Gas-phase Reactions of 2-Benzyl- and 2-Benzoyl-phenoxyl Radicals, and of 2-Phenoxybenzyl Radicals: Examples of New Hydrogen-transfer Processes[1]

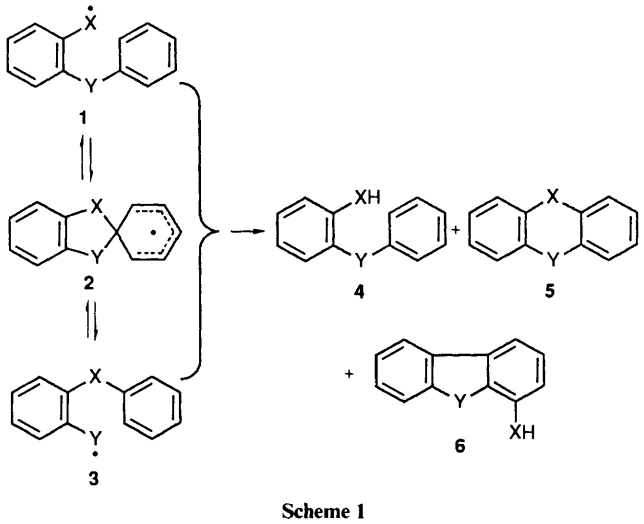
J. I. G. Cadogan,*[a] H. Susan Hutchison[b] and Hamish McNab*[b]
[a] *BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, UK*
[b] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*

Generation of the 2-benzylphenoxyl radical **23** or the 2-phenoxybenzyl radical **24** by flash vacuum pyrolysis of the ethers **8** or **9**, or the oxalate **19**, respectively, leads to fluoren-1-ol **22** together with 2-benzylphenol **7** and a low yield of xanthene **21**. Pyrolysis of the *para*-substituted derivatives **11** and **20** gives an analogous distribution of products, including two isomeric methylxanthenes **28** and **29** formed *via* the spirodienyl **27**. The reactions of the corresponding 2-benzoylphenoxyl radicals give information on the mechanisms of these processes. Thus the formation of the fluorenones **37** and **43** provides evidence for the hydrogen-abstraction mechanism (Scheme 4) of fluorene formation. Secondly, a detailed study of the ratios of xanthones **41** and **42** under a variety of pyrolysis conditions suggests that such 6-membered-ring products are formed by sigmatropic shifts in the spirodienyl, rather than direct cyclisation of the phenoxyl or benzoyl radicals.

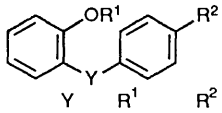
In recent papers we have explored the gas-phase generation, rearrangement, and cyclisation reactions of radicals of type **1**, and in particular the involvement of the spirodienyl **2** in these procsses.[2–4] Here we complete our current studies of these energy surfaces with full details[1] of the most complex case we have encountered, *viz.* that of the 2-benzylphenoxyl **1** (X = O, Y = CH_2) and 2-phenoxybenzyl **3** (X = O, Y = CH_2)[5] radical system together with the related case of 2-benzoylphenoxyl radicals. Particular features of interest include (i) the regiospecific formation of hydrogen-capture products **4**, (ii) the mechanism of formation of six-membered-ring products **5** including the extent of involvement of the spirodienyl **2**, the migratory aptitudes of X and Y, and the question of whether the final product is formed by sigmatropic migration directly from the spirodienyl **2** or by recyclisation of radical **1** or **3**, (iii) the mechanism of formation of the rearranged products **6**, and (iv) the effect of the heteroatoms X and Y in controlling the pathways which lead to the products **4**–**6** (Scheme 1).

Results and Discussion

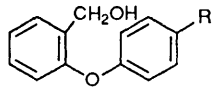
As before,[6] we have employed *O*-allyl derivatives and oxalates[5] as sources of the phenoxyl and benzyl radicals, respectively. In one case, an *O*-benzyl ether was also used. The precursor phenols **7** and **13** were commercially available: the *para*-methyl derivative **15** was made by Friedel–Crafts acylation of toluene with *o*-anisic acid chloride,[7] and the product was transformed into the diphenylmethane **10** by Wolff–Kischner reduction.[8] Alternatively, lithium aluminium deuteride–aluminium chloride reduction[9] of the 2-allyloxybenzophenone **14** gave the deuterium-labelled diphenylmethane **12**. The ethers **8**, **9**, **11**, **14** and **15** were obtained by treatment of the corresponding phenol with allyl or benzyl bromide in dimethylformamide (DMF) containing anhydrous potassium carbonate. The oxalates **19**[5] and **20** were made from the benzyl alcohols **17** and **18**, which themselves were obtained by lithium aluminium hydride reduction[10] of the corresponding benzoic acid.[11]



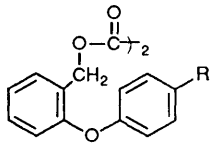
Scheme 1



	Y	R^1	R^2
7	CH_2	H	H
8	CH_2	allyl	H
9	CH_2	CH_2Ph	H
10	CH_2	H	Me
11	CH_2	allyl	Me
12	C^2H_2	allyl	H
13	CO	H	H
14	CO	allyl	H
15	CO	H	Me
16	CO	allyl	Me



17 R = H
18 R = Me

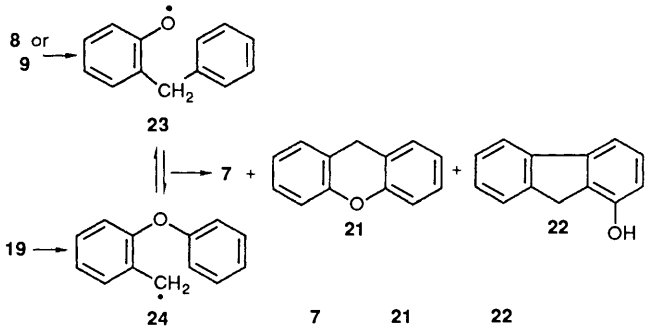


19 R = H
20 R = Me

The base peaks in the mass spectra of the 2-allyloxydiphenylmethanes **8** and **11** correspond to loss of the allyl fragment (M − 41). The corresponding benzophenones **14** and **16** also show this behaviour, but in addition intense peaks corresponding to $ArCO^+$ are observed, presumably owing to ionisation at the carbonyl group, followed by β-cleavage.[4]

Flash vacuum pyrolysis of the *O*-allyl compound **8**, the *O*-benzyl compound **9** or the oxalate **19** at 750 °C gave a similar range of products including the phenol **7**, xanthene **21** and fluoren-1-ol **22** (Scheme 2). The first two products were identified by comparison with authentic samples, and the structure of the third follows by analogy with the formation of related compounds reported in the preceding paper.[4] This latter assignment is fully supported by spectroscopic data, particularly

the mass spectrum [*m/z* 182 (M^+, 100%)], ^{1}H NMR spectrum [methylene protons at δ_H 3.84 (2 H) and hydroxy proton at δ_H 5.25], and ^{13}C NMR spectrum (7 methine, 5 quaternary and one methylene signal). The location of the hydroxy substituent was confirmed by the melting points of the fluorenol isomers {observed 118–120 °C [lit. (1-isomer[12]) 119–120 °C; (2-isomer[13]) 169–171 °C; (3-isomer[14]) 136–137 °C; (4-isomer[15]) 109–110 °C]}.



