Generation and contrasting gas-phase reactivity of 2-(2-alkenylpyrrol-1-yl)phenoxyl and thiophenoxyl radicals

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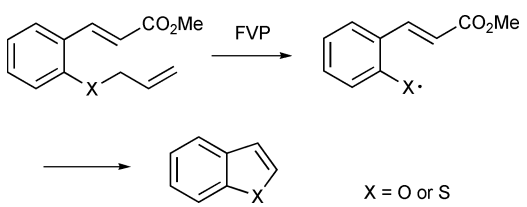
The pyrrolylacrylates **9** and **10** were synthesised and subjected to flash vacuum pyrolysis (FVP) at 650–700 °C to generate the radicals **11** and **18**, respectively. The phenoxyl **11** underwent hydrogen capture to give a mixture of the phenol **12** and the pyrrolobenzoxazine **13** in low yields, which were also obtained by a Wittig reaction of the 2-formylpyrrole **14**. The thiophenoxyl **18** gave a single major product in 41% yield which was identified as the pyrrolo[1,2-*a*]quinoline **17** by a sequence of NMR experiments. A mechanism for the formation of **17** by a rearrangement–sulfur extrusion sequence is proposed.

Introduction

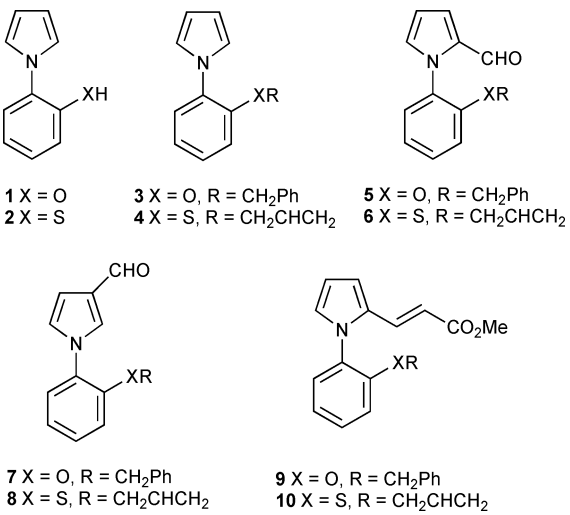
In previous work, we have shown that phenoxyl[1] and thiophenoxyl[2] radicals can interact with adjacent acrylate groups under flash vacuum pyrolysis (FVP) conditions to give benzofuran (X = O) and benzothiophene (X = S) ring systems respectively in good yield (Scheme 1). The loss of the entire ester function as a thermal radical leaving group is apparently highly favourable in these reactions and so we have explored the scope and limitations of this process by incorporating acrylate groups and radical generators into other molecular architectures. In this paper we report examples in which the radical site (phenoxyl or thiophenoxyl) and the acrylate unit are situated within an *N*-arylpyrrole framework which we hoped would lead to the creation of new seven-membered rings. In the event, these pyrolyses did not give the products expected by analogy with Scheme 1 but instead the behaviour of the phenoxyl and thiophenoxyl proved to be very different (*cf.* ref. 3 and 4) and an efficient sulfur extrusion—rather than ester extrusion—has been identified.



Scheme 1

Results and discussion

Our chosen substrates **9** and **10** were synthesised from the 1-arylpyrroles **1** and **2** by successive *O*- or *S*-alkylation, Vilsmeier formylation and Wittig olefination. The *O*-benzyl product **3** was chosen rather than the corresponding *O*-allyl derivative in an attempt to minimise the hydrogen atom flux during the FVP experiment.[1] In both cases the Vilsmeier reaction gave two products (**5** and **7**, and **6** and **8** respectively) due to competitive substitution at the 2- and 3-positions of the pyrrole ring. These products were easily separated by chromatography and the required 2-formylated products **5** and **6** were isolated in >70% yield. The position of the formyl group was determined by comparison of the ^{1}H NMR spectra of the products with those of the known spectra of 2- and 3-formyl-1-phenylpyrrole.[5] The chemical shifts of the 2-formyl protons at δ_H *ca.* 9.4–9.5 and those of the 3-formyl protons at δ_H *ca.* 9.7–9.8 ppm are particularly characteristic. Although the Wittig reactions were slow and required extended reaction times, **9** and **10** were obtained in 45% and 60% yields respectively after chromatography, exclusively as the *E*-isomers.



