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

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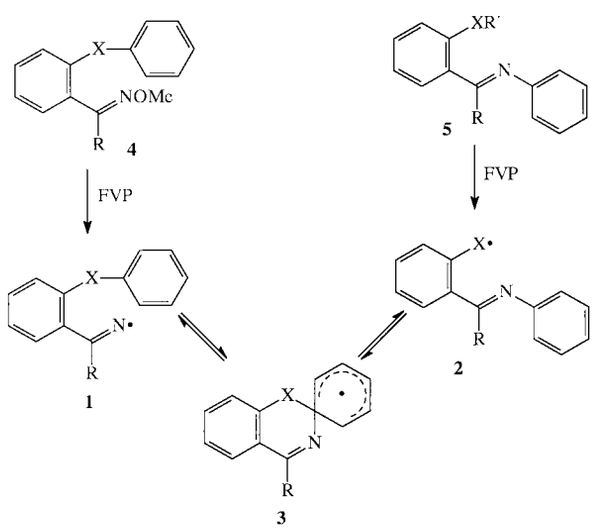
Flash vacuum pyrolysis (FVP) of the oxime ethers **12**–**14** and of the sulfides **18**–**20** at 650 °C (10^{-2}–10^{-3} Torr) gave products derived from the corresponding iminyl and thiophenoxyl radicals. In all cases, benz[*d*]isothiazoles (*e.g.*, **26**) are formed as major products *via* S_Hi 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_Hi 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 **1** and the phenoxyls and aminyls **2** (Scheme 1, X = O and NR respectively) *via* an intermediate spirodienyl radical **3**.[1–3] In the gas-phase 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 aminyl–iminyl 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 before[2] 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′ = CH_2Ph) 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]



Scheme 1

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′-nitroacetophenone[10] 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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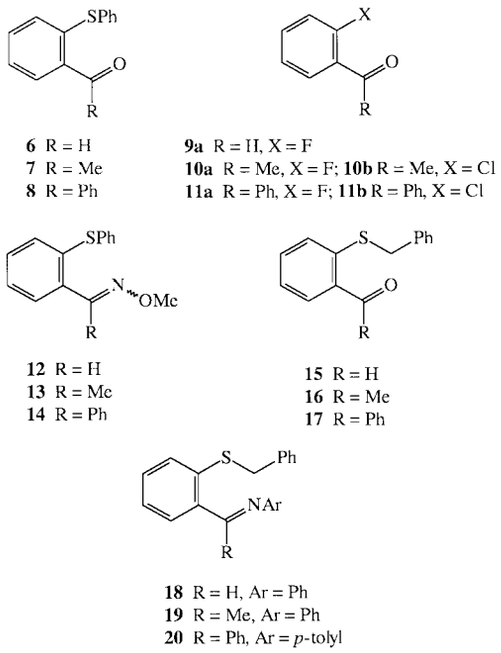
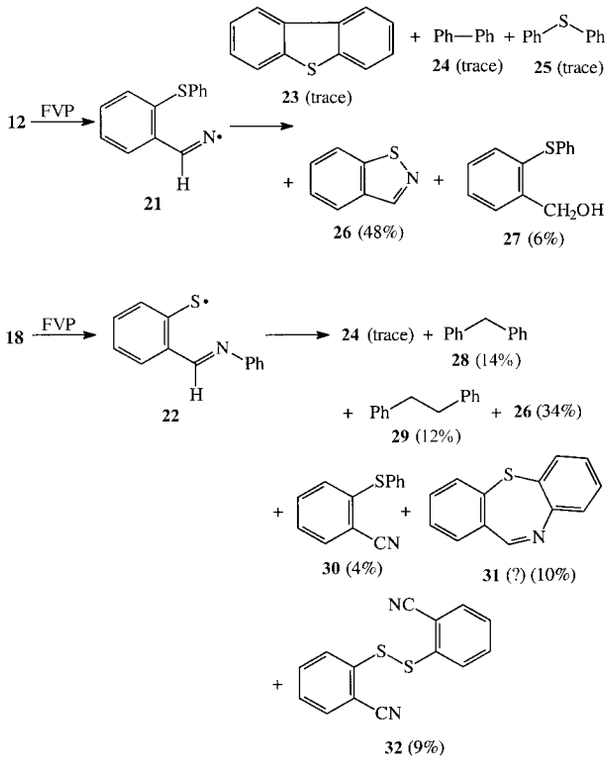


single isomer, but **19** was formed as *E* and *Z* isomers in a 3 : 1 ratio.

