A study of the gas-phase interconversion of 1-(2-aryloxyphenyl)-alkaniminyl and 2-(aryliminomethyl)phenoxyl radicals

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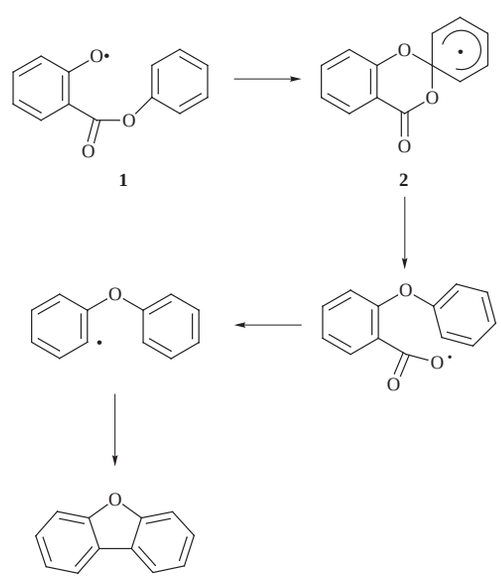
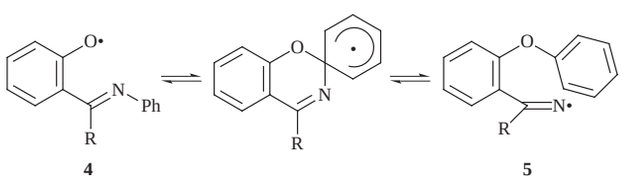
Flash vacuum pyrolysis of the allyl ethers 9–11 and of the oxime ethers 15–17 at 650 °C (5×10^{-2}–5×10^{-3} Torr) generates 2-(aryliminomethyl)phenoxyl radicals 4 and 1-(2-aryloxyphenyl)alkaniminyl radicals 5 respectively which can interconvert *via* a spirodienyl radical leading to common products which are generally isolated in low to moderate yield. The iminyls 5 normally undergo β-cleavage leading to nitriles (*e.g.* 21) and/or to benzofurans (*e.g.* 22) after cyclisation. The phenoxyls 4 show more complex behaviour dominated by hydrogen abstraction processes leading to products such as phenols (*e.g.* 32), the indole 27 or phenanthridines 34 and 35.

We have previously observed a preparatively useful gas-phase transformation of 2-aryloxycarbonylphenoxyl radicals **1** to dibenzofuran derivatives, *via ipso* attack of the radical on the 'ester' aryl group to give a spirodienyl intermediate **2**, followed



Scheme 1

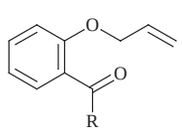
by extrusion of carbon dioxide and cyclisation (Scheme 1).[1] The radicals were generated by flash vacuum pyrolysis (FVP) of the appropriate *O*-allyl compound. The corresponding stilbene system **3** underwent intramolecular attack at the alkene function to give a route to benzofurans;[2] in these series, there were no complications of hydrogen abstraction which we have previously encountered with phenoxyls in the gas phase.[3] In this paper, we report the fate of the corresponding imine-substituted phenoxyls **4** in the gas phase, once again employing *O*-allyl ethers as the radical precursors.[4] Anticipating that the phenoxyls might undergo a rearrangement (Scheme 2) related



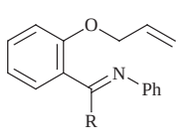
Scheme 2

to that of Scheme 1, we also generated the resulting iminyls **5** independently by pyrolysis of the appropriate oxime *O*-methyl ethers, which we have previously found to be the optimum iminyl source under FVP conditions.[4] In the accompanying papers we describe the results of our efforts to generate these intermediates in the solution phase,[5] together with related gas- and solution-phase work on 1-(2-arylaminophenyl)alkaniminyl radicals.[5,6]

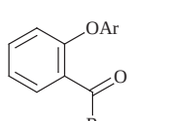
We chose to study three series of radicals, bearing a hydrogen atom, a methyl group and a phenyl group at the imine (or oxime) carbon atom. The anil precursors **9**–**11** were obtained



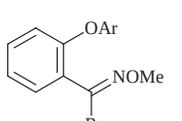
6 R = H
7 R = Me
8 R = Ph



9 R = H
10 R = Me
11 R = Ph



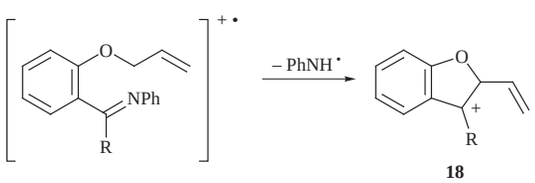
12 R = H, Ar = Ph
13 R = Me, Ar = Ph
14 R = Ph, Ar = *p*-MeC_6H_4



15 R = H, Ar = Ph
16 R = Me, Ar = Ph
17 R = Ph, Ar = *p*-MeC_6H_4

by condensation of aniline with the appropriate 2-allyloxy-benzaldehyde, -acetophenone or -benzophenone **6**–**8** in toluene solution with azeotropic removal of water. These reactions were not optimised and the benzophenone derivative **11** in particular was formed in very low yield (13%) though based on recovered starting material the conversion was acceptable. The allyloxy carbonyl compounds **6**–**8** were themselves made by alkylation of the corresponding phenol with allyl bromide under basic conditions. The acetophenone derivative **10** was obtained as a mixture of *Z* and *E* isomers which were not further identified. The oxime ether precursors **15**–**17** were made by reaction of the appropriate 2-aryloxy-benzaldehyde, -acetophenone or -benzophenone **12**–**14** with *O*-methylhydroxylamine in ethanol solution. In this case, an acceptable yield of the benzophenone derivative **17** was obtained *via* extended reaction times (48 h) and the use of pyridine as a co-solvent. The NMR spectra of the ketone derivatives **16** and **17** showed that mixtures of *Z* and *E* oxime isomers had been formed. The aldehyde **12** was synthesised by oxidation of the corresponding benzyl alcohol whereas the 2-aryloxy ketones **13**–**14** were obtained by copper-catalysed displacement of halide from a 2-halogeno carbonyl compound by the appropriate phenol under basic conditions (see Experimental section).

The mass spectra of the radical precursors show few major fragmentation peaks corresponding to the anticipated thermal breakdown. The major breakdown mechanism from the anils **10** and **11** involves loss of a PhNH (*m*/*z* 92) radical to give peaks at *m*/*z* 159 (57%) and 221 (100%) respectively, which may be drawn as the benzofuranyl cations **18** (R = Me or Ph) respectively (Scheme 3). The initial cleavage from the oxime ethers **16**

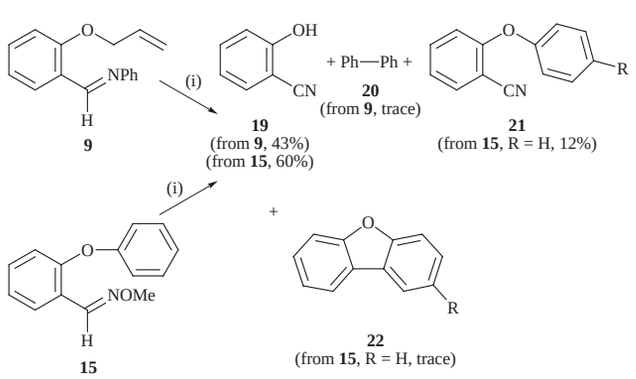


Scheme 3

and **17** is loss of a *m*/*z* 31 fragment (probably corresponding to inductive cleavage of MeO) to give peaks at *m*/*z* 210 (47%) and 286 (100%) respectively, but little pattern in further breakdown is apparent from the spectra.