The electron impact (EI) mass spectrum of the benzyloxy compound **9** is dominated by cleavage of the benzyl group (*m*/*z* 91, 100%) but there is also evidence of ionisation at the ester function giving small peaks at M − 31 and M − 59. The corresponding spectrum of the allylthio compound **10** shows initial loss of the allyl group (M − 41, 81%) followed by loss of a fragment of *m*/*z*

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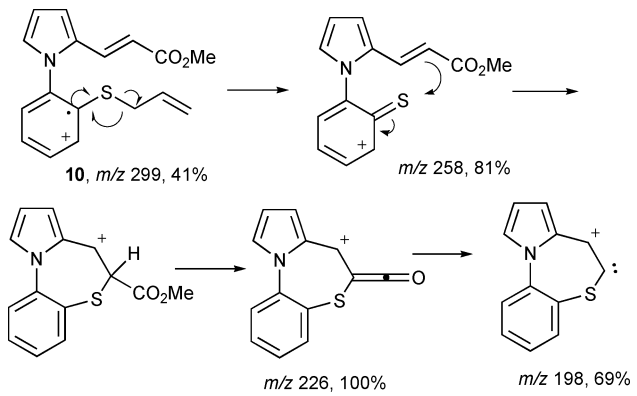
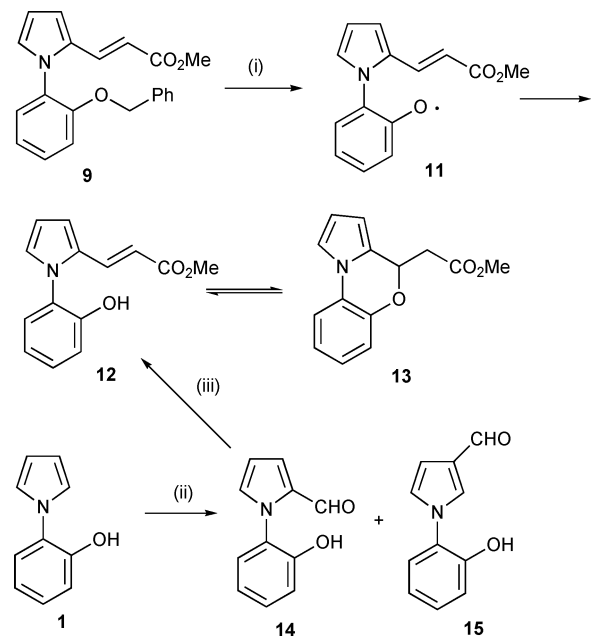
32 to give an ion at *m/z* 226 (100%). This may be rationalised by loss of the sulfur atom or by cleavage of methanol; the latter is more likely since the subsequent loss of CO (*m/z* 198, 69%) is then readily explained (Scheme 2).



Scheme 2

Flash vacuum pyrolysis of the *O*-benzyl compound **9** at 650 °C (0.005 Torr) was disappointing; apart from the inevitable formation of bibenzyl, only two significant products were obtained in low yield (<10%) and these proved to be the phenol **12** and the cyclic ether **13** (Scheme 3). Compound **12** could not be obtained in pure form, but was identified by comparison with an authentic sample (see below). The ether **13** was identified by its spectra; in particular the ^{1}H NMR spectrum showed three signals due to aliphatic protons (in addition to the seven due to the pyrrole and the benzene rings) which were shown to be a CH (δ_C 70.26), a CH_3 (δ_C 51.88) and a CH_2 (δ_C 38.72) by a ^{13}C NMR DEPT experiment. The ^{1}H and ^{13}C NMR chemical shifts of the CH group suggest that it is adjacent to an oxygen atom, as required for structure **13**.



Scheme 3 *Reagents and conditions*: (i) FVP (650 °C, 0.005 Torr); (ii) DMF–$POCl_3$; (iii) $Ph_3P{=}CHCO_2Me$.

The phenol **12** is probably formed by hydrogen atom capture by the phenoxyl radical **11**; such reactions are common in the gas-phase chemistry of phenoxyl radicals.[4] The source of the ether **13** is more ambiguous. It could be obtained by intramolecular conjugate addition of the radical centre of **11** onto the acrylate unit, followed by hydrogen atom capture. Alternatively, the phenol **12** may be the sole primary product of the pyrolysis, but may exist in equilibrium with the ether **13** by a heterolytic conjugate addition mechanism. A control experiment (Scheme 3) showed that the same mixture of **12** and **13** was formed when the aldehyde **14** was subjected to a Wittig reaction (see Experimental section), which suggests that **12** and **13** can indeed exist in equilibrium in solution, though they are stable to chromatography and can be separated. It therefore appears that intermolecular hydrogen capture[4] by the phenoxyl is the most likely product-forming route open to the radical derived from **9** and that processes related to the efficient cyclisation observed in Scheme 1 cannot take place with this system. In this context, the use of an *O*-benzyl (rather than an *O*-allyl) derivative as the radical precursor may have contributed to the low yields, since a benzyl radical leaving group is known to minimise the hydrogen atom flux under FVP conditions.[1]

In contrast, pyrolysis of the *S*-allyl derivative **10** at 650 °C (0.001 Torr) gave a single major product in 41% yield after dry-flash chromatography on silica. It was clear from its ^{1}H and ^{13}C NMR spectra that the 1,2-disubstituted pyrrole (AMX spin system) and 1,2-disubstituted aromatic (AKQX spin system) systems together with the ester function were still present but only one of the two alkene protons of the precursor **10** appeared in the product. Remarkably, its mass spectrum (*m/z* 225, M^+) suggested that the sulfur atom had been lost in the pyrolysis process as well as the allyl group and a hydrogen atom. This represents a very unusual example of a pyrolysis in which the atom bearing the original radical species is not present in the ultimate product. In addition, NOE experiments showed that the methyl group of the ester function was close in space to the pyrrole ring and not adjacent to the aromatic system. The two structures, **16** and **17**, which fulfil these requirements, are both unknown compounds and could not be distinguished from their routine NMR data or by comparison with the NMR spectra of model compounds. For example, the set of NOE data could be equally interpreted in terms of either structure (Fig. 1).