	7	21	22
From 8:	33%	2%	30%
From 9:	18%	13%	63%
From 19:	5%	9%	36%

Scheme 2

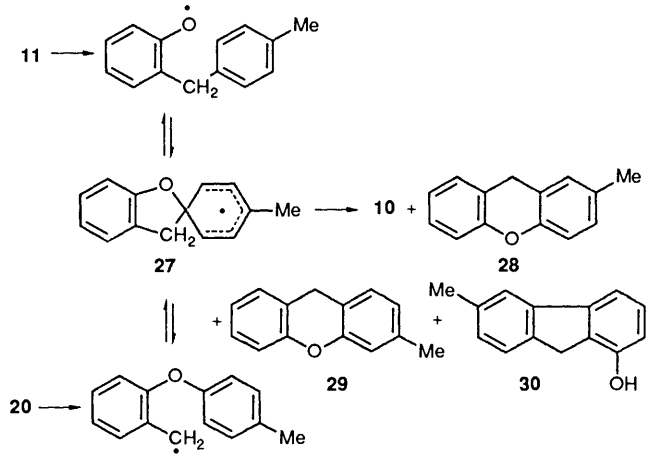
The formation of the phenol **7** from pyrolysis of the oxalate **19** is evidence for the interconversion of the benzyl **24** and phenoxyl **23** radicals, but the absence of the corresponding hydrogen-capture product **25** from the benzyl radical **24** in *any* of the pyrolysates is noteworthy. The high yield of the phenol **7** from the *O*-allyl compound **8** compared with that from the *O*-benzyl derivative **9** probably reflects a higher availability of hydrogen atoms from the co-formed allyl radical, compared with the co-formed benzyl radical (*cf.* ref 4). As expected, bibenzyl (39%) was also detected in the pyrolysate from compound **9**.

The low yield of the 'normal' cyclised product, xanthene **21** in all cases (2–13%) is in contrast with our earlier results[2–4] for related species.* Trahanovsky and Ong[5] also report a 13% yield of xanthene from the oxalate **19**, but did not identify any other products. However, all of these pyrolyses gave a consistently higher level of rearrangement product (fluoren-1-ol **22**) than we had observed previously,[2,4] and we have therefore used this series for a detailed study of the mechanism of this process (see below). The formation of the fluorenol **22** from the oxalate **19** is best rationalised by interconversion to the phenoxyl radical **23**: again, the product formed by analogous direct reaction of the benzyl radical (4-methyldibenzofuran **26**) is absent.

In view of the high yield of fluoren-1-ol **22** from the readily available *O*-benzyl ether **9** on a small scale, this reaction was briefly studied as a possible preparative method (see Experimental section). However, on a large (>1 g) scale the yield of base-soluble products had dropped to 54% of a 3:1 mixture of phenolic products **22** and **7**, which was only partially separable by recrystallisation. This aspect of the work was therefore not pursued further.

* Note, however, that corresponding products were also not obtained from 2-phenoxyaminyl radicals.[4]

In principle, the pyrolyses of the methyl-labelled derivatives **11** and **20** should allow determination of the migrating aptitude of the O and CH_2 groups in the spirodienyl **27** from the ratio of methylxanthenes **28** and **29** formed (Scheme 3). In practice, this proved extremely difficult owing to the low yields obtained, and the need to determine the ratio from the crude pyrolysate to avoid accidental concentration of one isomer during work-up. Fortunately, the resonances of the methylene carbon atoms of the xanthenes (δ_C 27–28) are well separated from other signals in the ^{13}C NMR spectrum of the pyrolysate, and we have shown that the methylene chemical shift can be a sensitive probe of the position of methyl substitution in related systems.[16] In the present series, the methylene chemical shift of authentic samples of xanthene (δ_C 27.76) and 2-methylxanthene[17] (δ_C 27.73) are closely similar as predicted,[16] whereas the signal for 3-methylxanthene would be expected to be shielded by *ca.* 0.4–0.5 ppm.[16] Indeed, small peaks corresponding to both 2- and 3-methyl isomers were found in the spectra of the pyrolysates (from **11**; δ_C 27.52 and 27.18: from **20**; δ_C 27.74 and 27.39). From these spectra, the approximate isomeric ratio **28**:**29** may be estimated as being 1:1 from **11**, and 2.5:1 from **20**. Though these absolute values are probably not reliable, both isomeric products are certainly formed, and the ratio is apparently dependent on the precursor: this may be due to some competing direct cyclisation of the initial radicals prior to formation of the spirodienyl.

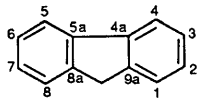


Scheme 3

Other products from the pyrolyses of substrates **11** and **20** include the phenol **10** and the fluorenol **30**, both formed in comparable yields to those obtained from the parent compounds **8** and **19**. The position of the methyl group in the fluorenol **30** was established by ^{1}H NMR (broad singlet at δ_H 7.59 indicates substitution in either the 6- or 7-position of the fluoren-1-ol nucleus) and ^{13}C NMR spectroscopy [additivity effects (Table 1), particularly at C-5a and C-8a which allow the 6- and 7-methyl isomers to be distinguished].

Any proposed mechanism for the formation of the rearrangement products **6** (*e.g.*, the fluorenols) must explain their selective occurrence, only when X = O[4] or (sometimes) NH,[2,4] and never with X = CH_2 or S,[3] and also the regiospecificity of the reaction, particularly with regard to the methyl-substituted derivatives. The simplest possible mechanism (Scheme 4) successfully predicts the regiochemistry, though the hydrogen-abstraction step to generate the phenyl radical **32** from the stabilised phenoxyl radical **31** must be highly endothermic. However, the observation that only phenoxyl (and to a lesser extent aminyl) radicals can accomplish this abstraction is consistent both with the equally specific occurrence of hydrogen-capture products from these radicals (*e.g.*, **7** formed in the *absence* of 2-phenoxytoluene **25**, from the

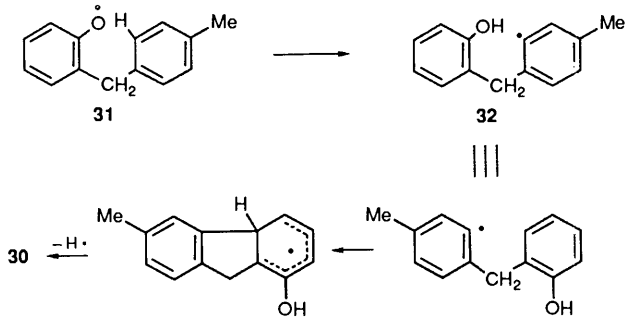
Table 1 Observed and estimated ^{13}C NMR chemical shifts for 6-methyl- and 7-methylfluoren-1-ol



	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9a	C-4a	C-5a	C-8a
Fluoren-1-ol[a]	152.01	113.41	128.41	112.83	120.06	126.61[b]	126.78[b]	124.93	128.23	143.79[c]	141.50	142.75[c]
Compound isolated from pyrolysate[a]	152.03	113.32	128.35	112.73	120.67	136.26	127.77	124.64	128.62	143.88	141.68	139.86
6-Methylfluoren-1-ol[d]	152.01	113.41	128.41	112.06	120.76	135.51	127.48	124.83	128.23	143.79	141.40	139.85
7-Methylfluoren-1-ol[d]	152.01	113.41	128.41	112.06	119.96	127.31	135.68	125.63	128.73	143.79	138.60	142.65

