Pyrolysis of *O*-Allyl Salicylic Amides and Esters, and Related Compounds: Formation of Isoindolones and Phthalides

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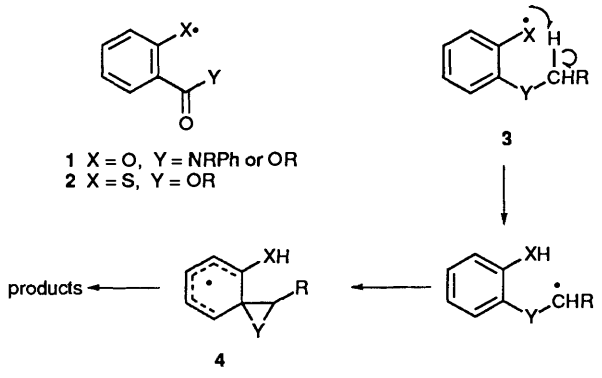
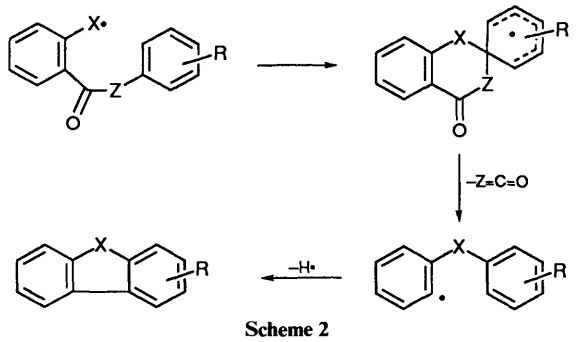
Flash vacuum pyrolysis of *O*-allyl salicylic alkylamides and alkyl esters gives isoindolones and phthalides, respectively, in low (20–40%) yield. The mechanism involves generation of the phenoxyl radical, regiospecific hydrogen-atom transfer from the alkylamide (or alkyl ester) group and cyclisation. A similar sequence was observed with thiophenoxyl radicals.

We report here the gas-phase hydrogen-transfer and cyclisation behaviour of the thermally generated phenoxyl **1** and thiophenoxyl **2** radicals. Our interest in these systems derives from our previous work on the gas-phase chemistry of *ortho*-



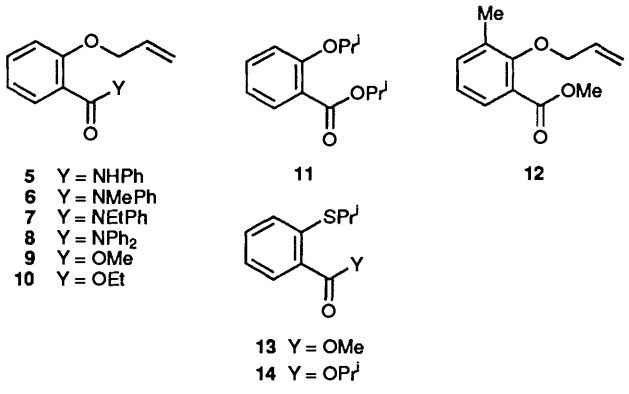
Scheme 1

substituted benzyl, phenoxyl, thiophenoxyl or aminyl radicals **3** (X = CH_2, O, S, NH respectively), which form products by hydrogen atom transfer (*via* a 6-membered ring transition state) and *ipso*-cyclisation to a spirodienyl system **4**[1] (Scheme 1). Any such process involving the alkyl groups of **1** and **2** will require (at least) a 7-membered ring transition state for hydrogen atom transfer, and *ipso*-attack will give a 4-membered ring spiro-system. We have also reported that under similar conditions, the radicals **1** (Y = OAr) and **2** (Y = OAr) undergo thermolysis to give dibenzofurans and dibenzothiophenes respectively, by an alternative *ispo*-attack followed by loss of CO_2[2] (Scheme 2; Z = O). An analogous route (with loss of an isocyanate) may be envisaged for the anilides **1** (Y = NRPh) *via* Scheme 2 (Z = NR).

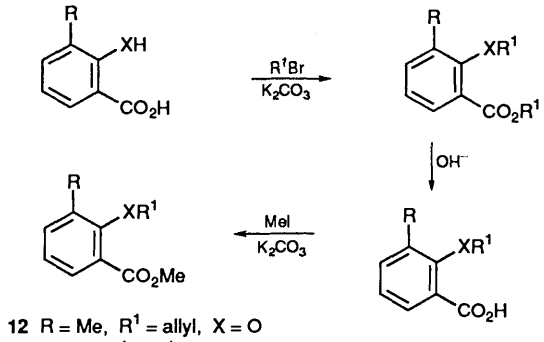


Scheme 2

As before,[1] we generated the radicals **1** and **2** by flash vacuum pyrolysis (FVP) of the corresponding *O*-allyl and *O*- and *S*-isopropyl compounds **5**–**14**, which were themselves normally



obtained by alkylation of the corresponding phenol or thiophenol (see Experimental section). In turn, the salicylanilide precursors of **5**–**8** were made from phenyl salicylate under standard conditions:[3] the esters **12** and **13** were made in three steps as shown in Scheme 3.



