Thermolysis of Polyazapentadienes. Part 9.[1] Gas Phase Thermolyses of Some Dienamines, Enaminones, and Enaminothiones

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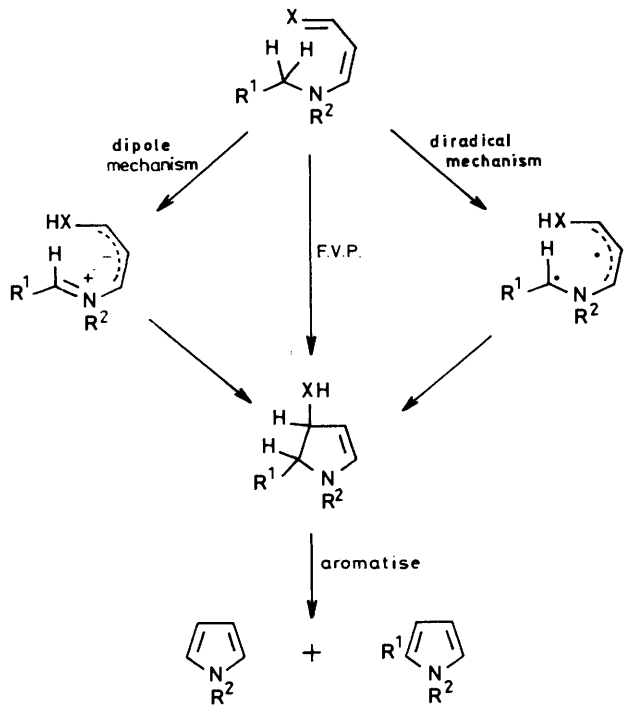
Thermolysis of the title compounds gives low yields of pyrroles by a hydrogen-transfer–cyclisation–aromatisation sequence. The results are best explained by a dipolar mechanism for the hydrogen-transfer step: competitive aromatisation routes account for the range of substituted pyrroles which were obtained.

In the preceding paper,[1] we described a new thermal cyclisation process of 1,5-diazapentadienes which results in the formation of pyrroles by functionalisation of otherwise unactivated *N*-alkyl groups. The mechanism is thought to involve three distinct steps (Scheme 1). First, hydrogen transfer from a site adjacent to

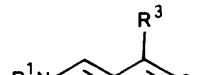


Scheme 1.

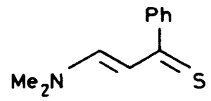
the nitrogen atom, to the terminus of the diazapentadiene chain (X = NPh) gives an intermediate (diradical or dipole, see below) which collapses to a dihydropyrrole in the second step of the sequence. Under the high temperature conditions required (800 °C at 10^{-3} Torr), the dihydro derivatives cannot be isolated, and aromatise by free-radical cleavage[2] of substituent groups (Scheme 1). Since there is no reason that this sequence should be confined to compounds with terminal imino functions (Scheme 1, X = NPh), we have now studied the pyrolyses of closely related dialkylaminobutadiene, dialkylaminoacrylaldehyde, and dialkylaminothioacrylaldehyde derivatives (Scheme 1, X = CH_2, O, and S, respectively). Low yields of pyrroles were obtained in each case, and an analysis of the results casts further light on the hydrogen-transfer and aromatisation steps of the mechanism (Scheme 1: *cf.* ref. 3).

The dienamines (**1**) and (**2**) were made by literature methods.[4,5] Although the dimethylamino compound (**1**) was isolated as an adduct with dimethylamine, the required diene was liberated by pyrolysis[4] (see Experimental section). Three procedures were used to prepare the enaminones (**3**)—(**6**). Dimethylaminoacrylaldehyde (**3**) was obtained by hydrolysis of a vinamidinium salt,[6] and the other acrylaldehyde derivatives (**4**)[7] and (**5**)[7] were obtained by *in situ* oxidation of prop-2-ynyl alcohol in the presence of the secondary amine.[8] The *C*-phenyl derivative (**6**) was made by condensation of acetophenone with

