Gas-phase cyclisation reactions of 1-(2-arylthiophenyl)alkaniminyl and 2-(aryliminomethyl)thiophenoxyl radicals

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Flash vacuum pyrolysis (FVP) of the oxime ethers **12–14** and of the sulfides **18–20** at 650 °C ($10^{-2}-10^{-3}$ Torr) gave products derived from the corresponding iminyl and thiophenoxyl radicals. In all cases, benz[*d*]isothiazoles (*e.g.*, **26**) are formed as major products *via* $S_{\rm H}$ i mechanisms though the yields are greatest with the iminyl precursors. Alternative pathways observed from the thiophenoxyls in specific cases include the formation of the anilinobenzothiophene **36** and of dibenzothiophene **23**, *via* an $S_{\rm H}$ i process and a spirodienyl rearrangement, respectively. There is no evidence for significant interconversion of the iminyl and thiophenoxyl species.

Introduction

We have previously examined the possibility of gas- and solution-phase interconversion of the iminyl radicals $\mathbf{1}$ and the phenoxyls and aminyls $\mathbf{2}$ (Scheme 1, X = O and NR respec-



tively) *via* an intermediate spirodienyl radical 3.¹⁻³ In the gasphase under flash vacuum pyrolysis (FVP) conditions, iminyl and phenoxyl precursors (**4** and **5**, X = O respectively) gave rise to common products, which suggested that the radicals equilibrated as shown in Scheme 1. However, in the aminyliminyl case (Scheme 1, X = NR) there was evidence for rearrangement only when the reaction was carried out in solution. In earlier work we have found that phenoxyls and thiophenoxyls often display very different chemistry, and so we have now investigated the gas-phase properties of the corresponding thiophenoxyl-iminyl system (Scheme 1, X = S). As before² we have employed FVP methods to generate the radicals and have used oxime ethers **4** as precursors to the iminyls **1**, and S-benzyl compounds (**5**, R' = CH₂Ph) as precursors to the thiophenoxyls 2 (Scheme 1). In order to be able to assess the generality of any new processes discovered, three precursors were prepared (Scheme 1, X = S, R = H, Me and Ph) in each series. The corresponding solution-phase behaviour of the iminyls was reported in the preceding paper in this issue.⁴

Results

The immediate precursors to the oxime ethers were the carbonyl compounds 6-8 These were made in 54-78% yield by the known displacement of halide ion from the ortho-halogenocarbonyl compounds 9a, 10b and 11b respectively (see Experimental section). In turn, the oxime ethers 12-14 were obtained in 60–67% yield by condensation of the aldehyde 6 or ketones 7 or 8 with O-methylhydroxylamine in ethanol or in a mixture of ethanol and pyridine. The aldoxime 12 was obtained as a single isomer, but the ketoximes 13 and 14 were formed as mixtures of E and Z isomers, each in a 3 : 1 ratio, which were not separated. The structures of the products followed immediately from their spectra (see Experimental section); for example, their mass spectra under electron impact (EI) conditions show weak molecular ions followed by loss of a fragment of m/z 31 or 32 (= MeO or MeOH respectively) to give the base peak. The oxime ethers 4 (X = O) show similar behaviour.²

Thiophenoxyl radicals have been generated in the gas-phase by pyrolysis of S-allyl or S-benzyl derivatives.^{5,6} Traditional syntheses of 2-(benzylthio)benzaldehyde 15 include multi-step routes ultimately based on reduction of thiosalicylic acid derivatives,^{7,8} though, more recently, a one-step route from 2-nitrobenzaldehyde has been developed.9 The corresponding acetophenone 16 has been made from 2'-nitroacetophenone¹⁰ or from 2'-bromoacetophenone.¹¹ The benzophenone 17 is unknown. However, we have found that displacement of fluoride from 9a-11a by phenylmethanethiol in isopropyl alcohol in the presence of anhydrous potassium carbonate, works smoothly to give 15, 16, and 17 in 67, 90 and 78% yield, respectively. The required anils 18-20 were then obtained by condensation with the appropriate aniline derivative, with azeotropic removal of water. The benzophenone derivative 20 formed sluggishly under these conditions and could not be purified satisfactorily. The anils 18 and 20 were obtained as a

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single isomer, but 19 was formed as E and Z isomers in a 3 : 1 ratio.

The mass spectra of 18-20, obtained under EI or fast-atom bombardment (FAB) conditions showed loss of the benzyl group as the initial breakdown peak. In addition, the base peak of 18 corresponds to loss of a fragment of m/z 93 from the molecular ion, which may be formed by an ortho hydrogen rearrangement followed by elimination of PhNH₂.

Flash vacuum pyrolysis of the oxime ethers 12-14 and the S-benzyl compounds 18-20 at 650 °C gave pyrolysates which showed no trace of starting material. The products, which are assumed to arise from the iminuls 21, 33 and 38 and the thiophenoxyls 22, 34 and 39, respectively, were separated by dry-flash chromatography.

