

Thermal Interconversion and Cyclisation Reactions of 2-(Arylthio)benzyl Radicals and 2-(Benzyl)thiophenoxy Radicals

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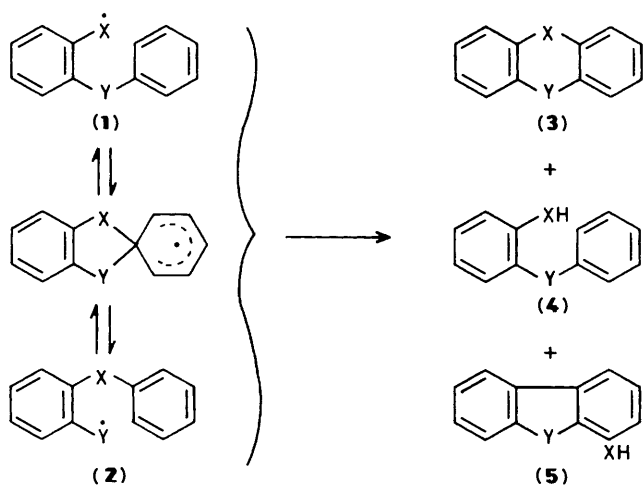
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Generation of the title radicals by flash vacuum pyrolysis leads to thioxanthene(s) as the sole significant product(s). Cyclisation takes place *via* an intermediate spirodienyl radical [*e.g.* (29)].

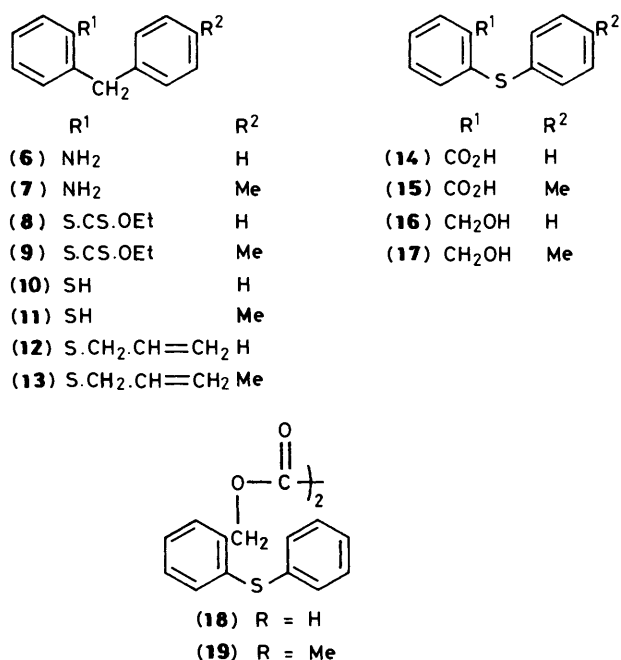
As a continuation of our recent studies¹⁻³ of the equilibration *via* spirodienyl species of *ortho*-substituted benzyl and related radicals in the gas phase (Scheme 1), we now report the gener-



Scheme 1.

ation and reactions of 2-(arylthio)benzyl radicals (1; X = CH₂, Y = S) and 2-(benzyl)thiophenoxy radicals (2; X = CH₂, Y = S). Three types of products were found in the previous work on related systems. The cyclisation product (3) was dominant where X = Y = NH, and it was shown by the use of a substituted and specifically ¹⁵N-labelled precursor, that complete equilibration of (1) and (2) took place prior to cyclisation.¹ Minor reaction pathways gave the hydrogen abstraction product (4) and the rearrangement product (5), but these routes assumed much greater importance in the cases of 2-benzylphenoxy radicals (1; X = O, Y = CH₂) and 2-phenoxybenzyl radicals (2; X = O, Y = CH₂).² Our aims for the present work, therefore, were to ascertain the importance of pathways leading to the anticipated products [(3)–(5); X, Y = CH₂, S], and by the use of appropriate substituted derivatives to define the extent of the equilibration (1) ⇌ (2).