R	
(**1**)	Me
(**2**)	Et



	R^1	R^2	R^3
(**3**)	Me	Me	H
(**4**)	Ph	Me	H
(**5**)	Ph	CH_2Ph	H
(**6**)	Me	Me	Ph

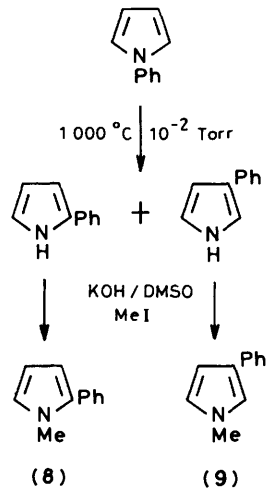


(**7**)

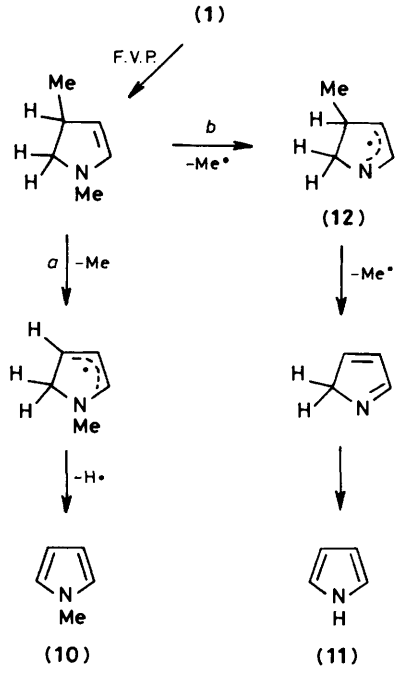
dimethylformamide diethyl acetal,[9] and was converted into the thione (**7**)[10] by treatment with Lawesson's reagent.[11]

Authentic samples of 2[12]- and 3[13]-methylpyrrole and 1-ethylpyrrole[14] were obtained conventionally. Flash vacuum pyrolysis conditions were optimised for the thermal rearrangement[15] of 1-phenylpyrrole to 2- and 3-phenylpyrroles (Scheme 2) together with conditions for the chromatographic separation of the isomers (see Experimental section). These were readily *N*-methylated, either separately or in an admixture, to give the derivatives (**8**) and (**9**), which were characterised by their ^1H n.m.r. spectra. The 3-phenyl derivative (**9**) shows two 1-proton deshielded triplets ($\delta_H > 6.5$; α-positions) and complex benzenoid resonances (δ_H 7.1—7.6) which indicate that conjugation between the two rings is readily achieved. In contrast, the 2-phenyl compound (**8**) shows a shielded 2-proton multiplet (δ_H 6.25; β-positions) together with a relatively sharp multiplet due to the phenyl group, which is twisted out-of-plane by the adjacent methyl group and therefore unable to conjugate effectively with the pyrrole ring.

Pyrolysis of the dienamine (**1**) at 850 °C (10^{-2} Torr) gave *N*-methylpyrrole (**10**; 8%) and pyrrole (**11**; 15%) together with trace amounts of *C*-methylpyrroles as the only significant products by g.c.–m.s. The formation of *N*-methylpyrrole (**10**) can be rationalised by the cyclisation mechanism (Scheme 1), followed by the expected[2] free-radical cleavage of the *C*-alkyl group (Scheme 3, route *a*). Secondary reaction of this product