The FVP experiments were all carried out at 650 °C (10^{-2}–10^{-3} Torr), to ensure that both the *O*-allylphenols and oxime ether radical precursors were completely decomposed under identical conditions.

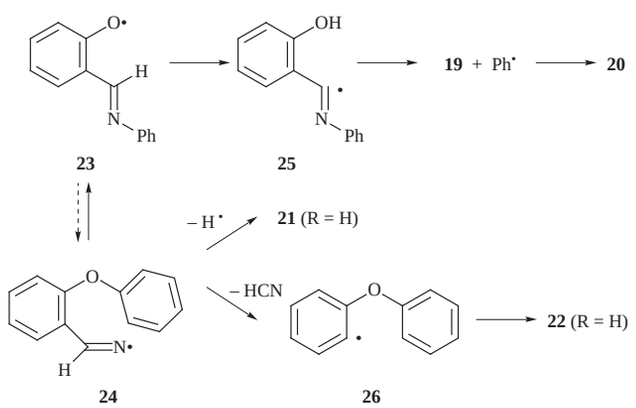
The results for the two aldehyde-derived precursors **9** and **15** are shown in Scheme 4. The anil **9** yielded 2-cyanophenol **19** as



Scheme 4 *Reagents and conditions*: (i) 650 °C, 0.01 Torr

the major product (43%) together with a trace of biphenyl. Pyrolysis of the complementary iminyl radical precursor **15** gave 2-cyanophenol **19** (60%) as found in the previous experiment, together with some 2-phenoxybenzonitrile **21** (R = H, 12%) (which is the major product from solution generation of the iminyl[5]) and a trace of dibenzofuran **22** (R = H). The NMR spectra of both these products were in line with those of literature values (see Experimental section).

The formation of 2-cyanophenol **19** may be rationalised by hydrogen abstraction by the phenoxyl radical **23** from the imine carbon atom, followed by β-cleavage of the resulting imidoyl **25** to give **19** and a phenyl radical. In agreement with this, a small amount of biphenyl **20** was also detected in the pyrolysate from **9**; phenyl radicals are known to couple inefficiently under FVP conditions, so the low level of this product was not unexpected.[4] The formation of 2-cyanophenol **19** from the iminyl precursor **15** can be readily explained by prior conversion of the iminyl **24** to the phenoxyl **23** (*cf.* Scheme 2). It is of interest that a hydrogen transfer mechanism again dominates the chemistry of the phenoxyl **23** whereas the corresponding stilbene derivative **3** shows none of this behaviour and forms cyclisation products exclusively.[2] The other products from **15** can be readily explained by β-cleavage mechanisms from the iminyl **24**, which can generate either HCN and the phenyl radical **26** [and hence dibenzofuran **22** (R = H) by a well-precedented cyclisation[1,7]] or a hydrogen atom and 2-phenoxybenzonitrile **21** (R = H) (Scheme 5). These β-cleavage routes from the iminyl are appar-

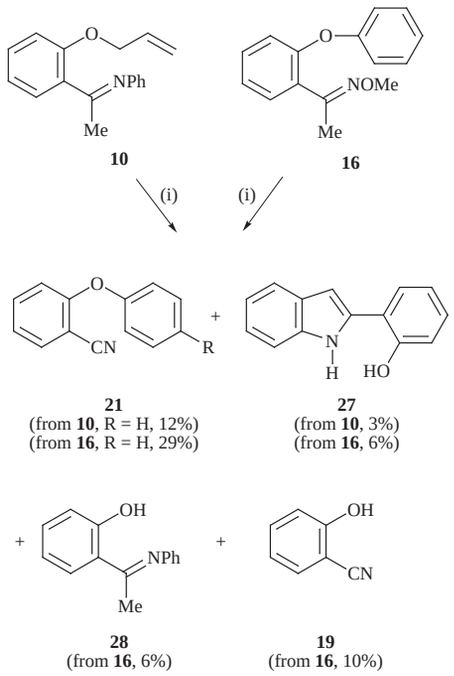


Scheme 5

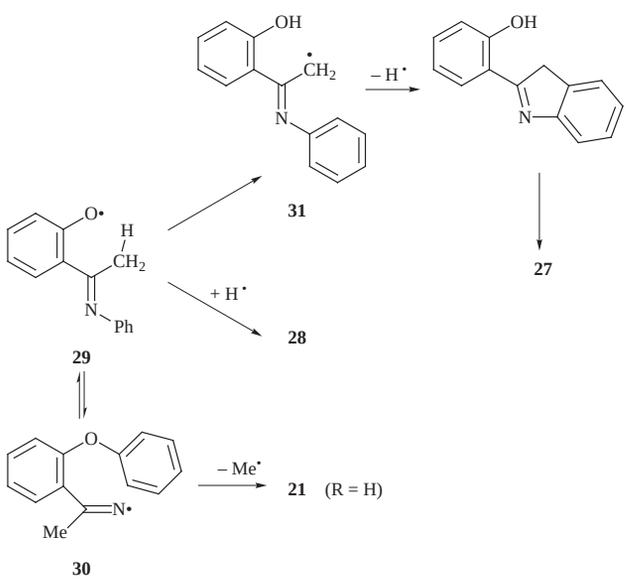
ently disfavoured relative to the spirodienyl rearrangement because of the high strengths of both C–H and C–aryl bonds. It is noteworthy that these iminyl-derived products are not formed *via* the phenoxyl **23** from the pyrolysis of **9** and it may be that the presence of only high energy product forming routes may also contribute to this occurrence. In conclusion, these results have established the viability of the conversion of iminyl **24** to phenoxyl **23**, but not the reverse.