The carbon connectivity is however different in these two isomers and so a 2D-INADEQUATE spectrum was obtained at natural abundance (40 mg) at 150 MHz, and optimized to give responses from single and double bonded pairs of carbon atoms. Interpretation was aided by prior identification of the methine carbon resonances, and thus the quaternary carbon resonances, from an HMQC ^{13}C–^{1}H correlation spectrum, and by the symmetrical disposition of coupled pairs of carbon-13 doublets about the diagonal of the 2-D INADEQUATE spectrum. The connectivity sequence obtained (Fig. 2) is consistent only with structure **17**.

Clear connectivities were observed for all carbons from the six-membered ring through to carbon C although that from E to the carbonyl carbon P was only identifiable from a very weak signal for E at the expected position. The connectivity from C to B was not observable; since the B and C carbon resonances are almost superimposed the anti-phase signals of the central lines of the AB system would effectively cancel. Structure **16** is clearly excluded

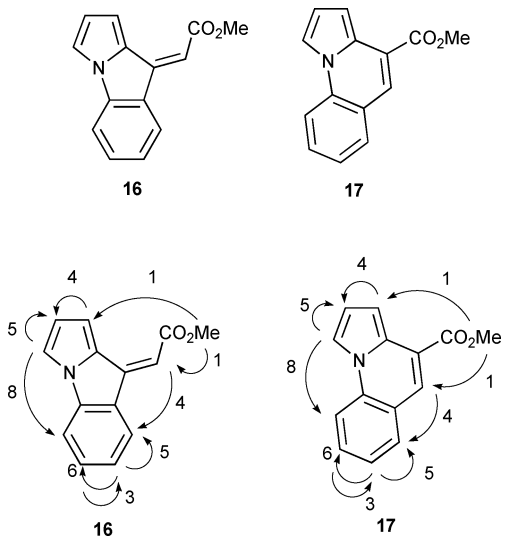


Fig. 1 NOE data (% enhancements) for the pyrolysis product of **10**, interpreted as structures **16** and **17**.

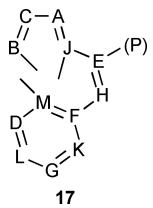
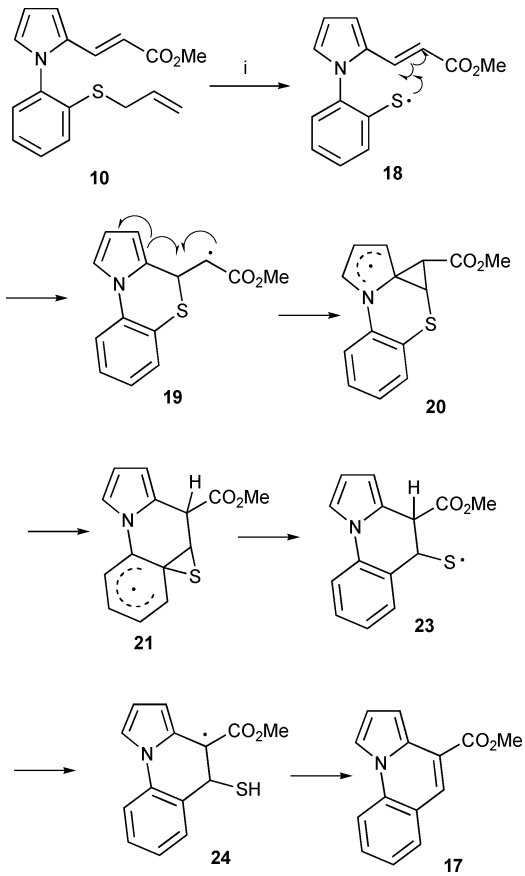


Fig. 2 Carbon connectivity of **17** as revealed by an INADEQUATE experiment.

since it requires an uninterrupted sequence of four quaternary carbon atoms. The full assignment of the NMR spectra of **17** is given in the Experimental section.

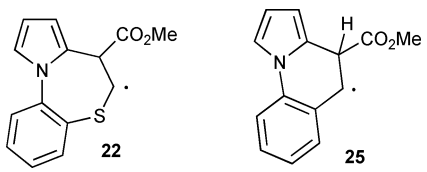
The formation of **17** from **10** requires an unusual and unexpected (yet efficient) rearrangement sequence, and a possible mechanism is shown in Scheme 4. The favoured 6-*exo*-*trig* cyclisation of the thiophenoxyl **18** to give **19** is followed by attack at the pyrrole system and a neophyl-type rearrangement to transform the connectivity of the precursor **10** into that of the product. Neophyl-type rearrangements are well known in aromatic systems (*e.g.* under FVP conditions[6]) yet apparently none of this type have been observed before in the sparse radical chemistry of the pyrrole ring system.[7] We believe that **20** is then transformed directly into **21** as a single step. By analogy with Scheme 1, our previous work suggests that the alternative formation of radicals with a β-carbomethoxy group such as **22** would be expected to suffer loss of the ester function leading to other products. For a similar reason, we favour the loss of the sulfur atom as the HS radical *via* **23** and **24** (Scheme 4), rather than as elemental sulfur,[8] because this latter process might be expected to generate the radical **25** which should again lead to loss of the ester function.