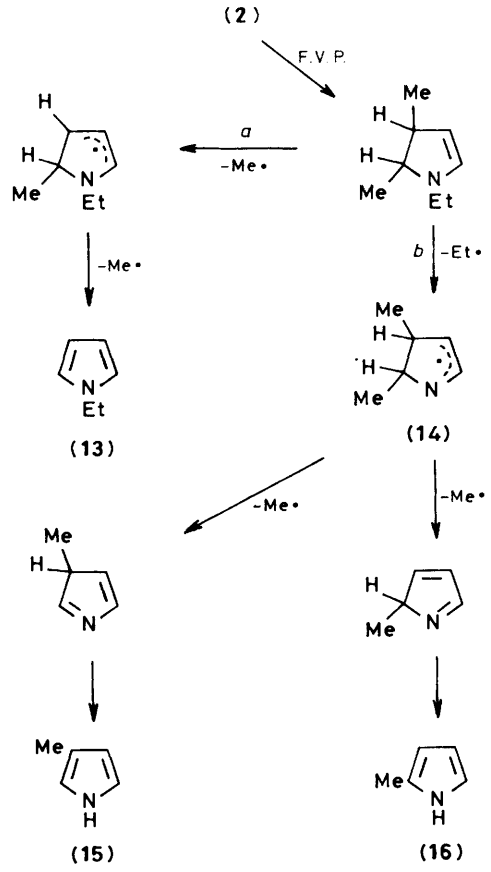
Scheme 2.



Scheme 3.

probably gives rise to the *C*-methylpyrroles, but a control experiment showed that this route is insufficient to account for the substantial proportion of pyrrole (**11**) itself. However, this formation can be explained by the competitive cleavage of the *N*-alkyl group in the dihydro intermediate to give the aza-allyl radical (**12**), which undergoes β-cleavage and aromatisation by 1,5-hydrogen shift (Scheme 3, route *b*). Three points are significant in relation to the imine work[1] (previous paper). First, the absence of route *b* products in that case is indicative of a more favourable aromatisation route, and supports our supposition of initial anilino radical cleavage (Scheme 1, initial cleavage of XH, where X = NPh). Second, the presence of secondary rearrangement products in the present examples only, suggests an increased level of 'chemical activation', for which there is a considerable precedent in the pyrrole series.[16] Third, since the pyrolysis as a whole can take place under significantly milder conditions than for the imines, it suggests that the initial hydrogen-transfer step may be more favourable in the present series.

These ideas are supported by the results of the pyrolysis of the *N*,*N*-diethyldienamine (**2**) at 800 °C (10^{-2} Torr), which gives a complex series of pyrroles, including the *N*-ethyl (14%), 2- and 3-methyl (17%), 2- and 3-ethyl (8.5%) derivatives, and pyrrole (6%) itself. The yields of the last three products were much reduced when the pyrolysis was conducted at a lower temperature (700 °C) and so they are likely to be formed by a secondary reaction of the *N*-ethylpyrrole (**13**) and this was confirmed by independent pyrolysis of compound (**13**). *N*-Ethylpyrrole (**13**) itself is logically formed by route *a* cleavage (Scheme 4); route *b*

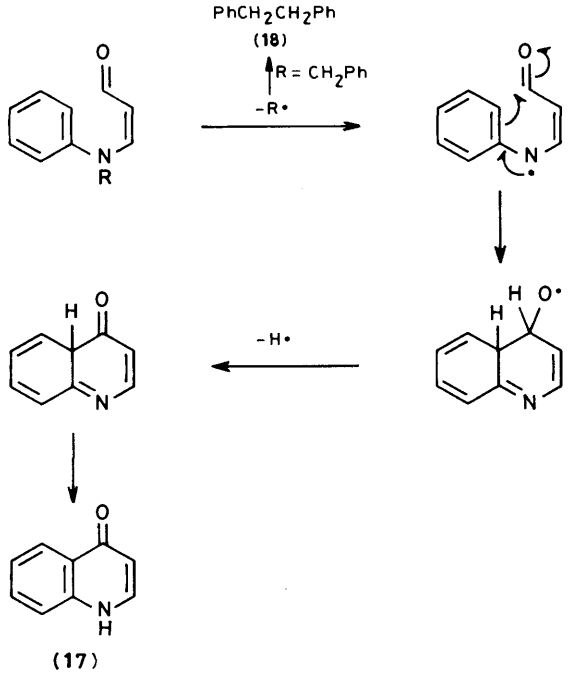


Scheme 4.

cleavage gives the aza-allyl radical (**14**) which can eject an alkyl radical in two ways to give 3-methylpyrrole (**15**) and predominantly, 2-methylpyrrole (**16**), after 1,5-hydrogen shift. The absence of *N*-methylpyrrole is consistent with this mechanism, since sigmatropic shifts of alkyl groups are disfavoured relative to those of hydrogen atoms.[17] Aromatisation by initial cleavage of the 2-methyl group is unlikely,[2] since it does not lead to a resonance-stabilised radical.

