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Formation of dibenzofurans by flash vacuum pyrolysis of aryl 2-(allyloxy)benzoates and related reactions†

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Flash vacuum pyrolysis (FVP) of aryl 2-(allyloxy)benzoates **5** and of the corresponding aryl 2-(allylthio)benzoates **6** at 650 °C, gives dibenzofurans **19** and dibenzothiophenes **20**, respectively. The mechanism involves generation of phenoxyl (or thiophenoxyl) radicals by homolysis of the *O*-allyl (or *S*-allyl) bond, followed by *ipso* attack at the ester group, loss of CO_2 and cyclisation of the resulting aryl radical. Synthetically, the procedure works well for *p*-substituted substrates, which lead to 2-substituted dibenzofurans **19b–f** (73–90%) and dibenzothiophenes **20b–c** (90–94%). Little selectivity is shown in the cyclisation of *m*-substituted substrates and competing interactions of the radical with the substituent—and *ipso*-attack—complicate the pyrolyses of *o*-substituted substrates. FVP of related radical precursors including 2-(allyloxy)phenyl benzoates **43** gave no dibenzofurans, whereas 2-(allyloxy-5-methyl)azobenzene **44** gave a much reduced yield. No carbazoles were obtained by FVP of 4-methylphenyl 2-(allylamino)benzoate **42**.

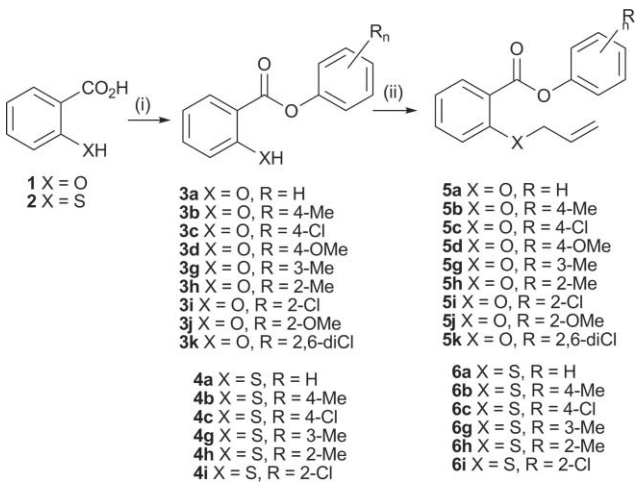
Introduction

The gas-phase behaviour of phenoxyl and thiophenoxyl radicals under flash vacuum pyrolysis (FVP) conditions often differ significantly. Whereas the former are prone to hydrogen atom abstraction processes,[1–5] the latter species are much more likely to undergo cyclisation. The formation of benzofurans[6] and benzothiophenes[7] from 2-allyloxy- and 2-allylthio-cinnamate esters, respectively, *via* the corresponding phenoxyl and thiophenoxyl species, is a notable exception. Here, we present full details of results published in a preliminary communication[8] where we showed that FVP of aryl esters of 2-allyloxy- and 2-allylthio-benzoic acids gives dibenzofurans and dibenzothiophenes, respectively, in good yields. We discuss the scope, limitations and mechanism of the process and a brief investigation of related radical precursors. This work complements our earlier study of the formation of dibenzofurans and dibenzothiophenes by direct cyclisation of aryl radicals.[9]

Standard routes to dibenzofurans[10] and dibenzothiophenes[11] include solution-phase free-radical cyclisations, but surprisingly few general methods are available, despite the environmental importance of many derivatives. Therefore, the development of concise and cost-effective synthetic methods from readily available starting materials was an important aim of this work.

Results and discussion

Most of the radical precursors, aryl 2-(allyloxy)benzoate esters **5** and the corresponding 2-(allylthio)benzoate esters **6**, were made by the sequence shown in Scheme 1, in which salicylic acid **1** (or thiosalicylic acid **2**) was first esterified using a modification of the *Organic Syntheses* procedure[12] to give the aryl esters **3** and **4**, respectively, which were treated with allyl bromide in DMF in the presence of potassium carbonate to provide the allyloxy and allylthio compounds **5** and **6**, respectively. Yields were variable (see Experimental section and ESI†) but no attempt was made to optimise the formation of these precursors. Substituents were chosen to provide a range of 2-, 3- and 4-substituted aryl esters and, in one case (**7**), a substrate with a further substituent on the salicylate ring was synthesised (see below).



Scheme 1 *Reagents and conditions*: (i) ArOH, $POCl_3$, 135 °C; (ii) allyl bromide, DMF, K_2CO_3, 20 °C.