The results of this study show that the intramolecular radical reactions of pyrrol-2-ylacrylate species such as **11** and **18** under FVP conditions are quite different from those of corresponding benzenoid systems. The behaviour of the phenoxyl and thiophenoxyl species is quite different and one unusual case of rearrangement and sulfur extrusion has been identified to give **17**. We conclude that cyclisation of radicals onto the 2-position of



Scheme 4 *Reagents and conditions*: (i) FVP (650 °C, 0.001 Torr).

an acrylate chain (as in Scheme 1) is sensitive to the structure of the precursor and that deviations from the optimum examples of benzofuran or benzothiophene formation is likely to result in reduced efficiency of the cyclisation process.



Experimental

^{1}H and ^{13}C NMR spectra were recorded at 250 (or 200) and 63 (or 50) MHz respectively for solutions in [^{2}H]chloroform unless otherwise stated. Coupling constants are quoted in Hz. ^{13}C NMR signals refer to CH resonances unless otherwise stated; in most cases assignments were confirmed by appropriate DEPT experiments. Mass spectra were obtained under electron impact conditions.

N-Arylpyrroles 1 and 2

A mixture of the appropriate 2-substituted aminophenol (33 mmol), 2,5-dimethoxytetrahydrofuran (3.96 g, 30 mmol) and glacial acetic acid (15 cm^3) in dioxane (30 cm^3) was heated under reflux for 4 h. The volatiles were then removed on a rotary evaporator and the residue was partitioned between ether (60 cm^3)

and aqueous sodium hydroxide (3%, 90 cm^3). The aqueous phase was separated, acidified (pH 4) and extracted with chloroform (3 × 50 cm^3). The combined extracts were washed with sodium hydrogen carbonate (1 M, 50 cm^3), dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. The crude product was then purified by bulb to bulb distillation.

2-Aminophenol (3.60 g, 33 mmol) gave *N*-(2-hydroxyphenyl)pyrrole **1** (2.95 g, 61%), bp 138–140 °C (0.03 Torr) (lit.,[9] mp 45–47 °C) (found: M^+ 159.0687. $C_{10}H_9NO$ requires M 159.0684); δ_H 7.35–7.26 (2H, m), 7.11–6.98 (2H, m), 6.94 (2H, t, ^3J 2.1) and 6.44 (2H, t, ^3J 2.1); δ_C 150.16 (quat), 128.70, 128.22 (quat), 126.58, 121.86 (2CH), 120.79, 116.81 and 110.12 (2CH); *m/z* 159 (M^+, 100%), 158 (11), 131 (27), 130 (41), 103 (10) and 51 (21).

2-Aminothiophenol (6.25 g, 50 mmol) gave *N*-(2-mercaptophenyl)pyrrole **2** (6.28 g, 72%), bp 110–115 °C (0.05 Torr) [lit.,[10] bp 119–121 °C (1.0 Torr)]; δ_H 7.41–7.20 (4H, m), 6.85 (2H, t, ^3J 2.1), 6.39 (2H, t, ^3J 2.2) and 3.41 (1H, s) spectrum consistent with literature data.[10]

N-[2-(Benzyloxy)phenyl]pyrrole 3, and *N*-[2-(allylthio)phenyl]pyrrole 4—general method

A suspension of potassium carbonate (1.1 equiv.) in DMF (10 cm^3 per gram) was stirred for 10 min. The appropriate phenol or thiophenol (1.0 equiv.) and the appropriate alkyl bromide (1.1 equiv.) were added and the mixture was stirred until TLC showed the disappearance of the *N*-arylpyrrole. Water (2 cm^3 per cm^3 DMF) was added and the mixture was extracted with ether [3 × (volume of water/3)]. The combined organic extracts were washed with water [3 × (volume of ether × 2/3)] and dried ($MgSO_4$). The solvent was removed on a rotary evaporator to yield the crude product which was purified by bulb to bulb distillation.

N-(2-Hydroxyphenyl)pyrrole **1** (0.80 g, 50 mmol) with benzyl bromide (1.03 g, 55 mmol) gave *N*-[2-(benzyloxy)phenyl]pyrrole **3** (1.05 g, 85%), bp 160–165 °C (0.005 Torr) (found C, 82.0; H, 6.2; N, 5.65. $C_{17}H_{15}NO$ requires C, 81.9; H 6.05; N, 5.6%); δ_H 7.42–7.05 (9H, m), 7.15 (2H, dd, ^3J 2.1), 6.42 (2H, dd, ^3J 2.1) and 5.13 (2H, s); δ_C 151.62 (quat), 136.54 (quat), 130.95 (quat), 128.38 (2CH), 127.69, 127.18, 126.85 (2CH), 125.69, 121.97 (2CH), 121.46, 114.71, 108.70 (2CH) and 70.81 (CH_2); *m/z* 249 (M^+, 15%), 172 (20), 158 (42), 91 (100), 77 (23), 65 (28), 63 (12), 51 (22) and 39 (26).