12 R = Me, R^1 = allyl, X = O
13 R = H, R^1 = Pi, X = S

Scheme 3

The mass spectra of the *O*-allyl precursors **5**–**10** often show normal carboxylic ester (or amide) behaviour, with ionisation at the carbonyl group followed by cleavage of the ester (or amide) bond, with subsequent loss of either CO or the allyl group. For example, the anilide **5** has its base peak at *m*/*z* 161 $(M - PhNH)^+$ and a significant fragment at *m*/*z* 133 $(M - PhNH - CO)^+$. The same ions are found in the spectrum of (for example) the ethyl ester **10**, though in this case the

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major breakdown peaks are around *m/z* 120 (M − OEt − allyl)$^+$. Similarly, the base peaks of the *S*-isopropyl compounds **13** and **14** are both at *m/z* 136, due to the ketene radical cation **15**.

The ^{13}C NMR chemical shift of the methylene carbon atom of the *O*-allyl group resonates characteristically at δ_C 68.5–69.5, though this may be shifted to higher frequency by hydrogen-bonding (in **5**) or the presence of an *ortho*-substituent (in **12**). The corresponding signal of allyl esters is in the region of δ_C 65.0 (see Experimental section and ref. 4).

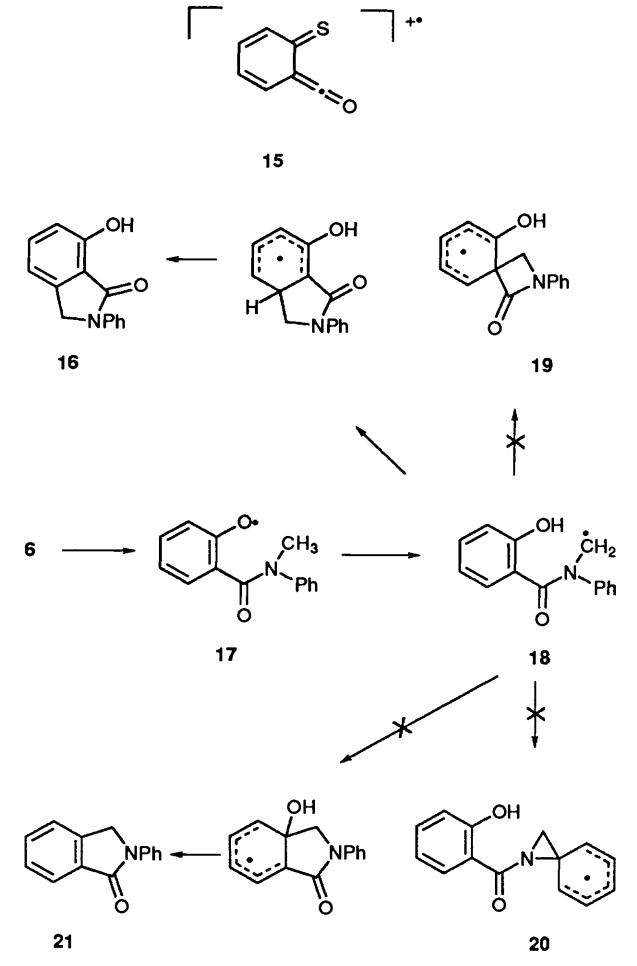
Pyrolysis of the anilide **5** was unsatisfactory. At 650 °C (5×10^{-3} Torr) considerable quantities of polymeric material were obtained together with some *C*-allyl compounds (possibly formed by Claisen rearrangement) which were not investigated further. At higher temperatures no volatile products could be detected by GLC. In particular, the absence of dibenzofuran confirms that *ipso*-attack of a phenoxyl radical and loss of HNCO does not take place in the same way as loss of CO_2 for the corresponding phenyl esters[2] (*cf.* Scheme 2, Z = NH). In similar fashion, neither phenyl isocyanate nor dibenzofuran could be detected from FVP of the diphenylamino derivative **8** at 650 °C and only diphenylamine (*m/z* 169) was identified by GC–MS of the pyrolysate.