Pyrolyses of the acetophenone-derived precursors **10** and **16** were more complex and the products are shown in Scheme 6. The imine **10** in particular was characterised by a very low recovery of products after chromatography, though these proved to be of interest mechanistically. The major products were 2-phenoxybenzonitrile **21** (R = H, 12%) (previously identified above) and 2-(2-hydroxyphenyl)indole **27** (3%) identical in all respects with an authentic sample prepared by a known method.[8] The recovery of products from the pyrolysis of the oxime ether **16** was higher, but the major products were again 2-phenoxybenzonitrile **21** (R = H, 29%) and the indole **10** (6%) together with *N*-[1-(2-hydroxyphenyl)ethylidene]aniline **28** (6%) (identical with an authentic sample[9]) and 2-cyanophenol **19** (10%); none of these products was identified when the iminyl **30** was generated in solution.[5]

These results are of particular interest since the nitrile **21** and the indole **27**, obtained in similar relative amounts from both precursors, are apparently derived from the iminyl radical **30** and the phenoxyl radical **29** respectively (Scheme 7). Thus β-cleavage of a methyl radical from **30** gives the nitrile **21** (R = H) directly; the relative ease of formation of methyl radical



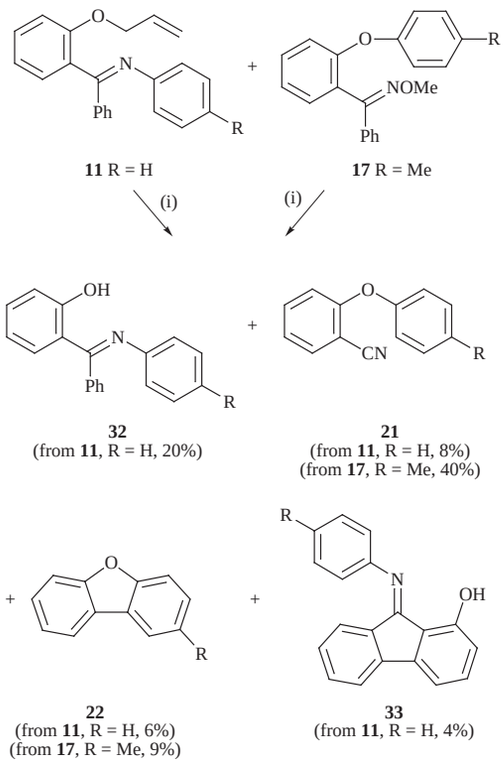
Scheme 6 *Reagents and conditions*: (i) 650 °C, 0.01 Torr

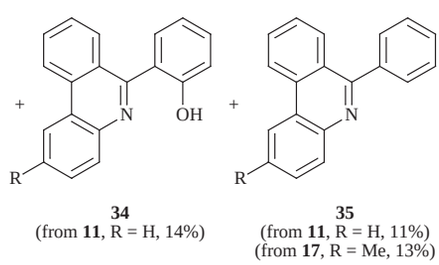


Scheme 7

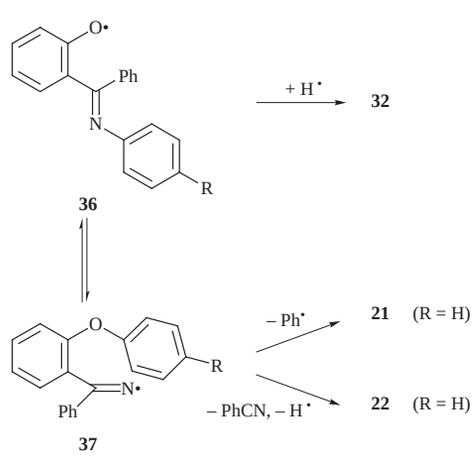
vis-à-vis hydrogen atoms (or phenyl radicals) provides a clear rationalisation of why this route has become viable in the gas phase (*cf.* above and ref. 10), though it does not occur in solution.[5] Alternatively, hydrogen transfer from the methyl group to the phenoxyl centre of **29** followed by cyclisation of the resulting azaallyl system **31** creates the indole skeleton of **27**. These results provide good evidence of complete equilibration of the phenoxyl **29** and the iminyl **30** in this series. Further evidence of the iminyl–phenoxyl interconversion is provided by the presence of the acetophenone-derived anil **28**—derived from well precedented hydrogen abstraction[3] by the rearranged phenoxyl **29**—in the pyrolysate from **16**. [Although this product was not identified in the complex pyrolysate from **10**, the corresponding material **32** was found to be the major product from the pyrolysis of the benzophenone-derived anil **11** (see below).] The source of the 2-cyanophenol **19** in the pyrolysate from the oxime ether **16** remains obscure.

The pyrolysis of the benzophenone-derived anil **11** gave a range of cyclised compounds (Scheme 8) though the major product was identified as *N*-(2-hydroxy-α-phenylbenzylidene)-





Scheme 8 *Reagents and conditions*: (i) 650 °C, 0.01 Torr



Scheme 9

aniline **32** (R = H, 20%) by comparison with an authentic sample,[11] and this is likely to be formed by simple hydrogen capture by the phenoxyl radical **36** (Scheme 9). In addition, benzofuran **22** (R = H, 6%) and 2-phenoxybenzonitrile **21** (R = H, 8%) were both present, which prove that the phenoxyl–iminyl interconversion is also viable in this series (Scheme 9). A fourth (insoluble) yellow component, present in very low yield (4%) and in insufficient quantity for NMR spectroscopy, was

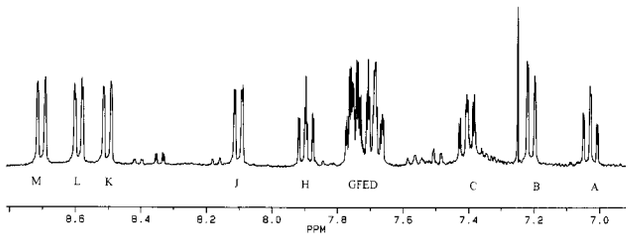


Fig. 1 Partial ^{1}H NMR Spectrum of **34** (R = H)

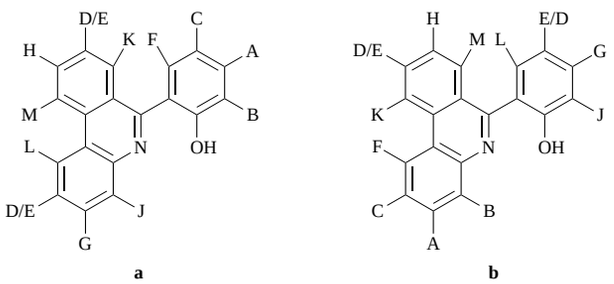
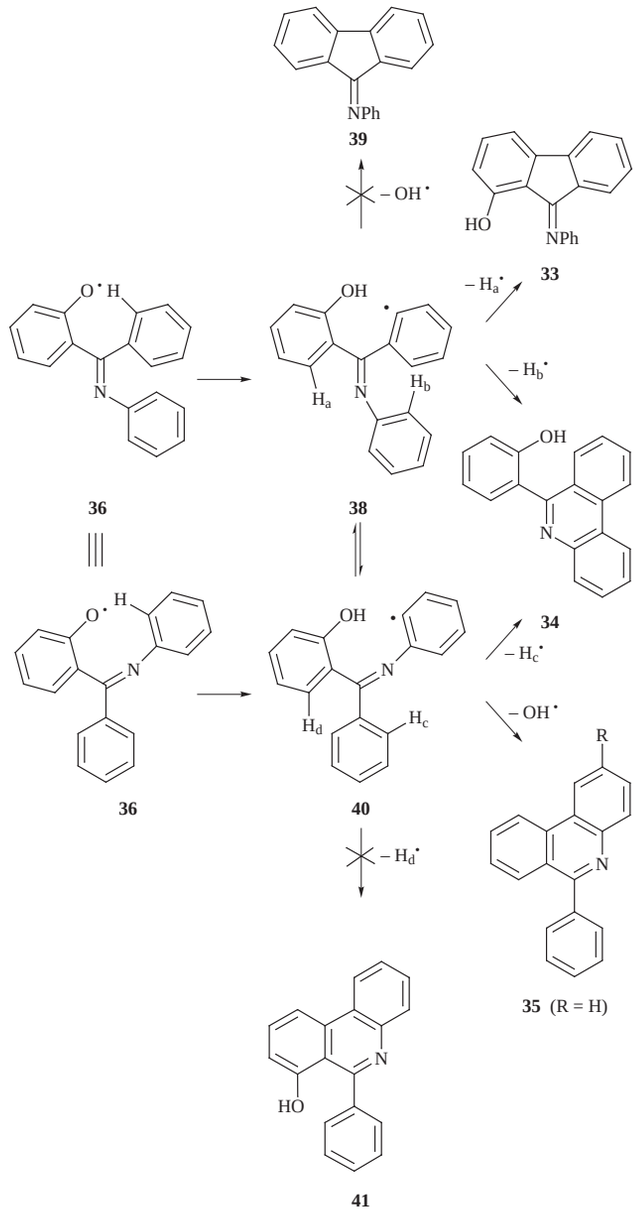