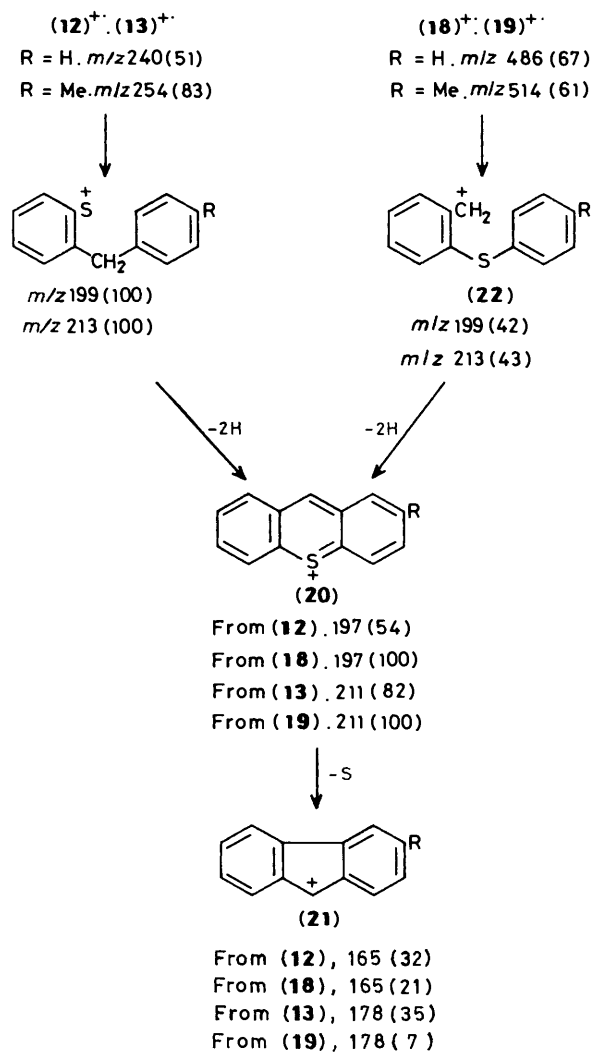
As thiophenoxy radical precursors, we required the allyl compounds (12) and (13), which would be expected^{3,4} to decompose by cleavage of the sulphur-allyl bond under flash vacuum pyrolysis (F.V.P.) conditions. These were synthesized, in three steps, from the amines (6) and (7); the latter compound was itself prepared by Wolff-Kischner reduction of the appropriate benzophenone.⁵ Diazotisation of the amines followed by reaction with potassium *O*-ethyl dithiocarbonate gave the esters (8) and (9) which were decomposed to the thiophenols (10) and (11) under hydrolytic⁶ and reductive^{7,8} conditions respectively. Both methods gave low yields in our



hands, though neither procedure was optimised. Nevertheless, sufficient material was obtained to give workable quantities of the *S*-allyl derivatives (12) and (13) after alkylation using allyl bromide and potassium carbonate in dimethylformamide.

From a synthetic point of view, the most convenient precursors of benzyl radicals in the gas phase are oxalate esters,^{3,9} which are readily available from the corresponding benzyl alcohol. The required 2-(thiophenoxy)benzyl alcohols (16) and (17) were prepared from anthranilic acid by diazotisation and reaction with the appropriate thiophenol¹⁰ followed by reduction of the resulting benzoic acids (14) and (15) with lithium aluminium hydride.¹¹ Treatment with oxalyl chloride and triethylamine in ether⁹ gave the esters (18) and (19) in 90 and 65% yield respectively.

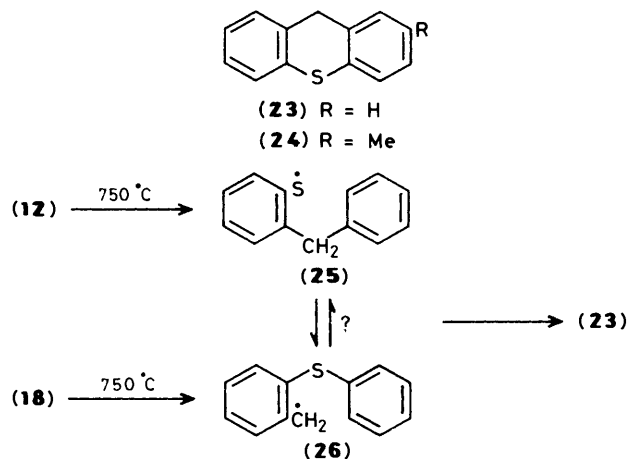
The mass spectra of the *S*-allyl compounds (12) and (13) and of the oxalates (18) and (19) show certain interesting similarities (Scheme 2). Thus cleavage of the allyl group from (12) and (13) leads to the base peak in both spectra, and this is followed by sequential loss of 2 H [*e.g.* from (12) *m*^{*} 195.0, 199→197 requires *m*^{*} 195.0] and S [*e.g.* from (12) *m*^{*} 138.3, 197→165 requires *m*^{*} 138.2; note that direct loss of H₂S from *m/z* 199 requires *m*^{*} 136.8] to give species best represented by the cyclised structures (20) and (21). Similarly, cleavage and loss of CO₂ from the oxalates (18) and (19) gives the benzyl cation (22) which shows similar cyclisation behaviour to its thiyli analogue (Scheme 2).