In contrast, a single major crystalline product was obtained by pyrolysis of the *N*-methylanilide **6**, and this was identified as the isoindolone **16** (33%) by its spectra and by correlation with literature data.[5] In particular, the ^{13}C (DEPT) NMR spectrum verified the presence of a methylene group (δ_C 51.11) and mass spectrometry confirmed the molecular weight and the presence of a free hydroxy group which gives rise to a breakdown peak at (M − 17)$^+$. The formation of **16** presumably occurs by intramolecular hydrogen atom transfer to the initial phenoxyl radical **17** *via* a 7-membered transition state, to give the key aminomethyl radical **18**, which can then cyclise at the free *ortho* position. It is of interest that three potential *ipso*-attack pathways do not lie on the main reaction coordinate (Scheme 4). First, a mechanism involving the 4-membered ring intermediate **19** should lead to two isomeric isoindolones (unless there was a wholly unprecedented difference in migration aptitude between the CH_2 and the CO groups in this series[6]) and these were not observed. Similarly, *ipso*-attack on the anilide ring to give the 3-membered ring intermediate **20**—well precedented in other cases[1] (Scheme 1)—does not take place to give products, and the absence of the parent indolone **21** confirms that cyclisation cannot occur by attack at the hydroxy position.

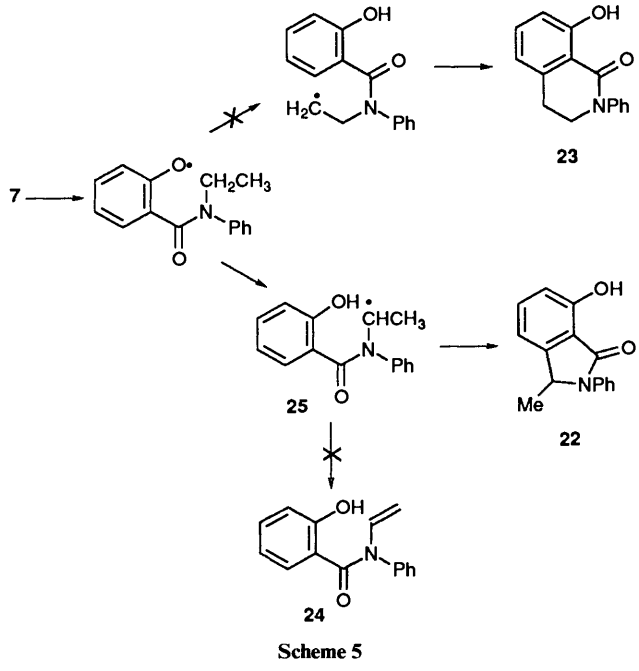
Two further features of the reaction were revealed by pyrolysis of the *N*-ethylanilide **7** (Scheme 5) which gave the methyl-substituted isoindolone **22** (19%). First, the absence of an isoquinolone product (*e.g.* **23**) confirms that hydrogen transfer *via* an 8-membered transition state cannot compete with the normal 7-membered process though the present results cannot distinguish possible stereochemical or electronic reasons for this. Second, no products derived from the enamine **24** could be detected, and so cyclisation of the aminoethyl radical **25** is kinetically favoured over hydrogen atom loss.

In the salicylic ester series, phenoxyl radicals derived from **9** and **10** underwent hydrogen transfer, cyclisation and loss of a hydrogen atom to give the 7-hydroxyphthalides **26** (25%) and **27** (trace): the major isolated product in the latter case was the carboxylic acid **28** (19%) which was formed by *cis*-elimination[7] from the ethyl ester. The presence of a methyl group *ortho* to the phenoxyl radical does not affect the major hydrogen-transfer route, and the phthalide **29** was obtained in 20% yield by pyrolysis of the ester **12**.

The 7-mercaptophthalide **30** (18%) was obtained by pyrolysis of the thiosalicylate **14** at 750 °C. This shows that transfer of a hydrogen atom from an *alkyl* group to a thiophenoxyl radical *via* a 7-membered transition state is more favourable than the corresponding abstraction from an aryl group (*cf.* refs. 6 and 8).



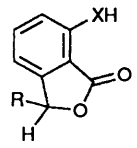
Scheme 4



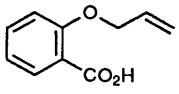
Scheme 5

However, attemps to observe generation and cyclisation of a tertiary radical by pyrolysis of the isopropyl esters **11** and **14** were unsuccessful, since only polymeric products were obtained.

In conclusion, we have generated phenoxyl (and thiophenoxyl) radicals with ester and amide groups in the *ortho*-



26 R = H, X = O
27 R = Me, X = O
30 R = H, X = S



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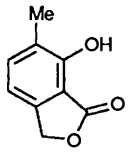

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position, and observed hydrogen transfer from *O*- or *N*-alkyl groups (exclusively *via* a 7-membered transition state) followed by direct cyclisation (without rearrangement) to create a new 5-membered heterocyclic ring. In principle, this provides a means of elaborating salicylic acid derivatives regiospecifically into 2,3-disubstituted phenols—including the 7-hydroxyphthalide natural products[9]—but in practice the consistently low yields associated with the present methodology are unattractive for synthetic applications.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz respectively for solutions in [^{2}H]chloroform.

2-Hydroxybenzamide Derivatives.—Phenyl salicylate (10 g, 0.047 mol) and the appropriate amine (0.059 mol) were heated together for 3 h at 180–200 °C, in a flask fitted with a short air condenser.[3] The hot melt was poured into ethanol (25 cm^3), charcoal was added to adsorb impurities and was then filtered off. The product then crystallised on cooling.