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 $PhNH_2$.

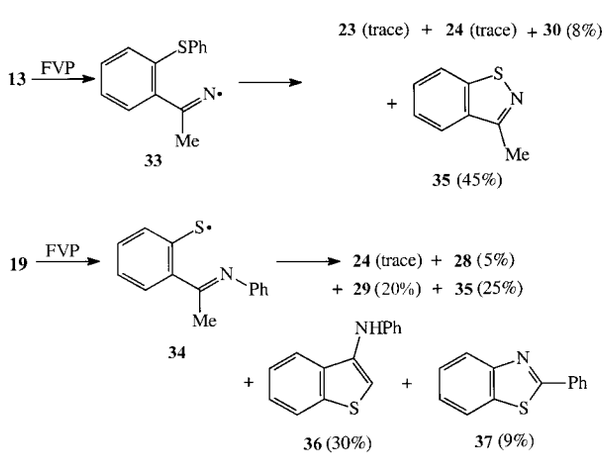
Flash vacuum pyrolysis of the oxime ethers **12**–**14** and the *S*-benzyl compounds **18**–**20** at 650 °C gave pyrolysates which showed no trace of starting material. The products, which are assumed to arise from the iminyls **21**, **33** and **38** and the thiophenoxyls **22**, **34** and **39**, 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** (≈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 ^{13}C NMR spectrum showed peaks identical with those of an authentic sample of 2-(phenylthio)benzonitrile **30** (see below). The following component was also impure (≈10%), but again showed a molecular ion at *m*/*z* 211, though in this case a singlet at δ_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** [δ_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 [ν_{max} 2221 cm^{-1} (CN)] and NMR comparison with reported data.[15]



Scheme 2

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



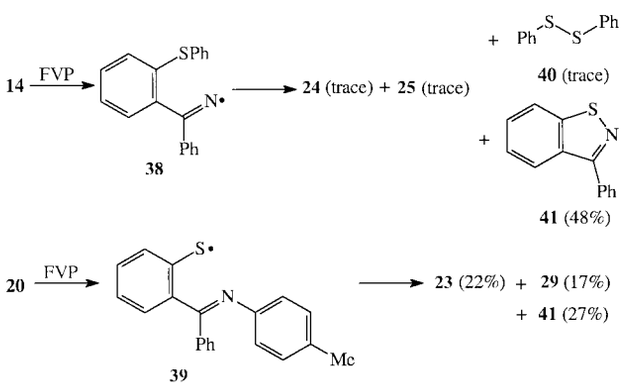
Scheme 3

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 (ν_{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 δ_H 6.71 which correlated with a carbon resonance at δ_C 110.14. The ^{1}H 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 (δ_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 3-position. 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 δ_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 δ_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

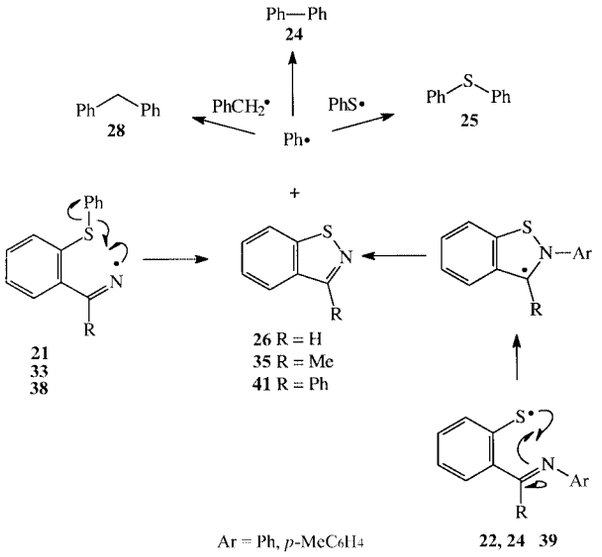


Scheme 4

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 solution[4] – though the yield appears to be greatest when the oxime ethers **12**–**14** are used. Such behaviour was never observed in the X = O or 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_Hi) 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