[a] $CDCl_3$ solution. [b,c] Assignments may be reversed. [d] Estimated from the observed spectrum of fluoren-1-ol, using the substituent effect of a methyl group.[18]

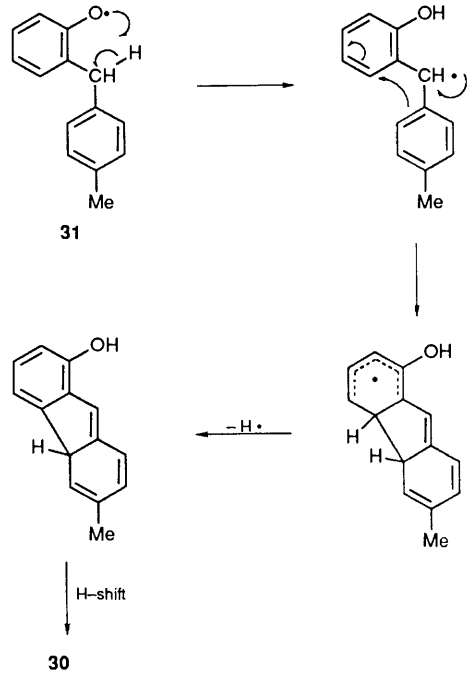
phenoxyl **23**), and the hard and soft acids and bases (HSAB) view of hydrogen, oxygen, and nitrogen atoms as 'hard' sites.[19]



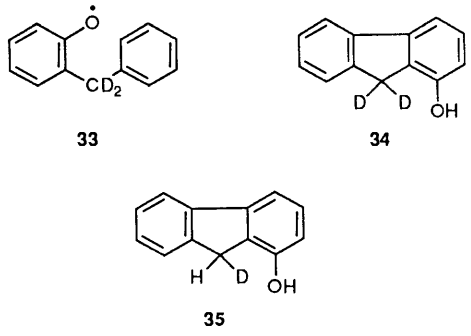
Scheme 4

An alternative mechanism (applicable to the fluorenols and aminocarbazole[2] examples, but not the aminodibenzothiophene[4] or hydroxycarbazole[4] ones) which avoids the endothermic hydrogen-transfer step is shown in Scheme 5. An attempt was made to distinguish the mechanisms of Schemes 4 and 5 by a deuterium-labelling experiment. Thus generation of the deuteriated radical **33** from the allyl precursor **12** should lead to the [9,9-$^2H_2$]fluorene **34** or the [9-^{1}H,9-^{2}H]fluorene **35** by the mechanisms of Schemes 4 and 5, respectively. In practice, however, *both* were formed, together with some unlabelled [9,9-$^1H_2$]fluoren-1-ol **22** (see Experimental section): it seems likely that secondary hydrogen-scrambling processes are taking place,* but in any event the presence of a substantial amount of the [9,9-$^2H_2$] compound **34** establishes that the sequence of Scheme 5 is unlikely to be the sole mechanism.

Further evidence that hydrogen atoms on the bridging group are not essential for the formation of these rearrangement products comes from a study of the pyrolyses of the benzophenone derivatives **14** and **16**. For these compounds, the absolute yields were not determined because of the absence of characteristic signals in the ^1H NMR spectra, but the components were isolated and identified in the usual way (see Experimental section). As expected, pyrolysis of compound **14** gave the phenol **13**, rather more of the cyclisation product xanthone **36** than from the diphenylmethane analogue, and a significant amount of 1-hydroxyfluorenone **37**, which clearly could not have been formed by the mechanism of Scheme 5. The increased level of cyclisation product may be connected with a reduction in 'hardness' of the radical centre owing to delocalisation to the carbonyl group. In addition, dibenzofuran **38** was isolated: control experiments at temperatures up to



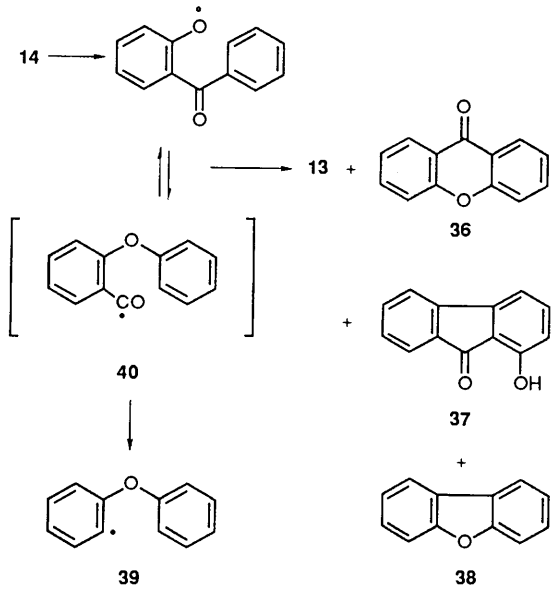
Scheme 5



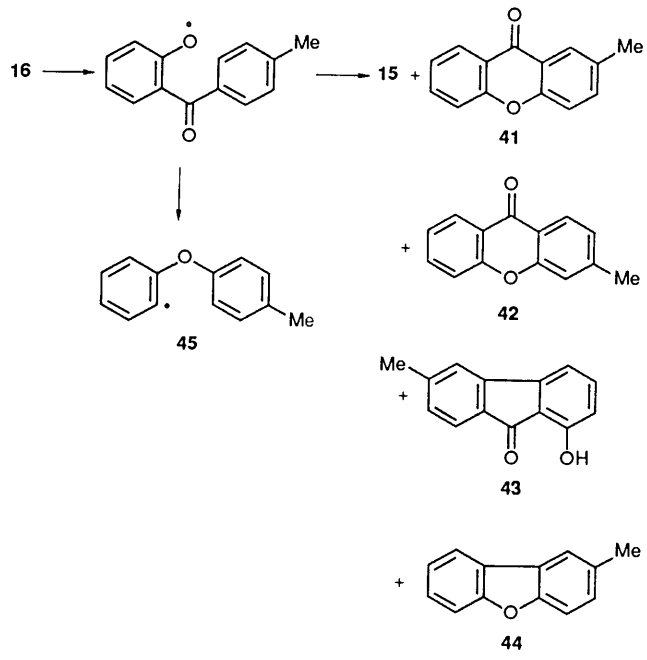
900 °C have shown that this cannot arise by decarbonylation of xanthone **36**, and cyclisation of the phenyl radical **39** generated by decarbonylation of the aroyl radical **40** or of the related spirodienyl is the most probable mechanism for its formation (Scheme 6). Decarbonylation of aroyl radicals is well established at 750 °C.[20]

These observations, applied to the *para*-methyl case (Scheme 7), provide a sensitive test of the mechanism for the formation of xanthones from the spirodienyl. Thus, reversion of the spirodienyl **47** to the aroyl radical **46** should be followed by decarbonylation to the phenyl radical **45**,[20] and cannot therefore lead to the rearranged xanthone **42** by recyclisation

* A control experiment has shown that pyrolysis of [9,9-$^2H_2$]fluorene itself at 750 °C does not lead to scrambling of the label into the aromatic rings.