Scheme 2.

Authentic samples of thioxanthene (23) and 2-methylthioxanthene (24) were synthesized by reduction of the corresponding thioxanthone using diborane in tetrahydrofuran,¹² and aluminium trichloride–lithium aluminium hydride¹³ respectively. As one means of analysing the pyrolysates, we intended to use the precise additivity effect of methyl substitution on the ¹³C n.m.r. chemical shift of the bridging methylene group of dihydroanthracenes and related compounds.¹⁴ Applicability in the thioxanthene series was confirmed with reference to (23) and (24), the 9-C atoms of which show identical chemical shifts (δ_C 39.08) which is within the limits of accuracy expected of the method (2-substitution; $\Delta\delta -0.04 \pm ca. 0.1$ p.p.m.¹⁴).

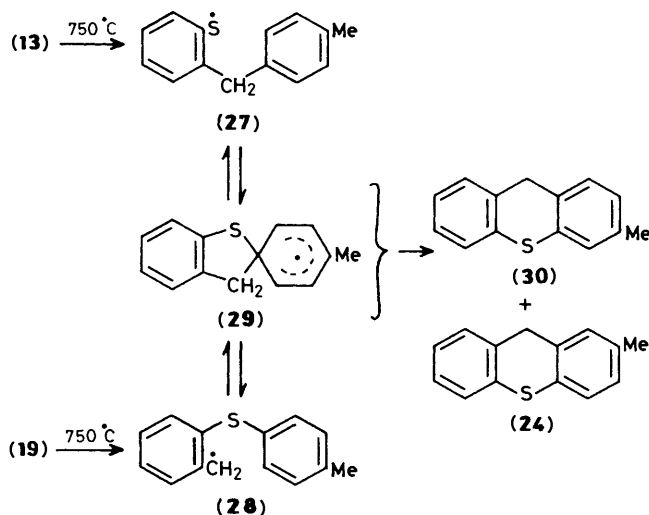
The thiophenoxy radical (25) and the benzyl radical (26) were generated under identical conditions (750 °C and 10⁻³ Torr), by pyrolysis of the *S*-allyl compound (12) and the oxalate (18) respectively (Scheme 3). In both cases, the major product in *ca.* 50% yield was thioxanthene (23), identical in all respects with an authentic sample. A trace of the thiophenol (10) was detected only in the pyrolysate of (12), presumably formed by hydrogen atom capture by the radical (25). The only substantial minor product (*ca.* 5%) from (18) was the benzyl alcohol (16), formed by a well known alternative cleavage of oxalate esters.⁹ It is noteworthy that products of type (5; X, Y = CH₂, S) were completely absent, and (4; X = S, Y = CH₂) was only



Scheme 3.

detectable in one case, in total contrast to the behaviour of the analogous phenoxy system [(1) and (2); X = O, Y = CH₂], where these routes give rise to the major products from both benzyl and phenoxy radical precursors.²

Pyrolysis of the *p*-substituted precursors (13) and (19) was undertaken to assess the possible equilibration of the thiophenoxy (27) and benzyl species (28) *via* the spirodienyl (29). Product distributions were very similar to those obtained from the parent compounds, with traces of the thiophenol (11) and the benzyl alcohol (17) being obtained from (13) and (19) respectively. The thioxanthene component, in both cases, consisted of an inseparable mixture of two isomers [single peak by g.l.c. (SE30); isomerism confirmed by m.s., *m/z* 212], which showed resolved methyl singlets in the ¹H n.m.r. spectrum (*e.g.* δ_H 2.32 and 2.34) and resolved methylene peaks in the ¹³C n.m.r. spectrum (*e.g.* δ_C 39.15 and 38.63). From a careful integration, after resolution enhancement and expansion of the above methyl signals in the crude pyrolysates, the ratio of the isomers from both precursors was found to be 1.00:1.02 ($\pm 5\%$), *i.e.* they were present in equal amounts, within experimental error. Preliminary analysis by the additivity effect of substitution on the ¹³C n.m.r. chemical shift of the methylene group¹⁴ suggested that the two isomers were the 2-methyl compound (24) [δ_C (calculated) 39.04; δ_C (observed) 39.15; δ_C (authentic sample) 39.08] and the 3-methyl derivative (30) [δ_C (calculated)



Scheme 4.