N-(2-Mercaptophenyl)pyrrole **2** (2.00 g, 11 mmol) gave *N*-[2-(allylmercapto)phenyl]pyrrole **4** (2.46 g, 100%), bp 118–120 °C (0.03 Torr) (found C, 72.3; H, 6.2; N, 6.35. $C_{13}H_{13}NS$ requires C, 72.5; H, 6.1; N, 6.5%); δ_H 7.47–7.26 (4H, m), 6.91 (2H, t, ^3J 2.2), 6.36 (2H, t, ^3J 2.2), 5.86 (1H, m), 5.17–5.03 (2H, m) and 3.35–3.30 (2H, m); δ_C 133.00, 132.78 (quat), 130.06, 127.50, 126.91, 126.53, 121.98 (2CH), 117.87 (CH_2), 108.96 (2CH), 108.80 (quat) and 35.86 (CH_2); *m/z* 215 (M^+, 8%), 175 (16), 174 (100), 173 (20), 45 (9), 41 (8) and 39 (18).

Formylation of *N*-arylpyrroles—general method

A solution of the appropriate *N*-arylpyrrole (3 mmol) in DMF (5 cm^3) was added to a solution of phosphoryl chloride (0.60 g, 3.9 mmol) in DMF (10 cm^3). After stirring for 1 h a further portion of phosphoryl chloride (0.60 g, 3.9 mmol) was added and stirring continued for 1 h. The mixture was then poured onto crushed ice, hydrolysed with sodium hydroxide solution (2 M, 25 cm^3) and then acidified to pH 6–7 with hydrochloric acid (2 M). The mixture was then extracted with ether (3 × 25 cm^3), the organic extracts were washed with water (3 × 50 cm^3) and dried ($MgSO_4$). TLC showed that formylation had occurred at both the 2- and 3-positions of the pyrrole ring, so the products were pre-adsorbed onto silica and separated by dry-flash chromatography (10% ethyl acetate–hexane: 5% gradient).

N-[2-(Benzyloxy)phenyl]pyrrole **3** (0.75 g, 3 mmol) gave 2-formyl-*N*-[2-(benzyloxy)phenyl]pyrrole **5** (0.64 g, 77%), bp 114–118 °C (3 Torr) (found: M^+ 277.1103. $C_{18}H_{15}NO_2$ requires M 277.1103); δ_H 9.49 (1H, s), 7.43–6.99 (11H, m), 6.42 (1H, dd, ^3J 4.1 and 2.6) and 5.05 (2H, s); δ_C 178.97, 153.44 (quat), 136.17 (quat), 133.02 (quat), 130.98, 129.61, 128.27 (2CH), 127.99, 127.61, 126.55 (2CH), 120.87, 120.55 (quat), 113.61, 110.32 and 70.32 (CH_2) (one CH overlapping); *m/z* 277 (M^+, 15%), 248 (23), 158 (16) and 91 (100) and 3-formyl-*N*-[2-(benzyloxy)phenyl]pyrrole **7** (0.12 g, 15%), bp 145–150 °C (2 Torr), (found: M^+ 277.1103. $C_{18}H_{15}NO_2$ requires M 277.1103); δ_H 9.81 (1H, s), 7.61 (1H, t, ^3J 1.7), 7.41–7.25 (7H, m), 7.14–6.98 (3H, m), 6.76 (1H, dd, ^3J 3.1 and 1.6) and 5.12 (2H, s); δ_C 185.32, 151.48 (quat), 135.84 (quat), 130.74, 129.13 (quat), 128.74, 128.42 (2CH), 127.87, 126.92 (quat), 126.68 (2CH), 125.52, 124.85, 121.40, 114.26, 107.60 and 70.68 (CH_2); *m/z* 277 (M^+, 75%), 186 (26), 158 (32), 92 (20), 91 (100) and 65 (30).