Fig. 2

tentatively identified as *N*-(1-hydroxyfluorenylidene)aniline **33** (R = H) on account of its physical properties and its mass spectrum (molecular ion at *m*/*z* 271 and loss of *m*/*z* 17 as the initial breakdown fragment being consistent with the presence of a phenol). From its mass spectrum, the fifth component was isomeric with the anil **33** (confirmed by accurate mass measurement) but was much less polar. It was identified as 6-(2-hydroxyphenyl)phenanthridine **34** (R = H, 14%) by the following NMR experiments. The ^{1}H NMR spectrum (Fig. 1) combined with the results of a homonuclear ^{1}H COSY experiment (summarised in Fig. 2), shows three four-proton spin systems, and the coupling patterns confirm the presence of three *ortho*-disubstituted aromatic rings. One of these, made up of signals A, B, C, and F, is located in the range δ_H 7.0–7.8; the second and third, made up of signals E/D, G, J and L, and D/E, H, K and M respectively are found in the range 7.6–8.7 ppm. A 2-dimensional NOESY experiment (2.5 s mixing time) showed that protons K and F are close in space, as are L and M. Both of the (hydroxyphenyl)phenanthridine assignments shown in Fig. 2 are consistent with these data, but that shown in Fig. 2a is preferred on chemical shift grounds, by comparison with the related compound **35** (see below). The final component of the pyrolysis (11%) was clearly very similar to the previous one from the characteristic high frequency multiplets in its ^{1}H NMR spectrum, but its mass spectrum (M^+ 255) showed that the oxygen atom of the starting material had been lost. Its constitution was conclusively proved to be 6-phenylphenanthridine **35** (R = H) by spectroscopic comparison with an authentic sample.[12] Again, none of these products were obtained from solution generation of the iminyl.[5]

The formation of the final three products **33**–**35** can be rationalised by the occurrence of hydrogen-transfer–cyclisation mechanisms which we have previously observed in phenoxyl radical chemistry[3] (Scheme 10), but of the five possible products only three were detected. Thus, hydrogen abstraction from the *C*-aryl group generates the radical **38** which can then cyclise at either of the two possible sites of the phenol ring to give **33** or **39** (with expulsion of H_a or the OH group respectively). Alternatively, cyclisation on the *N*-phenyl ring with loss of H_b gives the (hydroxyphenyl)phenanthridine **34**. We have previously shown that only 1-hydroxyfluorenone (and not fluorenone itself) is obtained from the pyrolysis of 1-allyloxybenzophenone,[3] so the presence of the anil **33** and the absence of **39** is not unexpected. There is no direct route to the deoxygenated phenanthridine **35** from **38** and hence hydrogen abstraction from the *N*-aryl ring must also take place. The direct intra-



Scheme 10

molecular abstraction of a hydrogen atom from the *N*-aryl ring to give the phenyl radical **40** requires an unlikely eight-membered transition state so it is perhaps more feasible that it is formed from **38** by phenyl radical equilibration *via* a seven-membered transition state (*cf.* ref. 7). Cyclisation of **40** gives an alternative route to the (hydroxyphenyl)phenanthridine **34** and also, by *ipso* attack, to 6-phenylphenanthridine **35** itself. The product formed by attack at the alternative *ortho* position of the phenol ring (**41**) was not observed in the pyrolysate. We have no explanation for such apparent selectivity, though there is some indication from this, and our previous work,[3,13] that phenyl radicals may cyclise with preferential displacement of a hydroxyl radical rather than a hydrogen atom to give six-membered rings, with the reverse selectivity when a five-membered ring is formed.

In view of the complexity of the analysis of some of the products in the previous pyrolysis it was decided to incorporate a *p*-methyl substituent into the precursor **17** of the final iminyl radical **37**. In the event, the pyrolysate proved difficult to analyse because of poor separation under our standard chromatographic conditions. The two major components which were identified were the nitrile **21** (R = Me, 40%) and the dibenzofuran **22** (R = Me, 9%) which would be expected as direct products from the iminyl **37** from the previous results.

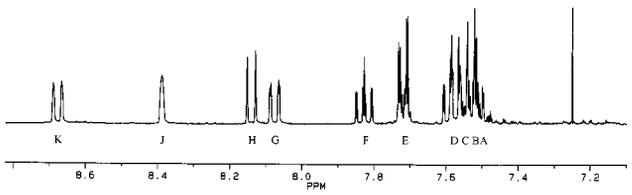


Fig. 3 Partial ^{1}H NMR Spectrum of **35** (R = Me)

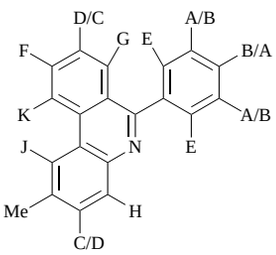


Fig. 4

One phenanthridine derivative was obtained in reasonably pure state from the column, and this was identified as the 2-methyl-6-phenyl compound **35** (R = Me, 13%) on the basis of its mass spectrum (molecular ion at *m/z* 269) and the following NMR results. The ^{13}C NMR spectrum showed 10 CH signals in total, (including two of double intensity indicating the presence of an unsubstituted phenyl group) together with 7 quaternaries and a methyl peak. The ^{1}H NMR spectrum (Fig. 3) showed three groups of benzenoid signals; the phenyl group (previously assigned *via* the ^{13}C NMR spectrum) (signals A, B and E), a 1,2,4-trisubstituted aromatic (signals C/D, H and J), and a 1,2-disubstituted aromatic system (signals D/C, F, G and K) were confirmed by a series of homonuclear decoupling experiments. In addition, irradiation of proton J in an NOE experiment showed enhancements of the methyl group (1.5%) and of proton K (20%). Similarly, irradiation of the doublet due to the *ortho*-protons of the phenyl group (E) caused a 6% enhancement of proton G. These results establish the connectivity shown in Fig. 4. The isolation of this compound provides good evidence for the iminyl–phenoxyl interconversion in this series (*cf.* Scheme 10).