The general method proved to be ineffective if the phenol contains an electron withdrawing group in the *para*-position. Instead, a Smiles rearrangement takes place under the basic conditions used for the allylation, to provide allyl esters (*e.g.* **8**). In their ^{13}C NMR spectra, allyl esters **8** show a signal at around

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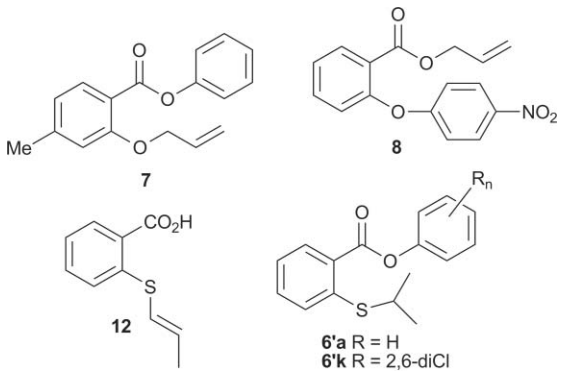
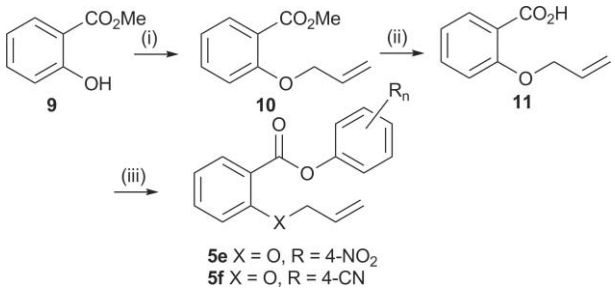
δ_C 65 ppm due to the *O*-CH_2, whereas the corresponding signal of the aryl ester system **5** appears around δ_C 70 ppm.



Compounds **5e** and **5f** were made by an alternative route (Scheme 2) in which the order of allylation and esterification was reversed. Because the phenol was introduced at the final stage of the sequence, this alternative route was advantageous for more complex phenols, though an additional step was required.

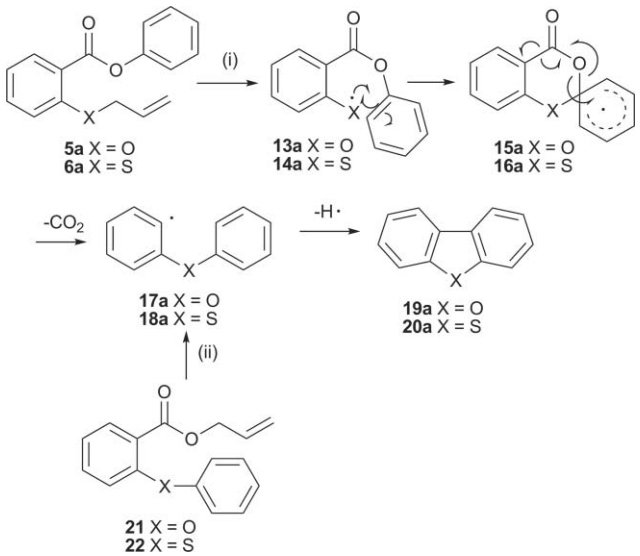


Scheme 2 *Reagents and conditions*: (i) allyl bromide, DMF, K_2CO_3, 20 °C; (ii) NaOH, H_2O–MeOH, reflux; (iii) $SOCl_2$, then ArOH, DMAP, Et_3N, 20 °C.

However, the alternative route (Scheme 2) proved unsuitable for *S*-allyl compounds because a rearrangement of the allyl group to a propenyl group (to give **12**) takes place under the basic conditions used for the ester hydrolysis. The unwanted rearrangement was avoided by using *S*-isopropyl derivatives **6′a** and **6′k** as alternative radical generators.

As expected from our earlier study of related alkyl benzoate systems,[13] the EI mass spectra of the precursors **5** and **6** display α-cleavage of the ester function to produce a peak at $(M\text{-}OAr)^+$, followed by loss of CO. Analogous processes are not found in the thermal behaviour of the substrates.

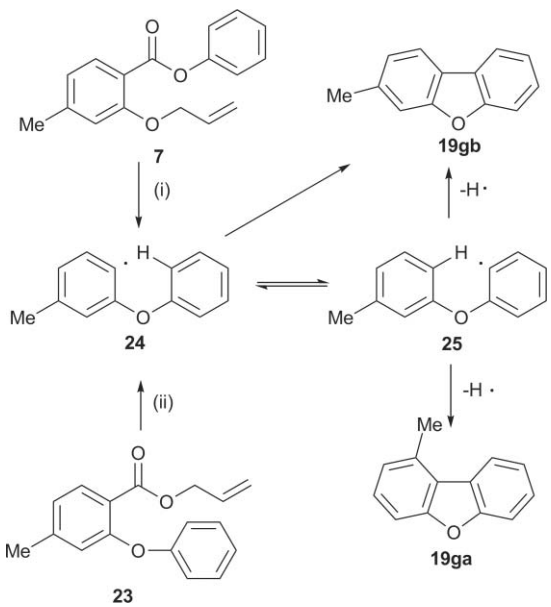
FVP of **5a** and of **6a** at 650 °C provides dibenzofuran (62%) and dibenzothiophene (88%) after purification. As usual for gas-phase pyrolyses, the Claisen rearrangement does not compete with radical formation.[5] The mechanism involves *ipso*-attack of the initial radicals **13** and **14**, respectively, to provide spirodienyl radicals **15** and **16**, which collapse with loss of CO_2 to generate the aryl radicals **17** and **18**, which cyclise (Scheme 3). The mechanism bears some resemblance to a radical variant of the Smiles rearrangement. We have previously shown that the key aryl radicals **17** and **18** can also be generated by FVP of allyl esters **21** and **22**, but the present method has the major advantage that the furnace temperature required for the reaction is *ca.* 200 °C lower than that needed for the previous method. Conditions