Products obtained from pyrolysis of the oxime ether 12 and of the S-benzyl anil 18 are shown in Scheme 2. The initial products to elute from the column from the pyrolysate of 12 were a number of trace components including dibenzothiophene 23, biphenyl 24, diphenyl sulfide 25, readily identified by their mass and NMR spectra (see Experimental section). The major component was identified as benz[d] isothiazole 26 (48%) by comparison of its NMR spectra with literature data.¹² Finally some 2-(phenylthio)
benzyl alcohol 27 (
 $\approx\!6\%$) was obtained; this was subsequently discovered to be a very minor impurity in the starting material. The pyrolysate from the corresponding thiophenoxyl generator 18 also gave minor radical coupling products (biphenyl 24, diphenylmethane 28, and bibenzyl 29) but again benz[d] isothiazole **26** (34%), identified as above, was found to be the major product. The next component (≈4%) was impure but showed a molecular ion at m/z 211 and its ¹³C NMR spectrum showed peaks identical with those of an authentic sample of 2-(phenylthio)benzonitrile 30 (see below). The following component was also impure ($\approx 10\%$), but again showed a molecular ion at m/z 211, though in this case a singlet at $\delta_{\rm H}$ 8.91 (corresponding to the CH of an imine function) was present. This compound may be the dibenzo[b,f][1,4]thiazepine 31 [$\delta_{\rm H}$ (lit.,¹³) 8.7] but the literature data for this compound are insufficiently precise to make an unambiguous identification. Nevertheless, this result defines the maximum limit of seven-membered ring formation in this study (cf. ref. 14). Finally, a small amount (9%) of the disulfide 32 derived by oxidative dimerisation of 2-cyanothiophenol, was identified from its mass spectrum (m/z 268, major breakdown peak at m/z 134), IR spectrum [v_{max} 2221 cm⁻¹ (CN)] and NMR comparison with reported data.







Results of the pyrolysis of the methyl-substituted oxime ether 13 and of the S-benzyl anil 19 are shown in Scheme 3. The



former compound gave trace quantities of dibenzothiophene 23 and of biphenyl 24, but the major product was the benz[d]isothiazole 35 (45%). This product was also a major component from the solution-phase study.⁴ In addition, a small amount of the nitrile 30 (8%) was isolated; the presence of the nitrile function was confirmed by IR spectroscopy (v_{max} 2219 cm⁻¹) and by comparison with literature data.¹⁶ Pyrolysis of the anil 19 gave the same set of radical coupling products as its analogue 18 (viz. 24, 28 and 29) but the major products were the benzisothiazole **35** (25%), *N*-benzo[*b*]thiophen-3-ylaniline **36** (30%) and 2-phenylbenzothiazole 37 (9%). Identification of 35 and 37 followed readily by comparison with literature data, but there are no meaningful NMR data reported for the benzothiophene 36. The structure was therefore established by its mass spectrum $(m/z 225, M^+)$ and by the following sequence of NMR experiments. A combination of COSY and HMQC experiments†

[†] COSY = 2D homonuclear chemical-shift correlation spectroscopy; HMQC = 2D heteronuclear multiple quantum coherence spectroscopy.

showed the presence of a phenyl group, a four-spin system (consistent with a 1,2-disubstituted aromatic) and an isolated proton at $\delta_{\rm H}$ 6.71 which correlated with a carbon resonance at $\delta_{\rm C}$ 110.14. The ¹H NMR spectrum showed the presence of an NH, and the HMQC correlation demonstrated that the ortho carbon resonances of the phenyl ring were substantially shielded ($\delta_{\rm C}$ 116.24), consistent with the presence of an anilino moiety. These data are consistent with a benzothiophene structure, substituted by an anilino group at either the 2- or the 3position. The 3-isomer 36 was confirmed by nuclear Overhauser enhancement (NOE) data which related the NH to (a) the ortho protons of the phenyl group (4% enhancement) (b) the *peri* proton at $\delta_{\rm H}$ 7.47 of the four-spin system (4% enhancement) (which excludes attachment of the anilino group at the 2-position of the benzothiophene) and (c) the isolated proton at $\delta_{\rm H}$ 6.71 (1% enhancement) (which is now assigned as the 2-proton of the benzothiophene).

Results of the pyrolysis of the phenyl-substituted oxime ether 14 and of the S-benzyl anil 20 are shown in Scheme 4. The



p-tolyl anil **20** was used in this case so that the fates of the *N*-aryl and *C*-aryl groups could be distinguished in the products. Thus, generation of the iminyl **38** again gave the corresponding benzisothiazole, in this case compound **41** (48%), as the major product, with small amounts of radical-coupling products including diphenyl disulfide **40**, which may have been present in the starting material. The thiophenoxyl **39**, generated from **20**, gave the expected benzisothiazole **41** (27%) and bibenzyl **29** (17%) but the major co-product was surprisingly dibenzothiophene **23** (22%). It is clear that the *N*-aryl group is not involved in this cyclisation since the methyl substituent is not present.