In conclusion, we have demonstrated that a reversible 1,5-aryl shift interconverting 1-(2-aryloxyphenyl)alkaniminyl radicals and 2-(aryliminomethyl)phenoxyl radicals *via* a spirodienyl radical is a viable and indeed a general process under gas-phase pyrolysis conditions, though it apparently does not take place to any significant extent when the intermediates are generated in solution.[5] The driving force for the direction of the reaction is apparently governed by the availability of product-forming pathways from the iminyl (generally β-cleavage leading to nitriles or to dibenzofurans) or the phenoxyl (generally hydrogen abstraction leading to cyclisation products) radical intermediates respectively. No examples of direct cyclisation of either the iminyl or the phenoxyls to give dibenzoxazepines were observed, even though iminyls (in particular) are well known to cyclise efficiently, at least to give six-membered ring products,[4] and analogous imidoyl radicals have been reported to give seven-membered cyclisation to dibenzoxazepines in solution.[14] The plethora of possible products from hydrogen-abstraction mechanisms—particularly from the benzophenone derivatives—considerably complicate the analysis of the pyrolysates. Although such reactions might have been anticipated from our earlier work on phenoxyls,[3] hydrogen abstraction does not take place at all in other closely related series[1,2] and it remains unclear as to which factors are responsible for this mechanistic dichotomy. In any event, our earlier work suggests that the use of 'soft' radical centres should circumvent the hydrogen abstraction problem, and consequently we are now investigating the chemistry of the related thiophenoxyls.

Experimental

^{1}H and ^{13}C NMR spectra were recorded in [^{2}H]chloroform at 200 (or 250) and 50 (or 63) MHz respectively unless otherwise stated. Dry-flash column chromatography was carried out on silica gel (GF_{254}) using a hexane–ethyl acetate gradient as eluent.

O-Allylation of phenols

This was carried out by the method previously reported for 2-allyloxybenzaldehyde.[2] Thus the phenol (0.035 mol) was added to a suspension of anhydrous potassium carbonate (9.70 g, 0.07 mol) in DMF (55 cm^3). Allyl bromide (4.23 g, 0.035 mol) was then added dropwise with stirring and the mixture was stirred at room temperature for a further 23 h. Water (65 cm^3) was added and the mixture was extracted with diethyl ether (3 × 20 cm^3). The combined ether extracts were washed with water (30 cm^3), dried ($MgSO_4$), the solvent was removed and the crude product was distilled. The following compounds were made by this method. Salicylaldehyde gave 2-allyloxybenzaldehyde **6**;[2] 2-hydroxyacetophenone gave 2-*allyloxyacetophenone* **7** (66%) bp 174–176 °C (0.4 Torr) (Found: M$^+$, 176.0842. $C_{11}H_{12}O_2$ requires *M*, 176.0837); δ_H 7.72 (1H, m), 7.42 (1H, m), 6.96 (2H, m), 6.07 (1H, m), 5.38 (2H, m), 4.63 (2H, m) and 2.63 (3H, s); δ_C 199.84 (q), 157.74 (q), 133.40, 132.46, 130.25, 128.41 (q), 120.60, 118.04, 112.58, 69.21 and 31.87; *m/z* 176 (M$^+$, 7%), 161 (15), 133 (24), 121 (100) and 105 (30); 2-hydroxybenzophenone gave 2-allyloxybenzophenone **8** as a yellow oil (44%) bp 200–201 °C (0.6 Torr) [lit.,[15] 145–147 °C (0.2 Torr)]; δ_H 7.84–6.86 (9H, m), 5.71 (1H, m), 5.00 (2H, m) and 4.44 (2H, m); δ_C 196.43 (q), 156.20 (q), 137.97 (q), 132.60, 132.18, 131.78, 129.65, 129.47, 129.06 (q), 128.00, 120.68, 116.69, 112.60 and 68.76; *m/z* 238 (M$^+$, 16%), 223 (20), 209 (18), 197 (63), 181 (46), 121 (56), 105 (100), 92 (23) and 77 (98).

N-(2-Allyloxybenzylidene)aniline 9

2-Allyloxybenzaldehyde **6** (0.81 g, 5 mmol) was dissolved in toluene (25 cm^3) and a trace of toluene-*p*-sulfonic acid was added. Aniline (0.47 g, 5 mmol) was then added and the reaction mixture was heated under reflux with azeotropic removal of water for 2 h. The cooled mixture was concentrated under reduced pressure and the residue was distilled to give the *anil* **9** as a yellow oil (54%) bp 130–131 °C (5 × 10^{-3} Torr) (Found: C, 80.8; H, 6.4; N, 5.95; $C_{16}H_{15}NO$ requires C, 81.0; H, 6.35; N, 5.9%) δ_H(200 MHz) 9.00 (1H, s), 8.21 (1H, m), 7.48–6.94 (8H, m), 6.08 (1H, m), 5.39 (2H, m) and 4.64 (2H, m); δ_C 158.53 (q), 156.10, 152.77 (q), 132.86, 132.32, 128.87, 127.60, 125.44, 120.99, 120.86, 117.49, 114.93 (q), 112.53 and 69.21; *m/z* 237 (M$^+$, 19%), 121 (90), 93 (100), 77 (52) and 41 (95).

N-[1-(2-Allyloxyphenyl)ethylidene]aniline 10

This product was prepared from 2-allyloxyacetophenone **7** (0.88 g, 5 mmol) as described above for the anil **9**, except that the reaction mixture was heated under reflux with azeotropic removal of water for 22 h. The cooled mixture was concentrated under reduced pressure to give the crude product which was distilled to give recovered **7** (0.45 g, 51%) [bp 108–110 °C (5 × 10^{-3} Torr)] followed by the *anil* **10** as a mixture of *Z* and *E* isomers (0.56 g, 45%) bp 123–124 °C (10^{-3} Torr) (Found: M$^+$, 251.1307. $C_{17}H_{17}NO$ requires *M*, 251.1310); δ_H(major isomer) 7.62–6.67 (9H, m), 6.06 (1H, m), 5.34 (2H, m), 4.61 (2H, m) and 2.22 (3H, s); δ_C(major isomer) 168.97 (q), 156.15 (q), 151.03 (q), 132.88, 131.40 (q), 130.35, 129.31, 128.73, 123.04, 120.83, 119.29, 117.25, 112.31, 68.98 and 20.99; δ_H(minor isomer) 7.62–6.67 (9H, m), 6.06 (1H, m), 5.34 (2H, m), 4.47 (2H, m) and 2.50 (3H, s); δ_C(minor isomer) 168.63 (q), 154.30 (q), 150.80 (q), 132.79, 130.23 (q), 129.10, 127.92, 122.92, 120.24, 120.15, 117.10, 111.46, 68.40 and 28.33 (one CH signal overlapping); *m/z* 251 (M$^+$, 3%), 167 (20), 158 (59), 131 (20), 121 (55), 105 (26), 93 (50), 77 (100) and 65 (31).

