrared and ultraviolet spectra were recorded on Unicam SP200 and SP800 spectrophotometers, respectively. ^{1}H and ^{13}C NMR spectra were obtained with Varian T60 and CFT-20 spectrophotometers, respectively, using tetramethylsilane as the internal standard. *J* Values are given in Hz. The ^{15}N NMR spectrum was produced by the Physico-Chemical Measurements Unit, Harwell, using [$^2H_3$]nitromethane as the internal standard. Mass spectra were determined at 70 eV with a Hitachi-Perkin-Elmer RMS4 spectrometer.

The 1-substituted pyrazoles **8**,[13] **14**,[14] **36**[15] and **41**[15] were prepared by known methods from the appropriate 1-unsubstituted pyrazole and one of these *N*-alkylation procedures[14] was used to obtain **21**–**23** and **31**–**33** from pyrazole and the appropriate arylalkyl chloride. The known 1-tritylpyrazole **11**, mp 203–204 °C (lit.,[16] mp 202–202.5 °C), was obtained from the silver derivative of pyrazole in a procedure adapted from that used to prepare 4-bromo-1-tritylpyrazole from 4-bromopyrazole.[16] The same method was used to obtain 1-benzhydrylpyrazole **12** (96%) from pyrazole silver salt and benzhydryl chloride. 1-Benzylindazole **38** was prepared from indazole as described.[17]

Authentic samples for comparison of their GLC retention distances, IR and/or NMR spectra with those of products isolated from pyrolysates were available from commercial sources, **9** and **45**; or from samples produced in our earlier work, **10**,[5] **13**,[5] **24**–**27**,[9] **37**,[9] **42**[18] and **44**,[5] or from the preparation of samples by literature methods, **15**,[19] **39**,[20] **40**[21] and **44**.[22] In the case of 1,6-diazacarbazole (9*H*-dipyrido[2,3-*b*:3′,4′-*b*]pyrrole) **34** identification was established by comparison of its UV and IR spectra with those of an authentic sample provided by Dr G. I. Gregory. The structures of the novel 2-(chlorophenyl)pyrimidines (**28**–**30**) and 1,7-diazacarbazole (9*H*-dipyrido[2,3-*b*:4′,3′-d]-pyrrole) **35** were assigned on the basis of their analytical and spectroscopic data.

General method for 1-trityl- and 1-benzhydryl-pyrazole 11 and 12
A mixture of pyrazole silver salt (prepared from pyrazole and silver nitrate by the procedure employed to obtain the silver salt from 4-bromopyrazole[16]), the alkyl chloride (1 mol equiv.) and benzene was refluxed in the absence of light for 6 h. The silver chloride was filtered off and the filtrate treated with decolourising charcoal, filtered and evaporated.

1-Tritylpyrazole 11. (98%), Mp 203–204 °C (benzene–light petroleum) (lit.,[16] 202–202.5 °C).

1-(Diphenylmethyl)pyrazole 12. The crude product was distilled (bp 228–230 °C/0.07 mmHg) to give the *title compound*, mp 65–65.5 °C (benzene–light petroleum); δ_H[$(CD_3)_2SO$] 6.30 (1H, t, *J* 2, 4-H), 6.94 (1H, s, Ph_2CH), 7.29 (10H, s, 2 × Ph), 7.55 (1H, d, *J* 2, 5-H), 7.68 (1H, d, *J* 2, 3-H); *m*/*z* 234 (M^+, 12%), 168 (25), 167 (100), 165 (50) (Found: M^+ 234.1156. $C_{16}H_{14}N_2$ requires *M*, 234.1157).

General method for 1-(arylmethyl)pyrazoles 21, 22, 23, 31, 32, 33
1-Substituted pyrazoles were prepared from pyrazole by the method employed to prepare 1-benzylpyrazole from pyrazole.[14]

1-(2-Chlorobenzyl)pyrazole 21. (77%), Bp 108 °C/0.9 mmHg; δ_H($CDCl_3$) 5.38 (2H, s, CH_2), 6.23 (1H, dd, *J* 2 and 2.5, 4-H), 7.08 (4H, m, C_6H_4), 7.38 (1H, d, *J* 2.5, 3-H), 7.53 (1H, d, *J* 2, 5-H) (Found: C, 62.44; H, 4.84; N, 14.21. $C_{10}H_9N_2Cl$ requires C, 62.34; H, 4.68; N, 14.59%).