N-[2-(Allylthio)phenyl]pyrrole **4** (0.75 g, 3 mmol) gave 2-formyl-*N*-[2-(allylthio)phenyl]pyrrole **6** (0.57 g, 77%), bp 124–128 °C (2 Torr) (found: M^+ 243.0713. $C_{14}H_{13}NOS$ requires M 243.0718); δ_H 9.42 (1H, s), 7.42–7.39 (2H, m), 7.28–7.24 (2H, m), 7.13 (1H, dd, ^3J 4.0 and 1.6), 6.95 (1H, m), 6.43 (1H, dd, ^3J 4.0 and 2.6), 5.73 (1H, m), 5.16–5.02 (2H, m) and 3.40–3.35 (2H, m); δ_C 178.70, 137.99 (quat), 135.02 (quat), 132.84 (quat), 132.64, 130.84, 129.26, 129.10, 128.05, 126.29, 120.64, 118.20 (CH_2), 110.63 and 35.65 (CH_2); *m/z* 243 (M^+, 43%), 214 (71), 174 (97), 173 (59), and 170 (100) and 3-formyl-*N*-[2-(allylthio)phenyl]pyrrole **8** (0.18 g, 23%), bp 136–140 °C (3 Torr) (found: M^+ 243.0726. $C_{14}H_{13}NOS$ requires M 243.0718); δ_H 9.79 (1H, s), 7.46–7.23 (5H, m), 6.84 (1H, m), 6.73 (1H, dd, ^3J 2.7 and 1.5), 5.68 (1H, m), 5.10–4.98 (2H, m) and 3.32 (2H, d, ^3J 6.8); δ_C 185.29, 139.00 (quat), 132.74 (quat), 132.46, 130.46, 130.27, 128.82, 127.16 (quat), 126.85, 126.69, 124.94, 118.30 (CH_2), 108.00 and 36.03 (CH_2); *m/z* 243 (M^+, 19%), 202 (84), 175 (19), 174 (100) and 173 (51).

Wittig reactions—general method

The appropriate 2-formyl-*N*-arylpyrrole (2 mmol) was dissolved in dry methylene chloride (50 cm^3). Methyl (triphenylphosphoranylidene)acetate (0.736 g, 2.2 mmol) was added and the mixture was then heated under reflux until TLC showed that all the aldehyde had been consumed. The mixture was pre-adsorbed onto silica and purified by dry-flash chromatography (10% ethyl acetate–hexane: 10% gradient).

2-Formyl-*N*-[2-(benzyloxy)phenyl]pyrrole **5** (0.554 g, 2 mmol) (48 h) gave methyl 3-{*N*-[2-(benzyloxy)phenyl]pyrrol-2-yl}propenoate **9** (0.300 g, 45%), bp 150–155 °C (0.05 Torr) (found: M^+ 333.1374. $C_{21}H_{19}NO_3$ requires M 333.1364); δ_H 7.42–7.20 (8H, m), 7.10–7.06 (2H, m), 6.92 (1H, m), 6.84 (1H, m), 6.38 (1H, m), 6.03 (1H, m, ^3J 15.8), 5.05 (2H, s) and 3.70 (3H, s); δ_C 167.97 (quat),

153.71 (quat), 136.25 (quat), 133.74, 130.22 (quat), 129.71, 128.93, 128.29 (2CH), 128.05 (quat), 127.61, 127.30, 126.58 (2CH), 121.13, 114.10, 112.03, 111.73, 110.05, 70.31 (CH_2) and 51.14 (CH_3); *m/z* 333 (M^+, 35%), 274 (12), 170 (34), 168 (23), 154 (23) and 91 (100).

2-Formyl-*N*-[2-(allylthio)phenyl]pyrrole **6** (0.486 g, 2 mmol) (8 h) gave methyl 3-{*N*-[2-(allylthio)phenyl]pyrrol-2-yl}propenoate **10** (0.342 g, 60%), bp 145–150 °C (0.05 Torr) (found: M^+ 299.0984. $C_{17}H_{17}NO_2S$ requires M 299.0980); δ_H 7.41 (2H, m), 7.27–7.14 (3H, m), 6.85–6.80 (2H, m), 6.36 (1H, dd, ^3J 3.3), 5.93 (1H, d, ^3J 15.9), 5.81–5.64 (1H, m), 5.18–5.03 (2H, m), 3.67 (3H, s) and 3.40 (2H, d, ^3J 6.6); δ_C 167.85 (quat), 137.36 (quat), 135.97 (quat), 133.08, 132.62, 129.88 (quat), 129.23, 128.88, 128.75, 127.04, 126.21, 118.24 (CH_2), 112.48, 112.13, 110.33, 51.20 (CH_3) and 35.40 (CH_2); *m/z* 299 (M^+, 41%), 258 (81), 226 (100), 199 (44), 198 (69), 197 (31), 186 (53), 167 (23) and 41 (22).

Flash vacuum pyrolysis experiments

The substrate was volatilised under vacuum through an electrically heated empty silica tube (35 × 2.5 cm) and the products were collected in a liquid nitrogen cooled U-tube, situated at the exit point of the furnace. Conditions for the pyrolyses were established in small-scale experiments in which the product(s) were dissolved in a deuterated solvent and analysed immediately by ^{1}H NMR spectroscopy. The precursor, pyrolysis conditions [quantity of precursor, furnace temperature (T_f), inlet temperature (T_i), pressure range (P) and pyrolysis time (t)] and, where appropriate, approximate yields are given.