Discussion

It is clear that the chemistry of the radicals 1 and 2 (Scheme 1) is considerably altered when X = S, by comparison with the cases where X = O or NR. The benz[d] isothiazole system (e.g., 26) is formed (25-48%) in the gas-phase pyrolyses of all six substrates 12-14 and 18-20 – and in solution⁴ – though the yield appears to be greatest when the oxime ethers 12-14 are used. Such behaviour was never observed in the X = Oor X = NR cases. The formation of the benz[d]isothiazoles involves creation of an N-S bond with expulsion of aryl radical (Scheme 5). The iminyls probably cyclise directly by an intramolecular homolytic substitution $(S_{\rm H}i)$ mechanism, though an addition-elimination route is possible for the thiophenoxyls (Scheme 5). For reasons explained below it seems likely that the thiophenoxyls and iminyls do not interconvert to any significant extent and therefore the benzisothiazoles are probably formed by these independent mechanisms. As a potential new synthetic method to benz[d] isothiazoles,¹⁷ the method at present suffers from the disadvantage of moderate yields and



the need for chromatographic separation of the products, though in principle these factors may be improved by alteration of the radical leaving group at the final cyclisation step.

The aryl radicals formed along with the benzisothiazoles give rise to a number of the minor products detected in the pyrolysates. Aryl radicals are known to couple with poor efficiency in the gas phase⁵ and so this accounts for the detection of biphenyl 24 in only trace amounts in most of the pyrolyses. Similarly, when the *S*-benzyl compounds 18-20 were used, the concomitant presence of benzyl radicals allows random radical coupling to provide diphenylmethane 28 and bibenzyl 29 as well as the biphenyl. Traces of diphenyl disulfide 40 as a contaminant of the precursors could explain its presence in the pyrolysate from 14, and, as a potential source of thiophenoxyl radicals, could account for diphenyl sulfide 25 through coupling with phenyl radicals.

The iminuls **21** and **33** may undergo β -cleavage reactions which lead to the formation of the nitrile **30** (8%) and ultimately to traces of dibenzothiophene **23** (Scheme 6). This



behaviour is expected from our previous work; indeed we have used these products as markers for the interconversion of phenoxyls and iminyls as shown in Scheme 1. Nitriles are often major products in cases where a relatively weak C-alkyl bond can be cleaved.¹⁸ The relatively low level of nitrile **30** (8%) is good evidence for the efficiency of the cyclisation to the benzisothiazole. Significantly, dibenzothiophene **23** was not observed amongst the products from the thiophenoxyls **22** or **34** and its presence in the pyrolysate from **39** must be due to an alternative mechanism (see below). Although the nitrile **30** was similarly not found in the pyrolysate from the thiophenoxyl **34** it could be detected in small amounts (4%) from the aldimine pre-

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cursor 18. The simplest explanation for its formation is by a thiophenoxyl-iminyl interconversion (see Scheme 1) followed by β -cleavage (Scheme 6). This is the only evidence that thiophenoxyl-to-iminyl interconversion may be a very minor pathway on this energy surface.

A number of other products were formed from the thiophenoxyls **22**, **34** and **39**. That these compounds were not detected in the pyrolysates from the iminyl generation is good evidence that iminyl-to-thiophenoxyl interconversion according to Scheme 1 does not occur. A possible route to the disulfide **32** from the thiophenoxyl **22** involves hydrogen abstraction followed by β -cleavage of the resulting imidoyl and aerial oxidation (Scheme 7); a related sequence has been observed in the phenoxyl series.³



The major product derived from the thiophenoxyl **19** was unexpectedly the anilinobenzothiophene **36**. This product may be formed by a formal $S_{\rm H}$ i ejection of one of the hydrogen atoms of the *C*-methyl group, and a tautomerisation step (Scheme 8), though the actual sequence of these steps remains



unknown. The presence of the benzothiazole **37** (9%) in this pyrolysis was also unexpected; overall, the reaction from **19** must involve the loss of a methyl group, a skeletal rearrangement and a phenyl migration but the nature of these steps is not obvious by inspection. One possible mechanism (Scheme 9)



involves initial ejection of the methyl radical followed by ring expansion of the thiete **42** to the stable carbene **43**, which collapses to the benzothiazole **37**. However, labelling studies would be required to substantiate the mechanism of such a deep-seated rearrangement.

Finally, the presence of dibenzothiophene 23 as a significant product (22%) in the pyrolysate from the *para*-substituted imine 20 must be explained. The mechanism shown in Scheme 10 takes account of the fact that the *N*-aryl ring is not found in the product and involves a thiophenoxyl–imidoyl interconversion as the key step. Cyclisation of 2-thiophenoxyaryl radicals to dibenzothiophenes is known to be efficient under FVP condi-



tions, 19 as is the formation of spirodienyl radicals related to $44.^{20}$

Conclusions

The major conclusion from this work, and from the accompanying paper,⁴ is that iminyls of type 1 (X = S) and thiophenoxyls of type 2 (X = S) do not interconvert *via* a spirodienyl system either in the gas-phase or in solution, in contrast to the cases of the corresponding phenoxyl and aminyl species.^{1,2} The creation of the benz[*d*]isothiazole system by an $S_{\rm Hi}$ mechanism is unexpectedly a common product-forming route both in solution and under FVP conditions and it is most efficient from the iminyl precursors 1 (X = S). The thiophenoxyls 2 (X = S) decompose to products by a variety of competitive routes which depend on the nature of the substituent attached to the imine function.

Experimental

¹H and ¹³C NMR spectra are recorded at 250 (or 200) and 63 (or 50) MHz respectively for solutions in [²H]chloroform unless otherwise stated. Coupling constants are quoted in Hz; ¹³C NMR signals refer to CH resonances unless otherwise stated. ¹H–¹³C HMQC experiments were performed at 360 MHz with gradient selection using the INV4GP sequence as provided by Bruker. Mass spectra were obtained under electron-impact conditions unless otherwise stated.