Table. Observed and estimated ^{13}C n.m.r. chemical shifts of 2-methyl- and 3-methylthioxanthene isomers^a

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
Thioxanthene	127.8	126.5	126.5	126.7	126.7	126.5	126.5	127.8
2-Methylthioxanthene (calculated) ^b	128.5		127.2	126.6	126.7	126.5		127.8
2-Methylthioxanthene (observed) ^c	128.61		127.2	126.56	126.75	126.33	126.33	127.78
3-Methylthioxanthene (calculated) ^b	127.7	127.2		127.4	126.7	126.5	126.5	127.8
3-Methylthioxanthene (observed) ^c	127.59	127.21		127.39	126.75	126.33	126.33	127.78

^a Quaternary signal chemical shifts could not be unambiguously assigned. ^b Estimated from the spectrum of thioxanthene,¹⁵ using the substituent effect of the methyl group. ¹⁶ ^c CDCl_3 Solution.

38.63; δ_{C} (observed) 38.63]. These assignments were confirmed by a more complete analysis of the ^{13}C n.m.r. spectra, summarized in the Table.

A control pyrolysis has shown that compound (24) is stable under our reaction conditions, and so we conclude that the radicals (27) and (28) proceed to the cyclic products (24) and (30) exclusively *via* a common intermediate (29) (Scheme 4). The sulphur and carbon atoms apparently have very similar migratory aptitudes in this system, leading to equal quantities of (24) and (30) from either precursor. Though we have no direct evidence for the mechanism of the cyclisation from the spirodienyl (29), the failure to detect any of the thiophenols (10) or (11) when the energy surface is entered from the benzyl radical side, would suggest that (29) does not revert to the thiophenoxy, and hence that the thioxanthene skeleton is formed by sigmatropic migration from (29) rather than by direct cyclisation of re-formed (27) or (28).

Experimental

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

2-Mercaptodiphenylmethane.—(a) **2-Benzylphenyl O-ethyl dithiocarbonate (8).** A solution of potassium O-ethyl dithiocarbonate (9.5 g, 0.06 mol) in water (12 ml) was warmed to 40–45 °C and was kept in that range during the slow addition of a cooled solution of diazonium salt obtained from 2-benzylaniline (9.1 g, 0.05 mol) and sodium nitrite (3.7 g, 0.05 mol). After an additional 30 min at this temperature to ensure complete decomposition, the red oily layer was separated and the aqueous layer was extracted with ether (2 × 10 ml). The combined oil and ether extracts were washed with aqueous sodium hydroxide (10%; 10 ml) and then with water until the water washings were neutral to litmus. The ether solution was dried (MgSO_4) and the solvent was evaporated under reduced pressure to give the required dithiocarbonate.

(b) **2-Mercaptodiphenylmethane (10)** (*cf.* ref. 6). The crude dithiocarbonate was dissolved in ethanol (150 ml) and the solution was heated until boiling. The source of heat was removed and potassium hydroxide pellets (12 g) were added to the hot solution at such a rate that it kept boiling. The mixture was then heated overnight under reflux by which time aliquots were completely soluble in water. Most of the ethanol was removed under reduced pressure, water (40 ml) was added, and the aqueous solution was extracted with ether (3 × 30 ml). The aqueous mixture was acidified, extracted with ether (3 × 100 ml), the ether extracts were dried (MgSO_4), and the solvent was evaporated under reduced pressure. A brown oil was obtained which partially solidified (2.38 g). On triturating the oily

mixture with light petroleum the required product was obtained as a pale brown solid (0.52 g, 5%), m.p. 44–47 °C (from light petroleum) (Found: C, 78.2; H, 6.05. $\text{C}_{13}\text{H}_{12}\text{S}$ requires C, 78.0; H, 6.0%). δ_{H} 7.13–7.50 (9 H, m), 4.19 (2 H, s), and 3.39 (1 H, s); δ_{C} 139.27 (q), 139.05 (q), 131.05, 130.83 (q), 130.49, 128.77, 128.39, 126.90, 126.11, and 40.35 (two signals are co-incident); m/z 200 (M^+ , 96%), 165 (50), and 122 (100).