Scheme 3 *Reagents and conditions*: (i) FVP, 650 °C; (ii) FVP, 850 °C.

are therefore compatible with substituents (*e.g.* methoxy-groups) which decompose at the higher temperatures.[9]

Our previous work has also demonstrated that aryl radicals of the type **17** can equilibrate by hydrogen atom abstraction from the neighbouring ring,[9] one of a class of hydrogen atom rearrangements which take place at high temperatures.[14] Thus, FVP of the allyl ester **23** at 850–1000 °C leads to the two isomeric methyl benzofurans **19gb** and **19ga** in a 3 : 1 ratio *via* equilibration and cyclisation of the two aryl radicals **24** and **25** (Scheme 4).[9] FVP of **7** at 650 °C also gave **19gb** and **19ga** in a 3 : 1 ratio, which suggests that the radicals are fully equilibrated even at 650 °C. This rearrangement can lead to regioselectivity problems for certain targets.



Scheme 4 *Reagents and conditions*: (i) FVP, 650 °C; (ii) FVP 850–1000 °C.

By employing substituents in the aryl ester ring, the method is synthetically useful for 2-substituted dibenzofurans **19b–f** and 2-substituted dibenzothiophenes **20b–c**. The reaction proceeds well,

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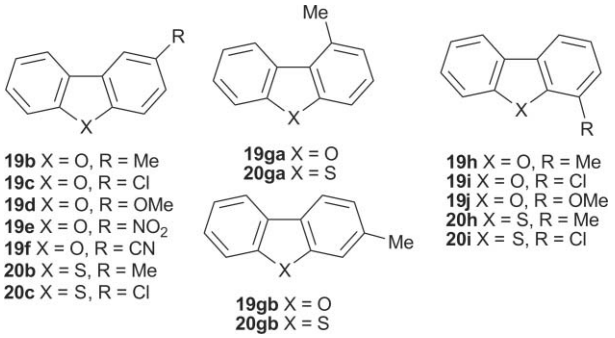
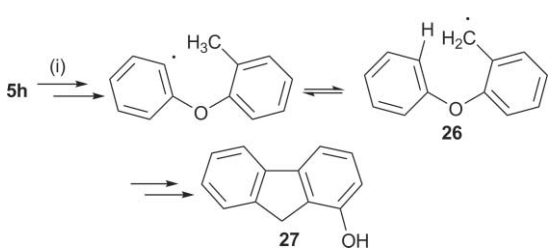
irrespective of the nature of the substituent, which includes an alkyl group (**19b**, 70%; **20b**, 90%) a halogen (**19c**, 75%; **20c**, 92%), an electron donating group (**19d**, 91%) and electron withdrawing groups (**19e**, 90%; **19f**, 73%). The only significant by-product is a trace of the phenol (see below), which can be easily removed on a preparative scale by base extraction. The method therefore provides a three-step route from a *p*-substituted phenol to a 2-substituted dibenzothiophene or dibenzofuran.

FVP of the 3-methyl precursors **5g** and **6g** showed little regioselectivity in the pyrolysis step, giving mixtures of 1- and 3-methyl isomers **19ga**, **19gb** and **20ga**, **20gb**, respectively, identified by the characteristic chemical shifts of the methyl groups.[9] No other 3-substituted substrates were investigated.

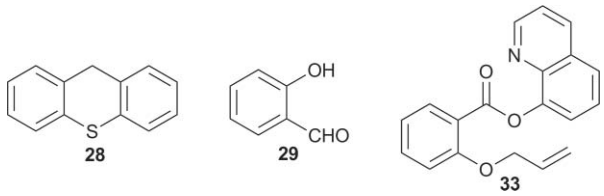


The 2-methyl precursors **5h** and **6h** gave the expected cyclised products **19h** (31%) and **20h** (39%), respectively, together with small amounts of *o*-cresol (*ca.*10%), and of the parent compounds **19a** and **20a**. The latter are formed by *ipso*-attack of the aryl radical at the site of the methyl group followed by ejection of the substituent; related sequences have been previously observed.[15] The ^{1}H NMR spectrum of the pyrolysate from **5h** suggested the presence of 1-hydroxyfluorene **27** (2%), formed by a known[4] sequence of hydrogen-transfer and rearrangement processes *via* the benzyl radical **26** (Scheme 5). In agreement with this mechanism, a trace of thioxanthene **28** was identified in the pyrolysate from **6h**; 2-(thiophenoxy)benzyl radicals are known to cyclise to thioxanthene.[2]

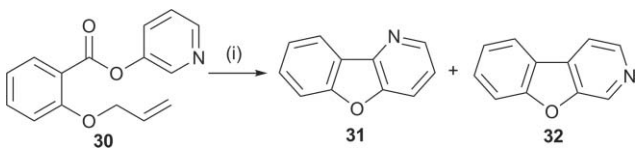


Scheme 5 *Reagents and conditions*: (i) FVP 650 °C.

