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Gas Phase Generation and Cyclisation Reactions of Some *o*-Substituted Phenyl Radicals

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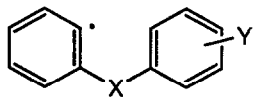
Abstract: Flash vacuum pyrolysis of the allyl esters 2 (X=O,S, CH_2, CO) at 900°C (10^{-2} Torr) gives dibenzofurans, dibenzothiophenes, fluorenes, and fluorenones respectively as the major products. The mechanism involves the phenyl radical intermediates 1 which equilibrate by intramolecular hydrogen transfer via six-membered transition states, prior to cyclisation.

The chemistry of aryl radicals in the gas phase under short contact time conditions has been little explored.[1] In contrast to the behaviour of benzyl radicals, which give high yields of intermolecular coupling products when generated by flash vacuum pyrolysis (FVP),[2] aryl radicals apparently undergo ill-defined hydrogen-abstraction processes, and only poor yields of biphenyls are obtained.[1] As a continuation of our work on intramolecular gas phase radical reactions,[3] we report here our results on the generation and properties of the *o*-substituted aryl radicals 1. In most cases, cyclisation products are obtained, though hydrogen-transfer processes are involved in the mechanism of the reactions.

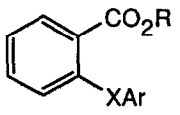


1

a X=O
b X=S
c X=NR
d X=CH_2
e X=CO

Dedicated to Professor C.W. Rees, with the greatest personal and professional respect

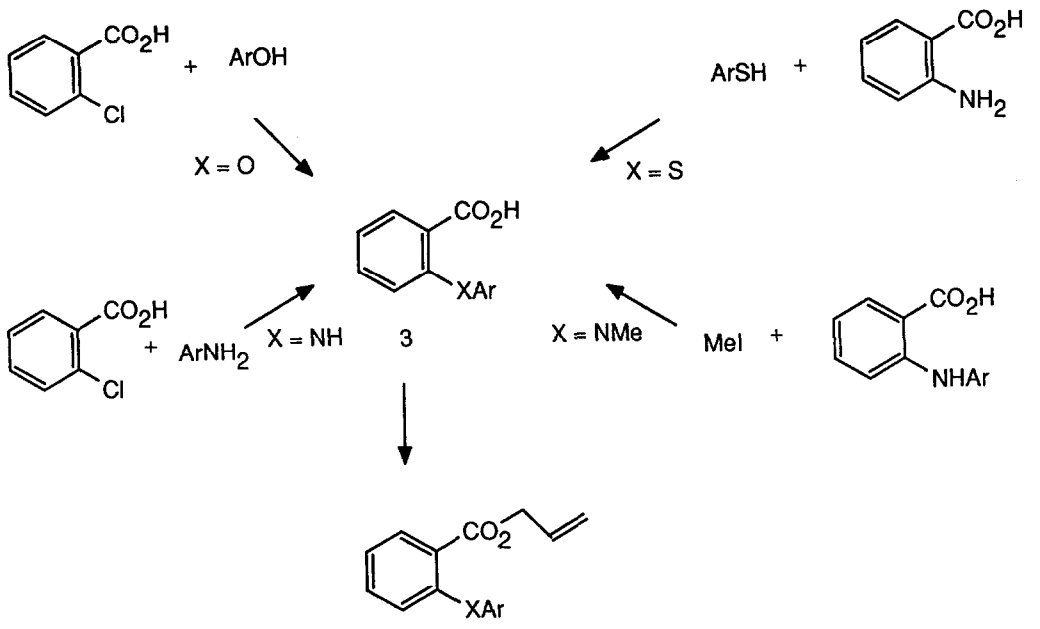
Potential gas-phase precursors of aryl radicals include[1] sulphones,[4], nitro-compounds,[5] and allyl esters.[6] For this study we chose the aryl



2 R=allyl
3 R=H

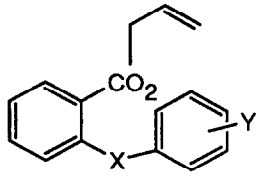
a X=O
b X=S
c X=NR
d X=CH_2
e X=CO

esters 2, because the corresponding acids 3 are readily available (Scheme 1 and Table 1). The allyl esters were obtained directly by reaction of the carboxylic acids 3 with allyl bromide in dimethylformamide in the presence of potassium carbonate.[3]



Scheme 1

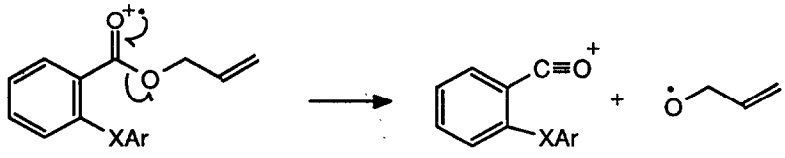
Table 1 Allyl esters



Ester	X	Y	Yield/%	Carboxylic Acid Precursor Reference
4	O	H	80	a
5	O	*p*-Me	63	7
6	O	*p*-COMe	44	8
7	O	*p*-OMe	73	8
8	O	*p*-Cl	81	9
9	O	*m*-Me	82	7
10	O	m-COMe	44	b
11	O	*o*-Me	82	7
12	S	H	75	10
13	S	*p*-Me	48	11
14	S	*p*-Cl	20	12
15	S	*m*-Me	52	b
16	S	*o*-Me	57	b
17	NH	*p*-Me	90	13
18	NMe	H	89	14
19	NMe	*p*-Me	93	b
20	CH_2	H	88	a
21	CO	H	97	a

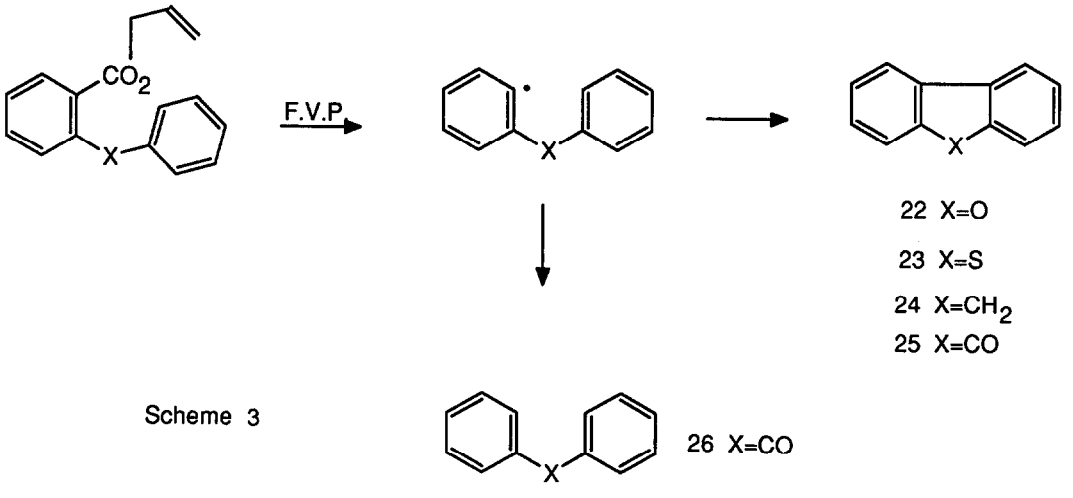
a Commercially available; b New compound - see Experimental section

The n.m.r. spectra of these esters are unexceptional (see Experimental section): the aliphatic CH_2 of the allyl function showed a characteristic ^{13}C n.m.r. signal at δ_C 65-66, whereas the corresponding peak of aryl allyl ethers occurs at δ_C 68-69.[3] In their mass spectra, all the allyl esters show significant molecular ions, and in the absence of special effects due to the substituents, loss of the entire *O*-allyl fragment is often a major breakdown. This suggests that ionisation under electron-impact conditions takes place at the ester carbonyl group (Scheme 2).