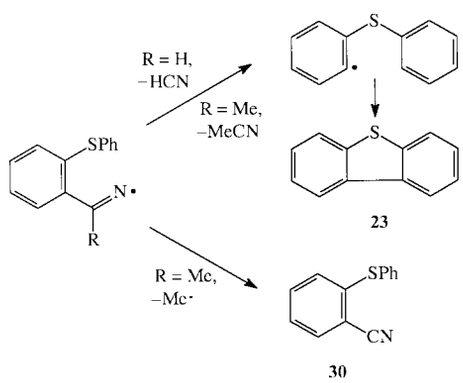


Scheme 5

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 phase[5] 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 iminyls **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

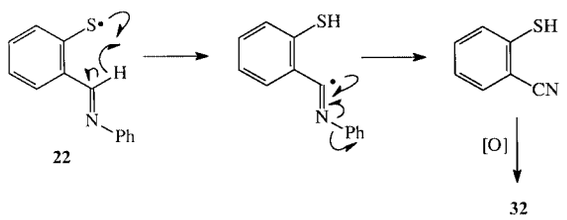


Scheme 6

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-

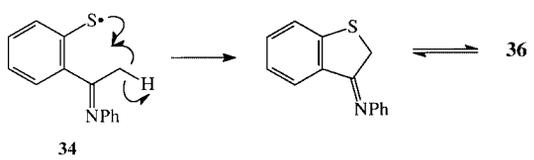
cursor **18**. The simplest explanation for its formation is by a thiophenoxyl–iminyl interconversion (see Scheme 1) followed by β-cleavage (Scheme 6). This is the only evidence that thiophenoxyl-to-iminyl interconversion may be a very minor pathway on this energy surface.

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]



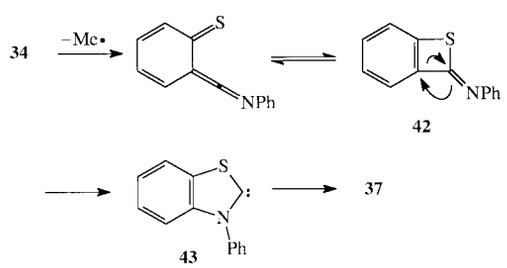
Scheme 7

The major product derived from the thiophenoxyl **19** was unexpectedly the anilinobenzothiophene **36**. This product may be formed by a formal S_Hi 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



Scheme 8

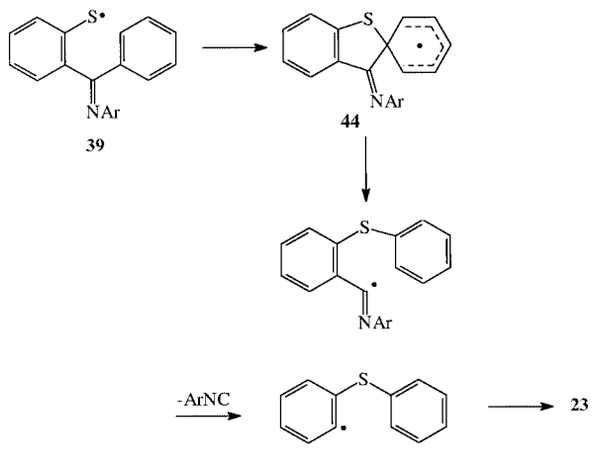
unknown. The presence of the benzothiazole **37** (9%) in this pyrolysis was also unexpected; overall, the reaction from **19** must involve the loss of a methyl group, a skeletal rearrangement and a phenyl migration but the nature of these steps is not obvious by inspection. One possible mechanism (Scheme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



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 conditions,[19] as is the formation of spirodienyl radicals related to **44**.[20]



Scheme 10

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_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

^{1}H and ^{13}C NMR spectra are 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. ^{1}H–^{13}C 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 cm^3) and potassium carbonate (6.07 g, 44 mmol) was stirred under reflux for 20 h, cooled, and poured into water (100 cm^3). The precipitated oil was extracted into chloroform and washed with water (2 × 25 cm^3), dried ($MgSO_4$), 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); δ_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 cm^3) was added a solution of 2′-chloroacetophenone **10b** (5.00 g, 32 mmol) in DMF (49 cm^3). 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 ($MgSO_4$), 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); δ_H 6.86–7.56 (9H, m) and 2.66 (3H, s).