Although the 4-chloro compounds **19i** and **20i** were both significant components of the pyrolysates from the 2-chloro substrates **5i** and **6i**, *ipso*-attack and ejection of the substituent also occurred, leading to the major product in the latter case. This problem could be overcome to some extent by FVP of the 2,6-dichloro compounds **5k** and **6′k**. FVP of the 2-methoxy-compound **5j** gave 4-methoxydibenzofuran **19j** (*ca.* 30%) as the major component. It is known that methoxy groups *ortho* to radical centres can rearrange to aldehydes,[16] so the detection of salicylaldehyde **29** (12%) confirms that the small amounts of phenols detected in these pyrolysates are formed by competitive radical cleavage of the aryl ester moiety followed by hydrogen atom abstraction (*cf.* ref. 1–5).

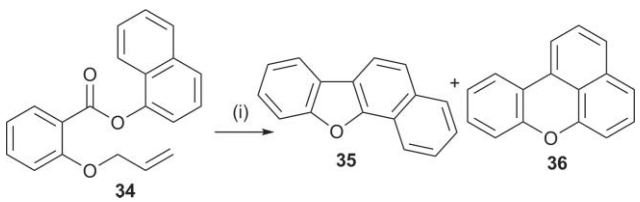


The scope of the reaction was further tested by extension to some more unusual ring systems. The heterocyclic and naphthyl precursors **30**, **33**, **34** and **37** were synthesised in the standard way and pyrolysed at 650 °C.



Scheme 6 *Reagents and conditions*: (i) FVP 650 °C.

FVP of the 3-pyridyl compound **30** gave a 55% yield of a 3 : 1 mixture of benzofuro[3,2-*b*]pyridine **31** and benzofuro[2,3-*c*]pyridine **32**, identified by their ^{13}C NMR spectra[17] and by isolation of the picrate salt of the minor isomer **32** (Scheme 6).[18] Formation of the major isomer therefore involves attack at C-2 of the pyridine ring, the preferred site for intramolecular radical attack of the pyridine system in solution-phase cyclisations.[19] In contrast, FVP of the quinolinyl system **33** gave 8-hydroxyquinoline (34%), by radical cleavage of the ester, rather than significant amounts of cyclised products.



Scheme 7 *Reagents and conditions*: (i) FVP 650 °C.

FVP of the α-naphthyl system **34** gave two isomeric cyclised products in 43% overall yield in *ca.* 1 : 1 ratio which were not separated (Scheme 7). One component was identified as benzo[*k*,*l*]xanthene **36** by comparison of the ^{13}C NMR spectrum of the mixture with reported data for **36**.[20] The remaining signals were tentatively assigned to benzo[*b*]naphtho[2,1-*d*]furan (α-brazan) **35** (see Experimental section). Two products (in 4 : 1 ratio) were also obtained by FVP of the β-naphthyl system **37** (91% overall yield). The minor isomer was isolated by recrystallisation and identified as benzo[*b*]naphtho[2,3-*d*]furan, (β-brazan) **39** (19%), so the major isomer is benzo[*b*]naphtho[1,2-*d*]furan (γ-brazan) **38** (Scheme 8). Intermolecular radical attack at the α- and β-positions of naphthalene in solution gives comparable regioselectivity to the present example.[21]

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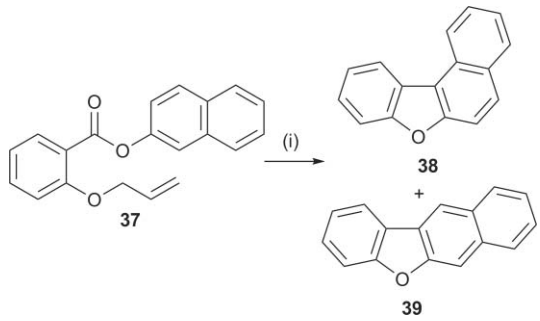
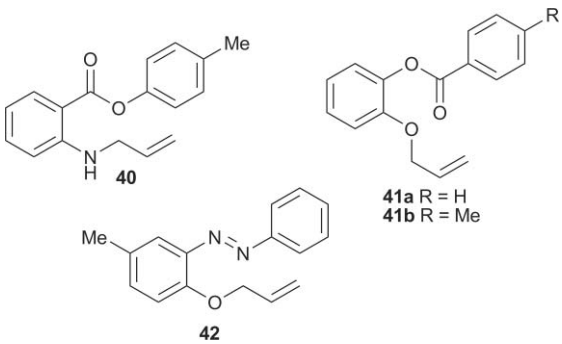


Scheme 8 *Reagents and conditions*: (i) FVP 650 °C.