2-(Phenylthio)benzaldehyde^{21a} 6

A mixture of 2-fluorobenzaldehyde **9a** (4.96 g, 40 mmol), thiophenol (4.84 g, 44 mmol), isopropyl alcohol (20 cm³) and potassium carbonate (6.07 g, 44 mmol) was stirred under reflux for 20 h, cooled, and poured into water (100 cm³). The precipitated oil was extracted into chloroform and washed with water (2×25 cm³), dried (MgSO₄), and concentrated. The product was distilled to give 2-(phenylthio)benzaldehyde **6** (6.97 g, 78%), mp 45–47 °C (lit.,^{21b} 47–48 °C); $\delta_{\rm H}$ 10.31 (1H, s) and 7.00–7.83 (9H, m).

2'-(Phenylthio)acetophenone 7

To a solution of sodium benzenethiolate [prepared from thiophenol (4.24 g, 38 mmol) and sodium hydride (60% in mineral oil; 1.1 g)] in DMF (49 cm³) was added a solution of 2'-chloroacetophenone **10b** (5.00 g, 32 mmol) in DMF (49 cm³). The mixture was stirred under reflux for 3 h, poured into water, and then extracted with toluene–hexane (4 : 1) mixture. The extract was washed with water, dried (MgSO₄), and concentrated. The solution was distilled to give 2'-(phenylthio)acetophenone **7** (3.94 g, 54%), mp 71–73 °C (lit.,²² 72–73 °C); $\delta_{\rm H}$ 6.86–7.56 (9H, m) and 2.66 (3H, s).

2-(Phenylthio)benzophenone²³ 8

A solution of sodium benzenethiolate [prepared from thiophenol (3.05 g, 28 mmol) and sodium hydride (60% in mineral oil; 1.1 g)] in DMF (35 cm³) was added to a solution of 2-chlorobenzophenone **11b** (5.00 g, 23 mmol) in DMF (35 cm³). The mixture was stirred under reflux for 3 h, poured into water, and then extracted with toluene–hexane (4 : 1) mixture. The extract was washed with water, dried (MgSO₄), and the solvent was evaporated off. The residue was distilled under high vacuum to give 2-(phenylthio)benzophenone **8** (5.12 g, 77%), mp 50–52 °C (lit.,²² 51–52 °C); $\delta_{\rm H}$ 7.21–7.83 (14H, m).

Formation of oxime ethers - general method

The carbonyl compound (8 mmol) and *O*-methylhydroxylamine hydrochloride (0.84 g, 10 mmol) were dissolved in ethanol (50 cm³) and the solution was stirred under reflux for the length of time stated. The mixture was concentrated under reduced pressure, the residue was treated with aq. sodium hydroxide (0.25 M; 40 cm³), and the mixture was extracted with diethyl ether (3×30 cm³). The combined extracts were dried (MgSO₄), concentrated, and distilled *in vacuo*. The following products were made by this method.

2-(Phenylthio)benzaldehyde **6** gave, after 1 h under reflux, 2-(*phenylthio*)benzaldehyde O-methyloxime **12** (66%) as a single isomer, bp 158–160 °C (1 Torr) (Found: M⁺, 243.0753. C₁₄H₁₃-NOS requires *M*, 243.0718); $\delta_{\rm H}$ 8.60 (1H, s), 7.15–7.92 (9H, m) and 3.96 (3H, s); $\delta_{\rm C}$ 173.96, 146.99, 136.11 (quat), 134.179, 133.88 (quat), 133.64 (quat), 130.23, 129.39, 129.12, 126.93, 126.51 and 61.98 (CH₃); *m*/*z* 243 (M⁺, 26%), 212 (100), 211(90), 109 (67) and 77 (69).

2'-(Phenylthio)acetophenone 7 gave, after 1.5 h under reflux, 2'-(*phenylthio*)acetophenone O-methyloxime **13** (60%) as two isomers in 3 : 1 ratio, bp 182–186 °C (1 Torr) (Found: M⁺, 257.0880. C₁₅H₁₅NOS requires M, 257.0874); $\delta_{\rm H}$ 7.06–7.29 (9H, m), 3.86 (0.75 × 3H, s, major isomer), 3.65 (0.25 × 3H, s, minor isomer), 2.14 (0.75 × 3H, s, major isomer) and 2.08 (0.25 × 3H, s, minor isomer); $\delta_{\rm C}$ (major isomer only) 155.93 (quat), 138.59 (quat), 135.50 (quat), 134.92 (quat), 131.78, 131.41, 128.96, 128.88, 126.99, 126.67, 61.60 (CH₃) and 15.93 (CH₃) (2 CH signals coincident); *m/z* 257 (M⁺, 15%), 226 (100), 225 (90), 185 (26) and 183 (23).