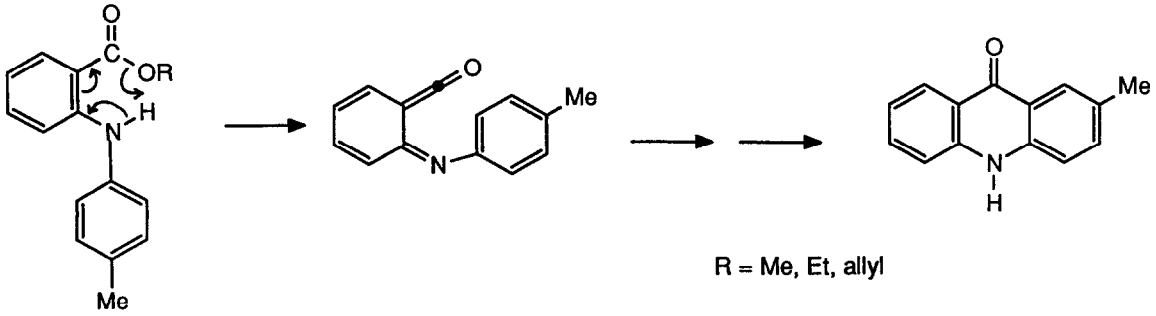
Scheme 2

Surprisingly, FVP of allyl esters in our apparatus requires very much higher furnace temperatures for complete reaction (900°C) than the corresponding allyl ethers (650°C), though the reasons for this behaviour are not clear. Despite these vigorous conditions, reasonable yields of dibenzofuran (22; 49% from 4), dibenzothiophene (23; 63% from 12) and fluorene (24; 40% from 20) were obtained after purification by crystallisation or chromatography (Scheme 3). No other significant products were identified, and it is clear that in these cases cyclisation of the intermediate aryl radical dominates any intermolecular hydrogen-capture process. The formation of the final product may occur by simple loss of a hydrogen atom from the cyclised radical, though an abstraction mechanism cannot be rigorously excluded. Fluorenone 25 obtained by pyrolysis of 21 was contaminated with benzophenone 26, and so the susceptibility of the radical towards external hydrogen capture is dependent to some extent on the nature of adjacent (hetero)-atoms (X).



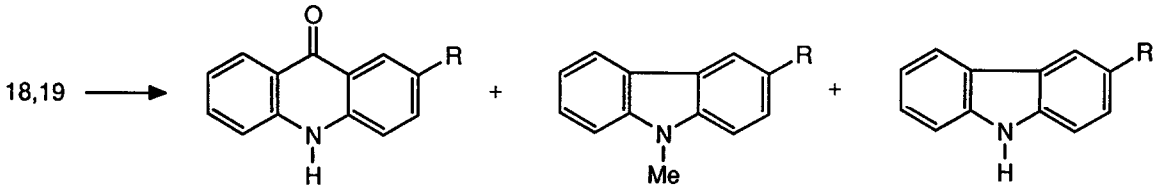
Scheme 3

Pyrolyses of the anthranilic esters 17-19 were more disappointing. It is known that methyl or ethyl *N*-arylanthranilates give acridones on pyrolysis at relatively modest temperatures,[15] (Scheme 4) and indeed this mode of reaction rather than radical formation was also observed for the allyl ester 17. The *N*-alkyl derivatives 18 and 19, however, cannot



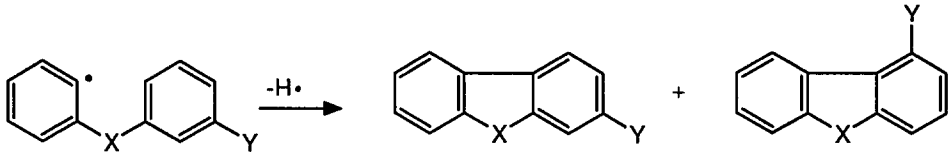
Scheme 4

formally react in this way, but nevertheless a mixture of the appropriate acridone, the *N*-methylcarbazole, and the *N*-unsubstituted carbazole was obtained in both cases (Scheme 5). Control experiments showed that both *N*-methylcarbazole and *N*-methylacridone are substantially demethylated under the reaction conditions (900°, 10^{-2} Torr), and because of these complications this route to carbazole derivatives was not further investigated.



Scheme 5

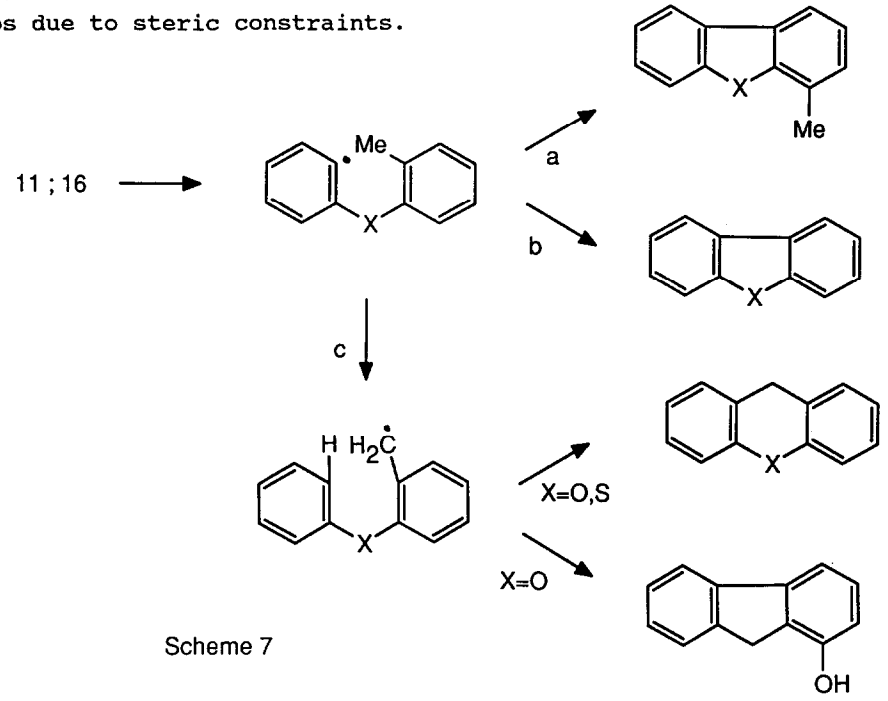
2-Substituted dibenzofurans and dibenzothiophenes were obtained in comparable yields to those of the parent compounds, by pyrolysis of the *p*-substituted derivatives 5, 6, 8, 13 and 14 (see Experimental section). The substituted dibenzofurans were always contaminated with a small amount (<10%) of dibenzofuran itself, which was removed by chromatography or crystallisation. No significant products were obtained from the *p*-methoxy derivative 7, owing to the instability of that functional group at high temperatures. Pyrolysis of the *m*-substituted precursors 9, 10 and 15, gave almost equal quantities of the two possible isomers (Scheme 6), which could not generally be separated. Some selectivity has been observed in related iminyl radical cyclisations,[16] and it is possible that the much higher temperatures used in this study may lead to the poor discrimination.



Scheme 6

A number of possible product-forming routes are open to the radicals derived from the *o*-tolyl derivatives 11 and 16 (Scheme 7). Direct cyclisation with loss of a hydrogen atom (route a) or a methyl radical (*cf* ref 16) (route b) gives 4-substituted or unsubstituted dibenzoheterocycles respectively. Alternatively, possible hydrogen abstraction from the

methyl group allows entry to the *o*-phenoxy- or *o*-thiophenoxy-benzyl radical energy surfaces (route c), from which the major products are, respectively, xanthene and 1-hydroxyfluorene[3] or thioxanthene.[17] In the event, both precursors **11** and **16** gave products derived from routes a and c only. These results show that phenyl radicals are capable of intramolecular hydrogen atom transfer *via* a 7-membered transition state, but that *ipso*-substitution with ejection of a methyl radical is disfavoured, perhaps due to steric constraints.



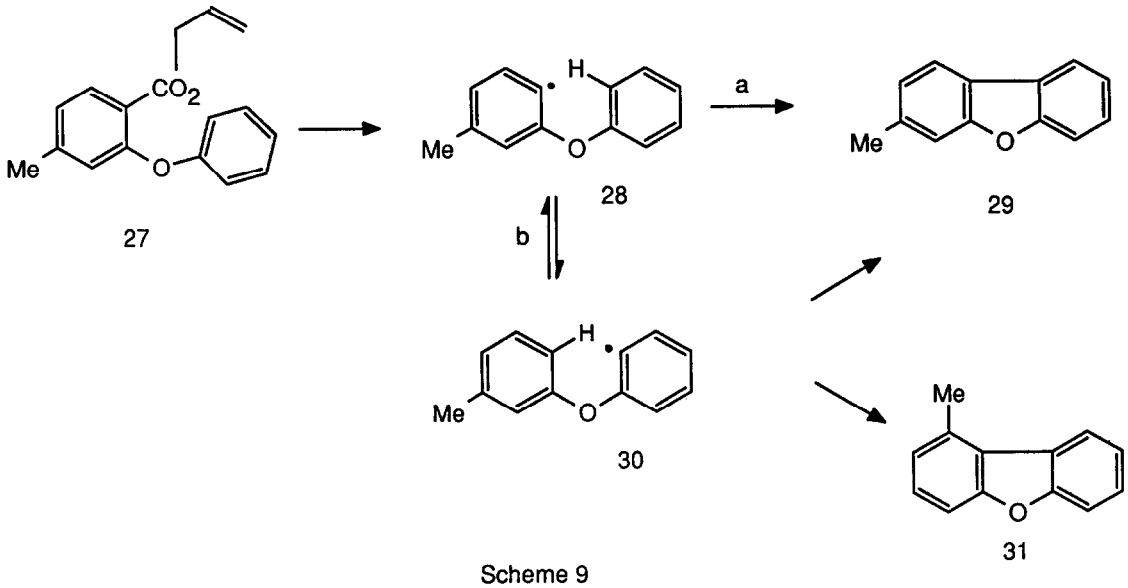
Scheme 7

Because of the hydrogen-transfer derived products obtained in the previous experiments, the possibility of direct equilibration of the aryl radicals (Scheme 8) was also studied. The symmetry of the intermediates was removed by the use of the methyl labelled precursor **27** which was made in the usual way from 2-chloro-4-methylbenzoic acid.[18] Thus, direct

Scheme 8

cyclisation of the initial radical **28** (Scheme 9) leads exclusively to 3-methylbenzofuran **29** (route a). Alternatively intramolecular hydrogen transfer, *via* a 6-membered transition state generates the isomeric radical **30** (route b) which has already been shown to give equal amounts of 3- and 1-methylbenzofuran **29** and **31** (*cf* Scheme 6). By experiment, both 3- and

1-methylbenzofuran isomers were indeed obtained by pyrolysis of 27 and their relative proportions (measured from integration of their characteristic methyl resonances at δ_H 2.55 and 2.81 respectively) at various temperatures are shown in Table 2. The observed ratio of 3:1 is independent of temperature and is consistent with complete equilibration of 28 and 30 prior to cyclisation.