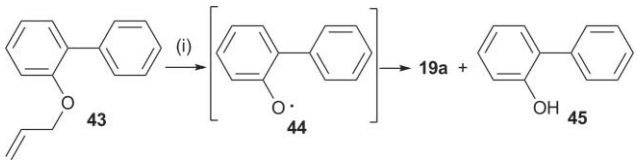
It was easy to show that the synthetic strategy shown in Scheme 3 is not applicable to the formation of carbazoles (see Experimental section). As previously found in the FVP reactions of anthranilic esters,[9,22] elimination of the phenol and formation of an unstable ketenimine by a cyclic transition state is probably the major pathway from **40**.



The FVP reactions of two related sets of precursors were studied in which the two aryl groups are again linked by a potential thermal leaving group. In the first of these, **41**, the leaving group is again CO_2 but arranged in the opposite fashion to that in **5**. The synthesis of these 'reversed esters' was achieved by standard esterification of 2-allyloxyphenol, itself obtained (20%) by reaction of catechol with a slight excess of allyl bromide (ESI†). FVP of **41a** or **41b** gave only traces of dibenzofurans and other monomeric products; considerable amounts of polymeric material were formed, which suggests that other reaction pathways are open to the phenoxyl radical, rather than *ipso*-attack. The nature of these pathways has not been investigated.

The second precursor related to **5** was the azo-compound **42**, designed so that any *ipso*-attack of the phenoxyl could be followed by extrusion of dinitrogen (ESI†). Compound **42** was synthesised by azo-coupling of benzenediazonium chloride with *p*-cresol followed by allylation. Although 2-methyldibenzofuran **19b** was indeed formed (28%) by FVP of **42** at 650 °C or higher, the yield was surprisingly much lower than when the ester **5b** was used as the precursor, despite the obvious efficiency of the leaving group. Clearly the juxtaposition of functionality in radicals **13** and **14** is ideally suited to the sequence of events shown in Scheme 3, leading to dibenzofurans and dibenzothiophenes.

Finally, the direct cyclisation of the 2-phenylphenoxyl radical **44**, generated by FVP of 2-allyloxybiphenyl **43**, gave dibenzofuran **19a** (65%) (ESI†). A considerable amount of hydrogen capture product, 2-hydroxybiphenyl **45** (17%) was also formed (Scheme 9), despite the proximity of the 2-phenyl group for cyclisation.



Scheme 9 *Reagents and conditions*: (i) FVP 650 °C.

Conclusions

In conclusion, the work reported in this paper defines the scope of a three step synthesis of dibenzofurans and dibenzothiophenes.[8] The key step involves radical generation, cyclisation, CO_2 extrusion, recyclisation and hydrogen atom expulsion, accomplished by FVP (650 °C) of aryl allyloxy- (or allythio)-benzoates **5** and **6**. If the aryl group contains a *para*-substituent, good yields of 2-substituted cyclised products are obtained, independent of the nature of the substituent. If the aryl group has an *ortho*- or *meta*- substituent, mixtures of products are usually obtained which, in principle, could be separated. FVP of the ester substrates **5** and **6** is a better route to dibenzofurans and dibenzothiophenes than that of corresponding azo-compounds (*e.g.* **42**) or of the 'reversed' esters **41**, and requires a much lower furnace temperature than that of the allyl esters **21** and **22**. The method was extended to some heterocyclic and polycyclic substrates.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, for solutions in [^{2}H]chloroform unless otherwise stated. Coupling constants are quoted in Hz. All mass spectra were recorded under electron impact conditions.

Aryl benzoates 3 and 4[12]

Salicyclic acid or thiosalicyclic acid (0.127 mol) was melted with the appropriately substituted phenol (0.127 mol) at 135 °C.[12] Phosphoryl chloride (7 g, 0.046 mol) was then added gradually and the temperature was moderated until the evolution of hydrogen chloride had ceased. The reaction mixture was cooled in ice, water (250 cm^3) was added and the product was obtained by trituration of the organic precipitate. The reaction mixture was then washed with aqueous sodium carbonate (4 M, 50 cm^3) to remove any unreacted acid.

If necessary, non-crystalline products were extracted with dichloromethane (3 × 50 cm^3), the extracts washed with water (2 × 50 cm^3), dried ($MgSO_4$), the solvent removed and the products purified by distillation. Typical products are reported here, the remainder are described in the ESI†:

4-Methylphenyl (2-hydroxy)benzoate 3b. (46%), mp 38–40 °C (from methanol) (lit.,[23] 38.5 °C); δ_H 10.56 (1H, br s), 8.09 (1H, m), 7.27–6.97 (7H, m) and 2.39 (3H, s); *m/z* 228 (M$^+$, 27%), 121 (100), 107 (24) and 93 (20).