1-(3-Chlorobenzyl)pyrazole 22. (67%), Bp 150 °C/18 mmHg; δ_H($CDCl_3$) 5.23 (2H, s, CH_2), 6.24 (1H, dd, *J* 1.8 and 2, 4-H), 7.10 (4H, m, C_6H_4), 7.36 (1H, d, *J* 2, 3-H), 7.52 (1H, d, *J* 1.8, 5-H) (Found: C, 62.14; H, 4.74; N, 14.34. $C_{10}H_9N_2Cl$ requires C, 62.34; H, 4.68; N, 14.54%).

1-(4-Chlorobenzyl)pyrazole 23. (69%), Bp 88 °C/0.45 mmHg; δ_H($CDCl_3$) 5.18 (2H, s, CH_2), 6.20 (1H, t, *J* 2, 4-H), 7.10 (4H, d, *J* 4.5, C_6H_4), 7.30 (1H, d, *J* 2, 3-H), 7.50 (1H, d, *J* 2, 5-H) (Found: C, 62.73; H, 4.66; N, 14.75. $C_{10}H_9N_2Cl$ requires C, 62.34; H, 4.68; N, 14.54%).

1-(2-Pyridylmethyl)pyrazole 31. (58%), Bp 104 °C/0.8 mmHg; δ_H(CCl_4) 4.50 (2H, s, CH_2), 6.20 (1H, t, *J* 2, 4-H), 6.98 (2H, m, 3′- and 5′-H), 7.46 (3H, m, 3- and 5-H, and 4′-H), 8.44 (1H, d, *J* 3.5, 6′-H) (Found: C, 68.10; H, 5.50; N, 26.32. $C_9H_9N_3$ requires C, 67.92; H, 5.66; N, 26.42%).

1-(3-Pyridylmethyl)pyrazole 32. (59%), Bp 112 °C/0.25 mmHg; δ_H(CCl_4) 5.23 (2H, s, CH_2), 6.20 (1H, t, *J* 2, 4-H), 7.14 (1H, dd, *J* 4.5 and 8, 5′-H), 7.42 (3H, m, 3- and 5-H, and 4′-H), 8.50 (1H, d, *J* 4.5, 6′-H), 8.52 (1H, s, 2′-H) (Found: C, 67.86; H, 5.78; N, 26.59. $C_9H_9N_3$ requires C, 67.92; H, 5.66; N, 26.42%).

1-(4-Pyridylmethyl)pyrazole 33. (50%), Bp 110 °C/0.35 mmHg; δ_H(CCl_4) 5.13 (2H, s, CH_2), 6.15 (1H, t, *J* 2, 4-H), 6.82 (2H, d, *J* 6, 3′- and 5′-H), 7.42 (2H, t, *J* 2, 3- and 5-H), 8.32 (2H, d, *J* 6, 2′- and 6′-H) (Found: C, 67.86; H, 5.47; N, 26.29. $C_9H_9N_3$ requires C, 67.92; H, 5.66; N, 26.42%).

Pyrolysis
The 'horizontal' pyrolysis system[3] with the reaction zone at 550-555 °C was used and the reactants were introduced into the preheater as a solution (Table 1).

The pyrolysis products (a solution in chloroform plus suspended solid) were filtered through Celite and the filtrate evaporated to give a black viscous residue which was treated with warm dilute hydrochloric acid. The insoluble, non-basic fraction was extracted into chloroform. The acidic solution was basified and extracted continuously with chloroform for 18 h. In the cases of the diazacarbazoles **34** and **35**, the concentrated chloroform extract deposited the solids after prolonged standing of the solution at −5 °C.

Products were analysed by GLC and usually isolated by preparative GLC (Tables 1 and 2) with instruments previously described.[23] In all but one case where a known compound was identified (the exception was **34**), the pyrolysis product was 'spiked' with the authentic sample and re-examined by analytical GLC in order to confirm the identity of the product.

Characterisation data for novel products 28, 29, 30, 35 formed as pyrolysis products

2-(2-Chlorophenyl)pyrimidine 28. δ_H($CDCl_3$) 7.30 (4H, m, 5-H and 3′-, 4′- and 5′-H), 7.68 (1H, m, 6′-H), 8.83 (2H, d, *J* 5, 4- and 6-H); *m*/*z* 192 (M^+ for ^{37}Cl, 35%), 191 (25%), (190 M^+ for ^{35}Cl, 100%), 157 (33), 155 (83), 137 (80) (Found: C, 62.71; H, 3.69; N, 14.48. $C_{10}H_7N_2Cl$ requires C, 62.99; H, 3.67; N, 14.70%).

2-(3-Chlorophenyl)pyrimidine 29. *m*/*z* 192 (M^+ for ^{37}Cl, 38%), 191 (26%), 190 (M^+ for ^{35}Cl, 100%), 139 (26), 137 (70), 135 (46) (Found: M^+ 190.0295. $C_{10}H_7N_3{}^{35}Cl$ requires *M*, 190.0297).