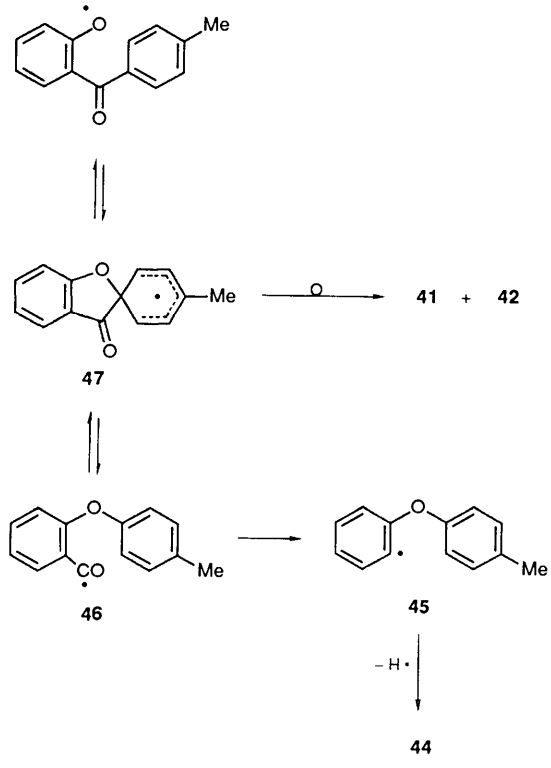
Scheme 6



Scheme 7

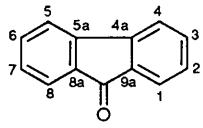
(Scheme 8). Even if some such cyclisation were possible, an increased pyrolysis temperature should lead to an increase in the dibenzofuran **44** *at the expense of the xanthone* **42** if both are formed competitively from aroyl radical **46**. By experiment, the expected products were isolated from the 750 °C pyrolysis, including the phenol **15**, the hydroxyfluorenone **43** [whose structure was confirmed by ^{13}C NMR spectroscopy in the usual way (Table 2)] and a unique dibenzofuran, *viz.* the 2-methyl isomer **44** (identified by comparison of ^{1}H and ^{13}C NMR spectra with samples of authentic[21] 1-, 2-, 3- and 4-methyldibenzofuran). This is the predicted isomer if the mechanism of formation *via* the phenyl radical **45** obtains. The final component isolated was a 1:1 mixture of *both* 2- and 3-methylxanthone **41** and **42**, identified by comparison of spectra with those of an authentic sample[22] and by calculation of the ^{13}C NMR chemical shifts (Table 3), respectively. At higher temperatures (Table 4), the ratio of 2-:3-methylxanthone remains constant despite the expected increase in the level of the dibenzofuran. Hence the aroyl radical **46** is *not* on the reaction co-ordinate to the xanthone **42**. The xanthones must therefore arise by direct sigmatropic migration from the spirodienyl **47**, the O and CO groups showing equal migration aptitude.

We conclude by returning to Scheme 1 and the points made in the first paragraph of this paper. It appears that the hydrogen-capture product **4** and the rearrangement product **6** are favoured relative to the cyclisation product **5** by 'hard' radical centres (X = O > N ⩾ S, CH_2), and that the relative amounts of products **4** and **6** are controlled by the availability of 'free' hydrogen atoms. The level of rearrangement product **6** is increased in the cases where the bridging group (Y) can donate its lone pair to increase the 'hardness' [thus for X = NH, compound **6** is formed only when Y = NH or S, and not when Y = CH_2 or CO[4]]. Conversely, the level of compound **6** is decreased when delocalisation is possible [thus for X = O the relative amounts of rearrangement product **6** to cyclisation products **5** decrease as Y is changed from NH, through CH_2, to CO]. The evidence for the formation of product **6** remains consistent with a hydrogen-abstraction mechanism (*cf.* Scheme 4) *via* a phenyl radical. We have positive evidence in one case (X = O, Y = CO) that the cyclisation product **5** is formed by sigmatropic migration from the spirodienyl rather than by recyclisation of radical **1** or **3**. The migration aptitudes of all the heteroatoms (X,Y) studied are remarkably similar (CH_2 = S; CO = O = NH), and though CH_2, S are consistently >NH, the effect is small and usually ⩽2:1. Hence, we believe that sufficient understanding of these systems has now been gained to allow reasonable prediction of product distribution from 'unknown' X,Y combinations (Scheme 1). Although these processes are only likely to be synthetically useful in isolated cases, the new reactions we have discovered point the way to more efficient exploitation of phenyl-radical cyclisation, which we shall report in detail in future publications.



Scheme 8

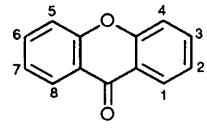
Table 2 Observed and estimated ^{13}C NMR chemical shifts of 1-hydroxy-6-methylfluorenone



	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-9a	C-4a	C-5a	C-8a
1-Hydroxyfluorenone[a]	157.25	118.01	137.22	112.59	120.80	134.44	128.89	123.85	196.07	117.28	143.69[b]	143.99[b]	134.11
Compound isolated from pyrolysate[a]	157.06	117.88	136.89	112.39	121.72	143.59	129.37	123.77	195.85	117.68	145.63	144.36	131.69
1-Hydroxy-6-methyl-fluorenone (calculated)[c]	157.25	118.01	137.22	112.59	121.50	143.34	129.59	123.75	196.07	117.28	143.99	143.59	131.21

[a] $CDCl_3$ solution. [b] Assignments may be reversed. [c] Estimated from the observed spectrum of 1-hydroxyfluorenone, using the substituent effect of a methyl group.[18]

Table 3 Observed and expected ^{13}C NMR methine chemical shifts for 3-methylxanthone



	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
Compound isolated[a]	126.41	125.17		117.70	117.49	134.36	123.50	126.46
3-Methylxanthone (calculated)[b]	126.5	124.5		118.5	117.8	134.5	123.8	126.6

[a] $CDCl_3$ solution. [b] Estimated using the reported spectrum of xanthone[23] and the substituent effect of a methyl group.[18]

Table 4 Effect of temperature on product proportions **41**, **42**, **44** obtained from compound **16**

	Relative proportions		
Temperature (°C)	2-Methylxanthone **42**	3-Methylxanthone **41**	2-Methyl dibenzofuran **44**
750	1	1	0.64
850	1	1	0.70
950	1	1	0.96

Experimental

Unless otherwise stated, ^1H NMR spectra were recorded at 80 or 200 MHz and ^{13}C NMR spectra were recorded at 20 or 50 MHz, for solutions in [^2H]chloroform. Light petroleum refers to the fraction boiling in the range 40–60 °C.