In an attempt to overcome the problems of multiple aromatisation mechanisms, the pyrolyses of the readily available enaminones (**3**) and (**6**) and the enaminothione (**7**) were carried out. Although the expected pyrroles were formed in each case, the low yields (< 3%), multiplicity of products [especially from (**6**) and (**7**)], and (in the oxygen series) severity of pyrolysis conditions are all indicative of the initial hydrogen-transfer step being unfavourable relative to other competitive processes. These were identified, in part, by a study of 3-(*N*-methylanilino)acrylaldehyde (**4**) which gave, on pyrolysis at 800 °C, aniline (13%) and *N*-methylaniline (7%) [presumably *via* free-

radical cleavage of the C(3)–N bond] together with quinoline (1%), quinolin-4-one (**17**; 9%) and *N*-phenylpyrrole (9%). The increased level of the pyrrole by comparison with other enaminone examples is consistent with stabilisation of the hydrogen-transfer intermediate (Scheme 1) by the *N*-aryl group. The formation of quinolin-4-one as a significant product is probably initiated by an alternative C–N bond fragmentation (Scheme 5). When this pathway is made more facile, as for the



Scheme 5.

pyrolysis of the *N*-benzyl derivative (**5**), the yield of quinolinone is increased to 57%, and bibenzyl (**18**; 28%) was detected in the pyrolysate.

In conclusion, we have shown in this, and the previous paper,[1] that pyrroles can be formed with varying degrees of efficiency, from a variety of 'heterodiene' substrates (Scheme 1, X = CH_2, NPh, O, S), *via* a hydrogen-transfer–cyclisation–aromatisation sequence. The last two steps are well behaved, although the plethora of aromatisation routes is primarily responsible for mixtures of products. The ease of hydrogen transfer is of particular interest with respect to the diradical or dipolar mechanism (Scheme 1), and is strongly dependent on the nature of the heteroatom (X). In view of complications due to competing reactions, the best criterion of this is probably the minimum pyrolysis temperature, with X = CH_2 ~ S < Nph < O. The relative order of the two cases in which reasonable yields of pyrroles are obtained (X = CH_2, NPh) is the *reverse* of that expected of the diradical mechanism (since the intermediate should be stabilised by electron donation from X[18]), but is consistent with the dipolar mechanism (in which the intermediate would be *destabilised* by electron donation from X) (Scheme 1). We tentatively conclude, therefore, that the 1,5-dipole mechanism (Scheme 1) best fits the available evidence for the hydrogen-transfer step; this is in agreement with other results on related systems.[7]

Experimental

Unless otherwise stated, ^1H n.m.r. spectra were recorded at 80 or 200 MHz, and ^{13}C n.m.r. spectra at 20 or 50 MHz, for solutions in [^2H]chloroform.

1-Dialkylaminobuta-1,3-dienes.—Treatment of diethylamine with crotonaldehyde in the presence of potassium carbonate[5] gave the diethylamino derivative (**2**) (40%), b.p. 115—125 °C (25 Torr) [lit.,[5] 64—66 °C (10 Torr)], δ_H 6.15—6.29 (2 H, m, 1- and 3-H), 5.01 (1 H, dd, *J* 13.3 and 10.5 Hz, 2-H), 4.68 (1 H, dd, *J* 16.8 and 1.9 Hz, 4-H), 4.43 (1 H, dd, *J* 10.1 and 1.9 Hz, 4-H), 3.04 (4 H, q), and 1.07 (6 H, t); δ_C 141.11, 137.20, 103.12, 98.00, 44.72, and 12.73.