Table 1 Pyrolysis reactants, basic products, analysis and isolation conditions

Pyrolysis[a]			Analysis Conditions		Isolation Conditions	
Reactant (g)	Contact time/s[b]	Basic product/g	Column[c]	Temperature/°C	Column[d]	Temperature/°C
8 (10)	5.7	5.2	1	150	A	170
11 (10)	7.75	2.0	1	142–266	B	140–266
12 (10)	6.5	4.2	1	204	A	225
14 (14.7)	5.5	6.2	1	145	C	220
21 (15)	6.4	5.7	1	200	C	250
22 (19.4)	3.5	14.9	1	200–230	C	250
23 (10)	5	4.2	1	180–250	C	250
31 (10)	4.7	6.75	1	180	C	250
32 (13.4)	4.9	7.0	2	200	**34** crystallised from $CHCl_3$	
33 (15)	3.7	10.4	2	200	**35** crystallised from $CHCl_3$	
36 (14.7)	4.3	4.4	1	200	**37** sublimed from residue after evap. of $CHCl_3$	
38 (12)	4.2	1.3	1	230	C	150–250
41 (20)	5.1	4.6	1	140	C	130–200

[a] A solution having a molar ratio of 5:1 for chloroform and reactant was introduced into the preheater of the reactor. [b] Contact (or space) time (c.t.) was calculated from the formula c.t. = time (s) taken to introduce the solution × volume of reactor at 550 °C (cm) ÷ total volume (cm^3) of vapourised solution and N_2 at 550 °C passing through the reactor in the time taken to introduce the sample. [c] Column 1 had 3% OV-17 on acid washed Diatomite C (60–80 mesh); column 2 had 3% OV-225 on the same support. Each column was conditioned at 250 °C before use. [d] All stationary phases were supported on acid washed Diatomite C (30–60 mesh) and the columns A and B were conditioned at 250 °C for 24 h before use. Column A had OV-17 at 20% loading, B had OV-17 (15%) and C had OV-17 (10%) and was conditioned at 300 °C.

Table 2 Composition of basic pyrolysates

Reactants	Products (%)[a]
8	**6** (24), **9** (40), **10** (36)[b]
11	**9** (94), **13** (6)
12	**9** (62), **13** (38)
14	**9** (11), **14** (20), **13** (23), **15** (46)
21	Pyrazole (6), **21** (13), **28** (27), **24** (54)
22	Pyrazole (10), **22** (39), **29** (9), **26** (25), **25** (17)
23	Pyrazole (6), **9** (2), **23** (16), **30** (32), **25** (44)
31	Pyrazole (5), **31** (50), five unidentified products
32	Pyrazole (5), **32** (93), **34** (2)
33	Pyrazole (2), **9** (2), **33** (86), **35** (10)
36	Pyrazole (2), **14** (6), **13** (3), **36** (22), **15** (12), **37** (55)
38	Indazole (17), **40** (6), **38** (2), **39** (63), unknown (12)
41	Pyrazole (7), **45** (7), **44** (16), **42** (28), **13** (7), **41** (15), **43** (20)

[a] Listed in order of increasing retention distance. [b] Isolated from the non-basic fraction of the pyrolysate.

2-(4-Chlorophenyl)pyrimidine 30. Mp 104–106 °C, $\delta_H(CDCl_3)$ 7.44 (2H, d, *J* 8.8, 3′- and 5′-H), 7.56 (1H, t, *J* 5, 5-H), 8.38 (2H, d, *J* 8.8, 2′- and 6′-H), 8.76 (2H, d, *J* 5, 4- and 6-H); *m*/*z* 192 (M^+ for ^{37}Cl, 33%), 191 (16), 190 (M^+ for ^{35}Cl, 100%), 139 (32), 137 (96) (Found: C, 62.75, H, 3.65; N, 14.90. $C_{10}H_7N_2Cl$ requires C, 62.99; H, 3.67; N, 14.70%).

9*H*-Dipyrido[2,3-*b*:4′,3′-*d*]pyrrole 35. The solid from the cold concentrated chloroform extract of the basic pyrolysis products was purified by column chromatography (alumina, ethyl acetate) to give the *title compound*, mp 260–262 °C; $\delta_H[(CD_3)_2SO]$ 7.42 (1H, dd, *J* 5 and 7, 3-H), 8.27 (1H, d, *J* 5, 5-H), 8.76 (4H, m, 2-, 4-, 6- and 8-H), 12.28 (1H, br s, NH exchanged with D_2O) (Found: C, 70.86; H, 4.05; N, 24.59. $C_{10}H_7N_3$ requires C, 71.01; H, 4.14; N, 24.85%).

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