2-(*Allyloxy*)-*diphenylmethane and -benzophenone Derivatives.*—The appropriate phenol (1.9 mmol) was treated with allyl bromide (2 mmol) in DMF (7 cm^3) containing potassium carbonate (2 mmol) as previously described.[24] The reaction mixture was stirred overnight at room temperature and the product was extracted into diethyl ether and purified by distillation. The following compounds were prepared by this method: 2-(*Allyloxy*)*diphenylmethane* **8** (83%), b.p. 138–140 °C (0.5 Torr) (Found: C, 85.65; H, 7.05. $C_{16}H_{16}O$ requires C, 85.7; H, 7.15%); δ_H 7.0–7.54 (9 H, m), 6.22 (1 H, m), 5.36–5.72 (2 H, m), 4.70 (2 H, m) and 4.28 (2 H, s); δ_C 156.15 (q), 140.89 (q), 133.35, 130.29, 129.89 (q), 128.83, 128.05, 127.16, 125.59, 120.52, 116.75, 111.59, 68.58 and 35.91; *m/z* 224 (M^+, 56%), 183 (100), 165 (30), 155 (22), 130 (37), 117 (59), 107 (13), 91 (70), 77 (50) and 41 (60).

2-(*Allyloxy*)-4′-*methyldiphenylmethane* **11** (83%) [from 2-(4-methylbenzyl)phenol **10**[16]], b.p. 156–158 °C (0.6 Torr) (Found: C, 85.55; H, 7.3. $C_{17}H_{18}O$ requires C, 85.7; H, 7.55%); δ_H 6.82–7.31 (8 H, m), 6.15 (1 H, m), 5.20–5.57 (2 H, m), 4.58 (2 H, m), 4.04 (2 H, s) and 2.37 (3 H, s); δ_C 156.30 (q), 137.92 (q), 135.01 (q), 133.54, 130.30, 129.24 (q), 128.80, 127.09, 120.63, 116.76, 111.82, 68.81, 35.47 and 20.83 (2 signals coincidental at δ_C 128.80); *m/z* 238 (M^+, 81%), 198 (33), 197 (100), 181 (30) and 131 (26).

2-(*Allyloxy*)*benzophenone* **14** (90%), b.p. 145–147 °C (0.2 Torr) (Found: C, 81.1; H, 5.85. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9%); δ_H 7.73–7.89 (2 H, m), 7.24–7.68 (5 H, m), 6.86–7.10 (2 H, m), 5.67 (1 H, m), 4.88–5.09 (2 H, m) and 4.42 (2 H, m); δ_C 196.06 (C=O), 156.21 (q), 138.05 (q), 132.39, 132.21, 131.59, 129.43, 129.30, 127.87, 120.61, 116.59, 112.77 and 68.86 (one quaternary signal is not apparent); *m/z* 238 (M^+, 19%), 223 (16), 208 (19), 198 (69), 197 (100), 181 (40), 121 (94), 105 (97) and 77 (91).

2-(*Allyloxy*)-4′-*methylbenzophenone* **16** (from 2-hydroxy-4′-methylbenzophenone **15**[7]) (90%), b.p. 140–142 °C (0.2 Torr) (Found: C, 81.2; H, 6.35. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.35%); δ_H 7.63–7.76 (2 H, m), 7.23–7.55 (4 H, m), 6.84–7.14 (2 H, m), 5.73 (1 H, m), 4.89–5.15 (2 H, m), 4.43 (2 H, m) and 2.37 (3 H, s); δ_C 195.79 (C=O), 156.09 (q), 143.31 (q), 135.44 (q), 132.39, 131.34, 129.64, 129.31, 128.66, 120.60, 116.63, 112.81, 68.93 and 21.37 (one quaternary signal is not apparent); *m/z* 252 (M^+, 30%), 237 (34), 222 (21), 211 (51), 209 (27), 208 (29), 181 (45), 121 (64), 120 (33), 119 (100) and 91 (78).

2(*Benzyloxy*)*diphenylmethane* **9**.—Prepared in 98% yield by the same method as the *O*-allyl compounds described above, this compound was obtained as an oil, b.p. 182–184 °C (0.1 Torr) (lit.,[25] m.p. 38 °C); δ_H 7.2–7.5 (12 H, m), 6.95 (2 H, t), 5.10 (2 H, s) and 4.09 (2 H, s); δ_C 156.46 (q), 140.96 (q), 137.22 (q), 130.46, 130.05 (q), 128.84, 128.26, 128.04, 127.55, 127.25, 127.09, 125.58, 120.69, 111.86, 69.98 and 36.10.

Benzyl Oxalates.—Symmetrical dibenzyl oxalates were prepared by the general method of Trahanovsky *et al.*[26] The following compounds were prepared by this method: Bis-(2-phenoxybenzyl) oxalate **19** (61%), m.p. 94–96 °C (from EtOH)

(lit.,[5] 94–96 °C); δ_H 6.80–7.51 (18 H, m) and 5.39 (4 H, s); δ_C 157.35 (q), 156.83 (q), 155.34 (q), 130.45, 130.19, 129.68, 125.36 (q), 123.38, 118.63, 118.48 and 63.71 (two signals are coincidental).

Bis-[2-(4-*methylphenoxy*)*benzyl*]*oxalate* **20** [from 2-(4-methylphenoxy)benzyl alcohol **18**[10]], m.p. 78–81 °C (from EtOH) (Found: C, 74.45; H, 5.35. $C_{30}H_{26}O_6$ requires C, 74.7; H, 5.4%); δ_H 6.76–7.50 (16 H, m), 5.41 (4 H, s) and 2.31 (6 H, s); δ_C 157.36 (q), 155.80 (q), 154.33 (q), 132.94 (q), 130.26, 130.11, 124.93 (q), 122.89, 118.79, 117.72, 63.70 and 20.50 (two signals are coincidental); *m/z* 482 (M^+, 46%), 286 (46), 242 (24), 198 (100) and 182 (23).

2-(*Allyloxy*)*diphenyl*[$^2H_2$]*methane* **12**.—A solution of 2-(allyloxy)benzophenone **14** (2.5 g, 0.01 mol) in dry diethyl ether (30 cm^3) was added dropwise to a stirred suspension of lithium aluminium deuteride (0.410 g, 0.01 mol) in dry diethyl ether (30 cm^3). After 40 min a solution of aluminium chloride (1.40 g, 0.01 mol) in dry diethyl ether (20 cm^3) was added *via* a dropping funnel.[9] The mixture was stirred at room temperature and monitored by GLC: after 5 h most of the starting material had reacted. Water (15 cm^3) was added to the reaction mixture, followed by sulphuric acid (6 mol dm^{-3}; 15 cm^3). The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 20 cm^3). The combined ethereal solutions were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The required product was isolated as an oil contaminated with minor impurities (crude wt 1.06 g), b.p. 130–132 °C (0.2 Torr), which were separated by dry-flash chromatography, with methylene dichloride–hexane (50:50) as eluant, to give the required deuteriated product as an oil (0.738 g, 31%), b.p. 133–135 °C (0.2 Torr), $\delta_D(CHCl_3)$ 3.91.

Pyrolysis Experiments.—NMR yields were obtained from small-scale pyrolyses with cyclohexane (5 mm^3) as integral calibrant. Results are quoted as follows: quantity of substrate, inlet temperature, furnace temperature, pressure, pyrolysis time, and products.

For the special case of the 2-(allyloxy)benzophenones **14** and **16**, for which there were no characteristic signals in the NMR spectra, the yields are quoted for isolated and purified material. Work-up involved separation and isolation of the phenolic components by base extraction, followed by dry-flash chromatography of both the neutral and the acidic fractions with the solvent system stated.