2-(Phenylthio)benzophenone[23] 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 cm^3) was added to a solution of 2-chlorobenzophenone **11b** (5.00 g, 23 mmol) in DMF (35 cm^3). 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 ($MgSO_4$), 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); δ_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 cm^3) 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 cm^3), and the mixture was extracted with diethyl ether (3 × 30 cm^3). The combined extracts were dried ($MgSO_4$), 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. $C_{14}H_{13}NOS$ requires *M*, 243.0718); δ_H 8.60 (1H, s), 7.15–7.92 (9H, m) and 3.96 (3H, s); δ_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 (CH_3); *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. $C_{15}H_{15}NOS$ requires *M*, 257.0874); δ_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); δ_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 (CH_3) and 15.93 (CH_3) (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. $C_{20}H_{17}NOS$ requires *M*, 319.1031); δ_H 7.17–7.52 (14H, m), 3.93 (0.25 × 3H, s, minor isomer) and 3.83 (0.75 × 3H, s, major isomer); δ_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 (CH_3); *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 cm^3) for the length of time stated, cooled, and poured into water (100 cm^3). 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 cm^3), 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); δ_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); δ_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 (CH_2).

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); δ_H 7.79–7.75 (1H, m), 7.40–7.15 (8H, m), 4.12 (2H, s) and 2.57 (3H, s); δ_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 (CH_2) and 28.21 (CH_3).

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 (CH_2) (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 cm^3), 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. $C_{20}H_{17}NS{\cdot}0.1H_2O$ requires C, 78.75; H, 5.7; N, 4.6%); δ_H 8.97 (1H, s), 8.20 (1H, m), 7.52–7.20 (13H, m) and 4.09 (2H, s); δ_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 (CH_2); *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 cm^3), 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. $C_{21}H_{19}NS{\cdot}0.1H_2O$ requires C, 79.0; H, 6.05; N, 4.4%) [Found: MH^+ (FAB), 318.1317. $C_{21}H_{19}NS$ requires *MH*, 318.1317]; δ_H 7.48–6.69 (14H, m), 4.14 (0.75 × 2H, s, major isomer), 4.07 (0.25 × 2H, s, minor isomer), 2.35 (0.25 × 3H, s, minor isomer) and 2.16 (0.75 × 3H, s, major isomer); δ_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 (CH_2) and 20.54 (CH_3); *m*/*z* (FAB) 318 (MH^+, 100%), 226 (71) and 91 (45).

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

2-(Benzylthio)benzophenone **17** (0.56 g, 1.85 mmol) was dissolved in commercial xylene (20 cm^3). *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. $C_{27}H_{23}NS$ requires *M*,

393.1551); δ_H 7.77–6.69 (18H, m), 3.91 (2H, s) and 2.22 (3H, s); δ_C 166.71 (quat), 147.99 (quat), 138.97 (quat), 138.06 (quat), 136.72 (quat), 134.56 (quat), 132.96 (quat), 130.4–120.5 (aromatics), 38.44 (CH_2) and 20.73 (CH_3); *m/z* 393 (M^+, 1%), 302 (55) and 91 (100).