2-(Phenylthio)benzophenone **8** was stirred under reflux for 2 days in a 2 : 1 mixture of ethanol and pyridine and gave after acid work-up 2-(*phenylthio*)benzophenone O-methyloxime **14** (67%) as two isomers in 3 : 1 ratio, bp 250 °C (1 Torr) (Found: M⁺, 319.1027. C₂₀H₁₇NOS requires *M*, 319.1031); $\delta_{\rm H}$ 7.17–7.52 (14H, m), 3.93 (0.25 × 3H, s, minor isomer) and 3.83 (0.75 × 3H, s, major isomer); $\delta_{\rm C}$ (major isomer only) 155.80 (quat), 136.30 (quat), 136.04 (quat), 135.60 (quat), 135.19 (quat), 132.8–127.2 (10 CH resonances) and 62.69 (CH₃); *m/z* 319 (M⁺, 12%), 318 (11), 288 (83), 287 (100), 210 (13), 183 (22), 77 (45) and 51 (30).

Reaction of phenylmethanethiol with o-fluorobenzaldehyde and related carbonyl compounds – general method ²¹

The *o*-fluoro-benzaldehyde, -acetophenone or -benzophenone **9a–11a** (40 mmol), phenylmethanethiol (4.96 g, 40 mmol) and potassium carbonate (6.01 g, 43.5 mmol) were stirred under reflux in isopropyl alcohol (35 cm³) for the length of time stated, cooled, and poured into water (100 cm³). The product generally crystallised and was filtered off. Alternatively, if no crystals formed, the mixture was extracted with dichloromethane, the organic extracts were washed with water (2×50 cm³), dried over magnesium sulfate, and the solvent was evaporated off. The following products were made by this method.

o-Fluorobenzaldehyde 9a gave, after 20 h under reflux and work-up by extraction into dichloromethane, o-(benzylthio)-

benzaldehyde **15** (67%) mp 73–74 °C (lit.,⁸ 77–79 °C); $\delta_{\rm H}$ 10.24 (1H, s), 7.82 (1H, m), 7.52–7.42 (2H, m), 7.34–7.23 (6H, m) and 4.12 (2H, s); $\delta_{\rm C}$ 191.32, 140.83 (quat), 135.95 (quat), 134.42 (quat), 133.79, 131.45, 129.65, 128.73, 128.45, 127.33, 125.92 and 38.67 (CH₂).

2'-Fluoroacetophenone **10a** gave, after 70 h under reflux, 2'-(benzylthio)acetophenone **16** (90%), which crystallised directly on addition to water, mp 142–145 °C (lit.,¹¹ 145 °C); $\delta_{\rm H}$ 7.79–7.75 (1H, m), 7.40–7.15 (8H, m), 4.12 (2H, s) and 2.57 (3H, s); $\delta_{\rm C}$ 199.16 (quat), 140.46 (quat), 136.05 (quat), 135.34 (quat), 131.85, 130.46, 128.85, 128.35, 127.07, 126.54, 123.95, 37.55 (CH₂) and 28.21 (CH₃).

2-Fluorobenzophenone **11a** gave, after 70 h under reflux 2-(*benzylthio*)*benzophenone* **17** (78%), which crystallised as the pure material on addition to water, mp 62–64 °C (Found: M⁺, 304.0918. $C_{20}H_{16}OS$ requires *M*, 304.0922); δ_H 7.88–7.18 (14H, m) and 4.06 (2H, s); δ_C 196.20 (quat), 139.99 (quat), 136.86 (quat), 136.35 (quat), 135.17 (quat), 132.67, 130.48, 130.07, 129.57, 128.52, 127.96, 126.73, 125.44, and 39.01 (CH₂) (2 sets of overlapping resonances); *m/z* 304 (M⁺, 10%), 213 (100), 105 (52) and 91 (67).

N-[(2-Benzylthio)benzylidene]aniline 18

2-(Benzylthio)benzaldehyde **15** (1.01 g, 4.42 mmol) was dissolved in toluene (25 cm³), then aniline (0.42 g, 4.51 mmol) and a trace of toluene-*p*-sulfonic acid (PTSA) were added. The reaction mixture was heated under reflux for 2 h with azeotropic removal of water. The resultant mixture was concentrated and the crude product was recrystallised from hexane and filtered hot to give *N*-*[*(2-benzylthio)benzylidene]aniline **18** (51%) as a single isomer, mp 51–54 °C (from hexane) (Found: C, 78.55; H, 5.65; N, 4.55. C₂₀H₁₇NS·0.1H₂O requires C, 78.75; H, 5.7; N, 4.6%); $\delta_{\rm H}$ 8.97 (1H, s), 8.20 (1H, m), 7.52–7.20 (13H, m) and 4.09 (2H, s); $\delta_{\rm C}$ 158.51, 151.74 (quat), 137.44 (quat), 136.75 (quat), 136.49 (quat), 132.35, 131.08, 128.83, 128.61, 128.26, 127.94, 127.26, 127.11, 125.81, 120.91 and 40.28 (CH₂); *m/z* 303 (M⁺, 1%), 214 (42), 213 (55), 212 (59), 210 (100), 109 (47), 91 (25) and 77 (45).