Phenyl (2-mercapto)benzoate 4a. (60%), mp 82–85 °C (from ethanol) (lit.,[24] 91 °C) δ_H 8.27 (1H, d), 7.49–7.20 (8H, m) and 4.47 (1H, s); *m/z* 230 (M$^+$, 89%), 137 (100) and 109 (82).

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Aryl 2-(allyloxy)benzoates 5 and aryl 2-(allylthio)benzoates 6

The following *S*- and *O*-allyl compounds were prepared by treatment of the appropriate aryl 2-mercaptobenzoate or aryl 2-hydroxybenzoate with allyl bromide in DMF in the presence of potassium carbonate as previously described.[25] Typical products are reported here, the remainder are described in the ESI†:

Phenyl 2-(allyloxy)benzoate 5a. (83%), bp 137–140 °C (0.4 Torr) (Found: C, 75.3; H, 5.45. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5%); δ_H 8.09 (1H, m), 7.68–6.95 (8H, m), 6.06 (1H, m), 5.66–5.23 (2H, m) and 4.64 (2H, m); δ_C 163.95 (quat), 158.22 (quat), 150.74 (quat), 133.58, 132.19, 131.58, 128.90, 125.16, 121.36, 120.01, 119.42 (quat), 116.83, 113.35 and 68.94; *m/z* 254 (M^+, 4%), 161 (100), 133 (13) and 92 (7).

Phenyl 2-(allylthio)benzoate 6a. (89%), mp 60–62 °C (from ethanol) (Found: C, 69.4; H, 5.2. $C_{16}H_{14}O_2S{\cdot}0.3H_2O$ requires C, 69.5; H, 5.3%); δ_H 8.19 (1H, m), 7.54–7.19 (7H, m), 6.00 (1H, m), 5.39–5.16 (2H, m) and 3.65 (2H, m); δ_H 164.54 (quat), 150.69 (quat), 141.74 (quat), 132.46, 131.41, 129.16, 126.52, 125.59 (quat), 124.05, 121.53, 118.31, 77.52, 76.88 and 35.34; *m/z* 270 (M^+, 1.5%), 177 (100), 149 (18) and 108 (26).

Base-promoted reaction of 4-nitrophenyl (2-hydroxy)benzoate and allyl bromide

Under the basic conditions employed in the general alkylation procedure this benzoate can undergo Smiles' rearrangement[26] and it is the rearranged product [2-(4-nitrophenoxy)benzoic acid] that is subsequently alkylated. Thus, allyl 2-(4-nitrophenoxy)benzoate **8** was obtained as a brown solid (72%), mp 63–65 °C (from ethanol) (Found: C, 64.0; H, 4.35; N, 4.7. $C_{16}H_{13}NO_5$ requires C, 64.2; H, 4.35; N, 4.7%); δ_H 8.16 (2H, m), 8.02 (2H, m), 7.60 (1H, m), 7.35 (1H, m), 7.13 (1H, m), 6.91 (2H, m), 5.78 (1H, m), 5.37–5.20 (2H, m) and 4.62 (2H, m); δ_C 164.14 (quat), 163.53 (quat), 153.37 (quat), 142.32 (quat), 134.22, 132.34, 131.40, 125.74 (2C), 124.01 (quat), 123.00, 118.47, 116.07 and 65.73; *m/z* 299 (M^+, 48%), 242 (46), 196 (100) and 168 (27).

2-(2-Propenylthio)benzoic acid 12

Thiosalicylic acid (6.17 g, 0.04 mol), allyl bromide (14.52 g, 0.12 mol) and anhydrous potassium carbonate (16.59 g, 0.12 mol) were reacted as described in ref. 27 After work-up, allyl 2-(allylthio)benzoate was obtained as a clear oil. (8.57 g, 87%), bp 155–160 °C (0.4 Torr) δ_H 7.95 (1H, m), 7.40–7.28 (2H, m), 7.12 (1H, m), 6.09–5.83 (2H, m), 5.43–5.12 (4H, m), 4.80 (2H, m) and 3.57 (2H, m). Crude allyl 2-(allylthio)benzoate (5.5 g, 0.024 mol) was then treated with aqueous sodium hydroxide (5 M, 30 cm^3) in methanol (100 cm^3) by the method previously described.[13] Work-up afforded 2-(2-propenylthio)benzoic acid **12** (3.87 g, 85%), mp 143–145 °C (from ethyl acetate) (lit.,[27] 144–146 °C); δ_H 9.60 (1H, br s), 8.09 (1H, m), 7.50–7.10 (3H, m), 6.30–6.12 (2H, m) and 1.90 (3H, d); *m/z* 194 (M^+, 100%) and 153 (32).