N-(2-Allyloxy-α-phenylbenzylidene)aniline 11

This product was prepared from 2-allyloxybenzophenone **8** (1.19 g, 5 mmol) as described above for the anil **10**, except that the reaction mixture was heated under reflux with azeotropic removal of water for 21 h. The cooled mixture was concentrated under reduced pressure and distilled to give a fraction which was predominantly recovered **8** (1.18 g) [bp 125–126 °C (5×10^{-3} Torr)] followed by the *anil* **11** as a yellow oil which solidified on standing (0.20 g, 13%) bp 139–140 °C (5×10^{-3} Torr) (Found: M^+, 313.1464. $C_{22}H_{19}NO$ requires *M*, 313.1467); δ_H 7.79–6.74 (14H, m), 5.75 (1H, m), 5.13 (2H, m) and 4.34 (2H, d); δ_C 166.12 (q), 155.44 (q), 151.41 (q), 139.27 (q), 132.73, 130.34, 129.93, 129.65, 128.32, 128.03, 127.98, 125.98 (q), 123.08, 120.16, 116.78, 111.81 and 68.47 (one CH signal overlapping); *m*/*z* 313 (M^+, 4%), 256 (15), 221 (100), 180 (18), 165 (15), 115 (26), 105 (32), 77 (84) and 51 (29).

2-Phenoxybenzaldehyde 12

A solution of 2-phenoxybenzyl alcohol (9.9 g, 0.045 mol) (itself prepared by diborane reduction of 2-phenoxybenzoic acid[16]) in dichloromethane (100 cm^3) was added dropwise at room temperature to a mechanically stirred suspension of chromium trioxide (27.0 g), pyridine (42.75 g) and dichloromethane (400 cm^3). After 2 h, the solvent was evaporated and the residue was filtered on silica gel. After removal of the solvent from the eluate, the residue was distilled to give the title aldehyde **12** (7.0 g, 78%), bp 114–116 °C [lit.,[17] 150–153 (1 Torr)].

2′-Phenoxyacetophenone 13

Prepared as described in ref. 18 by heating 2′-chloroacetophenone (10.00 g, 0.065 mol), phenol (7.65 g, 0.082 mol) and potassium carbonate (12.13 g, 0.088 mol) under reflux for 10 h in the presence of copper powder (0.61 g, 0.0096 mol). The initial product was distilled to give recovered 2′-chloroacetophenone (3.12 g, 31%) [bp 44–45 °C (5×10^{-2} Torr)] followed by 2′-phenoxyacetophenone **13** as a clear oil (6.87 g, 50%) bp 103–104 °C (5×10^{-2} Torr) [lit.,[18] 132–138 °C (3 Torr)]; δ_H 7.86–6.84 (9H, m) and 2.64 (3H, s); δ_C 199.00 (q), 156.28 (q), 156.22 (q), 133.53, 130.36, 130.21 (q), 129.89, 123.72, 123.28, 119.13, 118.72 and 31.44; *m*/*z* 212 (M^+, 61%), 197 (100), 141 (5), 119 (28), 94 (13), 77 (15), 65 (5) and 51 (23).

2-(4-Methylphenoxy)benzophenone 14

A mixture of 2-chlorobenzophenone (5.00 g, 0.023 mol), *p*-cresol (3.13 g, 0.029 mol) and potassium carbonate (4.30 g, 0.031 mol) was boiled for 10 h in the presence of copper powder (0.22 g, 0.0035 mol). After cooling, the mixture was filtered and the filter cake was washed with diethyl ether. The filtrate was concentrated under reduced pressure and the residue was distilled to give recovered 2-chlorobenzophenone (0.55 g, 11%) [bp 118–120 °C (5×10^{-2} Torr)] followed by 2-(4-*methylphenoxy*)-*benzophenone* **14** as a clear oil (3.10 g, 47%) bp 158–159 °C (5×10^{-2} Torr) (Found: M^+, 288.1143. $C_{20}H_{16}O_2$ requires *M*, 288.1150); δ_H 7.89–6.73 (13H, m) and 2.28 (3H, s); δ_C 195.66 (q), 155.19 (q), 153.85 (q), 137.38 (q), 132.97 (q), 132.83, 131.73, 130.45 (q), 129.92, 129.83, 129.54, 127.97, 122.67, 118.75, 117.87 and 20.43; *m*/*z* 288 (M^+, 78%), 211 (69), 181 (30), 168 (21), 152 (26), 105 (73), 77 (100), 65 (20) and 51 (29).

2-Phenoxybenzaldehyde *O*-methyloxime 15

A solution of 2-phenoxybenzaldehyde (2.0 g, 10 mmol) and *O*-methylhydroxylamine hydrochloride (1.25 g, 15 mmol) in ethanol (50 cm^3) containing pyridine (1.2 g, 15 mmol) was heated under reflux for 1 h. After cooling, the solvent was removed, the residue was treated with dilute hydrochloric acid [HCl (3 drops) in water (100 cm^3)] and extracted with ether to remove the remaining traces of pyridine. The organic layer was dried ($MgSO_4$) and concentrated to give the *oxime ether* **15** (1.2 g, 52%) as an oil (Found: M^+, 227.0946. $C_{14}H_{13}NO_2$ requires *M*, 227.0947); δ_H 8.45 (1H, s), 7.55 (1H, dd), 7.45–6.90 (8H, m) and 4.00 (3H, s); δ_C 157.20 (q), 154.68 (q), 143.93, 130.92, 129.67, 126.49 (q), 123.74, 123.12, 119.27, 118.48, 118.04 and 61.84; *m*/*z* 227 (M^+, 49%), 196 (100), 181 (32), 168 (13), 167 (11), 77 (46) and 51 (22).

2′-Phenoxyacetophenone *O*-methyloxime 16

2′-Phenoxyacetophenone **13** (0.50 g, 2.36 mmol) and *O*-methylhydroxylamine hydrochloride (0.40 g, 4.72 mmol) were dissolved in ethanol (25 cm^3) and heated under reflux for 1.5 h. The reaction mixture was concentrated under reduced pressure, the residue was treated with aqueous sodium hydroxide (0.25 M, 20 cm^3) and the mixture was extracted with diethyl ether (3×10 cm^3). The combined ether extracts were dried ($MgSO_4$), concentrated and distilled *in vacuo* to give the *oxime* **16** as a mixture of *Z* and *E* isomers in *ca.* 6:1 ratio (0.23 g, 40%) bp 124–125 °C (5×10^{-3} Torr) (Found: M^+, 241.1094. $C_{15}H_{15}NO_2$ requires *M*, 241.1103); δ_H(major isomer) 7.48–6.88 (9H, m), 3.94 (3H, s) and 2.19 (3H, s); δ_C(major isomer) 157.05 (q), 155.39 (q), 154.57 (q), 130.06, 129.85, 129.62, 128.71 (q), 123.57, 123.01, 119.28, 118.24, 61.65 and 15.70; δ_H(minor isomer) 7.48–6.88 (9H, m), 3.73 (3H, s) and 2.16 (3H, s); *m*/*z* 241 (M^+, 28%), 211 (48), 181 (28), 152 (29), 115 (31), 91 (31), 85 (26), 77 (100) and 69 (47).