FVP of methyl 3-{*N*-[2-(benzyloxy)phenyl]pyrrol-2-yl}propenoate 9

Methyl 3-{*N*-[2-(benzyloxy)phenyl]pyrrol-2-yl}propenoate **9** (0.204 g, 6 mmol) (T_f 650 °C, T_i 140–160 °C, P 0.005 Torr, t 20 min), gave a number of products, only three of which could be separated by dry-flash chromatography. The first to elute was bibenzyl. The second was methyl (4*H*-5-oxa-9*b*-aza-cyclopenta[*a*]naphthalen-4-yl)acetate **13** (0.006 g, 4%), bp 120–125 °C (0.05 Torr) (found: M^+ 243.0879. $C_{14}H_{13}NO_3$ requires M 243.0895); δ_H 7.33 (1H, m), 7.14 (1H, dd, ^3J 2.9 and ^4J 1.3), 7.05–7.00 (3H, m), 6.31 (1H, apparent t, ^3J 3.2), 6.01 (1H, dt, ^3J 3.5 and ^4J 1.3), 5.61 (1H, apparent t, ^3J 6.3), 3.76 (3H, s) and 2.99 (2H, m); δ_C 170.26 (quat), 144.88 (quat), 126.25 (quat), 126.09 (quat), 124.98, 122.31, 118.16, 114.90, 114.57, 110.48, 104.18, 70.26, 51.88 (CH_3) and 38.72 (CH_2); *m/z* 243 (M^+ 30%), 171 (13) and 170 (100). The third product could not be isolated in a pure form but was identified as methyl 3-[1-(2-hydroxyphenyl)pyrrol-2-yl]propenoate **12** by comparison with authentic data (see below); δ_H 7.06–6.99 (2H, m), 6.87 (1H, m), 6.80 (1H, m), 6.35 (1H, t), 5.99 (1H, d, ^3J 15.8) and 3.68 (3H, s) two aryl protons, one alkenyl proton and OH not assigned; *m/z* 243 (M^+).

2-Formyl-*N*-(2-hydroxyphenyl)pyrrole 14

Application of the general formylation procedure described above to *N*-(2-hydroxyphenyl)pyrrole **1** gave, after dry flash chromatography (15% ethyl acetate–hexane: 5% gradient), 2-formyl-1-(2-hydroxyphenyl)pyrrole **14** (0.092 g, 25%), bp 134–139 °C (0.2 Torr) (found: M^+ 187.0644. $C_{11}H_9NO_2$ requires M 187.0633); δ_H 9.42 (1H, s), 7.39–6.94 (4H, m) and 6.46–6.25 (3H, m) (OH not apparent); δ_C 178.40, 150.39 (quat), 131.16, 129.29, 127.26, 120.13, 116.98, 113.92 and 110.78 (two quaternaries not apparent); *m/z* 187 (M^+, 100%), 170 (28), 159 (93), 158 (50), 131 (23) and 130 (55), and 3-formyl-*N*-(2-hydroxyphenyl)pyrrole **15** (0.058 g, 16%), bp 150–155 °C (0.5 Torr), (found: M^+ 187.0625. $C_{11}H_9NO_3$ requires M 187.0633); δ_H 9.69 (1H, s), 7.72 (1H, t, ^4J 1.8), 7.30–6.91 (5H, m) and 6.76 (1H, dd, ^3J 3.0 and ^4J 1.8) (OH not apparent); δ_C 186.45, 149.91 (quat), 131.11, 129.03, 128.88 (quat), 128.06 (quat), 125.42, 124.78, 120.51, 117.41 and 108.68; *m/z* 187 (M^+, 92%), 170 (40), 159 (100), 158 (60), 130 (32) and 94 (27).

Methyl 3-{*N*-(2-hydroxyphenyl)pyrrol-2-yl}propenoate 12 and methyl (4*H*-5-oxa-9*b*-aza-cyclopenta[*a*]naphthalen-4-yl)acetate 13

2-Formyl-1-(2-hydroxyphenyl)pyrrole **14** (0.070 g, 0.37 mmol) was dissolved in dry THF (50 cm^3). Methyl (triphenylphosphoranylidene)acetate (0.38 g, 1.12 mmol) was added and the mixture was then heated under reflux until TLC showed that all the aldehyde had been consumed (36 h). The mixture was pre-adsorbed onto silica (1 g) and purified by dry-flash chromatography (20% ethyl acetate–hexane: 5% gradient). This gave two products: methyl (4*H*-5-oxa-9*b*-aza-cyclopenta[*a*]naphthalen-4-yl)acetate **13** (0.031 g, 34%), bp 130–135 °C (0.1 Torr) (found: M^+ 243.0883. $C_{14}H_{13}NO_3$ requires M 243.0895); δ_H 7.33 (1H, m), 7.15 (1H, dd, ^3J 2.9 and 1.4), 7.09–7.00 (3H, m), 6.32 (1H, t, ^3J 3.4), 6.02 (1H, dt, ^3J 3.5 and ^4J 1.3), 5.62 (1H, ddd, ^3J 7.0 and 6.0, ^4J 0.7), 3.77 (3H, s) and 3.00 (2H, m); δ_C 170.24 (quat), 144.85 (quat), 126.24 (quat), 126.07 (quat), 124.95, 122.28, 118.12, 114.91, 114.58, 110.51, 104.15, 70.25, 51.83 (CH_3) and 38.72 (CH_2); *m/z* 243 (M^+, 30%), 171 (15) and 170 (100), and methyl 3-[*N*-(2-hydroxyphenyl)pyrrol-2-yl]propenoate **12** (0.024 g, 27%), bp 145–150 °C (0.1 Torr) (found: M^+ 243.0887. $C_{14}H_{13}NO_3$ requires M 243.0895); δ_H 7.33–7.12 (3H, m), 7.01–6.97 (2H, m), 6.87 (1H, m), 6.80 (1H, d, ^3J 3.8), 6.38 (1H, t, ^3J 3.0), 6.16 (1H, br), 5.97 (1H, d, ^3J 15.7) and 3.66 (3H, s); *m/z* 234 (M^+, 10%), 241 (13), 227 (21), 226 (78), 213 (86), 198 (100), 197 (75) and 183 (56). These data are consistent with those reported above for the pyrolysis of **9**.