Treatment of crotonaldehyde with dimethylamine under the same conditions as above gave a mixture which was predominantly 1,3-bis(dimethylamino)but-1-ene,[4] b.p. 90—100 °C (35 Torr), δ_H 5.86 (1 H, d, *J* 13.8 Hz, 1-H), 4.02 (1 H, dd, *J* 13.8 and 8.4 Hz, 2-H), 2.73 (1 H, m), 2.50 (6 H, s), 2.16 (6 H, s), and 1.07 (3 H, d). The mixture could be substantially converted into 1-dimethylaminobuta-1,3-diene (**1**) by heating[4] [δ_H 6.12—6.26 (2 H, m), 4.98 (1 H, dd), 4.63 (1 H, dd), 4.47 (1 H, dd), and 2.64 (6 H, s) assignments as for the diethylamino compound (above)], and by flash vacuum pyrolysis, and so no attempt was made to obtain completely pure diene for the high temperature pyrolysis work (below).

Preparation of Enaminones.—3-Dimethylaminoacrylaldehyde (**3**) was obtained by hydrolysis of 1,1,5,5-tetramethyl-1,5-diazapentadienium perchlorate as described. previously.[6] 3-(Dimethylamino)acrylophenone (**6**), m.p. 85—88 °C (lit.,[9] 90 °C) was prepared by a literature method,[9] whereas 3-(*N*-methylanilino)acrylaldehyde(**4**)[7] and 3-(*N*-benzylanilino)-acrylaldehyde (**5**)[7] were synthesized by treatment of the appropriate amine with prop-2-ynyl alcohol in the presence of an excess of manganese dioxide (*cf.* ref. 8).

3-(*Dimethylamino*)*thioacrylophenone* (**7**).—The corresponding acrylophenone (1.75 g, 10 mmol) was added to a suspension of Lawesson's reagent[11] (2.02 g, 5 mmol) in dry benzene. The mixture was stirred at room temperature for 18 h and concentrated under reduced pressure. The residue was dissolved in methylene dichloride (50 ml) and the resulting solution poured into dilute aqueous sodium hydroxide (0.05M; 100 ml). The aqueous layer was extracted thrice with methylene dichloride and the combined organic extracts were dried ($MgSO_4$) and concentrated. The crude product (1.77 g) was chromatographed on 6% deactivated alumina [eluant methylene dichloride–light petroleum (b.p. 40—60 °C) 3:1] to give the red thioacrylophenone (0.23 g, 12%), m.p. 109—111 °C (lit.,[10] 115—116 °C); δ_H 7.1—7.9 (6 H, m), 6.54 (1 H, d, *J* 11.7 Hz, 2-H), 3.21 (3 H, s), and 3.00 (3 H, s); *m/z* 191 (M^+, 62%), 158 (100), 121 (30), and 115 (36).

2-Phenyl- and 3-Phenyl-pyrrole.—*N*-Phenylpyrrole (2.14 g, 15 mmol) was sublimed at 60—80 °C during 1 h into a silica furnace tube (2.5 × 30 cm) which was kept at 1 000 °C and 10^{-2} Torr. The products were condensed in a U-tube, cooled by liquid nitrogen, and consisted of a mixture of 1-, 2-, and 3-phenylpyrroles. If required, these could be separated by column chromatography on 6% deactivated alumina [eluant ether–light petroleum (b.p. 40—60 °C) 2:3]. The first component was recovered starting material, followed by the major fraction, 2-phenylpyrrole (0.64 g, 30%); δ_H 8.4 (1 H, br s), 7.0—7.6 (5 H, m), 6.84 (1 H, m), 6.52 (1 H, m), and 6.29 (1 H, m); the next component to be eluted was 3-phenylpyrrole (0.28 g, 13%); δ_H 8.1 (1 H, br s), 7.2—7.6 (5 H, m), 7.07 (1 H, m), 6.82 (1 H, m), and 6.56 (1 H, m).