2-(*Allyloxy*)*diphenylmethane* **8** (0.089 g, 0.397 mmol), 130–140 °C, 750 °C, 1 × 10^{-3} Torr, 20 min: 2-benzylphenol (33%), *m/z* 184; fluoren-1-ol (30%), *m/z* 182; xanthene (2%), *m/z* 182. On a preparative scale the ether (2.164 g, 9.66 mmol) was distilled at 5 × 10^{-3} Torr into a furnace at 750 °C over a period of 2 h. The entire pyrolysate was chromatographed on a column of alumina, with diethyl ether–light petroleum (50:50) as eluant. The following components were isolated: 2-benzylphenol (0.30 g, 17%), b.p. 119–120 °C (0.5 Torr), which could not be obtained in crystalline form; δ_H 6.74–7.43 (9 H, m), 5.06 (1 H, br s) and 4.07 (2 H, s); δ_C 153.50 (q), 139.78 (q), 130.83, 128.54, 128.46, 127.66, 126.91 (q), 126.16, 120.82, 115.57 and 36.12. However, the ^1H NMR and ^{13}C NMR were identical with those of an authentic sample; [δ_H 6.73–7.36 (9 H, m), 4.84 (1 H, s) and 4.06 (2 H, s); δ_C 153.51 (q), 139.75 (q), 130.83, 128.65, 128.56, 127.68, 126.87 (q), 126.18, 120.84, 115.58 and 36.14]; fluoren-1-ol (0.127 g, 7%). The crude isolated material was purified by distillation, b.p. 130–132 °C (0.5 Torr) to give the pure product (0.095 g), m.p. 118–120 °C (from water) (lit.,[12] 119–120 °C); δ_H 7.80 (1 H, d), 7.57 (1 H, d), 7.26–7.55 (4 H, m), 6.78 (1 H, d), 5.25 (1 H, br s), and 3.84 (2 H, s); δ_C 152.01 (q), 143.79 (q), 142.75 (q), 141.50 (q), 128.41, 128.23 (q). 126.78, 126.61, 124.98, 120.06, 113.41, 112.83 and 33.41; *m/z* 182 (M^+, 100%), 165 (38), 152 (86), 91 (41) and 77 (46).

In a replicate experiment, the entire pyrolysate was dissolved in methylene dichloride and was extracted with sodium hydroxide (1 mol dm^{-3}; 100 cm^3) to remove the phenolic components. The neutral fraction was chromatographed on a column of alumina and eluted with light petroleum. The xanthene (*ca.* 4%) isolated from the column was recrystallised from ethanol to give a yellow solid which was still impure; δ_H 7.01–7.49 (8 H, m) and 4.05 (2 H, s); δ_C 151.00 (q), 128.78, 127.50, 122.83, 120.48 (q), 116.34 and 27.78, though the ^1H NMR and ^{13}C NMR data were compatible with those of an authentic sample: [δ_H 7.00–7.23 (8 H, m) and 4.05 (2 H, s); δ_C 151.88 (q), 128.77, 127.50, 122.81, 120.45 (q), 116.34 and 27.76].

2-(*Benzyloxy*)*diphenylmethane* **9** (0.049 g, 0.18 mmol), 140–150 °C, 750 °C, 3 × 10^{-3} Torr, 20 min: the following components were identified by ^1H NMR spectral comparison with the results of the preceding pyrolysis: 2-benzylphenol (18%); fluoren-1-ol (63%); xanthene (13%); and in addition bibenzyl (δ_H 2.98) (39%) was also identified.

On a preparative scale, the benzyl ether (1.10 g, 4 mmol) was distilled at 170–190 °C during 45 min into the furnace tube which was maintained at 750 °C (2 × 10^{-3} Torr). The pyrolysate was dissolved in methylene dichloride (10 cm^3) and extracted with dil. aq. sodium hydroxide (2 mol dm^{-3}; 2 × 10 cm^3). The basic extracts were acidified (HCl), and extracted with methylene dichloride (2 × 20 cm^3), and the combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to give a brown solid (0.40 g, 54%). This material was a 3:1 mixture of fluoren-1-ol and 2-benzylphenol: the level of the fluorene was substantially increased by recrystallisation from cyclohexane.

2-(*Allyloxy*)-4′-*methyldiphenylmethane* **11** (0.129 g, 0.542 mmol), 120–130 °C, 750 °C, 1 × 10^{-3} Torr, 25 min: 2-(4′-methylbenzyl)phenol (22%), *m/z* 198; 6-methylfluoren-1-ol (26%), *m/z* 196; 2-methylxanthene (2%); and 3-methylxanthene (2%), *m/z* 196. On a larger scale the phenol (1.534 g, 6.43 mmol) was pyrolysed at 750 °C, 2 × 10^{-3} Torr over a period of 1.5 h. The entire pyrolysate was dissolved in methylene dichloride and was extracted with aq. sodium hydroxide (1 mol dm^{-3}; 100 cm^3). The base extract was neutralised, extracted with methylene dichloride, dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was chromatographed on a column of alumina, with diethyl ether/light petroleum (50:50) as eluant. The following components were isolated: 2-(4′-methylbenzyl)phenol (0.10 g, 8%), b.p. 174–176 °C (0.7 Torr), [lit.,[27] 73–76 °C (0.05 Torr)]; δ_H 6.77–7.31 (8 H, m), 5.07 (1 H, br s), 4.06 (2 H, s) and 2.43 (3 H, s); δ_C 153.64 (q), 136.55 (q), 135.78 (q), 130.79, 129.24, 128.44, 127.65, 127.08 (q), 120.79, 115.66, 35.89 and 20.86. The ^1H NMR and ^{13}C NMR spectra were identical with those of an authentic sample: [δ_H 6.80–7.36 (8 H, m), 4.56 (1 H, br s), 4.09 (2 H, s) and 2.42 (3 H, s); δ_C 153.64 (q), 136.54 (q), 135.81 (q), 130.78, 129.26, 128.43, 127.65, 127.06 (q), 120.79, 115.65, 35.90 and 20.87]: 6-*methylfluoren*-1-*ol* **30**; the crude product was purified by sublimation at 173–175 °C (0.7 Torr) to give the pure material as a light brown solid (0.121 g, 10%), m.p. 119–121 °C (Found: C, 85.55; H, 6.3. $C_{14}H_{12}O$ requires C, 85.7; H, 6.1%); δ_H 7.60 (1 H, s), 7.30–7.50 (2 H, m), 7.08–7.27 (2 H, m), 6.75 (1 H, d), 5.07 (1 H, s), 3.79 (2 H, s) and 2.47 (3 H, s); δ_C 152.03 (q), 143.88 (q), 141.68 (q), 139.86 (q), 136.26 (q), 128.62 (q), 128.35, 127.77, 124.64, 120.67, 113.32, 112.73, 33.00 and 21.35; *m/z* 196 (M^+, 90%), 181 (100), 165 (21) and 152 (29).