2-Mercapto-4'-methylidiphenylmethane.—(a) **2-Amino-4'-methylidiphenylmethane (7).** A mixture of 2-amino-4'-methylbenzophenone⁵ (7.5 g, 35.5 mmol), hydrazine hydrate (4.5 ml), and potassium hydroxide pellets (5.38 g, 96 mmol) in diethylene glycol (65 ml) was heated under reflux for 1 h. The mixture was then distilled until the temperature of the liquid rose to 190 °C and reflux was continued for a further 3 h. The solution was cooled, added to water (50 ml), and was extracted with ether (3 × 30 ml). The ether extracts were washed with water, dried (MgSO_4), and the solvent evaporated under reduced pressure. The light brown solid obtained was purified by sublimation, 156–158 °C (0.2 Torr) to give the pure product as a yellow solid (4.5 g, 61%), m.p. 56–60 °C (from hexane) (Found: C, 85.0; H, 7.85; N, 7.05. $\text{C}_{14}\text{H}_{15}\text{N}$ requires C, 85.3; H, 7.6; N, 7.1%). δ_{H} 6.66–7.25 (8 H, m), 3.91 (2 H, s), 3.42 (2 H, br s), and 2.37 (3 H, s); δ_{C} 144.53 (q), 136.10 (q), 135.68 (q), 130.66, 129.19, 128.22, 127.41, 125.18 (q), 118.54, 115.73, 37.52, and 20.83; m/z 197 (M^+ , 100%), 182 (29), 164 (35), and 106 (21).

(b) **2-Mercapto-4'-methylidiphenylmethane (11).** 2-Amino-4'-methylidiphenylmethane (4.5 g, 23 mmol) was diazotised and was treated with potassium O-ethyl dithiocarbonate (4.38 g, 23 mmol), as previously described for the parent compound. The O-ethyl dithiocarbonate so obtained was dissolved in dry ether (45 ml) and was added dropwise to a stirred slurry of lithium aluminium hydride (0.95 g, 25 mmol) in dry ether (45 ml) at such a rate that the ether refluxed gently.⁷ The mixture was stirred at room temperature for a further 1.5 h. The excess of lithium aluminium hydride was destroyed by the dropwise addition of water (7 ml), with rapid stirring. The resulting solid was destroyed by the addition of sulphuric acid (10%; 25 ml), the ether layer was separated, and the aqueous layer was extracted with ether (3 × 40 ml). The oily mixture obtained by concentrating the dried (MgSO_4) combined ether layers was dissolved in methylene dichloride and extracted with aqueous sodium hydroxide (1M; 80 ml). The basic solution was neutralised, extracted with methylene dichloride, dried (MgSO_4), and the solvent was evaporated under reduced pressure to leave an orange oil (crude wt. 0.86 g). The crude product was purified by distillation at 0.1 Torr to leave 2-mercapto-4'-methylidiphenylmethane as a pale yellow liquid which crystallised on cooling (0.72 g, 15%). A small amount was further purified, for characterisation, by dry-flash chromatography eluting with methylene dichloride–hexane (30:70). The

clear oil was distilled, b.p. 140–142 °C (0.1 Torr), to give the pure product, on cooling, as a colourless solid, m.p. 39–41 °C (from light petroleum) (Found: C, 78.8; H, 6.65. $C_{14}H_{14}S$ requires C, 78.5; H, 6.55%); δ_H 7.09–7.31 (8 H, m), 4.04 (2 H, s), 3.30 (1 H, s), and 2.33 (3 H, s); δ_C 139.31 (q), 136.22 (q), 135.66 (q), 131.02, 130.92 (q), 130.51, 129.19, 128.73, 126.90, 126.11, 40.03, and 20.95; m/z 214 (M^+ , 94%), 197 (24), 181 (19), 165 (59), and 122 (100).