2-(4-Methylphenoxy)benzophenone *O*-methyloxime 17

2-(4-Methylphenoxy)benzophenone **14** (1.01 g, 3.5 mmol) and *O*-methylhydroxylamine hydrochloride (0.65 g, 7.8 mmol) were dissolved in a mixture of ethanol (20 cm^3) and pyridine (10 cm^3) and heated under reflux for 2 days. The reaction mixture was concentrated under reduced pressure, the residual solid was treated with slightly acidified water (30 cm^3) and then extracted with diethyl ether (3×15 cm^3). The combined ether extracts were dried ($MgSO_4$), concentrated and distilled to give the *oxime* **17** as a mixture of *Z* and *E* isomers in *ca.* 1.5:1 ratio (0.84 g, 76%) bp 163–165 °C (0.1 Torr) (Found: M^+, 317.1407. $C_{21}H_{19}NO_2$ requires *M*, 317.1416); δ_H(major isomer) 7.58–6.54 (13H, m), 3.90 (3H, s) and 2.29 (3H, s); δ_H(minor isomer) 7.58–6.54 (13H, m), 3.96 (3H, s) and 2.27 (3H, s); the ^{13}C NMR spectrum was complex and showed the following peaks, some of which were due to overlapping signals: δ_C 155.52 (q), 154.79 (q), 154.51 (q), 154.35 (q), 153.81 (q), 135.58 (q), 133.63 (q), 132.63 (q), 132.34 (q), 131.08, 130.31, 129.97, 129.79, 129.70, 129.04, 128.94, 128.66, 128.06, 127.51, 126.88, 124.98 (q), 123.01, 122.54, 119.04, 118.76, 118.30, 118.00, 62.17, 62.13, 20.54 and 20.50; *m*/*z* 317 (M^+, 33%), 286 (100), 245 (47), 214 (30), 180 (10), 105 (10), 91 (11), 77 (47) and 51 (22).

Pyrolysis experiments

The substrates were sublimed or distilled under reduced pressure through a silica tube (35 × 2.5 cm) which was held at the required temperature by an electrical tube furnace. Products were collected in a U-tube trap cooled by liquid nitrogen which was situated immediately after the hot zone. Work-up involved dissolution of the pyrolysate in dichloromethane followed by dry-flash chromatography over silica using hexane–ethyl acetate mixtures as eluent. Results are quoted as follows: quantity of substrate, inlet temperature, furnace temperature, pressure, pyrolysis time and products (quoted in the order of elution from the column).

Pyrolysis of *N*-(2-allyloxybenzylidene)aniline 9. (0.49 g, 2.1 mmol), 85–90 °C, 650 °C, 5×10^{-3} Torr, 2 h: 2-cyanophenol **19** (0.108 g, 43%) mp 91–94 °C (lit.,[19] 93–96 °C); δ_H 7.52–7.43 (2H, m) 7.02–6.95 (2H, m) and 6.18 (1H, br s); δ_C 158.22 (q), 134.62, 132.71, 120.94, 116.46 and 99.43 (q) (one quaternary not apparent) (^1H and ^{13}C NMR spectra are consistent with literature values[20]); *m*/*z* 119 (M^+, 100%), 91 (87), 64 (30) and 38 (14). A trace of biphenyl **20** was detected by GC and by comparison with an authentic sample.

Pyrolysis of *N*-[1-(2-allyloxyphenyl)ethylidene]aniline 10. (0.41 g, 1.6 mmol), 150–160 °C, 650 °C, 10^{-2} Torr, 2 h: 2-phenoxybenzonitrile **21** (R = H) (0.037 g, 12%); δ_H 7.66 (1H, m), 7.50–7.34 (3H, m), 7.28–7.05 (4H, m) and 6.83 (1H, m) [lit.,[21] δ_H 7.6–7.8 (m)]; *m*/*z* 195 (M^+, 100%), 167 (53), 77 (66), 63 (17) and 51 (61): 2-(2-hydroxyphenyl)indole **27** (0.010 g, 3%); δ_H(200 MHz) 9.28 (1H, s) and 7.72–6.85 (10H, m); *m*/*z* 209 (M^+, 100%), 180 (38), 152 (9), 105 (6), 89 (11), 77 (19) and 51 (9). The ^{1}H NMR and mass spectra were identical with those of an authentic sample prepared according to ref. 8 [δ_H 9.33 (1H, s) and 7.71–6.84 (10H, m); *m*/*z* 209 (M^+, 100%), 180 (33), 152 (4), 105 (5), 89 (8), 77 (7), 63 (4) and 51 (2).]

Pyrolysis of *N*-(2-allyloxy-α-phenylbenzylidene)aniline 11. (0.16 g, 0.52 mmol), 160–165 °C, 650 °C, 5×10^{-3} Torr, 30 min: an initial insoluble compound, tentatively identified on account of its mass spectrum as *N*-(1-hydroxyfluorenylidene)aniline **33** (R = H) (0.005 g, 4%), was filtered off before column chromatography; *m*/*z* 271 (M^+, 51%), 270 (100), 254 (32) and 135 (28): dibenzofuran **22** (R = H) (0.005 g, 6%); δ_H 7.96 (2H, m), 7.57 (2H, m), 7.45 (2H, m) and 7.34 (2H, m); *m*/*z* 168 (M^+, 100%), 139 (69), 113 (12) and 84 (27). The ^{1}H NMR spectrum was identical with that of an authentic sample; [δ_H 7.98 (2H, m), 7.61 (2H, m), 7.48 (2H, m) and 7.36 (2H, m)]: *N*-(2-hydroxy-α-phenylbenzylidene)aniline **32** (R = H) (0.028 g, 20%); δ_H 7.47–6.74 (14H, m); *m*/*z* 273 (M^+, 46%), 272 (52), 196 (33), 181 (27), 180 (26) and 77 (100); spectra consistent with those of an authentic sample[11] [δ_H 14.53 (1H, br s) and 7.40–6.71 (14H, m); δ_C 173.19 (q), 162.42 (q), 146.73 (q), 134.01 (q), 133.12, 132.12, 128.73, 128.65, 128.34, 128.02, 124.36, 122.28, 119.82 (q) and 117.87, *m*/*z* 273 (M^+, 100%), 272 (63), 196 (35), 181 (14), 180 (14) and 77 (53)]: 2-phenoxybenzonitrile **21** (R = H) (0.008 g, 8%) δ_H 7.65 (1H, m), 7.49–7.36 (3H, m), 7.28–7.05 (4H, m) and 6.85 (1H, m) (^{1}H NMR spectrum is consistent with that quoted in the previous paragraph): 6-(2-*hydroxyphenyl*)*phenanthridine* **34** (R = H) (0.02 g, 14%) (Found: M^+, 271.0991; $C_{19}H_{13}NO$ requires *M*, 271.0997); δ_H(360 MHz) 8.69 (1H, d, ^3J 8.2), 8.58 (1H, dd, ^3J 8.1, ^4J 1.1), 8.49 (1H, d, ^3J 7.5), 8.09 (1H, dd, ^3J 8.0, ^4J 1.4), 7.90 (1H, ddd, ^3J 8.2 and 7.1, ^4J 1.2), 7.80–7.65 (4H, m), 7.40 (1H, ddd, ^3J 7.8 and 7.3, ^4J 1.5), 7.21 (1H, dd, ^3J 7.8, ^4J 1.5) and 7.03 (1H, td, ^3J 7.8, ^4J 1.2); δ_C 158.97 (q), 157.71 (q), 145.98 (q), 141.16 (q), 134.58 (q), 131.51, 130.87, 128.97, 128.84, 128.60, 127.10, 127.02, 123.66 (q), 122.29, 121.78, 121.01 (q), 118.55 and 117.93 (one CH signal overlapping); *m*/*z* 271 (M^+, 56%), 270 (100), 241 (19), 151 (9), 135 (27) and 121 (17): 6-phenylphenanthridine **35** (R = H) (0.015 g, 11%); δ_H(360 MHz) 8.70 (1H, d, ^3J 8.3), 8.62 (1H, dd, ^3J 8.0, ^4J 1.4), 8.26 (1H, dd, ^3J 8.0, ^4J 1.3), 8.10 (1H, d, ^3J 8.4) and 7.90–7.50 (9H, m); δ_C 143.46 (q), 139.42 (q), 133.35 (q), 130.54, 130.05, 129.60, 128.85, 128.77, 128.65, 128.30, 127.75 (q), 127.04, 126.87, 125.68 (q), 123.63 (q), 122.07 and 121.83; *m*/*z* 255 (M^+, 58%), 254 (100) and 127 (29). The ^{1}H NMR and mass spectra of this compound are identical with those of an authentic sample[12] [δ_H(360 MHz) 8.69 (1H, d, ^3J 8.3), 8.61 (1H, dd, ^3J 8.0, ^4J 1.4), 8.26 (1H, dd, ^3J 8.2, ^4J 1.3), 8.09 (1H, d, ^3J 8.3) and 7.85–7.50 (9H, m); *m*/*z* 255 (M^+, 54%), 254 (100) and 127 (16)].