The following compounds were prepared by this method:

2-Hydroxy-*N*-phenylbenzamide (70%), m.p. 129–131 °C (from ethanol) (lit.,[3] 131–132 °C); δ_H 9.79 (1 H, br, s, OH), 8.03–6.89 (9 H, m) and 3.82 (1 H, br s, NH); *m/z* 213 (M$^+$, 20%), 121 (33) and 93 (100): 2-hydroxy-*N*-methyl-*N*-phenylbenzamide (69%), m.p. 107–109 °C (from ethanol) (lit.,[10] 111–112 °C); δ_H 10.87 (1 H, br s, OH), 7.57–6.20 (9 H, m) and 3.57 (3 H, s); *m/z* 227 (M$^+$, 15%), 121 (44), 107 (100), 93 (10) and 77 (12): 2-hydroxy-*N*,*N*-diphenylbenzamide (21%), m.p. 193–194 °C (from ethanol) (lit.,[11] 193 °C); δ_H 10.70 (1 H, br s, OH) and 7.44–6.44 (14 H, m); δ_C 172.30 (q), 161.24 (q), 143.83 (q), 133.22, 130.51, 129.26, 127.15, 126.71, 117.92, 117.81 and 116.09 (q); *m/z* 289 (M$^+$, 100%), 169 (100), 121 (88), 93 (28) and 77 (26): *N*-ethyl-2-hydroxy-*N*-phenylbenzamide (15%), m.p. 74–76 °C (from ethanol); δ_H 10.98 (1 H, br s, OH), 7.33–6.33 (9 H, m), 4.03 (2 H, q) and 1.21 (3 H, t); δ_C(DEPT 3π/4) 132.39, 130.11, 129.42, 127.32, 127.06, 117.57, 117.47, 46.31 and 12.35. This compound was characterised as its allyl ether derivative (see below).

2-Allyloxybenzamides and Alkyl 2-Allyloxy- (or 2-Isopropoxy)benzoates.—The appropriate amide (0.02 mol) or ester (0.02 mol) was added to dimethylformamide (50 cm^3), containing anhydrous potassium carbonate (2.76 g, 0.02 mol).[12] Allyl bromide (2.42 g, 0.02 mol) or isopropyl bromide (2.46 g, 0.02 mol) was added dropwise to the mixture which was then stirred at room temperature for 21 h. After dilution with water (100 cm^3) the solution was extracted with ether (3 × 50 cm^3). The combined organic extracts were washed with water (3 × 50 cm^3), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The following compounds were prepared by this method:

2-Allyloxy-N-phenylbenzamide **5** (82%), m.p. 51–53 °C (from hexane–ethyl acetate) (Found: C, 76.2; H, 5.65; N, 5.5. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 5.9; N, 5.55%); δ_H 9.97 (1 H, br s, NH), 8.89 (1 H, m), 7.69–7.63 (2 H, m), 7.48–7.29 (3 H, m), 7.14–6.96 (3 H, m), 6.18 (1 H, m), 5.57–5.41 (2 H, m) and 4.69 (2 H, m); δ_C 162.92 (q), 156.11 (q), 138.24 (q), 132.85, 132.15, 131.55, 128.69, 123.74, 121.90 (q), 121.53, 119.88, 119.69, 112.72 and 69.98; *m/z* 253 (M$^+$, 40%), 161 (100) and 133 (27): *2-allyloxy-N-methyl-N-phenylbenzamide* **6** (98%), m.p. 68–70 °C (from hexane–ethyl acetate) (Found: C, 76.8; H, 6.35; N, 5.2. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.4; N, 5.25%); δ_H 7.31–6.80 (9 H, m), 5.93 (1 H, m), 5.43–5.18 (2 H, m), 4.35 (2 H, m) and 3.46 (3 H, s); δ_C 168.86 (q), 153.95 (q), 143.67 (q), 132.98, 129.85, 128.46, 128.20, 127.03 (q), 126.48, 126.24, 120.27, 116.90, 111.85, 68.66 and 36.91; *m/z* 267 (M$^+$, < 1%), 227 (17), 161 (8) and 107 (100): *2-allyloxy-N,N-diphenylbenzamide* **8** (80%), m.p. 95–97 °C (from ethanol) (Found: C, 80.1; H, 5.75; N, 4.15. $C_{22}H_{19}NO_2$ requires C, 80.25; H, 5.8; N, 4.25%); δ_H 7.60–6.59 (14 H, m), 5.98 (1 H, m), 5.44–5.24 (2 H, m) and 4.30 (2 H, m); δ_C 168.87 (q), 154.07 (q), 142.93 (q), 132.93, 130.34, 129.08, 128.37, 127.37, 127.16 (q), 126.09, 120.34, 117.13, 111.78 and 68.70; *m/z* 329 (M$^+$, 20%), 167 (20), 162 (100), 133 (10) and 121 (10): *2-allyloxy-N-ethyl-N-phenylbenzamide* **7** (68%), m.p. 39–41 °C (from ethanol) (Found: C, 77.3; H, 6.95; N, 4.9. $C_{18}H_{19}NO_2$ requires C, 76.9; H, 6.75; N, 4.9%); δ_H 7.39–6.98 (7 H, m), 6.75 (1 H, m), 6.56 (1 H, m), 5.98 (1 H, m), 5.33–5.22 (2 H, m), 4.35 (2 H, m), 3.95 (2 H, q) and 1.21 (3 H, t); δ_C 188.62 (q), 179.50 (q), 177.54 (q), 175.41, 175.20, 168.37, 153.90, 142.08, 133.04 (q), 132.47, 131.46, 121.64, 116.87, 68.69, 43.89 and 12.98; *m/z* 281 (M$^+$, 26%), 161 (100), 133 (15) and 41 (30): *methyl 2-allyloxybenzoate* **9** (89%), b.p. 140–144 °C (1.5 Torr) (Found: C, 68.7; H, 6.3. $C_{11}H_{12}O_3$ requires C, 68.8; H, 6.25%); δ_H 7.77 (1 H, m), 7.40 (1 H, m), 6.98–6.90 (2 H, m), 5.99 (1 H, m), 5.54–5.23 (2 H, m), 4.59 (2 H, m) and 3.86 (3 H, s); δ_C 166.52 (q), 157.94 (q), 132.95, 132.69, 131.39, 120.84 (q), 120.26, 117.01, 113.75, 69.46 and 51.56; *m/z* 192 (M$^+$, 28%), 161 (44), 120 (85), 92 (43) and 41 (100): *ethyl 2-allyloxybenzoate* **10** (84%), b.p. 129–133 °C (1.5 Torr) (Found: M$^+$ 206.0946. $C_{12}H_{14}O_3$ requires *M*$^+$, 206.0943); δ_H 7.77 (1 H, m), 7.35 (1 H, m), 6.99–6.90 (2 H, m), 6.08 (1 H, m), 5.54–5.23 (2 H, m), 4.59 (2 H, m), 4.35 (2 H, q) and 1.36 (3 H, t); δ_C 166.21 (q), 157.84 (q), 132.99, 132.62, 131.40, 120.85 (q), 120.22, 117.20, 113.43, 69.29, 60.63 and 14.15; *m/z* 206 (M$^+$, 38%), 161 (59), 133 (22), 121 (100), 120 (96), 92 (49) and 41 (81): *isopropyl 2-isopropoxybenzoate* **11** (using 2 mol equiv. of isopropyl bromide) (54%), b.p. 115–120 °C (2.0 Torr) (Found: M$^+$, 222.1095. $C_{13}H_{18}O_3$ requires *M*$^+$, 222.1099); δ_H 7.68 (1 H, m), 7.41 (1 H, m), 6.97–6.92 (2 H, m), 5.25 (1 H, m), 4.57 (1 H, m) and 1.34 (12 H, d); *m/z* 222 (M$^+$, 10%), 180 (29), 163 (15), 120 (100) and 92 (47); *isopropyl (2-isopropylthio)benzoate* **14** (using thiosalicylic acid and 2 mol equiv. of isopropyl bromide) (79%), b.p. 150–154 °C (0.4 Torr) (Found: C, 65.7; H, 7.85. $C_{13}H_{18}O_2S$ requires C, 65.5; H, 7.6%); δ_H 7.79 (1 H, m), 7.32–7.29 (2 H, m), 7.06 (1 H, m), 5.18 (1 H, m), 3.42 (1 H, m) and 1.27 (12 H, d); δ_C 165.80 (q), 139.54 (q), 131.23, 130.29, 129.80 (q), 127.39, 123.80, 68.17, 35.03, 22.22 and 21.48; *m/z* 238 (M$^+$, 30%), 179 (9), 136 (100) and 108 (12).

Methyl 2-Allyloxy-3-methylbenzoate **12**.—(i) *Allyl 2-allyloxy-3-methylbenzoate.* The general method given above was applied, using 3-methylsalicylic acid and 2 equiv. each of allyl bromide and anhydrous potassium carbonate. The *benzoate* was obtained as a yellow oil (91%), b.p. 140–145 °C (1.2 Torr) (Found: M$^+$, 232.1099. $C_{14}H_{16}O_3$ requires *M*$^+$, 232.1099); δ_H 7.63 (1 H, m), 7.31 (1 H, m), 7.03 (1 H, m), 6.05 (2 H, m), 5.44–5.19 (4 H, m), 4.78 (2 H, m), 4.42 (2 H, m) and 2.29 (3 H, s); δ_C 165.89 (q), 156.92 (q), 134.93, 133.72, 132.77 (q), 132.02, 128.97, 124.77 (q), 123.41, 118.32, 117.30, 74.77, 65.47 and 16.17; *m/z* 232 (M$^+$, < 1%), 175 (14), 134 (100), 106 (43), 91 (12) and 41 (87).