FVP of methyl 3-{*N*-[2-(allylthio)phenyl]pyrrol-2-yl}propenoate 10

Methyl 3-{*N*-[2-(allylthio)phenyl]pyrrol-2-yl}propenoate **10** (0.250 g, 8 mmol) (T_f 650 °C, T_i 140–160 °C, P 0.001 Torr, t 20 min), gave one major product which was purified by dry-flash chromatography (1% ethyl acetate–hexane: 10% gradient) and identified as methyl pyrrolo[1,2-*a*]quinoline-4-carboxylate **17** (see discussion) (0.084 g, 41%) bp 125–130 °C (0.2 Torr) (found: M^+ 225.0784. $C_{14}H_{11}NO_2$ requires M 225.0790); δ_H (600 MHz, [$^2H_6$]acetone, see Fig. 2 for atom labels) 8.11 (1H, dd, ^3J 2.9 and ^4J 1.5, proton B), 8.08 (1H, br. d, ^3J 8.5, proton D), 7.87 (1H, s, proton H), 7.83 (1H, ddt, ^3J 7.8, ^4J 1.4, ^nJ 0.7 and 0.7, proton K), 7.63 (1H, ddd, ^3J 8.5 and 7.2, ^4J 1.4, proton L), 7.36 (1H, ddd, ^3J 7.8 and 7.2, ^4J 1.1, proton G), 7.21 (1H, dd, ^3J 3.9 and ^4J 1.5, proton A), 6.83 (1H, dd, ^3J 3.9 and 2.9, proton C) and 3.95 (3H, s); δ_C (150 MHz, [$^2H_6$]acetone, see Fig. 2 for atom labels) 165.5 (quat P), 134.8 (quat M), 131.1 (L), 130.8 (K), 127.9 (quat

J), 125.2 (H), 124.5 (G), 122.3 (quat F), 121.0 (quat E), 115.0 (D), 113.7 (C), 113.6 (B), 105.6 (A) and 52.3 (CH_3); *m/z* 225 (M^+ 100%), 194 (7), 168 (7), 167 (63), 166 (49), 140 (13) and 139 (12).

NMR spectroscopic analysis of 17

The NMR spectra were measured on [$^2H_6$]acetone solutions using a Varian INOVA 600 MHz spectrometer operating at 599.9 MHz for protons and 150.9 MHz for ^{13}C nuclei.

The 2-D proton detected one-bond ^1H–^{13}C correlation (HMQC) spectra were obtained using the sequence:[11] *D*l–90°(^1H)–*D*2–180°(^1H); 180° (^{13}C)–*D*2–90°(^1H)–*D*3–90°(^1H)–*D*2–90°(^{13}C)–t_1/2–180°(^1H)–t_1/2–90°(^{13}C)–*D*2–AQ. The delays used were *D*l = 1.5 s, *D*2 = 3.7 ms ($1/2\ ^1J_{CH}$) and *D*3 = 1 s (to minimise signals from protons bonded to ^{12}C nuclei). The experiment was preceded by 64 dummy scans to establish thermal equilibrium. A 4-step phase cycle (hypercomplex acquisition) was used with ^{13}C broad band decoupling during acquisition of the proton signals. Other parameters were SW(^1H) = 5000 Hz; 2 K data points; 400 increments; SW(^{13}C) = 20000 Hz, AQ = 0.205 s. The data were processed using shifted sine-bell squared functions in both dimensions with zero filling of the F_1 data from 400 W to 1024 W before transformation.

The 2-D INADEQUATE spectrum was obtained on a 40 mg sample of **17** over a period of 64 h using the pulse sequence:[12] *D*l–90°–*D*2–180°–*D*2–90°-t_1–90°–AQ, with a 16 step phase cycle (absolute value mode) and where *D*l = 1.3 s (relaxation delay), *D*2 = 5.55 ms ($1/4\ ^1J_{CC}$), AQ = 0.3 s (acquisition time) and t_1 is the incremented delay. WALTZ-16 broad band proton decoupling was employed during AQ. Other parameters were SW2 = 23000 Hz; 13 K data points; SW1 = 40000 Hz; 128 FIDs each with 144 transients. The data were processed using optimized decreasing exponential window functions in both dimensions with zero filling of the F_1 data from 128 W to 512 W.

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