N-{1-[2-(Benzylthio)phenyl]ethylidene}aniline 19

o-(Benzylthio)acetophenone 16 (1.98 g, 8.15 mmol) was dissolved in toluene (50 cm³), and aniline (0.78 g, 8.38 mmol) and a trace of PTSA were added. The reaction mixture was heated under reflux for 48 h with azeotropic removal of water. The resultant mixture was concentrated and the crude product was recrystallised from hexane to give N-{1-[2-(benzylthio)phenyl]ethylidene}aniline 19 (64%) as two isomers in 3:1 ratio, mp 102-104 °C (from hexane) (Found: C, 78.85; H, 6.1; N, 4.2. C₂₁H₁₉NS·0.1H₂O requires C, 79.0; H, 6.05; N, 4.4%) [Found: MH⁺ (FAB), 318.1317. C₂₁H₁₉NS requires MH, 318.1317]; $\delta_{\rm H}$ 7.48–6.69 (14H, m), 4.14 (0.75 × 2H, s, major isomer), 4.07 $(0.25 \times 2H, s, minor isomer), 2.35 (0.25 \times 3H, s, minor isomer)$ and 2.16 (0.75 × 3H, s, major isomer); $\delta_{\rm C}$ (major isomer only) 168.38 (quat), 150.49 (quat), 142.30 (quat), 137.12 (quat), 135.02 (quat), 130.01, 128.99, 128.84, 128.77, 128.32, 127.70, 126.98, 125.87, 123.34, 119.29, 39.54 (CH₂) and 20.54 (CH₃); m/z (FAB) 318 (MH⁺, 100%), 226 (71) and 91 (45).

N-[2-(Benzylthio)-a-phenylbenzylidene]-4-methylaniline 20

2-(Benzylthio)benzophenone **17** (0.56 g, 1.85 mmol) was dissolved in commercial xylene (20 cm³). *p*-Toluidine (0.20 g, 1.88 mmol) and a trace of PTSA acid were added. The reaction mixture was heated under reflux for 70 h with azeotropic removal of water. The solvent was then removed to give N-[2-(benzylthio)- α -phenylbenzylidene]-4-methylaniline **20** (80%) as a thick oil which could not be purified by bulb-to-bulb distillation or by crystallisation; apparently only a single isomer was obtained (Found: M⁺, 393.1566. C₂₇H₂₃NS requires *M*,

Pyrolysis experiments

The substrates were sublimed or distilled under reduced pressure through a silica tube $(35 \times 2.5 \text{ cm})$ which was held at the required temperature by an electrical tube furnace. Products were collected in a U-tube trap cooled by liquid nitrogen that was situated immediately after the hot zone. The work-up involved dissolution of the pyrolysate in dichloromethane followed by dry-flash chromatography over silica, unless otherwise stated using hexane–ethyl acetate mixtures as eluent (starting with 99.5% hexane and increasing the proportion of the more polar solvent by 0.1% each time). Results are quoted as follows: quantity of substrate, furnace temperature ($T_{\rm f}$), inlet temperature ($T_{\rm i}$), pressure range (P), pyrolysis time ($t_{\rm p}$) and products (quoted in the order of elution from the column).

Pyrolysis of 2-(phenylthio)benzaldehyde O-methyloxime 12. 2-(Phenylthio)benzaldehyde O-methyloxime 12 (0.50 g, 2.1 mmol) (T_f 650 °C; T_i 50 °C; P 0.01 Torr; t_P 30 min) gave a mixture of products which was separated by dry-flash chromatography: dibenzothi
ophene **23** (trace), $\delta_{\rm H}$ 7.85–8.20 (8H, m); $\delta_{\rm C}$ 139.33 (quat), 135.43 (quat), 126.58, 124.23, 122.67 and 121.44 (NMR data consistent with literature values²⁴): biphenyl 24 (trace), m/z 154 (M⁺): diphenyl sulfide 25 (trace), m/z 186 (M⁺): benz[d]isothiazole **26** (0.231 g, 48%), $\delta_{\rm H}$ 8.89 (1H, s), 7.90-8.04 (2H, m) and 7.28-7.56 (2H, m) (data consistent with literature values¹²); $\delta_{\rm C}$ 154.67, 151.40 (quat), 135.80 (quat), 127.48, 124.60, 123.76 and 119.29; m/z 135 (M⁺): 2-(phenylthio)benzyl alcohol **31**, $\delta_{\rm H}$ 7.17–7.49 (9H, m) and 4.76–4.79 (2H, d, ³J 5.6); $\delta_{\rm C}$ (quaternary signals not reported) 133.98, 129.34, 129.15, 128.53, 128.44, 126.53 and 63.64 (CH₂) (two peaks overlapping) (NMR data consistent with literature values²⁵); $m/z 216 (M^+).$