After base extraction the methylene dichloride layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue consisted of a mixture of both 2-methylxanthene and 3-methylxanthene but was contaminated with a large number of impurities. Even after column chromatography on

alumina and dry-flash chromatography, the isomeric mixture was still impure (0.081 g, 6%). The ^{1}H NMR spectrum of the mixture showed two methyl peaks, at δ_H 2.36 and 2.39 and a peak at δ_H 4.04 corresponding to the methylene protons [δ_H (authentic 2-methylxanthene) 6.88–7.25 (7 H, m), 4.00 (2 H, s) and 2.31 (3 H, s)]. Assignments were made using data from the ^{13}C NMR spectrum, which showed two methylene peaks, at δ_C 27.18 and 27.52. These can be assigned to 3-methylxanthene and 2-methylxanthene, respectively, by using additivity effects[16] (see Discussion section) [δ_C (authentic 2-methylxanthene) 152.02 (q), 149.73 (q), 132.09 (q), 129.08, 128.78, 128.05, 127.40, 122.59, 120.43 (q), 120.02 (q), 116.28, 116.01, 27.73 and 20.46].

For these pyrolyses absolute yields of all the products could not be obtained by standard methods because of coincidence of peaks in both the ^{1}H NMR spectrum and the GLC traces. However, the absolute yield of the appropriate fluorene could be obtained directly by ^{1}H NMR spectroscopy, and the relative yields of the other products were estimated from the ^{13}C NMR spectrum of the mixture.

Bis-(2-phenoxybenzyl) oxalate **19** (0.108 g, 0.238 mmol), 140–160 °C, 750 °C, 1 × 10^{-3} Torr, 40 min: 2-benzylphenol (5%), *m/z* 184; fluoren-1-ol (36%), *m/z* 182; xanthene (9%), *m/z* 182; 2-phenoxybenzyl alcohol (trace), *m/z* 200. On a preparative scale the benzyl oxalate (2.064 g, 4.54 mmol) was distilled at 5 × 10^{-3} Torr into a furnace at 750 °C over a period of 1.5 h. The entire pyrolysate was chromatographed on a column of alumina and eluted with diethyl ether–light petroleum (50:50). The following components were isolated: 2-benzylphenol (0.19 g, 11%), b.p. 120–121 °C (0.5 Torr) which could not be obtained in crystalline form; δ_H 6.72–7.38 (9 H, m), 4.90 (1 H, br s) and 4.03 (2 H, s); δ_C 153.61 (q), 139.81 (q), 130.84, 128.51, 127.67, 126.91 (q), 126.19, 120.78, 115.59 and 36.17 (two peaks coincidental at δ_C 128.51). However, the ^{1}H NMR and ^{13}C NMR data were compatible with those of an authentic sample (see above); fluoren-1-ol (crude wt 0.39 g). The crude material was purified by distillation, b.p. 132–134 °C (0.5 Torr), to give the pure product as a pale brown solid (0.15 g, 10%), m.p. 118–120 °C (from water) (lit.,[12] 119–120.5 °C); δ_H 7.78 (1 H, m), 7.55 (1 H, m), 7.18–7.41 (4 H, m), 6.75 (1 H, d), 4.90 (1 H, br s) and 3.84 (2 H, s); δ_C 152.04 (q), 143.83 (q), 142.76 (q), 141.54 (q), 128.44, 128.21 (q), 126.79, 126.64, 125.01, 120.09, 113.42, 112.86 and 33.43: xanthene, contaminated with a large number of impurities; attempts to purify the crude material by distillation at 73–75 °C (0.6 Torr), then by recrystallisation from ethanol, gave xanthene as a yellow solid which was still impure (0.09 g, 5%); δ_H 6.94–7.53 (8 H, m) and 4.05 (2 H, s); δ_C 151.84 (q), 128.76, 127.47, 122.79, 120.43 (q), 116.32 and 27.70. The ^{1}H NMR and ^{13}C NMR spectral data were compatible with those of an authentic sample (see above).

Bis-[2-(4-methylphenoxy)benzyl] oxalate **20** (0.078 g, 0.161 mmol), 170–200 °C, 750 °C, 1 × 10^{-3} Torr, 50 min: 2-(4′-methylbenzyl)phenol (6%), *m/z* 198; 6-methylfluoren-1-ol (48%), *m/z* 196; 2-methylxanthene (14%); and 3-methylxanthene (5%), *m/z* 196; 2-(4-methylphenoxy)benzyl alcohol (trace), *m/z* 214. The oxalate (1.082 g, 2.24 mmol) was pyrolysed on a larger scale at 750 °C and 3 × 10^{-3} Torr over a period of 2.5 h. The components of the pyrolysate were separated by column chromatography on alumina, with light petroleum–diethyl ether (50:50) as eluant. The following components were isolated: 2-(4′-methylbenzyl)phenol (0.064 g, 7%), b.p. 161 °C (0.6 Torr) [lit.,[27] 73–76 °C (0.05 Torr)]; δ_H 6.72–7.38 (8 H, m), 3.98 (2 H, s) and 2.36 (3 H, m); δ_C 153.73 (q), 136.59 (q), 135.78 (q), 130.78, 129.25, 128.44, 127.64, 127.07 (q), 120.73, 115.65, 35.90 and 20.87. The ^{1}H NMR and ^{13}C NMR spectra were identical with those of the authentic sample previously quoted. The ^{1}H NMR and ^{13}C NMR spectra of this component also showed peaks at δ_H 4.79 and 2.34 and δ_C 61.31 and 20.53, respectively, which correspond to the methyl and methylene signals of 2-(4-methylphenoxy)benzyl alcohol [authentic sample; δ_H 7.42 (1 H, m), 7.0–7.3 (4 H, m), 6.75–6.95 (3 H, m), 4.75 (2 H, s), 3.16 (1 H, br s) and 2.34 (3 H, s); δ_C 155.16 (q), 154.54 (q), 132.86 (q), 131.44 (q), 130.18, 129.03, 128.79, 123.23, 118.45, 117.85, 61.19 and 20.52]: 6-methylfluoren-1-ol (crude wt 0.160 g). The crude material was purified by sublimation at 159–162 °C (0.7 Torr) to give the pure material as a light brown solid (0.121 g, 10%). The sublimed material had m.p. 118–120 °C; δ_H 7.61 (1 H, s), 7.28–7.49 (2 H, m), 7.08–7.27 (2 H, m), 6.75 (1 H, d), 5.07 (1 H, br s), 3.79 (2 H, s) and 2.47 (3 H, s); δ_C 152.09 (q), 143.92 (q), 141.73 (q), 139.86 (q), 136.32 (q), 128.59 (q), 128.39, 127.81, 124.69, 120.69, 113.33, 112.75, 33.02 and 21.37; the ^{1}H NMR and ^{13}C NMR spectra are identical with those previously quoted: 2-methylxanthene and 3-methylxanthene isolated in a mixture contaminated with a large number of impurities. Attempts to purify the mixture, both by distillation and preparative TLC, were again unsuccessful, the impure mixture being isolated as a yellow oily solid (0.054 g, 6%). The ^{13}C NMR spectrum of the mixture showed a large peak at δ_C 27.67 assigned to the methylene resonance of 2-methylxanthene, and a smaller peak at δ_C 27.33 assigned to 3-methylxanthene.

Absolute yields of these pyrolysis products were obtained by use of both ^{13}C and ^{1}H NMR spectral data as previously outlined.