Scheme 9

Table 2 Amounts of 1- and 3-methylbenzofuran from pyrolysis of 27

Temperature/°C	29/%	31/%
850	74	26
900	75	25
950	75	25
1000	75	25

In conclusion, we have shown that in the absence of competing reactions of substituents, cyclisation reactions of aryl radicals to 5-membered ring products can compete effectively with *intermolecular* hydrogen abstraction processes, though equilibration *via intramolecular* hydrogen transfer is involved in the reaction mechanism. The synthetic potential of the cyclisation is limited both by this process, and by the

harsh conditions which we employed to generate the radicals (see, however, ref 19).

Experimental

^{1}H N.m.r. spectra were recorded at 80 or 200 MHz and ^{13}C n.m.r. spectra at 50 MHz, for solutions in [^{2}H]chloroform, unless otherwise stated.

Preparation of Substituted 2-Phenoxybenzoic acids. - The appropriate phenol (65 mmol) was reacted with the potassium salt of *o*-chlorobenzoic acid (25 mmol) and copper bronze (0.1 g), in methanolic sodium methoxide [from sodium (25 mmol) in methanol (15 ml)].[20] After work-up the required product was purified by recrystallisation. The following compounds were prepared by this method: 2-(4-methylphenoxy)benzoic acid (3.05 g, 53%), m.p. 123-127°C [from light petroleum (b.p. 80-100°C)] (lit.,[7] 118.5°C), δ_H 10.14 (1H, br.s), 8.06-8.18 (1H, dd), 6.78-7.55 (7H, m) and 2.34 (3H, s); δ_C 166.20 (C=O), 157.56 (q), 152.05(q), 135.16(q), 134.61, 133.30, 130.62, 123.21, 120.04, 117.18 and 20.66 (one quaternary signal is not apparent); 2-(4-acetylphenoxy)benzoic acid (2.85 g, 45%), m.p. 184-185°C [from methanol/water (70:30)] (lit.,[8] 182°C), δ_H ([$^2H_6$]DMSO): 7.75 (1H, d), 7.35-7.6 (2H, m), 7.20 (1H, d), 6.81-6.92 (4H, s), 6.79 (1H, s), and 3.68 (3H, s); δ_C ([$^2H_6$]DMSO): 195.43 (C=O), 166.11 (C=O), 162.08(q), 153.40(q), 134.08, 131.81, 131.37(q), 130.66, 125.50, 125.17(q), 122.77, 116.28 and 26.56: 2-(4-chlorophenoxy)benzoic acid (4.03 g, 65%), m.p. 110-111°C (from aqueous ethanol) (lit.,[9] 114-115°C), δ_H ([$^2H_6$]DMSO): 7.83 (1H, d), 7.27-7.69 (4H, m) and 6.78-7.19 (3H, m); δ_C ([$^2H_6$]DMSO): 166.25 (C=O), 156.68(q), 154.29(q), 133.72, 131.50, 129.63, 126.45(q), 124.75(q), 124.60, 121.56 and 118.96: 2-(4-methoxyphenoxy)benzoic acid (4.70 g, 78%), m.p. 140-141°C [from light petroleum/xylene (50:50)] (lit.,[8] 144°C), δ_H ([$^2H_6$]DMSO): 7.75 (1H, dd), 7.05-7.58 (3H, m), 6.79-6.91 (4H, s) and 3.63 (3H, s); δ_C ([$^2H_6$]DMSO): 166.87 (C=O), 156.33(q), 155.46(q), 150.29(q), 133.28, 132.94, 123.78(q), 123.00, 119.93, 119.16, 115.11 and 55.53: 2-(3-methylphenoxy)benzoic acid (3.00 g, 53%), m.p. 91-93°C [from methanol/water (80:20] (lit.,[7] 95°C), δ_H ([$^2H_6$]DMSO): 7.85 (1H, dd), 7.55 (1H, t), 7.03-7.34 (3H, m), 6.94 (1H, s), 6.64-6.85 (2H, m) and 2.27 (3H, s); δ_C ([$^2H_6$]DMSO): 167.65 (C=O), 157.28(q), 155.11(q), 140.32(q), 134.51, 133.01, 129.64, 120.50, 123.19, 120.26, 119.97(q), 118.31, 116.59 and 21.15: *2-(3-acetylphenoxy)benzoic acid* (2.82 g, 44%), m.p. 105-107°C ([from methanol/water (70:30)] (Found: C, 68.6; H, 4.55. $C_{15}H_{12}O_4.0.33H_2O$ requires C, 68.7; H, 4.85%) (consistently analyses with 0.33 mol water); δ_H ([$^2H_6$]DMSO): 7.85 (1H, dd), 7.26-7.71 (5H, m), 7.00-7.19 (2H, m) and 2.50 (3H, s); δ_C ([$^2H_6$]DMSO): 184.45 (C=O), 166.34 (C=O), 158.14(q), 154.23(q), 138.56(q), 133.82, 131.61, 130.38, 124.92(q), 124.77, 122.97, 122.09, 121.75, 115.86 and 26.83: *m/z* 256 (M^+, 44%), 241(49), 152(20), 139(29) and 136(100): 2-(2-methylphenoxy)benzoic acid (4.08 g, 72%), m.p. 133.5-134°C [from benzene/light petroleum (50:50)] (lit.,[7] 133.5°C), δ_H 9.74 (1H, br.s), 8.16 (1H, dd), 6.91-7.53 (6H, m), 6.69 (1H, d) and 2.23 (3H, s); δ_C 167.35 (C=O), 157.44(q), 152.37(q), 134.58, 133.26, 131.75, 130.19(q), 127.45, 125.50, 122.66, 120.48, 118.85(q), 116.16 and 15.88: *2-phenoxy-4-methylbenzoic acid* (55%) (made from 2-chloro-4-methylbenzoic acid[18]), m.p. 130-133°C (from acetonitrile) (Found: C, 73.7; H, 5.25. $C_{14}H_{12}O_3$ requires C, 73.7; H, 5.25%); δ_H 8.03 (1H, s), 7.38 (2H, m), 7.20 (1H, m), 7.02 (3H, m), 6.66 (1H, s) and 2.29 (3H, s); δ_C 166.64 (C=O), 157.00(q), 155.11(q), 145.98(q), 133.09, 129.94, 124.70, 124.47, 119.62, 118.64 and 21.38 (one quaternary signal not apparent); *m/z* 228 (M^+, 39%) and 135(100).

Preparation of Allyl 2-phenoxybenzoates. - The appropriate benzoic acid (0.01 mol) was reacted with allyl bromide (0.02 mol) in dimethylformamide (25 ml) containing potassium carbonate (0.02 mol) as previously described.[3] The reaction mixture was stirred overnight at room temperature and the product was purified by distillation. The following compounds were prepared by this method: *allyl 2-phenoxybenzoate* (1.90 g, 80%), b.p. 134-136°C (0.4 Torr) (Found: C, 75.7; H, 5.55.