2-(Allylthio)diphenylmethanes (12) and (13).—The appropriate thiophenol (1.9 mmol) was treated with allyl bromide (2 mmol) in dimethylformamide (7 ml) containing potassium carbonate (2 mmol) as previously described.⁴ The reaction mixture was stirred overnight at room temperature and the product was purified by distillation. The following compounds were prepared by this method. **2-(Allylthio)diphenylmethane (71%)**, b.p. 140 °C (0.1 Torr) (Found: C, 79.8; H, 6.75. $C_{16}H_{16}S$ requires C, 80.0; H, 6.65%); δ_H 7.19–7.52 (9 H, m), 5.72–6.02 (1 H, m), 5.07–5.31 (2 H, m), 4.28 (2 H, s), and 3.55 (2 H, d); δ_C 141.11 (q), 140.32 (q), 135.22 (q), 133.37, 130.11, 128.90, 128.20, 126.65, 126.28, 125.86, 117.52, 39.54, and 37.15 (two peaks co-incident at 130.11); m/z 240 (M^+ , 51%), 199 (100), and 165 (32). **2-(Allylthio)-4'-methyl-diphenylmethane (55%)**, b.p. 140 °C (0.1 Torr). The isolated oil was further purified by dry-flash chromatography, with methylene dichloride–hexane (30:70) as eluant, to give the required product as a clear oil, b.p. 151 °C (0.1 Torr) (Found: C, 80.6; H, 7.2. $C_{17}H_{18}S$ requires C, 80.3; H, 7.1%); δ_H 7.39–7.43 (1 H, d), 7.14–7.26 (7 H, m), 5.91 (1 H, m), 5.09–5.22 (2 H, m), 4.18 (2 H, s), 3.53 (2 H, d), and 2.37 (3 H, s); δ_C 141.32 (q), 137.22 (q), 135.30 (q), 135.21 (q), 133.41, 130.01, 129.98, 128.93, 128.79, 126.57, 126.23, 117.52, 39.11, 37.11, and 20.87; m/z 254 (M^+ , 83%), 214 (47), 213 (100), 211 (82), 197 (61), 178 (35), 165 (74), and 112 (31).

Bis[2-(thiophenoxy)benzyl] Oxalates⁹ (18) and (19).—A solution of oxalyl chloride (4 mmol) in dry ether (9 ml) was added dropwise over a period of ca. 5 min to a stirred, ice-cold solution of the appropriate benzyl alcohol^{11,17} (9 mmol) and triethylamine (12 mmol) in dry ether (90 ml), and the mixture was stirred, at room temperature, for 2 h. At the end of the reaction water was added until the precipitate had dissolved and the ether layer was separated. The aqueous layer was extracted with ether (2 × 40 ml), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The following compounds were prepared by this method. **Bis[2-(thiophenoxy)benzyl] oxalate (18)** (98%), m.p. 117–120 °C (from ethanol) (Found: C, 68.8; H, 4.5. $C_{28}H_{22}O_4S_2$ requires C, 69.15; H, 4.55%); δ_H 7.49 (3 H, m), 7.16–7.41 (15 H, m), and 5.44 (4 H, s); δ_C 157.04 (C=O), 135.82 (q), 135.62 (q), 134.20 (q), 133.93, 129.81, 129.41, 129.11, 128.18, 126.67, and 66.40 (signals correspond to two carbon atoms at 129.81, 129.41, and 129.11); m/z 486 (M^+ , 67%), 197 (100), 184 (17), 165 (21), and 104 (17). **Bis[2-(4-methylthiophenoxy)benzyl] oxalate (19)** (63%), m.p. 130–132 °C (from acetonitrile) (Found: C, 69.5; H, 5.1. $C_{30}H_{26}O_4S_2 \cdot 0.25H_2O$ requires C, 69.45; H, 5.1% (analyses consistent with 0.25 mol water); δ_H 7.45–7.51 (2 H, m), 7.04–7.34 (14 H, m), 5.48 (4 H, s), and 2.32 (6 H, s); δ_C 157.13 (C=O), 137.10 (q), 135.48 (q), 134.97 (q), 132.70, 131.37 (q), 130.96, 129.92, 129.19, 127.47, 66.30, and 20.81 (signals correspond to two carbon atoms at 130.96, 129.92, and 129.19); m/z 514 (M^+ , 61%), 392 (27), 302 (23), 211 (100), 181 (7), and 91 (36).

2-Methylthioxanthene (24).—Prepared as a faint yellow solid by the literature method,¹³ this compound had m.p. 75–77 °C (lit.,¹³ 79.5–81.5 °C); δ_H 7.17–7.52 (6 H, m), 7.04 (1 H, d), 3.85 (2 H, s), and 2.37 (3 H, s); δ_C 136.24 (q), 136.06 (q), 134.19 (q), 130.34 (q), 128.57, 127.73, 127.12, 126.69, 126.50, 126.28, 39.08,

and 20.78 (two signals co-incident at 126.28; two quaternary signals co-incident at 136.24).

Pyrolysis Experiments.—Yields were obtained from small-scale pyrolyses using cyclohexane (5 μ l) as internal calibrant. Results are quoted as follows: quantity of substrate, inlet temperature, furnace temperature, pressure, pyrolysis time, and products.