Pyrolysis of 2'-(phenylthio)acetophenone *O*-methyloxime 13. 2'-(Phenylthio)acetophenone *O*-methyloxime 13 (0.50 g, 1.9 mmol) ($T_{\rm f}$ 650 °C; $T_{\rm i}$ 105 °C; *P* 0.01 Torr; $t_{\rm p}$ 30 min) gave a mixture of products which was separated by dry-flash chromatography: dibenzothiophene 23 (trace), $\delta_{\rm H}$ 7.8–8.2 (8H, m); *m/z* 184 (M⁺): biphenyl 24 (trace), *m/z* 154 (M⁺): 3-methylbenz-[*d*]isothiazole 35 (0.135 g, 45%), $\delta_{\rm H}$ 7.95–7.88 (2H, m), 7.55–7.25 (2H, m) and 2.74 (3H, s); $\delta_{\rm C}$ 162.71 (quat), 151.92 (quat), 134.91 (quat), 127.33, 124.31, 123.26, 119.71 and 17.26 (CH₃) (spectra consistent with literature values²⁶); *m/z* 149 (M⁺, 100%), 148 (26), 121 (33) and 108 (21): 2-(phenylthio)benzonitrile **30** (0.024 g, 8%), $\delta_{\rm H}$ 7.09–7.65 (9H, m) (consistent with literature data²⁷); $\delta_{\rm C}$ 142.24 (quat), 133.53, 133.45, 132.85, 131.70 (quat), 129.78, 129.64, 128.79, 126.32, 116.82 (quat) and 112.70 (quat); *m/z* 211 (M⁺, 100%), 210 (40) and 184 (24); $\nu_{\rm max}$ 2219 cm⁻¹ (lit.,¹⁶ 2220 cm⁻¹).

Pyrolysis of 2-(phenylthio)benzophenone *O*-methyloxime 14. 2-(Phenylthio)benzophenone *O*-methyloxime 14 (0.50 g, 1.6 mmol) ($T_{\rm f}$ 650 °C; $T_{\rm i}$ 115 °C; *P* 0.01 Torr; $t_{\rm p}$ 30 min) gave a mixture of products which was separated by dry-flash chromatography: biphenyl 24 (trace), m/z 154 (M⁺): diphenyl sulfide 25 (trace), m/z 186 (M⁺): diphenyl disulfide 40 (trace), m/z 218 (M⁺): 3-phenylbenz[*d*]isothiazole 41 (0.037 g, 48%), $\delta_{\rm H}$ 8.18 (1H, m), 7.98 (1H, m), 7.90–7.85 (2H, m) and 7.59–7.42 (5H, m) (spectrum consistent with literature data²⁸); $\delta_{\rm C}$ 164.25 (quat), 153.36 (quat), 135.07 (quat), 133.65 (quat), 129.20, 128.67, 128.57, 127.36, 124.87, 124.71 and 119.81; m/z 211 (M⁺, 100%), 210 (80), 184 (11), 105 (15) and 77 (18).

Pyrolysis of N-[(2-benzylthio)benzylidene]aniline 18. N-[(2-Benzylthio)benzylidene]aniline 18 (0.40 g, 1.32 mmol) ($T_{\rm f}$ 650 °C; T_i 165 °C; P 0.005 Torr; t_p 15 min) gave a mixture of products which was separated by dry-flash column chromatography (0.5% ethyl acetate-hexane, 10% gradient): biphenyl **24** (trace), $\delta_{\rm H}$ 7.6–7.2 (10H, m); $\delta_{\rm C}$ 141.10 (quat), 128.63, 127.12 and 127.04; m/z 154 (M⁺): diphenylmethane 28 (0.030 g, 14%), $\delta_{\rm H}$ 7.5–7.2 (10H, m) and 4.05 (2H, s); $\delta_{\rm C}$ 140.99 (quat), 128.80, 128.33, 125.94 and 41.81 (CH₂) (spectra consistent with literature data²⁴); m/z 168 (M⁺): bibenzyl **29** (0.030 g, 12%), $\delta_{\rm H}$ 7.47– 7.22 (10H, m) and 3.00 (4H, s); $\delta_{\rm C}$ 141.65 (quat), 128.33, 128.21, 125.79 and 37.83 (CH₂) (spectra consistent with literature data²⁴); *m*/z 182 (M⁺): benz[*d*]isothiazole **26** (0.060 g, 34%), $\delta_{\rm H}$ 8.91 (1H, s), 8.07-7.92 (2H, m) and 7.56-7.38 (2H, m) (spectrum consistent with literature data as above¹²); $\delta_{\rm C}$ 154.81, 151.49 (quat), 135.88 (quat), 127.61, 124.72, 123.90 and 119.42; m/z 135 (M⁺, 100%), 108 (17) and 91 (15): an impure fraction which contained a small amount of 2-(phenylthio)benzonitrile **30** (\approx 0.010 g, 4%), $\delta_{\rm H}$ 7.65–7.05 (aromatics); $\delta_{\rm C}$ (CH resonances only) 133.51, 133.43, 132.82, 129.76, 129.62, 128.76 and 126.29 (data consistent with those reported above for this compound): an impure fraction which may contain dibenzo[b,f][1,4]thiazepine **31** ($\approx 10\%$) $\delta_{\rm H}$ 8.91 (1H, s), 8.15 (1H, m) and 7.49–7.10 (aromatics) [lit.,¹³ 8.7 (1H, s) and 7.40–7.05 (8H, m)]; m/z 211 (M⁺, 67%), 210 (100), 184 (10) and 91 (32): 2,2'disulfanediyldibenzonitrile 32 (0.032 g, 9%) (Found: M⁺, 268.0129. $C_{14}H_8N_2S_2$ requires *M*, 268.0129); v_{max} 2221 cm⁻¹ (lit.,¹⁵ 2220 cm⁻¹); $\delta_{\rm H}$ 7.79–7.25 (8H, m); $\delta_{\rm C}$ 139.76 (quat), 133.63, 133.46, 129.77, 128.26, 116.08 (quat) and 113.01 (quat) (¹H NMR spectrum consistent with literature data,¹⁵ though the ¹³C NMR spectrum¹⁵ shows discrepancies at $\delta_{\rm C}$ 129 and 110); *m*/*z* 268 (M⁺, 100%) and 134 (29).