$C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5%); δ_H 7.95 (1H, dd), 7.10-7.54 (5H, m), 6.85- 7.03 (3H, m), 5.86 (1H, m), 5.07-5.43 (2H, m) and 4.70 (2H, d); δ_C 165.18 (C=O), 157.48(q), 155.95(q), 133.39, 131.83, 131.69, 129.50, 123.33, 123.19(q), 122.84, 120.78, 117.91 and 65.44 (two signals co-incidental at δ117.91); *m/z* 254 (M^+, 45%), 197(100) and 115(21): *allyl 2-(4-methylphenoxy)benzoate* (1.84 g, 63%), b.p. 141-143°C (0.4 Torr) (Found: C, 76.5; H, 6.0. $C_{17}H_{16}O_3$ requires C, 76.1; H, 5.95%); δ_H 7.94 (1H, dd), 7.38 (1H, td), 6.81-7.21 (6H, m), 5.90 (1H, m), 5.09-5.46 (2H, m), 4.74 (2H, m) and 2.31 (3H, s); δ_C 165.37 (C=O), 156.68(q), 154.98(q), 133.33, 132.61(q), 131.97, 131.64, 130.06, 122.85, 120.02, 118.30, 117.86, 65.45 and 20.50 (one quaternary signal not apparent); *m/z* 268 (M^+, 68%), 211(65), 192(27), 151(30), 155(100), 121(49) and 120(46): *allyl 2-(4-acetylphenoxy)benzoate* (1.26 g, 44%), b.p. 139-141°C (0.2 Torr) (Found: C, 73.4; H, 5.5. $C_{18}H_{16}O_4$ requires C, 73.0; H, 5.4%); δ_H 7.81-8.04 (3H, m), 6.83-7.56 (5H, m), 5.50-6.25 (1H, m), 5.06-5.36 (2H, m), 4.61 (2H, m) and 2.53 (3H, s); δ_C 196.18 (C=O), 164.45 (C=O), 162.09(q), 154.14(q), 133.72, 131.96, 131.61, 130.29, 124.81, 124.00(q), 122.41, 118.03, 116.23, 65.47 and 26.04 (one quaternary signal not apparent); *m/z* 296 (M^+, 50%), 281(100) and 197(34): *allyl 2-(4-chlorophenoxy)benzoate* (2.34 g, 81%), b.p. 150-153°C (0.1 Torr) (Found: C, 67.0; H, 4.5. $C_{16}H_{13}ClO_3$ requires C, 65.55; H, 4.5%); δ_H 7.93 (1H, dd), 7.25-7.56 (4H, m), 6.74-7.14 (3H, m), 5.84 (1H, m), 5.07-5.38 (2H, m) and 4.68 (2H, m); δ_C 164.84 (C=O), 156.34(q), 155.41(q), 133.55, 131.83, 131.75, 129.44, 127.76(q), 123.91, 123.39(q), 121.09, 118.86, 118.03 and 65.50; *m/z* 290 (27%), 288 (M^+, 75), 246(25), 231(100) and 197(40): *allyl 2-(4-methoxyphenoxy)benzoate* (2.08 g, 73%), b.p. 107-109°C (0.3 Torr) (Found: C, 71.6; H, 5.65. $C_{17}H_{16}O_4$ requires C, 71.85; H, 5.65%); δ_H 7.81-7.93 (1H, m), 6.71-7.46 (7H, m), 5.75-6.20 (1H, m), 5.09-5.43 (2H, m), 4.74 (2H, m) and 3.71 (3H, s); δ_C 165.38 (C=O), 157.37(q), 155.68(q), 150.34(q), 133.23, 131.94, 131.54, 122.36, 122.17(q), 120.02, 118.94, 117.81, 114.69, 65.39 and 55.47; *m/z* 284 (M^+, 2%), 192(20) and 135(100): *allyl 2-(3-methylphenoxy)benzoate* (2.21 g, 82%), b.p. 130-133°C (0.3 Torr) (Found: C, 76.3; H, 5.95. $C_{17}H_{16}O_3$ requires C, 76.1; H, 5.95%); δ_H 7.94 (1H, dd), 6.72-7.56 (7H, m), 5.83 (1H, m), 5.10-5.43 (2H, m), 4.73 (2H, d) and 2.31 (3H, s); δ_C 165.23 (C=O), 157.38(q), 156.16(q), 139.68(q), 133.32, 131.93, 131.64, 129.21, 128.19(q), 123.73, 123.14, 120.65, 118.74, 117.82, 115.03, 65.42 and 21.28; *m/z* 268 (M^+, 35%), 212(88), 211(82), 197(23), 180(35), 151(41) and 105(100): *allyl 2-(3-acetylphenoxy)benzoate* (1.56 g, 56%), b.p. 142°C (0.4 Torr); a colourless crystalline solid was obtained, m.p. 32-34°C (from light petroleum) (Found: C, 72.9; H, 5.35. $C_{18}H_{16}O_4$ requires C, 72.8; H, 5.4%); δ_H 7.92 (1H, dd), 7.60 (1H, d), 7.21-7.49 (3H, m), 7.05-7.18 (2H, d), 6.96 (1H, d), 5.80 (1H, m), 5.19 (2H, m), 4.64 (2H, m) and 2.49 (3H, s); δ_C 194.71 (C=O), 164.83 (C=O), 158.12(q), 155.21(q), 138.71(q), 133.69, 131.97, 131.77, 129.72, 124.15, 123.51(q), 122.66, 122.16, 121.34, 118.06, 116.94, 65.52 and 26.51; *m/z* 296 (M^+, 59%), 239(50), 221(43), 211(32), 197(68), 161(84), 135(64) and 121(100): *allyl 2-(2-methylphenoxy)benzoate* (2.20 g, 82%), b.p. 111-113°C (0.4 Torr) (Found: C, 75.7; H, 6.0. $C_{17}H_{16}O_3$ requires C, 76.1; H, 5.95%); δ_H 7.96 (1H, dd), 7.02-7.52 (5H, m), 6.75-6.98 (2H, m), 5.93 (1H, m), 5.12-5.49 (2H, m), 4.78 (2H, m) and 2.30 (3H, s); δ_C 165.64 (C=O), 156.70(q), 154.61(q), 133.28, 132.00, 131.74, 131.27, 129.28(q), 126.92, 123.66, 122.31, 121.98(q), 118.50, 118.37, 117.84, 65.40 and 15.99; *m/z* 268 (M^+, 85%), 211(62), 197(23), 191(31), 183(65), 162(61), 139(88) and 135(100): *allyl 2-phenoxy-4-methylbenzoate* (69%), b.p. 141-143°C (0.2 Torr) (Found: C, 75.9; H, 6.0. $C_{17}H_{16}O_3$ requires C, 76.1; H, 5.95%); δ_H 7.87 (1H, d), 7.30 (2H, m), 6.92-7.09 (4H, m), 6.81 (1H, s), 5.85 (1H, m), 5.13-5.35 (2H, m), 4.70 (2H, m) and 2.31 (3H, s); δ_C 165.01 (C=O), 157.77(q), 155.96(q), 144.58(q), 132.06, 131.76, 129.43, 124.36, 122.60, 121.54, 120.45(q), 117.74, 117.62, 65.19 and 21.33; *m/z* 268 (M^+, 53%), 211(100), 175(29) and 119(29).

Preparation of Substituted 2-Thiophenoxybenzoic acids. - The appropriate thiophenol (0.09 mol) was reacted with the diazonium salt of anthranilic acid in sodium hydroxide solution.[10] After work-up the required product was washed with light petroleum then purified by

sublimation or recrystallisation. The following compounds were prepared by this method: 2-thiophenoxybenzoic acid (4.93 g, 50%), m.p. 159-160°C (from methanol) (lit.,[10] 160°C), δ_H 9.80 (1H, br.s), 8.13 (1H, d), 7.56-7.71 (2H, m), 7.41-7.47 (3H, m), 7.10-7.32 (2H, m) and 6.82 (1H, d): 2-(4-methylthiophenoxy)benzoic acid (4.61 g, 44%), m.p. 210-212°C (from methanol) (lit.,[11] 215-216°C), δ_H ([$^2H_6$]DMSO): 7.90 (1H, d), 7.13-7.44 (6H, m), 6.70 (1H, d), 3.36 (1H, br.s) and 2.36 (3H, s); 2-(4-chlorothiophenoxy)benzoic acid (5.92 g, 49%), m.p. 222-226°C (from aqueous ethanol) (lit, 239-242°C); δ_H ([$^2H_6$]DMSO); 7.90 (1H, d), 7.34-7.86 (5H, m), 7.25 (1H, m) and 6.76 (1H, d); δ_C ([$^2H_6$]DMSO); 167.25 (C=O), 140.18(q), 136.15, 133.95(q), 132.29, 131.74(q), 130.66, 129.86, 128.58(q), 127.53 and 125.12: *2-(3-methylthiophenoxy)benzoic acid* (5.9 g, 54%), purified by sublimation, 136-138°C (0.15 Torr), to leave the required product as a colourless crystalline solid, m.p. 174-176°C (from ethanol) (Found: C, 67.9; H, 5.0. $C_{14}H_{12}O_2S.0.25H_2O$ requires C, 67.6; H, 5.0%) (analyses consistently with 0.25 mol H_2O); δ_H 8.12 (1H, d), 7.25-7.40 (5H, m), 7.17 (1H, t), 6.82 (1H, d) and 2.37 (3H, s); δ_C ([$^2H_6$]DMSO); 167.28(C=O), 141.44(q), 139.39(q), 135.18, 132.06, 131.85, 130.63, 129.77, 129.66, 128.01(q), 127.06, 124.54 and 20.65 (one quaternary signal not apparent); *m/z* 244 (M^+, 100%), 184(28), 149(22) and 137(44): *2-(2-methylthiophenoxy)benzoic acid* (4.95 g, 48%), purified by sublimation, 138-140°C (0.2 Torr), to leave the required product as a colourless powdery solid, m.p. 171-173°C (from ethanol) (Found: C, 68.6; H, 4.75. $C_{14}H_{12}O_2S$ requires C, 68.85; H, 4.9%); δ_H ([$^2H_6$]DMSO): 7.94 (1H, d), 7.52 (1H, d), 7.37 (2H, m), 7.25-7.33 (2H, m), 7.16 (1H, m), 6.52 (1H, d) and 2.25 (3H, s); δ_C ([$^2H_6$]DMSO): 167.29 (C=O), 142.11(q), 140.90(q), 136.29, 132.20, 131.08, 130.98, 129.81, 127.62(q), 127.34, 125.85, 125.68(q), 124.34 and 19.94; *m/z* 244 (M^+, 100%), 226(24), 197(32), 193(45), 149(56), 137(23) and 91(59).