2-(Allylthio)diphenylmethane (12). 0.014 g (0.058 mmol), 100–110 °C, 750 °C, 1×10^{-3} Torr, 35 min: thioxanthene (50%) and 2-mercaptodiphenylmethane (trace). On a larger scale the substrate (0.086 g, 0.36 mmol) was distilled at 5×10^{-3} Torr into a furnace at 750 °C over a period of 1.5 h. The entire pyrolysate was dissolved in methylene dichloride and was extracted with aqueous sodium hydroxide. The remaining methylene dichloride solution was dried ($MgSO_4$), the solvent was evaporated under reduced pressure, and the residue was purified by dry-flash chromatography, using methylene dichloride–hexane (50:50) as eluant. The major component of the residue was thioxanthene (crude wt. 0.036 g). The crude product was recrystallised from methanol to give pure thioxanthene (0.016 g, 23%), m.p. 129–130 °C, mixed m.p. 129–130 °C (lit.,¹⁸ 128–130 °C); δ_H 7.40–7.48 (2 H, m), 7.26–7.34 (2 H, m), 7.14–7.25 (4 H, m), and 3.86 (2 H, s); δ_C 136.01 (q), 133.71 (q), 127.72, 126.66, 126.38, 126.11, and 39.02. The ¹H n.m.r. and ¹³C n.m.r. spectra were identical with those of an authentic sample. The remainder of the residue consisted of minor components, isolated in less than 5% yield, which were not identified.

The base extract from the pyrolysate was acidified, extracted with methylene dichloride (3 × 15 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The residue (0.008 g), was shown by g.c. to be 2-mercaptodiphenylmethane, contaminated with impurities, which was not purified further.

2-(Allylthio)-4'-methyl-diphenylmethane (13). 0.016 g (0.063 mmol), 110–120 °C, 750 °C, 1×10^{-3} Torr, 40 min: 2-methylthioxanthene (29.5%), 3-methylthioxanthene (29.5%), and 2-mercapto-4'-methyl-diphenylmethane (6%). The pyrolysis was carried out on a larger scale, the substrate (0.173 g, 0.68 mmol) being distilled (1×10^{-3} Torr) through the furnace tube (750 °C) over a period of 120 min. The entire pyrolysate was dissolved in methylene dichloride and extracted with aqueous sodium hydroxide (1M; 50 ml). The methylene dichloride was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The components of the residue were separated by dry-flash chromatography with methylene dichloride–hexane (70:30) as eluant. The major component was a mixture of 2-methylthioxanthene and 3-methylthioxanthene, obtained as a white crystalline solid (0.033 g, 23%). The ¹H n.m.r. spectrum showed two methyl peaks at 2.32 and 2.34, which were tentatively assigned to the 2-methyl and 3-methyl isomers respectively, a peak at 3.82 attributed to the methylene signals for the two compounds, and aromatic signals between 6.99 and 7.46. The ¹³C n.m.r. spectrum showed two methylene peaks at 39.15 and 38.63, assigned to the 2-methyl and 3-methyl isomers respectively (see Discussion section), and a signal at 20.80 attributed to the methyl signals of both isomers. The remainder of the signals in the aromatic region could be assigned to the respective isomers: 2-methylthioxanthene; 136.32 (2q), 136.14 (q), 134.25 (q), 130.40 (q), 128.61, 127.78, 127.17, 126.75, 126.56, and 126.33 (two signals co-incident at 126.33: 3-methylthioxanthene; 133.94 (q), 133.59 (q), 133.07 (q), 127.78, 127.59, 127.29, 127.21, 126.75, and 126.33 (the remainder of the quaternary signals could not be unambiguously assigned; two signals co-incident at 126.33). The ¹³C n.m.r. spectrum for the 2-methyl isomer is compatible with that previously quoted for the authentic compound. The remainder of the components

separated by chromatography were isolated in less than 5% yield and were not identified.

The base extract was neutralised, extracted with methylene dichloride (3 × 25 ml), dried, and the solvent was evaporated. The residue was identified by g.c. and ¹H n.m.r. spectroscopy, as 2-mercapto-4'-methylthiophenylmethane (0.026 g) contaminated with impurities; δ_H 7.03–7.34 (8 H, m), 4.02 (2 H, s), 3.29 (1 H, s), and 2.32 (3 H, s). The ¹H n.m.r. spectrum is identical with that obtained for the authentic compound.