Pyrolysis of *N*-{1-[2-(benzylthio)phenyl]ethylidene}aniline 19. N-{1-[2-(Benzylthio)phenyl]ethylidene}aniline 19 (0.51 g, 1.61 mmol) ($T_{\rm f}$ 650 °C; $T_{\rm i}$ 195 °C; P 0.005 Torr; $t_{\rm p}$ 15 min) gave a mixture of products which was separated by dry-flash column chromatography (0.5% ethyl acetate-hexane, 10% gradient): biphenyl 24 (trace); m/z 154 (M⁺): diphenylmethane **28** (0.015 g, 5%), $\delta_{\rm H}$ 7.4–7.2 (10H, m) and 4.01 (2H, s); *m*/*z* 168 (M⁺): bibenzyl **29** (0.060 g, 20%), $\delta_{\rm H}$ 7.4–7.2 (10H, m) and 2.95 (4H, s); m/z 182 (M⁺): N-benzo[b]thiophen-3-ylaniline 36 (0.107 g, 30%), mp (crude sample) 66-68 °C (lit.,²⁹ 88 °C); $\delta_{\rm H}$ 7.85 (1H, m), 7.66 (1H, m), 7.40–7.25 (5H, m) 7.03–6.87 (3H, m) and 5.73 (1H, br s); $\delta_{\rm C}$ 144.52 (quat), 138.70 (quat), 134.86 (quat), 134.42 (quat), 129.23, 124.72, 123.76, 123.06, 120.45, 119.99, 115.94 and 108.90; $\delta_{\rm H}$ ([²H₆]benzene; 360 MHz) 7.67 (1H, m), 7.47 (1H, m), 7.26-7.18 (4H, m), 6.92 (1H, m), 6.86-6.82 (2H, m), 6.71 (1H, s) and 5.18 (1H, br s); $\delta_{\rm C}$ ([²H₆]benzene; 90 MHz) 145.18 (quat), 139.28 (quat), 135.41 (quat), 135.12 (quat), 129.41, 124.91, 123.87, 123.22, 121.19, 120.12, 116.24 and 110.14; *m/z* 225 (M⁺, 100%), 224 (97), 183 (13) and 91 (17): 3-methylbenz[d]isothiazole **35** (0.060 g, 25%), $\delta_{\rm H}$ 8.12–6.85 (4H, m) and 2.75 (3H, s); $\delta_{\rm C}$ 162.71 (quat), 151.93 (quat), 134.92 (quat), 127.35, 124.32, 123.27, 119.72 and 17.26 (CH₃) (spectra consistent with literature values²⁶); m/z 149 (M⁺, 100%), 121 (12) and 108 (8): 2-phenylbenzothiazole 37 (0.030 g, 9%), $\delta_{\rm H}$ 8.14–7.88 (4H, m) and 7.56–7.34 (5H, m); $\delta_{\rm C}$ 167.96 (quat), 154.01 (quat), 134.93 (quat), 133.49 (quat), 130.86, 128.91, 127.44, 126.20, 125.08, 123.11 and 121.51 (spectra consistent with literature values²⁴); m/z 211 (M⁺, 37%), 210 (100) and 108 (12).

Pyrolysis of *N*-[2-(benzylthio)-α-phenylbenzylidene]-4methylaniline 20. *N*-[2-(Benzylthio)-α-phenylbenzylidene]-4methylaniline 20 (0.47 g {80% pure}, 0.96 mmol) ($T_{\rm f}$ 650 °C; $T_{\rm i}$ 285 °C; *P* 0.006 Torr; $t_{\rm p}$ 20 min) gave a mixture of products which was separated by dry-flash column chromatography (0.5% ethyl acetate–hexane, 10% gradient): dibenzothiophene 23 (0.038 g, 22%), $\delta_{\rm H}$ 8.18–8.14 (2H, m), 7.88–7.84 (2H, m) and 7.49–7.44 (4H, m); $\delta_{\rm C}$ 139.29 (quat), 135.40 (quat), 126.57, 124.22, 122.68 and 121.44 (as above²⁴); *m/z* 184 (M⁺, 59%): bibenzyl **29** (0.030 g, 17%), $\delta_{\rm H}$ 7.62–7.09 (10H, m) and 2.92 (4H, s); $\delta_{\rm C}$ 141.63 (quat), 128.53, 128.30, 128.18 and 37.81 (CH₂) (as above²⁴); *m*/*z* 182 (M⁺, 39%) and 91 (100): 3-phenylbenz-[d]isothiazole **41** (0.054 g, 27%), $\delta_{\rm H}$ 8.19 (1H, m), 7.99 (1H, m), 7.90–7.84 (2H, m) and 7.59–7.43 (5H, m) (as above 28); $\delta_{\rm C}$ 164.28 (quat), 153.38 (quat), 135.08 (quat), 133.67 (quat), 129.22, 128.69, 128.58, 127.38, 124.89, 124.73 and 119.83; m/z 211 (M⁺, 27%), 210 (100), 184 (12), 105 (30), and 77 (30).

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