Pyrolysis of 2-phenoxybenzaldehyde *O*-methyloxime 15. (0.69 g, 3 mmol), 90 °C, 650 °C, 5×10^{-3} Torr, 1 h: 2-cyanophenol **19** (0.21 g, 60%) mp 93–94 °C (lit.,[19] 93–96 °C) (spectroscopic data as reported above): 2-phenoxybenzonitrile **21** (R = H) (0.07 g, 12%) as an oil, [lit.,[21] bp 142 °C (3 Torr)]; *m*/*z* 195 (M^+, 100%), 167 (60), 77 (58) and 51 (36) (other spectra consistent with those reported in other sections of this paper): dibenzofuran **22** (R = H) (trace) spectra as above.

Pyrolysis of 2′-phenoxyacetophenone *O*-methyloxime 16. (0.18 g, 0.75 mmol), 150–160 °C, 650 °C, 10^{-2} Torr, 30 min: *N*-[1-(2-hydroxyphenyl)ethylidene]aniline **28** (0.009 g, 6%); δ_H 7.71–6.84 (9H, m) and 2.33 (3H, s); *m*/*z* 211 (M^+, 92%), 210 (76), 196 (100), 120 (25), 77 (74), 65 (10), 51 (30) and 39 (13), spectra identical with an authentic sample[9] [δ_H 14.65 (1H, br s), 7.65–6.85 (9H, m) and 2.33 (3H, s); δ_C 171.03 (q), 161.86 (q), 146.88 (q), 132.91, 128.93, 128.79, 124.66, 121.15, 119.63 (q), 118.12, 117.99 and 16.90; *m*/*z* 211 (M^+, 100%), 210 (61), 196 (82), 120 (22), 77 (73) and 51 (29)]: 2-phenoxybenzonitrile **21** (R = H) (0.042 g, 29%); δ_H 7.64 (1H, m), 7.50–7.35 (3H, m), 7.25–7.04 (4H, m) and 6.84 (1H, m); δ_C 159.66 (q), 154.94 (q), 134.05, 133.74, 129.98, 124.90, 122.66, 119.91, 116.88, 115.85 (q) and 103.65 (q) (spectra consistent with reported data[21,22]); *m*/*z* 195 (M^+, 100%), 167 (31), 77 (45), 63 (5) and 51 (28) (^{1}H NMR and mass spectra are also identical with those previously quoted): 2-(2-hydroxyphenyl)indole **27** (0.010 g, 6%); δ_H 9.36 (1H, s) and 7.72–6.83 (10H, m); *m*/*z* 209 (M^+, 100%), 180 (83), 152 (14), 105 (7), 89 (9) and 77 (12) (the ^{1}H NMR and mass spectra are consistent with those of the authentic sample previously quoted): 2-cyanophenol **19** (0.009 g, 10%); δ_H 7.60–7.34 (2H, m) and 7.05–6.94 (2H, m); *m*/*z* 119 (M^+, 100%), 91 (65) and 77 (9) (the spectra are consistent with those previously quoted).

Pyrolysis of 2-(4-methylphenoxy)benzophenone *O*-methyloxime 17. (0.37 g, 1.17 mmol), 170–175 °C, 650 °C, 5×10^{-2} Torr, 1 h: 2-methyldibenzofuran **22** (R = Me) (0.019 g, 9%); δ_H 7.96–7.23 (7H, m) and 2.51 (3H, s); δ_C 156.33 (q), 132.05 (q), 128.07, 127.03 (q), 126.79, 124.05 (q), 122.38, 120.49, 120.39, 111.49, 111.01 and 21.21 (one quaternary signal missing); *m*/*z* 183 (M^+, 48%), 182 (94), 181 (100), 168 (69), 154 (40) and 139 (14) (the spectra are consistent with those previously reported[7]): 2-(4-methylphenoxy)benzonitrile **21** (R = Me) (*ca.* 40%) δ_H 6.6–7.7 (8H, m) and 2.36 (3H, s) [lit.,[21] 6.7–7.6 (8H, m) and 2.33 (3H, s)]; δ_C(CH and CH_3 signals only) 130.41, 128.91, 128.58, 128.04, 122.25, 119.93 and 20.63; *m*/*z* 209 (M^+, 100%), 91 (60) and 65 (23): 2-*methyl*-6-*phenylphenanthridine* **35** (R = Me) (0.04 g, 13%) (Found: M^+ 269.1207; $C_{20}H_{15}N$ requires *M*, 269.1205); δ_H(360 MHz) 8.68 (1H, d, ^3J 8.3), 8.39 (1H, s), 8.14 (1H, d, ^3J 8.3), 8.07 (1H, dm, ^3J 8.3), 7.83 (1H, ddd, ^3J 8.3, 7.0, ^4J 1.3), 7.73–7.70 (2H, m), 7.61–7.48 (5H, m) and 2.64 (3H, s); δ_C 160.14 (q), 141.76 (q), 139.52 (q), 136.70 (q), 133.00 (q), 130.44, 130.23, 129.70, 129.57, 128.68, 128.47, 128.22, 126.81, 125.09 (q), 123.41 (q), 121.98, 121.40 and 21.85; *m*/*z* 269 (M^+, 68%), 268 (100), 253 (10), 196 (5), 119 (16), 91 (17) and 77 (7).

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