Preparation of Allyl 2-thiophenoxybenzoates. - The appropriate benzoic acid (5 mmol) was reacted with allyl bromide (10 mmol) in dimethylformamide (15 ml) containing potassium carbonate (10 mmol) as described above to give *allyl 2-thiophenoxybenzoate* (75%), b.p. 179-181°C (0.4 Torr) (Found: C, 71.6; H, 5.25. $C_{16}H_{14}O_2S$ requires C, 71.1; H, 5.15%); δ_H 7.97 (1H, m), 7.31-7.62 (5H, m), 7.07-7.25 (2H, m), 6.93 (1H, m), 6.04 (1H, m), 5.19-5.55 (2H, m) and 4.85 (2H, m); δ_C 165.91 (C=O), 143.09(q), 135.34, 132.55(q), 132.17, 132.02, 130.89, 129.58, 128.89, 127.43, 126.79(q), 124.20, 118.39 and 65.68; *m/z* 270 (M^+, 25%), 213(51), 184(37), 146(35), 138(31), 118(90), 109(26) and 91(100): *allyl 2-(4-methylthiophenoxy)benzoate* (48%), purified by sublimation, 157-159°C (0.3 Torr) to give a yellow solid, m.p. 60-62°C (from methanol) (Found: C, 71.9; H, 5.75. $C_{17}H_{16}O_2S$ requires C, 71.85; H, 5.65%); δ_H 8.02 (1H, dd), 7.98 (2H, d), 7.04-7.46 (4H, m), 6.81 (1H, d), 6.05 (1H, m), 5.26-5.49 (2H, m), 4.85 (2H, m) and 2.38 (3H, s); δ_C 165.76 (C=O), 143.79(q), 139.12(q), 135.48, 131.99, 131.89, 130.80, 130.33, 128.62(q), 126.89, 126.31(q), 123.81, 118.23, 65.50 and 21.05; *m/z* 284 (M^+, 94%), 246(22), 227(100) and 184(44): *allyl 2-(4-chlorothiophenoxy)benzoate* (20%), purified by distillation, 160-162°C (0.1 Torr), to give the required product, on cooling, as a yellow solid, m.p. 58-61°C (from methanol) (Found: C, 63.1; H, 4.25; N, 0.45. $C_{16}H_{13}ClO_2S.0.1$ mol $HCON(CH_3)_2$ requires C, 62.8; H, 4.4; N, 0.45%) (consistently analyses with 0.1 mol dimethylformamide); δ_H 8.02 (1H, dd), 7.29-7.99 (4H, m), 7.09-7.27 (2H, m), 6.81 (1H, d), 6.04 (1H, m), 5.25-5.48 (2H, m) and 4.84 (2H, m); δ_C 165.76 (C=O), 142.07(q), 136.24, 135.12(q), 132.19, 131.92, 131.42(q), 130.91, 129.73, 129.27(q), 127.62, 124.57, 118.38 and 65.67; *m/z* 306 (37%), 304 (M^+, 100), 247(90), 184(46), 143(22) and 108(35): *allyl 2-(3-methylthiophenoxy)benzoate* (52%), b.p. 175-178°C (0.2 Torr) (Found: C, 71.7; H, 5.65. $C_{17}H_{16}O_2S$ requires C, 71.8; H, 5.6%); δ_H 8.04 (1H, m), 7.01-7.97 (6H, m), 6.83 (1H, m), 6.05 (1H, m), 5.20-5.56 (2H, m), 4.85 (2H, m) and 2.36 (3H, s); δ_C 165.73 (C=O), 143.16(q), 139.31(q), 135.71, 132.21, 132.09(q), 132.00, 131.93, 130.72, 129.61, 129.26, 127.32, 126.65(q), 123.97, 118.19, 65.49 and 20.97; *m/z* 284 (M^+, 83%), 246(38), 227(100) and 184(25): *allyl 2-(2-methylthiophenoxy)benzoate* (51%), b.p. 155-157°C (0.1 Torr) (Found: C, 72.0; H, 5.65. $C_{17}H_{16}O_2S$ requires C, 71.85; H, 5.65%); δ_H 7.98 (1H, m), 7.31-7.57 (1H, m), 7.21-7.27 (2H, m), 7.01-7.18 (3H, m), 6.59

(1H, m), 6.02 (1H, m), 5.16-5.51 (2H, m), 4.82 (2H, m) and 2.30 (3H, s); δ_C 165.72 (C=O), 142.79(q), 142.54(q), 136.65, 132.12, 131.99, 131.23(q), 131.00, 130.74, 129.53, 126.95, 126.45(q), 126.22, 123.78, 118.14, 65.44 and 20.29; *m/z* 284 (M^+, 74%), 246(63), 227(50), 197(37), 164(29), 149(29), 137(32) and 123(100).

N-Methyl-N-(p-tolyl)anthranilic acid. - A mixture of *N-p*-tolylanthranilic acid[13] (5 g, 0.023 mol), sodium hydroxide (1 g, 0.025 mol), methyl iodide (11 g, 0.080 mol) and water (30 ml) was reacted, as previously described for the unsubstituted system.[14] The methyl ester of the required product was isolated, after dry-flash chromatography, with chloroform/hexane (60:40) as eluant, and the ester was hydrolysed to the required acid by heating under reflux with sodium hydroxide solution (20%, 15 ml) for 1 h. After dilution with water (100 ml) and acidification, the reaction mixture was extracted with ether (3 x 50 ml), dried ($MgSO_4$) and the solvent was removed *in vacuo*. An oily solid was thus obtained which was recrystallised from light petroleum/ether (50:50) to give the required *product* as a yellow crystalline solid (0.673 g, 12%), m.p. 86-88°C (Found: C, 74.6; H, 6.25; N, 5.9. $C_{15}H_{16}NO_2$ requires C, 74.7; H, 6.2; N, 5.8%); δ_H 12.65 (1H, br.s), 8.31 (1H, dd), 7.44 (2H, m), 7.08 (3H, m), 6.81 (2H, m), 3.16 (3H, m) and 2.26 (3H, s); δ_C 166.06 (C=O), 150.98(q), 145.66(q), 134.67, 132.91(q), 132.26, 129.78, 127.64, 126.61, 125.95(q), 118.66, 42.05 and 20.38; *m/z* 241 (M^+, 100%), 196(29), 194(19), 181(33) and 180(29).

Preparation of Allyl 2-(4-methylphenylamino)benzoate and Related N-Methyl Derivatives. - The appropriate benzoic acid (3 mmol) was reacted with allyl bromide (6 mmol) in dimethylformamide (10 ml) containing potassium carbonate (6 mmol) as before, to give *allyl 2-(4-methylphenylamino)benzoate* (90%) (from *N-p*-tolylanthranilic acid[13]), b.p. 153-155°C (0.2 Torr) (Found: C, 76.6; H, 6.25; N, 5.3. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.4; N, 5.25%); δ_H 8.11 (1H, dd), 7.28 (6H, m), 7.25 (1H, br.s), 6.79 (1H, t), 6.16 (1H, m), 5.35-5.57 (2H, m), 4.91 (2H, m) and 2.44 (3H, s); δ_C 167.97 (C=O), 148.66(q), 137.84(q), 134.00, 133.36(q), 132.27, 131.44, 129.78, 123.15, 117.88, 116.42, 113.58, 111.18(q), 64.94 and 20.71; *m/z* 267 (M^+, 74%), 209(100), 180(22) and 167(17): *allyl N-methyl-N-phenylanthranilate* (89%) (from *N*-methyl-*N*-phenylanthranilic acid[14]), b.p. 168-170°C (0.2 Torr) (Found: M^+ 267.1247; $C_{17}H_{16}NO_2$ requires M^+ 267.1259); δ_H 7.87 (1H, m), 7.45-7.64 (1H, m), 7.06-7.36 (4H, m), 6.60-6.86 (3H, m), 5.69 (1H, m), 5.08-5.37 (2H, m), 4.52 (2H, m) and 3.31 (3H, s); δ_C 166.22 (C=O), 148.99(q), 147.87(q), 132.91, 131.89, 131.10, 129.59(q), 128.93, 128.56, 125.04, 117.87, 117.62, 113.93, 65.33 and 40.00; *m/z* 267 (M^+, 100%), 226(21), 210(25), 208(25), 179(50), 180(54), 177(21) and 105(21): *allyl N-methyl-N-(4-methylphenyl)-anthranilate* (93%), b.p. 177-179°C (0.3 Torr) (Found: C, 77.2; H, 6.7. $C_{18}H_{19}NO_2$ requires C, 76.9; H, 6.75%); δ_H 7.82 (1H, m), 7.49 (1H, m), 7.32 (1H, s), 6.95-7.24 (4H, m), 6.61 (1H, m), 5.80 (1H, m), 5.11-5.38 (2H, m), 4.51 (2H, m), 3.30 (3H, s) and 2.27 (3H, s); δ_C 166.76 (C=O), 164.78(q), 148.38(q), 147.01(q), 132.90, 132.03, 131.13, 129.28, 128.14, 127.33(q), 124.48, 118.06, 114.88, 32.54, 40.46 and 20.20; *m/z* 281 (M^+, 100%), 224(21), 222(27), 210(27), 195(27), 194(42) and 180(36).