(ii) *2-Allyloxy-3-methylbenzoic acid.* Allyl 2-allyloxy-3-methylbenzoate (7 g, 0.03 mol) was added to methanol (130 cm^3) followed by aqueous sodium hydroxide (5 mol dm^{-3}; 30 cm^3), and the mixture was heated under reflux for 5 h. Methanol was then removed under reduced pressure to leave a

dense white residue. This was dissolved in water (50 cm^3) and the solution was acidified with aqueous sulfuric acid (2 mol dm^{-3}; *ca.* 50 cm^3) and extracted with ether (3 × 20 cm^3). The combined organic extracts were washed with water (50 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to provide the *product* as a pink solid (5.71 g, 99%), m.p. 52–54 °C (from hexane) (Found: C, 68.6; H, 6.3. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.25%); δ_H 7.94 (1 H, m), 7.42 (1 H, m), 7.18 (1 H, m), 6.09 (1 H, m), 5.49–5.28 (2 H, m), 4.49 (2 H, m) and 2.35 (3 H, s) (the hydroxy signal is not apparent); δ_C 166.99 (q), 156.31 (q), 136.62, 131.73, 130.41, 124.69, 122.56 (q), 119.87, 75.85 (q), 75.67 and 16.00; *m/z* 192 (M^+, 32%), 152 (13), 134 (100) and 106 (78).

(iii) *Methyl 2-allyloxy-3-methylbenzoate* **12**. The general method of alkylation was employed, using methyl iodide (2.13 g, 0.015 mol), anhydrous potassium carbonate (2.07 g, 0.015 mol) and 2-allyloxy-3-methylbenzoic acid (2.88 g, 0.015 mol). The *benzoate* was obtained as a yellow oil (2.78 g, 90%), b.p. 117–120 °C (2.0 Torr) (Found: M^+, 206.0944. $C_{12}H_{14}O_3$ requires M^+, 206.0943); δ_H 7.62 (1 H, m), 7.32 (1 H, m), 7.03 (1 H, m), 6.05 (1 H, m), 5.42–5.20 (2 H, m), 4.41 (2 H, m), 3.87 (3 H, s) and 2.29 (3 H, s); δ_C 166.76 (q), 156.84 (q), 134.88, 133.70, 132.75 (q), 128.94, 124.69 (q), 123.40, 117.33, 74.80, 51.92 and 16.15; *m/z* 206 (M^+, 13%), 175 (23), 134 (63), 106 (67), 91 (20) and 41 (100).

Methyl (2-Isopropylthio)benzoate **13**.—(i) *(2-Isopropylthio)benzoic acid*. Hydrolysis of isopropyl (2-isopropylthio)benzoate using aqueous sodium hydroxide as described above for an allyl benzoate gave the *acid* (85%), m.p. 110–112 °C (from ethanol) (Found: C, 61.5; H, 6.2. $C_{10}H_{12}O_2S$ requires C, 61.2; H, 6.1%); δ_H 8.07 (1 H, m), 7.46–7.38 (2 H, m), 7.21 (1 H, m), 4.74 (1 H, br s, OH), 3.51 (1 H, m) and 1.36 (6 H, m); δ_C 170.78 (q), 140.41 (q), 132.63, 132.26, 128.26, 128.02 (q), 124.60, 36.00 and 22.46; *m/z* 196 (M^+, 20%), 153 (19), 136 (100) and 108 (31).

(ii) *Methyl (2-isopropylthio)benzoate* **13**. The general method of alkylation described above was employed using 2-isopropylthiobenzoic acid (1.96 g, 0.01 mol), methyl iodide (1.42 g, 0.01 mol), and anhydrous potassium carbonate (1.38 g, 0.01 mol). The *benzoate* was obtained as a yellow oil (1.62 g, 77%), b.p. 126–133 °C (1.8 Torr) (Found: C, 63.1; H, 6.9. $C_{11}H_{14}O_2S$ requires C, 62.85; H, 6.65%); δ_H 7.86 (1 H, m), 7.34 (2 H, m), 7.14–7.06 (1 H, m), 3.85 (3 H, s), 3.46 (1 H, m) and 1.31 (6 H, d); δ_C 166.81 (q), 140.20 (q), 131.69, 130.74, 128.85 (q), 127.25, 123.89, 51.78, 35.09 and 22.34; *m/z* 210 (M^+, 88%), 136 (100) and 108 (36).