Aryl 2-(allyloxy)benzoates 5 and aryl 2-(isopropylthio)benzoates 6′

2-Allyloxybenzoic acid[13] **11** (3.56 g, 0.02 mol) and thionyl chloride (2.86 g, 0.024 mol) were heated under reflux for 30 min. Excess thionyl chloride was removed *in vacuo* (using a water pump). The acid chloride thus formed was dissolved in dichloromethane (25 cm^3) and 4-dimethylaminopyridine (DMAP) (0.02 g, 0.0002 mol) was added, followed by the addition of the appropriate phenol (0.02 mol). Triethylamine (2.02 g, 0.02 mol) in dichloromethane (25 cm^3) was added dropwise and the solution was stirred for 3 h. The dense white precipitate of triethylamine hydrochloride was removed by filtration and the filtrate was washed with water (3 × 15 cm^3), dried ($MgSO_4$) and the solvent removed *in vacuo*.. Typical products are reported here, the remainder are described in the ESI†:

4-Nitrophenyl 2-(allyloxy)benzoate 5e. (70%) mp 62–64 °C (from ethanol) (lit.,[28] 62–63 °C) (Found: C, 64.0; H, 4.4; N, 4.7. $C_{16}H_{13}NO_5$ requires C, 64.2; H, 4.35; N, 4.7%); δ_H 8.11 (1H, m), 7.55 (1H, m), 7.17–7.05 (2H, m), 6.99–6.93 (3H, m), 6.08 (1H, m), 5.52–5.39 (2H, m) and 4.80 (2H, m); δ_C 167.20 (quat), 162.38 (quat), 157.44 (quat), 140.90 (quat), 135.49, 133.47, 130.59, 125.96, 122.37, 120.52, 117.14 (quat), 115.64, 113.17 and 70.86; *m/z* 299 (M^+, 0.3%), 161 (100), 133 (12) and 41 (20).

The following compounds were prepared using 2-isopropylthiobenzoic acid[13] in place of 2-allyloxybenzoic acid, by the same method:

Phenyl 2-(isopropylthio)benzoate 6′a. (75%) mp 57–59 °C (from ethanol) (Found: C, 68.9; H, 5.4. $C_{16}H_{16}O_2S{\cdot}0.4H_2O$ requires C, 68.8; H, 6.0%); δ_H 8.14 (1H, m), 7.58–7.19 (8H, m), 3.55 (1H, m) and 1.38 (6H, m); δ_C 164.89 (quat), 150.73 (quat), 141.23 (quat), 132.31, 131.33, 129.23, 127.89, 125.98 (quat), 125.67, 124.25, 121.65, 35.56 and 22.52; *m/z* 272 (M^+, 13%), 179 (100), 137 (64) and 109 (22).

2,6-Dichlorophenyl 2-(isopropylthio)benzoate 6′k. (73%), mp 65–67 °C (from ethanol) (Found: C, 56.7; H, 4.2. $C_{16}H_{14}C1_2O_2S$ requires C, 56.3; H, 4.1%); δ_H 8.33 (1H, m), 7.53–7.11 (6H, m), 3.57 (1H, m) and 1.38 (6H, m); δ_C 162.27 (quat), 143.99 (quat), 142.80 (quat), 132.98, 132.09, 129.08 (quat), 128.45, 127.40, 127.00, 126.03 (quat), 124.05, 35.26 and 22.46; *m/z* 340 (M^+, 5%), 179 (100), 161 (45), 137 (80) and 136 (22).

FVP experiments

The precursors were distilled under vacuum through a silica pyrolysis tube (35 × 2.5 cm), which was heated by a laboratory tube furnace. Products were collected in a U-tube trap cooled by liquid nitrogen and situated at the exit point of the furnace. Upon completion of the pyrolysis, the trap was allowed to warm up to room temperature under nitrogen and the product was removed from the trap. Pyrolysis parameters are quoted as follows: furnace temperature (T_f) inlet temperature (T_i), pressure (range if appropriate) (*P*) and reaction time (*t*).

When the FVP reaction was carried out on >100 mg scale, the entire pyrolysate was dissolved in dichloromethane (*ca.* 30 cm^3) and the solution washed with aqueous sodium hydroxide (2 M, 15 cm^3) to remove phenols. The neutral fraction was washed with water (2 × 15 cm^3), dried ($MgSO_4$) and the solvent removed *in vacuo* to give the non-acidic components. Typical products are reported here, the remainder are described in the ESI†:

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FVP of phenyl 2-(allyloxy)benzoate 5a

FVP of **5a** [1.106 g (5 mmol), T_i 160 °C, T_f 650 °C, P 0.005 Torr, t 40 min] provided phenol (0.03 g, 6%) and dibenzofuran **19a** (0.52 g, 62%) mp 79–81 °C (from ethanol) (lit.,[29] 83–84 °C); δ_C 156.02 (quat), 126.97, 124.06 (quat), 122.52, 120.49 and 111.50.