Bis[2-(thiophenoxy)benzyl] oxalate (**18**). 0.024 g (0.049 mmol), 140–230 °C, 750 °C, 5 × 10⁻³ Torr, 140 min: thioxanthene (53%) and 2-(thiophenoxy)benzyl alcohol (5%). On a preparative scale the oxalate (0.992 g, 2.04 mmol) was distilled at 1 × 10⁻³ Torr into a furnace at 750 °C over a period of 250 min. The entire pyrolysate was dissolved in methylene dichloride and was extracted with aqueous sodium hydroxide (1M; 50 ml). After extraction the methylene dichloride was dried (MgSO₄), the solvent was evaporated under reduced pressure, and the residue was separated by dry-flash chromatography, using methylene dichloride–hexane (70:30) as eluant. The following components were isolated: thioxanthene (0.470 g), which was recrystallised from methanol to give the pure material (0.15 g, 18%), m.p. 125–126 °C, mixed m.p. 126–128 °C (lit.,¹⁸ 128–130 °C); δ_H 7.40–7.58 (2 H, m), 7.31–7.38 (2 H, m), 7.18–7.29 (4 H, m), and 3.90 (2 H, s); δ_C 136.05 (q), 133.76 (q), 127.78, 126.71, 126.44, 126.38, and 39.11. The ¹H and ¹³C n.m.r. spectra are identical with those of the authentic compound: 2-(thiophenoxy)benzyl alcohol (0.058 g, 13%), contaminated with minor impurities which could not be separated. This component was not obtained in crystalline form, b.p. 135–136 °C (0.2 Torr) (lit.,¹¹ m.p. 44 °C); δ_H 7.15–7.58 (9 H, m), 4.77 (2 H, s), and 2.30 (1 H, br s); δ_C 142.36 (q), 135.98 (q), 133.84, 132.35 (q), 129.37, 129.05, 128.30, 126.44, and 63.35. The ¹H and ¹³C n.m.r. spectra are identical with those of the authentic sample.

The neutralised base extract from the pyrolysate (0.011 g) was examined by t.l.c. and g.c. and was found to contain a number of minor components which were not identified.

Bis[2-(4-methylthiophenoxy)benzyl] oxalate (**19**). 0.029 g (0.056 mmol), 220–230 °C, 750 °C, 1 × 10⁻³ Torr, 40 min: 2-methylthioxanthene (25%), 3-methylthioxanthene (25%), and 2-(4-methylthiophenoxy)benzyl alcohol (8%). On a preparative scale the oxalate (0.713 g, 1.39 mmol) was pyrolysed at 750 °C, 1 × 10⁻³ Torr over a period of 165 min. The components of the pyrolysate were separated by dry-flash chromatography, using methylene dichloride–hexane (50:50) as eluant. The major component was a mixture of 2-methylthioxanthene and 3-methylthioxanthene, isolated as a white solid contaminated with some minor impurities which were not further separated (0.13 g, 44%). The ¹H n.m.r. spectrum shows two methyl peaks at 2.41 and 2.42 which could not be unambiguously assigned, a peak at 3.90 attributed to the methylene signals for the two isomers, and aromatic signals between 7.07 and 7.56. The signals in the ¹³C n.m.r. spectrum of the mixture were assigned to each isomer as above: 2-methylthioxanthene, δ_C (DEPT, 3π/4) 128.68, 127.86, 127.22, 126.80, 126.60, 126.39 (two signals co-incident), 39.17, and 20.94; 3-methylthioxanthene, δ_C (DEPT, 3π/4) 127.86, 127.65, 127.35, 127.27, 126.80, 126.39 (two signals co-incident), 38.65, and 20.94. The ¹³C n.m.r. spectrum for the

2-methyl isomer is compatible with that of the authentic compound: 2-(4-methylthiophenoxy)benzyl alcohol (0.05 g, 15%), contaminated with minor impurities, isolated as a yellow oil, b.p. 154–155 °C (0.5 Torr) [lit.,¹⁷ 185–188 °C (5 Torr)], δ_H 7.08–7.46 (8 H, m), 4.79 (2 H, s), 2.34 (3 H, s), and 2.27 (1 H, br s); δ_C 141.50 (q), 136.89 (q), 133.69 (q), 132.64, 131.67 (q), 130.53, 129.91, 129.25, 128.16, 127.66, 63.37, and 20.82. The ¹H and ¹³C n.m.r. spectra were identical with those of the authentic sample.

The remainder of the components separated by chromatography were isolated in less than 5% yield and were not identified.

Control pyrolysis of 2-methylthioxanthene (24). 0.059 g (0.28 mmol), 90 °C, 750 °C, 1 × 10⁻³ Torr, 20 min. The ¹H and ¹³C n.m.r. spectra of the crystalline pyrolysate showed the presence of starting material uncontaminated by the 3-methyl isomer [e.g. δ_C(methylene region) 39.07, with the level of any signal at ca. δ_C 38.6 ≤ 3%].

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