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 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_f), inlet temperature (T_i), pressure range (P), pyrolysis time (t_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: dibenzothiophene **23** (trace), δ_H 7.85–8.20 (8H, m); δ_C 139.33 (quat), 135.43 (quat), 126.58, 124.23, 122.67 and 121.44 (NMR data consistent with literature values[24]): biphenyl **24** (trace), *m/z* 154 (M^+): diphenyl sulfide **25** (trace), *m/z* 186 (M^+): benz[*d*]isothiazole **26** (0.231 g, 48%), δ_H 8.89 (1H, s), 7.90–8.04 (2H, m) and 7.28–7.56 (2H, m) (data consistent with literature values[12]); δ_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**, δ_H 7.17–7.49 (9H, m) and 4.76–4.79 (2H, d, ^3J 5.6); δ_C (quaternary signals not reported) 133.98, 129.34, 129.15, 128.53, 128.44, 126.53 and 63.64 (CH_2) (two peaks overlapping) (NMR data consistent with literature values[25]); *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_f 650 °C; T_i 105 °C; P 0.01 Torr; t_p 30 min) gave a mixture of products which was separated by dry-flash chromatography: dibenzothiophene **23** (trace), δ_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%), δ_H 7.95–7.88 (2H, m), 7.55–7.25 (2H, m) and 2.74 (3H, s); δ_C 162.71 (quat), 151.92 (quat), 134.91 (quat), 127.33, 124.31, 123.26, 119.71 and 17.26 (CH_3) (spectra consistent with literature values[26]); *m/z* 149 (M^+, 100%), 148 (26), 121 (33) and 108 (21): 2-(phenylthio)benzonitrile **30** (0.024 g, 8%), δ_H 7.09–7.65 (9H, m) (consistent with literature data[27]); δ_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); ν_{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_f 650 °C; T_i 115 °C; P 0.01 Torr; t_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%), δ_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 data[28]); δ_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_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), δ_H 7.6–7.2 (10H, m); δ_C 141.10 (quat), 128.63, 127.12 and 127.04; *m/z* 154 (M^+): diphenylmethane **28** (0.030 g, 14%), δ_H 7.5–7.2 (10H, m) and 4.05 (2H, s); δ_C 140.99 (quat), 128.80, 128.33, 125.94 and 41.81 (CH_2) (spectra consistent with literature data[24]); *m/z* 168 (M^+): bibenzyl **29** (0.030 g, 12%), δ_H 7.47–7.22 (10H, m) and 3.00 (4H, s); δ_C 141.65 (quat), 128.33, 128.21, 125.79 and 37.83 (CH_2) (spectra consistent with literature data[24]); *m/z* 182 (M^+): benz[*d*]isothiazole **26** (0.060 g, 34%), δ_H 8.91 (1H, s), 8.07–7.92 (2H, m) and 7.56–7.38 (2H, m) (spectrum consistent with literature data as above[12]); δ_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** (≈0.010 g, 4%), δ_H 7.65–7.05 (aromatics); δ_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** (≈10%) δ_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); ν_{max} 2221 cm^{-1} (lit.,[15] 2220 cm^{-1}); δ_H 7.79–7.25 (8H, m); δ_C 139.76 (quat), 133.63, 133.46, 129.77, 128.26, 116.08 (quat) and 113.01 (quat) (^{1}H NMR spectrum consistent with literature data,[15] though the ^{13}C NMR spectrum[15] shows discrepancies at δ_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_f 650 °C; T_i 195 °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); *m/z* 154 (M^+): diphenylmethane **28** (0.015 g, 5%), δ_H 7.4–7.2 (10H, m) and 4.01 (2H, s); *m/z* 168 (M^+): bibenzyl **29** (0.060 g, 20%), δ_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); δ_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); δ_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; δ_H ([$^2H_6$]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); δ_C ([$^2H_6$]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%), δ_H 8.12–6.85 (4H, m) and 2.75 (3H, s); δ_C 162.71 (quat), 151.93 (quat), 134.92 (quat), 127.35, 124.32, 123.27, 119.72 and 17.26 (CH_3) (spectra consistent with literature values[26]); *m/z* 149 (M^+, 100%), 121 (12) and 108 (8): 2-phenylbenzothiazole **37** (0.030 g, 9%), δ_H 8.14–7.88 (4H, m) and 7.56–7.34 (5H, m); δ_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 values[24]); *m/z* 211 (M^+, 37%), 210 (100) and 108 (12).

Pyrolysis of *N*-[2-(benzylthio)-α-phenylbenzylidene]-4-methylaniline 20. *N*-[2-(Benzylthio)-α-phenylbenzylidene]-4-methylaniline **20** (0.47 g {80% pure}, 0.96 mmol) (T_f 650 °C; T_i 285 °C; P 0.006 Torr; t_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%), δ_H 8.18–8.14 (2H, m), 7.88–7.84 (2H, m) and

7.49–7.44 (4H, m); δ_C 139.29 (quat), 135.40 (quat), 126.57, 124.22, 122.68 and 121.44 (as above[24]); *m*/*z* 184 (M^+, 59%): bibenzyl **29** (0.030 g, 17%), δ_H 7.62–7.09 (10H, m) and 2.92 (4H, s); δ_C 141.63 (quat), 128.53, 128.30, 128.18 and 37.81 (CH_2) (as above[24]); *m*/*z* 182 (M^+, 39%) and 91 (100): 3-phenylbenz-[*d*]isothiazole **41** (0.054 g, 27%), δ_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]); δ_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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