FVP of phenyl 2-(allylthio)benzoate 6a

FVP of **6a** [1.037 g (4 mmol), T_i 150 °C, T_f 650 °C, P 0.001 Torr, t 75 min] gave dibenzothiophene **20a** as a white solid (0.62 g, 88%), mp 96–99 °C (from ethanol), mixed mp 96–98 °C (lit.,[29] 98–100 °C) δ_C 139.21 (quat), 135.32 (quat), 126.45, 124.11, 122.55 and 121.34, compatible with published data.[9]

FVP of 3-pyridyl 2-(allyloxy)benzoate 30

FVP of **30** [0.831 g (4 mmol), T_i 150 °C, T_f 650 °C, P 0.001 Torr, t 60 min] gave, after work-up a 3 : 1 mixture of isomers (0.37 g, 55%), which can be distinguished by ^{13}C NMR (DEPT) spectroscopy: benzofuro[3,2-*b*]pyridine **31** (major); δ_C 144.99, 129.01, 123.39, 121.06, 120.95, 118.39 and 111.95 (consistent with reported data[17]); benzofuro[2,3-*c*]pyridine **32** (minor); δ_C 142.77, 134.20, 129.74, 123.22, 121.88, 114.97 and 112.25 (consistent with reported data[17]).

The picrate mixture was made as follows:[30] picric acid (wet with ethanol) (0.6 g, 2.6 mmol) was dissolved in acetone (0.6 cm^3) and added to the isomeric mixture (0.21 g, 1.2 mmol). The addition of ether (6 cm^3) completed the crystallisation of the products (0.74 g, 72%). The picrate of the minor isomer **32** was partially purified by recrystallisation (0.26 g, 25%), mp 204–207 °C (from nitromethane) (lit.,[18] 240–241 °C). In solution one drop of trifluoroacetic acid was added to maintain the protonation δ_H (d_6-DMSO) 9.63 (1H, s), 8.92–8.81 (2H, m), 8.58 (2H, s), 8.54 (1H, m), 8.04 (1H, m), 7.95 (1H, m) and 7.65 (1H, m); the singlet at δ_H 9.63 defines the regiochemistry of this product.

FVP of 1-naphthyl 2-(allyloxy)benzoate 34

GC analysis of the pyrolysate from FVP of **34** [0.425 g (1.4 mmol), T_i 150 °C, T_f 650 °C, P 0.005 Torr, t 60 min] suggests the presence of two isomers and a trace of 1-naphthol. After work-up, the pyrolysate was chromatographed on a silica dry-flash column, however the two isomers were not separated (combined yield 0.13 g, 43%). The ^{13}C NMR spectrum of the mixture indicated the presence of benzo[*k*,*l*]xanthene **36** δ_C(DEPT) 129.67, 127.17 (2 CH), 125.52, 123.23, 122.66, 119.64, 117.07, 113.97 and 107.78 (data within 0.06 ppm of those reported[20]). The remaining signals were tentatively assigned to benzo[*b*]naphtho[2,1-*d*]furan **35**, whose ^{13}C NMR spectrum has not been previously reported δ_C(DEPT) 128.31, 126.35, 126.04, 125.95, 122.81, 120.77, 120.17, 118.35 and 111.70 (one CH overlapping).

FVP of 2-naphthyl 2-(allyloxy)benzoate 37

FVP of **37** [0.052 g (0.17 mmol), T_i 130 °C, T_f 650 °C, P 0.005 Torr, t 60 min] showed a trace of β-naphthol (detected by GC) however the ^{13}C NMR (DEPT) spectrum indicates that a major and a minor isomer are present, δ_C (major isomer) 129.08, 128.43, 127.02, 125.74, 124.26, 123.33, 123.03, 121.81, 112.58 and 111.75 (consistent with a spectrum of γ-brazan **38** prepared by a different method[31]); δ_C (minor isomer) 128.20 (2C), 127.35, 125.72, 124.15, 122.82, 121.13, 118.97, 111.41 and 106.77, consistent with the spectrum of isolated β-brazan **39** reported below.

On a preparative scale [0.448 g (1.5 mmol), T_i 130 °C, T_f 650 °C, P 0.001 Torr, t 60 min], work-up afforded both isomers (0.30 g, 91%) and the minor isomer was isolated by recrystallisation to constant melting point and thus identified as β-brazan **39** (0.061 g, 19%), mp 201–202 °C (from ethanol–acetic acid) (lit.,[32] 209.2–209.8 °C); δ_C 157.55 (quat), 154.76 (quat), 132.96 (quat), 130.08 (quat), 128.22 (2C), 127.65, 125.66, 125.33 (quat), 124.17, 123.81 (quat), 122.63, 121.15, 119.00, 111.44 and 106.80, consistent with published data.[33]

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Notes and references

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