Preparation of Allyl 2-benzylbenzoate. - Allyl bromide (2.28 g, 17 mmol) was added dropwise to a stirred mixture of 2-benzylbenzoic acid (2.11 g, 9.9 mmol) in dimethylformamide (20 ml) containing potassium carbonate (2.06 g, 17 mmol). After stirring overnight at room temperature, the crude product was isolated as before and purified by distillation to give a colourless *oil* (2.21 g, 88%), b.p. 138-140°C (0.1 Torr) (Found: C, 80.91 H, 6.6. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.35%); δ_H 7.99 (1H, d), 7.44 (1H, m), 7.09-7.35 (7H, m), 5.99 (1H, m), 5.26-5.43 (2H, m), 4.78 (2H, d) and 4.44 (2H, s); δ_C 167.09 (C=O), 142.12(q), 140.78(q), 132.10, 131.85, 131.45, 130.55, 129.97(q), 128.83, 128.19, 126.12, 125.81, 118.13, 65.36 and 39.44; *m/z* 252 (M^+, 8%), 211(100), 193(24), 194(44), 165(52) and 133(58).

Preparation of Allyl 2-benzoylbenzoate. - Prepared as above, using allyl bromide (0.02 mol) and 2-benzoylbenzoic acid (0.02 mol), in dimethylformamide (25 ml) containing potassium carbonate (0.02 mol), the crude isolated product was purified by distillation to give *allyl*

2-benzoylbenzoate as a colourless oil (2.60 g, 97%), b.p. 145-147°C (0.2 Torr) (Found: C, 77.0; H, 5.25. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.25%); δ_H 8.03 (1H, m), 7.22-7.77 (8H, m), 5.45-5.92 (1H, m), 4.97-5.25 (2H, m) and 4.41-4.50 (2H, m); δ_C 195.13 (C=O), 165.33 (C=O), 141.51(q), 136.98(q), 132.82, 132.19, 131.11, 129.90, 129.36, 129.16, 128.23, 127.56, 118.36 and 65.78 (one quaternary signal not apparent); *m/z* 266 (M^+, 13%), 210(88), 209(67), 105(79), 77(60) and 41(100).

Pyrolysis Experiments

The precursor was distilled or sublimed at 10^{-2}-10^{-3} Torr into a silica furnace tube (30 x 2.5 cm) held at 900°C, and the products were trapped in a 'U'-tube cooled by liquid nitrogen. Minor components of the pyrolysate were removed either by sublimation and recrystallisation or by chromatography followed by recrystallisation. The yields quoted are for the isolated and purified compound. The pyrolysis details are reported as [precursor, (amount pyrolysed), inlet temperature, pyrolysis time].

Benzofurans

The following dibenzofurans were made by pyrolysis: dibenzofuran (0.28 g, 49%), sublimed, 125-128°C (0.3 Torr), to give a yellow solid, m.p. 80-81°C (from methanol) (lit.,[21] 82-83°C), δ_H 7.92-8.05 (2H, m) and 7.26-7.72 (6H, m); δ_C 156.12(q), 126.92, 124.12(q), 122.49, 120.42 and 111.47; [from allyl 2-phenoxybenzoate (0.866 g, 3.41 mmol), 150-160°C, 1h]: 2-methyldibenzofuran (0.26 g, 38%), sublimed, 103-105°C (0.4 Torr), to give a yellow solid, m.p. 38-40°C (from ethanol) (lit.,[22] 44-45°C), δ_H 7.96 (1H, d), 7.78 (1H, s), 7.29-7.64 (5H, m) and 2.56 (3H, s); δ_C 156.36(q), 154.43(q), 132.03(q), 128.06, 126.99(q), 126.78, 124.13(q), 122.38, 120.48, 120.41, 111.50, 111.01 and 21.18; [from allyl 2-(4-methylphenoxy)benzoate (1.00 g, 3.73 mmol), 140-160°C, 90 min]; 2-acetyldibenzofuran (0.15 g, 35%) by column chromatography on alumina with ether/light petroleum (20:80) as eluant to give a white solid, m.p. 77-79°C (from methanol) (lit.,[23] 81°C), δ_H 8.54 (1H, s), 7.92-8.14 (2H, m), 7.32-7.61 (4H, m) and 2.68 (3H, s); δ_C 194.81 (C=O), 158.79(q), 156.75(q), 132.43(q), 127.83, 124.46(q), 123.63(q), 123.25, 121.44, 120.80, 111.81, 111.43 and 26.60 (two signals co-incidental at δ 127.83); [from allyl 2-(4-acetylphenoxy)benzoate (0.665 g, 2.25 mmol), 150-170°C, 160 min]; 2-chlorodibenzofuran (0.30 g, 56%) by column chromatography on alumina eluted with ether/light petroleum (50:50) to give a colourless solid, m.p. 100-101°C (from methanol) (lit.,[24] 100°C), δ_H 7.88-7.93 (2H, m) and 7.31-7.59 (5H, m); δ_C 156.68(q), 154.38(q), 128.10(q), 127.73, 127.00, 125.53(q), 123.23(q), 122.86, 120.66, 120.33, 112.50 and 111.72; [from allyl 2-(4-chlorophenoxy)benzoate (0.750 g, 2.60 mmol), 140-160°C, 105 min].

The following mixtures of dibenzofurans were obtained: 1-methyl- and 3-methyl-dibenzofuran [from allyl 2-(3-methylphenoxy)benzoate (0.645 g, 2.4 mmol) 90 min]. The mixture was partially separated using the different physical characteristics of the isomers, since the 3-methyl isomer crystallised on cooling the liquid 1-methyl isomer could be removed by pipette: 1-methyldibenzofuran (0.164 g, 37%) (contaminated with some 3-methyldibenzofuran), δ_H 8.05 (1H, d), 7.38-7.59 (5H, m), 7.17-7.26 (1H, t) and 2.86 (3H, s); δ_C 156.18(q), 156.08(q), 133.43(q), 126.79, 126.39, 124.83(q), 123.82, 122,48, 122.21, 111.38, 108.91 and 19.61 (one quaternary signal not apparent): 3-methyldibenzofuran (0.127 g, 29%) (contaminated with some 1-methyldibenzofuran), δ_H 7.96-8.00 (2H, m), 7.69 (2H, t), 7.39-7.59 (2H, m), 7.17-7.26 (1H, t) and 2.61 (3H, s); δ_C 156.60(q), 156.15(q), 137.48(q), 126.35, 124.31(q), 123.77, 122.40, 121.59(q), 120.11, 119.97, 111.79, 111.38 and 21.70. The assignment is in agreement with literature ^{1}H nmr data:[25] 1-acetyl- and 3-acetyldibenzofuran [from allyl 2-(3-acetylphenoxy)benzoate (0.634 g, 2.1 mmol) 3 h]: The components of the crude pyrolysate were separated by dry-flash chromatography, using methylene chloride/hexane (50:50) as eluant. The following components were separated: 1-acetyldibenzofuran[26] (0.027 g, 6%), b.p. 157-159°C (0.3 Torr) isolated as a pale yellow oil, δ_H 8.80 (1H, dd), 7.24-7.95 (6H, m) and 2.75 (3H, s); δ_C 199.04 (C=O), 156.98(q), 156.81(q), 133.60(q), 128.24, 126.35, 126.03, 124.84, 123.04(q), 122.94(q), 122.72, 115.82, 110.98 and 28.24; 3-acetyldibenzofuran (0.028 g, 6%), m.p. 145-147°C (from methanol) (lit.,[27] 144°C) isolated as a

colourless solid, δ_H 8.15 (1H, s), 7.93-8.05 (3H, m), 7.37-7.60 (3H, m) and 2.69 (3H, s); δ_C 196.97 (C=O), 157.56(q), 155.87(q), 136.15(q), 128.45, 123.23(q), 123.05, 122.97, 121.27, 120.25, 119.02(q), 111.88, 111.64 and 26.59.