1-Methyl-2-phenyl- (**8**) *and 1-Methyl-3-phenyl-pyrrole* (**9**) (*cf.* Ref. 14).—The crude mixture of pyrroles from the above pyrolysis (1.43 g, 10 mmol) was added to a suspension of crushed potassium hydroxide (2.24 g, 40 mmol) in dimethyl sulphoxide (50 ml). The mixture was stirred for 45 min after which iodomethane (2.84 g, 20 mmol) was added with cooling,

and the stirring was continued for a further 45 min. The mixture was diluted with water (100 ml) and extracted with ether (3 × 50 ml) and the combined organic extracts were washed with water (50 ml), dried ($MgSO_4$), and concentrated to give a mixture of 2- and 3-phenyl-1-methylpyrroles (1.42 g, 90%). Pure samples of the isomers were obtained by preparative g.l.c. on 10% Carbowax 20 M at 200 °C. The first component was 1-methyl-2-phenylpyrrole, δ_H 7.3—7.5 (5 H, m), 6.74 (1 H, t), 6.25 (2 H, m), and 3.68 (3 H, s); *m/z* 157 (M^+, 100%), followed by 1-methyl-3-phenylpyrrole, δ_H 7.1—7.6 (5 H, m), 6.90 (1 H, t), 6.62 (1 H, t), 6.43 (1 H, dd), and 3.67 (3 H, s); *m/z* 157 (M^+, 100%).

Pyrolysis Experiments.—These were carried out on a *ca.* 1 mmol scale as described previously.[19] Products were identified by g.l.c. (5% Carbowax or 5% SE30) and by g.l.c.–m.s. comparison with authentic samples, unless otherwise stated. Characteristic signals of the products in the ^1H n.m.r. spectra of the pyrolysates were used to estimate the yields, generally with cyclohexane (5 μl) or methylene dichloride (10 μl) as internal 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.l.c.–m.s.

1-*Dimethylaminobuta*-1,3-*diene* (**1**) (0.13 g, 1.1 mmol); 30 °C; 850 °C; 10^{-2}—10^{-3} Torr; 10 min; *N*-methylpyrrole (**10**) (8%), *m/z* 81; pyrrole (**11**) (15%), *m/z* 67; 2- (**16**) and/or 3-methylpyrrole (**15**) (trace), *m/z* 81 (identified by g.l.c.–m.s.; level too low for confirmation by ^1H n.m.r. spectroscopy). Significant peaks at δ_H 2.0—2.5 were not obviously associated with the g.l.c.–m.s. components, and may be due to more volatile (or involatile) materials. Similar results were obtained at a furnace temperature of 700 °C. A control pyrolysis of *N*-methylpyrrole under more extreme conditions (900 °C; pyrolysis tube packed with silica wool) gave pyrrole and *C*-methylpyrroles in *ca.* 1:2.5 ratio.

1-*Diethylaminobuta*-1,3-*diene* (**2**) (0.12 g, 0.99 mmol); 30 °C; 800 °C; 10^{-2}—10^{-3} Torr; 10 min; *N*-ethylpyrrole (**13**) (14%), *m/z* 95; pyrrole (6%), *m/z* 67; 2- and 3-methylpyrrole (17%), *m/z* 81, 2-ethylpyrrole (7.5%), *m/z* 95; 3-ethylpyrrole (2%), *m/z* 95. The assignment of the last two components may be reversed: however, they are formed in a similar ratio, together with pyrrole, by independent pyrolysis of *N*-ethylpyrrole at 800 °C. 2-and 3-Methylpyrrole were distinguished by comparison of the chemical shifts of their *C*-methyl signals in the ^1H n.m.r. spectrum of the pyrolysate, with those of authentic samples. [δ_H(3-methylpyrrole)[13] 6.70 (1 H, m), 6.75 (1 H, m), (2-and 5-H), 6.09 (1 H, m, 4-H), and 2.16 (3 H, s); δ_H(2-methylpyrrole)[12] 6.67 (1 H, m, 5-H), 6.14 (1 H, m), 5.92 (1 H, m), (3- and 4-H), and 2.30 (3 H s). The pyrolysate showed singlets at δ_H 2.29 and 2.16 in a 2:1 ratio corresponding to the 2- and 3-methyl isomers, respectively].