Pyrolysis Experiments.—Flow pyrolyses were carried out by distillation of the substrate *in vacuo* through a hot silica furnace tube (35 × 2.5 cm) and the products were trapped at liquid nitrogen temperature. Results are quoted as follows: substrate, quantity, inlet temperature, furnace temperature, pressure, pyrolysis time and products. Small-scale pyrolyses (50–100 mg) were generally analysed by GLC (5% Carbowax) and NMR spectroscopy: on a larger scale, products were isolated and characterised in the usual way.

2-Allyloxy-N-phenylbenzamide. 0.59 g (2.3 mmol), 120 °C, 650 °C, 5 × 10^{-3} Torr, 60 min. ^{1}H NMR spectroscopy indicated the presence of *C*-allyl compound(s); δ_H 7.40–6.80 (9 H, m), 6.05 (1 H, m), 5.25–5.10 (2 H, m) and 3.40 (2 H, m).

Pyrolysis was repeated at furnace temperatures of 750 and 850 °C. In each case, ^{1}H NMR spectroscopy revealed the absence of starting material, and showed a series of broad peaks, indicative of polymer formation. Furthermore, the GLC of each pyrolysate indicated the absence of volatile products.

2-Allyloxy-N-methyl-N-phenylbenzamide. 1.234 g, (4.6 mmol) 100 °C, 650 °C, 1 × 10^{-3} Torr, 40 min. An involatile solid and red droplets were produced. The solid was scraped from the trap and identified as 2,3-dihydro-7-hydroxy-2-phenylisoindol-1-one **16** (0.34 g, 33%), m.p. 204–207 °C (from ethyl acetate) (lit.,[5] 216 °C) (Found: C, 74.9; H, 4.9; N, 6.25. $C_{14}H_{11}NO_2$ requires C, 74.6; H, 4.8; N, 6.2%); δ_H 8.77 (1 H, s, OH), 7.83–7.73 (2 H, m), 7.50–7.35 (3 H, m), 7.18 (1 H, m), 7.00–6.85 (2 H, m) and 4.80 (2 H, s); δ_C 169.29 (q), 156.29 (q), 140.13 (q), 138.71 (q), 134.26, 129.04, 124.52, 119.07, 117.37 (q), 114.55, 113.63 and 51.11 (CH_2, from a DEPT experiment); *m/z* 225 (M^+, 100%), 208 (8), 196 (14) and 77 (41).

The red liquid (0.18 g) was analysed by ^{1}H NMR spectroscopy and GLC but no significant products were detected.

2-Allyloxy-N,N-diphenylbenzamide. 0.052 g (0.15 mmol), 150 °C, 650 °C, 1 × 10^{-3} Torr, 30 min. A black oil and a yellow gummy material were deposited in the cold trap. ^{1}H NMR spectroscopy indicated that in each fraction, starting material was absent and GC–MS showed that diphenylamine (*m/z* 169) was formed.

2-Allyloxy-N-ethyl-N-phenylbenzamide. 0.133 g (0.47 mmol), 100 °C, 650 °C, 1 × 10^{-3} Torr, 60 min. A thick yellow gum and a yellow solid were obtained. The solid was scraped from the trap and was identified by its NMR and mass spectra as 2,3-dihydro-7-hydroxy-3-methyl-2-phenylisoindol-1-one **22** (0.033 g, 29%), m.p. 143–145 °C (from ethanol); δ_H 8.76 (1 H, br s, OH), 7.60–7.40 (5 H, m), 7.23 (1 H, m), 6.97–6.87 (2 H, m), 5.20 (1 H, q) and 1.56 (3 H, d); *m/z* 239 (M^+, 17%), 224 (38) and 77 (100), but was not fully characterised. Analysis of the gum-like fraction by GLC suggested that polymeric-type products had been formed.

Methyl 2-Allyloxybenzoate. 2.586 g (13 mmol), 150 °C, 650 °C, 1 × 10^{-3} Torr, 30 min. A yellow solid and a brown oil were deposited in the cold trap. The oil (0.45 g) was removed, and the solid was washed out with chloroform (25 cm^3), dried ($MgSO_4$), and the solvent was removed *in vacuo*, leaving a dark crystalline material, identified as 7-hydroxyphthalide **26** (0.49 g, 25%), m.p. 132–134 °C (from ethanol) (lit.,[13] 136–137 °C); δ_H 7.76 (1 H, br s, OH), 7.54 (1 H, m), 6.97–6.89 (2 H, m) and 5.30 (2 H, s); δ_C 172.25 (q), 156.59 (q), 146.57 (q), 136.66, 115.12, 113.07, 110.84 (q) and 70.30.

The liquid fraction was anlysed by GLC and ^{1}H NMR spectroscopy, but no significant products could be identified.

Ethyl 2-allyloxybenzoate. 0.309 g (1.5 mmol), 120 °C, 650 °C, 1 × 10^{-3} Torr, 30 min. A yellow solid and a yellow oil were obtained. The entire pyrolysate was washed out of the trap with chloroform (20 cm^3) and extracted with aqueous sodium carbonate (2 mol dm^{-3}; 10 cm^3) to remove any acidic compounds. Phenolic compounds were then removed from the organic layer following extraction with aqueous sodium hydroxide (2 mol dm^{-3}; 10 cm^3).