Pyrolysis of allyl-2-(2-methylphenoxy)benzoate (0.907 g, 3.36 mmol) at 900°C and 1 x 10^{-3} Torr (inlet temperature 110-120°C) over 2 h gave 4-methyldibenzofuran, 1-hydroxyfluorene and xanthene. The entire pyrolysate was chromatographed on a column of alumina and eluted with ether (30%) in light petroleum to give 4-methyldibenzofuran (crude wt = 0.371 g) (contaminated with xanthene which could not be separated by further chromatography). The mixture was partly separated by distillation to give impure 4-methyldibenzofuran as a yellow oil (0.202 g, 33%), b.p. 106-108°C (0.2 Torr) [lit.,[22] 105°C (0.2 Torr)], δ_H 8.08 (1H, dd), 7.93 (1H, m), 7.80 (1H, m), 7.40-7.66 (4H, m) and 2.80 (3H, s); δ_C 155.96(q), 127.98, 126.76, 124.51(q), 123.51(q), 122.50, 122.42, 121.73(q), 120.56, 117.86, 111.50 and 15.09 (one quaternary signal not apparent). The ^{13}C n.m.r. spectrum also shows CH peaks at δ_C 128.76, 127.49, 122.79 and 116.32 which correspond to those of xanthene. The second component from the column was 1-hydroxyfluorene (crude wt = 0.062 g), which was purified by distillation at 146-148°C (0.4 Torr), to give the product as a yellow solid (0.045 g, 7%), m.p. 114-116°C (from water) (lit.,[28] 119-120°C), δ_H 7.79 (1H, d), 7.55 (1H, d), 7.23-7.47 (4H, m), 6.78 (1H, d), 5.10 (1H, br.s) and 3.84 (2H, s); δ_C 152.32(q), 143.90(q), 142.91(q), 141.71(q), 128.05, 126.81, 126.66, 125.04, 120.11, 113.61, 112.81 and 33.54 (one quaternary signal not apparent).

Pyrolysis of allyl 2-phenoxy-4-methylbenzoate (0.073 g, 0.27 mmol), at 900°C (5 x 10^{-3} torr) during 35 min gave 1-methyldibenzofuran (25%) and 3-methyldibenzofuran (75%) (relative yields are quoted from the ^1H n.m.r. spectrum of the crude pyrolysate). Similar experiments conducted at furnace temperatures of 850°C, 950°C (with and without silica wool packing of the furnace tube) and 1000°C gave identical results (±1%).

Dibenzothiophenes

The following dibenzothiophenes were made by pyrolysis: dibenzothiophene (0.201 g, 63%), m.p. 96-98°C (from ethanol), mixed m.p. 98-100°C (lit.,[21] 99.7°C); δ_H 8.18 (2H, m), 7.88 (2H, m) and 7.48 (4H, m); δ_C 139.34(q), 135.44(q), 126.49, 124.15, 122.61 and 121.37. The ^1H n.m.r. and ^{13}C n.m.r. spectra are identical with those of an authentic sample: δ_H 8.19 (2H, m), 7.90 (2H, m) and 7.50 (4H, m); δ_C 139.25(q), 135.34(q), 126.40, 124.06, 122.50 and 121.31; [from allyl 2-thiophenoxybenzoate (0.467 g, 1.73 mmol), 140-170°C, 95 min]: 2-methyldibenzothiophene (0.088 g, 56%), m.p. 80-83°C (from ethanol) (lit.,[29] 86°C), δ_H 8.13 (1H, m), 7.97 (1H, s), 7.85 (1H, m), 7.75 (1H, d), 7.45 (2H, m), 7.28 (1H, d) and 2.55 (3H, s); δ_C 139.79(q), 136.40(q), 135.66(q), 135.39(q), 133.98(q), 128.08, 126.38, 124.06, 122.69, 122.29, 121.65, 121.33 and 21.30; [from allyl 2-(4-methylthiophenoxy)benzoate (0.225 g, 0.79 mmol), 140-160°C, 85 min]: 2-chlorodibenzothiophene (0.046 g, 36%), m.p. 122-123°C (from ethanol) (lit.,[29] 125-126°C), δ_H 7.94-8.07 (2H, m), 7.60-7.88 (2H, m) and 7.30-7.53 (3H, m); δ_C 140.03(q), 137.36(q), 136.73(q), 134.38(q), 130.50(q), 127.12, 126.70, 124.41, 123.52, 122.69, 121.56 and 121.27; [from allyl 2-(4-chlorothiophenoxy)benzoate (0.180 g, 0.59 mmol), 130-160°C, 1.5 h].

The following mixture of dibenzothiophenes was obtained: 1-methyl- and 3-methyl-dibenzothiophene [from allyl 2-(3-methylthiophenoxy)benzoate 150-170°C, 75 min]. The entire pyrolysate was dissolved in methylene chloride and was washed with sodium carbonate solution (10%, 50 ml). The residue was purified by dry-flash chromatography eluting with methylene chloride/hexane (50:50) to leave a clean mixture of 1-methyldibenzothiophene and 3-methyldibenzothiophene in 1.2:1.0 ratio (0.234 g, 48%) which could not be further separated. The ^1H n.m.r. spectrum showed two methyl peaks at δ_H 2.99 and 2.59, the former due to the 1-methyl isomer (lit. chemical shift,[30] δ 2.82) and the latter due to the 3-methyl isomer (lit. chemical shift,[31] δ 2.45). The ^{13}C n.m.r. spectrum showed methyl peaks at δ_C 22.24 and 21.35, assigned to the 1-methyl and 3-methyl isomers respectively.

Pyrolysis of allyl 2-(2-methylthiophenoxy)benzoate (0.546 g, 1.92

mmol), at 900°C, (2 x 10^{-3} Torr) during 140 min gave 4-methyldibenzothiophene and thioxanthene in 2.4:1.0 ratio. The pyrolysate was purified by dry-flash chromatography using methylene chloride/hexane (30:70) as eluant to give 4-methyldibenzothiophene (0.221 g) separated from minor impurities as a yellow crystalline solid though it was still contaminated with thioxanthene. Attempts to separate the mixture by both distillation and recrystallisation proved unsuccessful. The 4-methyldibenzothiophene had δ_H 8.06-8.23 (2H, m), 7.79-7.99 (2H, m), 7.30-7.58 (3H, m) and 2.61 (3H, s); δ_C 139.49(q), 139.14(q), 135.29(q), 132.11(q), 127.16(q), 126.88, 126.41, 124.59, 124.21, 122.70, 121.66, 118.93 and 20.34. The ^{1}H n.m.r. spectrum also shows a single peak at δ_H 3.92 which is coincidental with the methylene signal in authentic thioxanthene. The ^{13}C n.m.r. spectrum also shows the following peaks which are coincidental with those observed for authentic thioxanthene[17] δ_C 136.10(q), 133.78(q), 127.80, 126.73, 126.52, 126.41 and 39.06.

Attempted Preparation of Carbazoles

Pyrolysis of allyl 2-(4-methylphenylamino)benzoate [(0.106 g, 0.397 mmol), 140-160°C, 650°C, 1 x 10^{-3} Torr, 45 min] gave a yellow solid around the entrance to the trap which was scraped out, recrystallised from ethanol, and identified as 2-methylacridone (0.02 g, 24%), m.p. 318-320°C (lit.,[32] 338°C), δ_H ([$^2H_6$]DMSO): 11.61 (1H, br.s), 8.16-8.28 (1H, m), 8.01 (1H, s), 7.30-7.72 (4H, m), 7.10-7.28 (1H, m) and 2.40 (3H, s); δ_C ([$^2H_6$]DMSO): 176.58 (C=O), 140.81(q), 139.00(q), 134.84, 133.14, 130.59(q), 126.00, 125.06, 120.66, 120.41(q), 117.24 and 20.54 (two signals co-incidental at 117.24 and two quaternary signals co-incidental at 120.41); *m/z* 209 (M^+, 86%), 181(36), 180(43), 122(43) and 105(100). The ^{13}C n.m.r. spectrum is identical with that of an authentic sample; δ_C ([$^2H_6$]DMSO): 176.62 (C=O), 140.86(q), 139.06(q), 134.96, 133.26, 130.13(q), 126.08, 125.14, 120.76, 120.44(q), 117.33 and 20.65 (co-incidental signals as above).