Broadly similar results were obtained at a furnace temperature of 700 °C, although the levels of secondary products (pyrrole, and 2- and 3-ethylpyrrole) were substantially lower. Recovered starting material was obtained at temperatures below 650 °C.

3-*Dimethylaminoacrylaldehyde* (**3**) (0.13 g, 1.28 mmol); 110 °C; 800 °C; 5 × 10^{-3} Torr; 10 min; *N*-methylpyrrole (2.2%), *m/z* 81; pyrrole (trace), *m/z* 67; 2- and/or 3-methylpyrrole (0.8%), *m/z* 81. Only *N*-methylpyrrole was clearly identified by ^1H n.m.r. spectroscopy. Unchanged starting material was also present (< 1%) at 800 °C. No peaks corresponding to products present in > 3% yield could be detected by g.l.c. (Carbowax) after the solvent ($CHCl_3$) had been eluted. Pyrolysis at 700 °C gave recovered starting material only.

3-(*Dimethylamino*)*acrylophenone* (**6**) (0.19 g, 1.09 mmol); 150 °C; 850 °C; 10^{-3} Torr; 20 min; a large number of components were present in < 5% yield of which ethylbenzene (*m/z* 106), styrene (*m/z* 104), indene (*m/z* 116), and naphthalene (*m/z* 128) could be identified by their g.c. retention times and their characteristic breakdown patterns in g.c.–m.s. Similarly, 1-methyl-3-phenylpyrrole (**9**) (*ca.* 3%), *m/z* 157, was identified by comparison with an authentic sample. Some starting material was recovered when the pyrolysis was conducted at 750 °C.

3-(*Dimethylamino*)*thioacrylophenone* (**7**) (7.7 mg, 0.040 mmol); 150 °C; 650 °C; 10^{-3} Torr; 15 min. The only product identified in this extremely complex pyrolysate was 1-methyl-3-phenylpyrrole (*ca.* 3%), *m/z* 157, identical (g.l.c. and g.c.–m.s.) with an authentic sample. No starting material was present, even after pyrolysis at temperatures as low as 650 °C.

3-(N-*Methylanilino*)*acrylaldehyde* (**4**) (67 mg, 0.42 mmol); 150 °C; 800 °C; 5 × 10^{-3} Torr; 20 min; aniline (13%), *N*-methylaniline (7%), quinoline (1%), and *N*-phenylpyrrole (9%) were identified by g.l.c. comparison with authentic samples. The level of expected secondary products (2- and 3-phenylpyrroles) was low under these conditions. In addition, a colourless, crystalline, chloroform-insoluble material was obtained at the exit point of the furnace, which was identified as quinolin-4-one (**17**) (9%) by comparison of its spectra with those of an authentic sample[20] [δ_H([$^2H_6$]DMSO) 11.73 (1 H, br s), 8.08 (1 H, dd), 7.89 (1 H, d, *J* 7.3 Hz, 2-H), 7.64 (1 H, t of d), 7.53 (1 H, d), 7.30 (1 H, t of d), and 6.02 (1 H, d, *J* 7.3 Hz, 3-H); δ_C([$^2H_6$]DMSO), DEPT, 139.24, 131.49, 124.85, 122.92, 118.14, and 108.59].

3-(N-*Benzylanilino*)*acrylaldehyde* (**5**) (11 mg, 0.046 mmol); 160 °C; 800 °C; 2 × 10^{-3} Torr; 30 min; the major chloroform-soluble component was bibenzyl (**18**) (δ_H 2.92; 28%). Quinolin-4-one, spectroscopic parameters identical with those quoted above, was obtained in 57% yield.

Acknowledgements

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