The remaining organic extract containing non-acidic compounds only, was washed with water (10 cm^3), dried ($MgSO_4$), and the solvent was evaporated under reduced pressure to afford a viscous brown oil (0.062 g). However, no significant products could be detected by GLC or ^{1}H NMR spectroscopy.

The phenolic and acidic fractions were each acidified with aqueous hydrochloric acid (2 mol dm^{-3}; 10 cm^3) and extracted with chloroform (2 × 10 cm^3). The combined organic extracts, in each case, were washed with water (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Thus were obtained 2-allyloxybenzoic acid (0.052 g, 19%), m.p. 63–64 °C (from hexane) (lit.,[14] 64–65 °C); δ_H 7.47–6.73 (4 H, m), 6.02 (1 H, m), 5.20–5.10 (2 H, m), 4.98 (1 H, br s, OH) and 3.41 (2 H, m); and a small quantity of impure 7-hydroxy-3-methylphthalide **27**, which was identified only by its NMR spectra; δ_H 7.54–6.80 (3 H, m), 5.56 (1 H, q) and 1.63 (3 H, d); δ_C 171.92 (q), 156.41 (q), 151.40 (q), 136.86, 129.54 (q), 115.27, 112.73, 79.13 and 20.13.

Methyl 2-allyloxy-3-methylbenzoate. 0.308 g (1.5 mmol), 120 °C, 650 °C, 1 × 10^{-3} Torr, 30 min. A yellow solid and

a red oil were obtained. The oil was removed (0.09 g) and GC–MS indicated that methyl 2-hydroxy-3-methylbenzoate was present: *m/z* 166 (M^+, 47%), 134 (100) and 106 (86). No other significant products were identified by GLC or ^1H NMR spectroscopy.

The solid was washed from the trap with methylene dichloride (15 cm^3) and then was washed with aqueous sodium hydroxide (2 mol dm^{-3}; 10 cm^3) to remove any acidic compounds. The basic extract was acidified with aqueous hydrochloric acid (2 mol dm^{-3}; *ca.* 10 cm^3) and was then extracted with methylene dichloride (15 cm^3). The extract was washed with water (10 cm^3) dried ($MgSO_4$), and the solvent was evaporated under reduced pressure to afford a brown solid. This was identified as *7-hydroxy-6-methylphthalide* **29** (0.048 g, 20%), m.p. 127–129 °C (from ethanol) (Found: M^+, 164.0466. $C_9H_8O_3$ requires M^+, 164.0473); δ_H 7.85 (1 H, br s, OH), 7.38 (1 H, d), 6.83 (1 H, d), 5.25 (2 H, s) and 2.27 (3 H, s); δ_C 172.88 (q), 154.39 (q), 143.91 (q), 137.97, 124.68 (q), 112.65, 110.24 (q), 70.27 and 14.36; *m/z* 164 (M^+, 92%), 163 (14) and 135 (100).

Isopropyl 2-isopropoxybenzoate. 0.069 g (0.31 mmol), 100 °C, 750 °C, 2 × 10^{-3} Torr, 30 min. ^1H NMR spectroscopy revealed that no starting material was recovered, and that polymeric-type products may have been formed. GC–MS indicated the presence of phenol (*m/z* 94) as a major volatile component, but no other products could be identified.

Isopropyl (2-isopropylthio)benzoate. 0.047 g (0.19 mmol), 100 °C, 750 °C, 5 × 10^{-3} Torr, 30 min. No starting material was recovered, as indicated by ^1H NMR spectroscopy and GC–MS, and no other compounds could be identified.

Methyl (2-isopropylthio)benzoate. 0.176 g (0.84 mmol), 100 °C, 750 °C, 5 × 10^{-3} Torr, 60 min. A crystalline solid and a yellow oil were obtained. The entire pyrolysate was washed out of the trap with chloroform (15 cm^3) and the acidic and non-acidic compounds were separated, as above.

The non-acidic fraction afforded a thick yellow oil (0.18 g). Analysis by ^1H NMR spectroscopy and GLC indicated that polymeric material may have been formed.

A yellow crystalline solid was obtained from the acidic fraction. This was identified as *7-mercaptophthalide* **30** (0.025 g, 18%), m.p. 114–116 °C (from ethanol) (Found: C, 57.8; H, 3.7. $C_8H_6O_2S$ requires C, 57.8; H, 3.6%); δ_H 7.46 (1 H, m), 7.27 (1 H, m), 7.15 (1 H, m), 6.25 (1 H, s, SH) and 5.24 (2 H, s); δ_C 133.87, 128.31, 117.51 and 68.61 (no quaternaries were apparent at this concentration); *m/z* 166 (M^+, 100), 137 (93) and 109 (36).

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