Pyrolysis of allyl *N*-methyl-*N*-phenylanthranilate [(0.192 g, 0.72 mmol), 120-125°C, 900°C, 5 x 10^{-3} Torr, 100 min] gave acridone, carbazole and *N*-methylcarbazole. The trap was washed with chloroform to remove the soluble components and an insoluble yellow solid was left in the trap. This solid was identified as acridone (0.045 g, 32%), m.p. 326-330°C (decomp), mixed m.p. 332-335°C (decomp) (lit.,[33] 344-346°C); δ_H ([$^2H_6$]DMSO): 8.23 (2H, d), 7.72 (2H, m), 7.54 (2H, d) and 7.25 (2H, t), identical with that of an authentic sample. The remainder of the pyrolysate was chromatographed by dry-flash chromatography, with chloroform/hexane (30:70) as eluant to give *N*-methylcarbazole (0.006 g, 5%), m.p. 80-82°C (lit.,[14] 88-89°C); δ_H 8.09 (2H, d), 7.37-7.48 (6H, m) and 3.85 (3H, s), identical with that of an authentic sample; and carbazole (0.031 g, 26%) as a colourless solid after sublimation [174-176°C (0.3 Torr)], m.p. 238-240°C, mixed m.p. 240-243°C (lit.,[34] 245°C), δ_H 8.00-8.14 (2H, m) and 7.11-7.49 (6H, m), identical with that of an authentic sample.

Pyrolysis of allyl *N*-methyl-*N*-(4-methylphenyl)anthranilate [0.240 g, (0.854 mmol), 130-150°C, 900°C, 1 x 10^{-3} Torr, 110 min] gave 2-methylacridone, 3-methylcarbazole and 3,9-dimethylcarbazole. Similar work-up to the previous experiment gave a chloroform-insoluble solid, which was identified as 2-methylacridone (0.052 g, 30%), m.p. 325-328°C (lit.,[32] 335°C), δ_H ([$^2H_6$]DMSO): 11.62 (1H, br.s), 8.23 (1H, d), 8.02 (1H, s), 7.30-7.74 (4H, m), 7.13-7.24 (1H, m) and 2.42 (3H, s), identical with that of an authentic sample. The remainder of the pyrolysate was chromatographed by dry-flash chromatography, with chloroform/hexane (30:70) as eluant, to give 3,9-dimethylcarbazole (0.009 g, 6%) (Found: M^+ 195.1052. $C_{14}H_{13}N$ requires M^+ 195.1048); δ_H 8.06 (1H, d), 7.89 (1H, s), 7.13-7.45 (5H, m), 3.82 (3H, s) and 2.54 (3H, s); *m/z* 195 (M^+, 100%), 194(52), 44(38) and 40(33) and 3-methylcarbazole (0.039 g, 26%), m.p. 200-201°C (from methanol) (lit.,[35] 199-203°C), δ_H 8.07 (1H, d), 7.87 (1H, s), 7.36-7.44 (2H, m), 7.17-7.33 (3H, m) and 2.53 (3H, s), identical with that of an authentic sample.

A control pyrolysis of *N*-methylacridone [0.053 g (0.253 mmol), 140-180°C, 900°C, 1 x 10^{-3} Torr, 1 h] gave acridone as the sole product: *N*-methylacridone was detected (δ_H ([$^2H_6$]DMSO): 11.69 (1H, br.s), 8.23

(2H, m), 7.73 (2H, m), 7.52 (2H, m) and 7.23 (2H, t)).

Similarly, a pyrolysis of *N*-methylcarbazole [0.030 g, (0.166 mmol),130-140°C, 900°C, 5 x 10^{-3} Torr, 20 min] gave carbazole contaminated with *ca* 20% *N*-methylcarbazole.

Fluorenes

Pyrolysis of allyl 2-benzylbenzoate (0.527 g, 2.1 mmol) at 900°C (1 x 10^{-3} Torr) during 105 min gave fluorene. The main component of the pyrolysate was isolated by dry-flash chromatography with methylene chloride/hexane (50:50) as eluant and recrystallised from ethanol, to give pure fluorene as a pale yellow crystalline solid (0.139 g, 40%), m.p. 110-112°C, mixed m.p. 111-112°C (lit.,[36] 115-116°C), δ_H 7.81 (2H, d), 7.56 (2H, d), 7.28-7.44 (4H, m) and 3.92 (2H, s).

Pyrolysis of allyl 2-benzoylbenzoate (0.630 g, 2.37 mmol) at 900°C (5 x 10^{-3} Torr) over a period of 2 h gave a mixture of fluorenone contaminated with *ca* 10% benzophenone. Attempts to separate this component by column chromatography on alumina, with light petroleum/ether (50:50) as eluant, proved unsuccessful as did repeated recrystallisation from ethanol. A pure sample of each compound was however obtained by preparative g.c., using a 10% SE30 column: fluorenone; δ_C (DEPT) 134.48, 128.90, 124.14 and 120.12, [identical with that of an authentic sample; δ_C (DEPT) 134.46, 128.85, 124.06 and 120.10]: benzophenone: δ_C (DEPT) 132.19, 129.86 and 128.08, [identical with that of an authentic sample: δ_C (DEPT) 132.16, 129.79 and 128.05].

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References

1. J.I.G. Cadogan, C.L. Hickson and H. McNab, *Tetrahedron*, 1986, 42, 2135.
2. W.S. Trahanovsky, C.C. Ong and J.A. Lawson, *J. Am. Chem. Soc.*, 1968, 90, 2839.
3. J.I.G. Cadogan, H.S. Hutchison and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1991, 385, and earlier papers cited therein.
4. F.A. Davis, T.W. Panunto, S.B. Awad, R.L. Billmers and T.G. Squires, *J. Org. Chem.*, 1984, 49, 1228.
5. For example, E.K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, 1967, 89, 724.
6. R.A. Marty and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 1971, 127.
7. F. Ullmann and M. Zlokasoff, *Ber. Deut. Chem. Ges.*, 1905, 38, 2111.
8. M. Oki and M. Hirota, *Bull. Chem. Soc., Jpn.*, 1964, 37, 209.
9. R.H. Thomson and A.G. Wylie, *J. Chem. Soc. (C)*, 1966, 321.
10. W.S. Weedon and H.W. Doughty, *Am. Chem. Journal*, 1905, 33, 393.
11. J. Goldberg, *Ber. Deut. Chem. Ges.*, 1904, 37, 4527.
12. J.O. Jilek, M. Rajsner, J. Pomykacek and M. Protiva, *Cesk. Farm.*, 1965, 14, 294.
13. F. Ullman, *Liebigs Ann. Chem.*, 1907, 355, 312.
14. H. Gilman and S.M. Spatz, *J. Org. Chem.*, 1952, 17, 860.
15. Y. Mao and V. Boekelheide, *J. Org. Chem.*, 1980, 45, 1547.

16. H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1941.
17. J.I.G. Cadogan, H.S. Hutchison and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2875.
18. A. Claus and N. Davidson, *J. Prakt. Chem.*, 1846, 39, 491.
19. M. Black, J.I.G. Cadogan and H. McNab, *J. Chem. Soc., Chem. Commun.*, 1990, 395.
20. F.E. Ray and C.F. Hull, *J. Org. Chem.*, 1949, 14, 394.
21. A. Luttringhaus and K. Hauschild, *Ber. Deut. Chem. Ges.*, 1940, 73, 145.
22. S. Trippett, *J. Chem. Soc.*, 1957, 419.
23. N.P. Buu-Hoi, L. Petit and D.C. Thang, *J. Org. Chem.*, 1964, 29, 762.
24. G.G. Choudhry, G. Sundström, F.M.W. van der Wielen and O. Hutzinger, *Chemosphere*, 1977, 6, 327.
25. D.E. Ames and A. Opalko, *Synthesis*, 1983, 234.
26. A.A. Pashchenko, A.G. Khaitbaeva and K.Y. Yuldashev, *Dokl. Akad. Nauk. Uzb. SSR*, 1978, 40.
27. J.N. Chatterjea, *J. Indian Chem. Soc.*, 1956, 33, 447.
28. E.K. Weisburger and J.H. Weisburger, *J. Org. Chem.*, 1953, 18, 864.
29. S. Oae, K. Iida, K. Shinhama and T. Takata, *Bull. Chem. Soc., Jpn.*, 1981, 54, 2374.
30. J. Ashby, M. Ayad and O. Meth-Cohn, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1744.
31. E. Campaigne and J. Ashby, *J. Heterocycl. Chem.*, 1969, 6, 517.
32. S. Kahn, *Liebigs Ann. Chem.*, 1894, 279, 270.
33. C.F.H. Allen and G.H.W. McKee, *Org. Synth. Coll. Vol. II*, 1943, 15.
34. S.H. Tucker, *J. Chem. Soc.*, 1926, 546.
35. B.M. Barclay and N. Campbell, *J. Chem. Soc.*, 1945, 530.
36. M. Orchin, *J. Am. Chem. Soc.*, 1945, 67, 499.