2-(*Allyloxy*)*benzophenone* **14** (0.452 g, 1.9 mmol), 130–140 °C, 750 °C, 1 × 10^{-3} Torr, 120 min: 2-hydroxybenzophenone (8%); 1-hydroxyfluorenone (9%); xanthone (14%); and dibenzofuran (6%). The following components were separated from the base extract, after elution with methylene dichloride–hexane (50:50): 2-hydroxybenzophenone (0.030 g, 8%), b.p. 124–126 °C (0.2 Torr) [lit.,[28] 175 °C (14 Torr)]; δ_H 12.03 (1 H, s), 7.45–7.70 (7 H, m), 7.07 (1 H, d) and 6.87 (1 H, t); δ_C 201.42 (C=O), 163.10 (q), 137.82 (q), 136.09, 133.39, 131.69, 128.95, 128.14, 119.03 (q), 118.42 and 118.25. The ^{1}H NMR and ^{13}C NMR spectra were identical with those of an authentic sample: [δ_H 12.07 (1 H, s), 7.44–7.69 (7 H, m), 7.06 (1 H, d) and 6.86 (1 H, t); δ_C 201.42 (q), 163.12 (q), 137.79 (q), 136.13, 133.42, 131.74, 129.00, 128.17, 119.02 (q), 118.47 and 118.24]: 1-hydroxyfluorenone (crude wt 0.05 g). The crude solid was recrystallised from aqueous ethanol to give 1-hydroxyfluorenone as a yellow, crystalline solid (0.034 g, 9%), m.p. 115–117 °C (lit.,[29] 115 °C); δ_H 8.41 (1 H, s), 7.58 (1 H, d), 7.44 (2 H, m), 7.21–7.36 (2 H, m), 6.97 (1 H, d) and 6.72 (1 H, d); δ_C 196.07 (C=O), 157.25 (q), 143.99 (q), 143.69 (q), 137.22, 134.44, 134.11 (q), 128.89, 123.85, 120.80, 118.01, 117.28 (q) and 112.59. The following components were separated from the neutral fraction, after elution with methylene dichloride–hexane (50:50): dibenzofuran (0.02 g, 6%), m.p. 72–74 °C (from MeOH) (lit.,[30] 83–84 °C); δ_H 7.96–8.1 (2, H, m) and 7.28–7.63 (6 H, m); δ_C 156.14 (q), 127.00, 124.15 (q), 122.57, 120.51 and 111.55. The ^{1}H NMR and ^{13}C NMR spectra are identical with those of an authentic sample; [δ_H 7.9–8.1 (2 H, m) and 7.2–7.6 (6 H, m); δ_C 156.18 (q), 127.01, 124.19 (q), 122.57, 120.51 and 111.56]; xanthone (crude wt 0.068 g). The crude solid was recrystallised from ethanol to give xanthone as fine needles (0.052 g, 14%), m.p. 174–175 °C, mixed m.p. 174.5–176 °C (lit.,[31] 173–174 °C); δ_H 8.29 (2 H, d), 7.68 (2 H, m) and 7.29–7.45 (4 H, m); δ_C 176.89 (C=O), 155.98 (q), 134.55, 126.52, 123.68, 121.70 (q) and 117.76. The ^{1}H NMR and ^{13}C NMR data were identical with those of an authentic sample: [δ_H 8.28 (2 H, d), 7.67 (2 H, m) and 7.28–7.44 (4 H, m); δ_C 176.87 (C=O), 155.95 (q), 134.53, 126.50, 123.66, 121.69 (q) and 117.74].

2-(*Allyloxy*)-4′-*methylbenzophenone* **16** (0.568 g, 2.25 mmol), 120–160 °C, 750 °C, 5 × 10^{-3} Torr, 130 min: 2-hydroxy-4′-methylbenzophenone (5%); 1-hydroxy-6-methylfluorenone (9%); 2-methyldibenzofuran (3%); 2-methylxanthone and 3-methylxanthone (18%). The following components were isolated from the base extract, after elution with methylene

dichloride–hexane (70:30): 2-hydroxy-4′-methylbenzophenone (crude wt 0.028 g); the orange oil obtained was triturated with light petroleum to give the product as a yellow solid (0.016 g, 5%), m.p. 54–57 °C (lit.,[7] 61.5 °C); δ_H 12.02 (1 H, s), 6.75–7.67 (8 H, m) and 2.45 (3 H, s); δ_C 197.41 (C=O), 163.09 (q), 142.56 (q), 135.90, 135.19 (q), 133.36, 129.33, 128.89, 119.29 (q), 118.38, 118.26 and 21.43. The ^1H and ^{13}C NMR spectra were identical with those of an authentic sample: [δ_H 12.02 (1 H, s), 6.75–7.65 (8 H, m) and 2.45 (3 H, s); δ_C 190.72 (C=O), 163.03 (q), 142.58 (q), 135.93, 135.11 (q), 133.36, 129.33, 128.87, 119.19 (q), 118.40, 118.22 and 21.44]: *1-hydroxy-6-methylfluorenone* **43** (crude wt 0.08 g); the crude solid was recrystallised from ethanol to give pure 1-hydroxy-6-methylfluorenone **42** as fine yellow needles (0.041 g, 9%), m.p. 104–106 °C (from EtOH) (Found: 79.4; H, 4.75%; M^+, 210.0677. $C_{14}H_{10}O_2$ requires C, 80.00; H, 4.75%; M, 210.0681); δ_H 8.42 (1 H, s), 7.46 (1 H, d), 7.24–7.33 (2 H, m), 7.04 (1 H, m), 6.94 (1 H, d), 6.71 (1 H, d) and 2.38 (3 H, s); δ_C 195.84 (C=O), 157.06 (q), 145.63 (q), 144.36 (q), 143.59 (q), 136.89, 131.69 (q), 129.37, 123.77, 121.72, 117.88, 117.68 (q), 112.39 and 21.90; *m/z* 210 (M^+, 100%) and 182 (27). The following components were separated by chromatography from the neutral residue after base extraction, methylene dichloride–hexane (50:50) being the eluting solvent: 2-methyldibenzofuran (crude wt 0.028 g), b.p. 119–121 °C (0.2 Torr), to give a yellow oily solid which could not be obtained in crystalline form (0.012 g, 3%); δ_H 7.93 (1 H, d), 7.75 (1 H, s), 7.23–7.59 (5 H, m) and 2.52 (3 H, s); δ_C(DEPT) 128.05, 126.76, 122.35, 120.46, 120.37, 111.47, 110.99 and 21.18. The ^1H and ^{13}C NMR spectra were identical with those of an authentic sample:[21] 2-methylxanthone and 3-methylxanthone (0.078 g, 16%) obtained as a mixture of isomers. A small amount of 3-methylxanthone (0.01 g, 2%) was also isolated, free from contamination with the 2-methyl isomer. From the ^1H and ^{13}C NMR spectra obtained for the mixture and the separated isomer the peaks for both isomers could be assigned: 3-methylxanthone; δ_H 8.32 (1 H, dd), 8.12 (1 H, d), 7.68 (1 H, m), 7.16–7.49 (4 H, m) and 2.50 (3 H, s); δ_C(DEPT) 134.36, 126.46, 126.41, 125.17, 123.50, 117.70, 117.49 and 21.73; 2-methylxanthone; δ_H 8.27 (1 H, m), 8.03 (1 H, s), 7.58–7.67 (1 H, m), 7.07–7.46 (4 H, m) and 2.39 (3 H, s); δ_C(DEPT) 135.79, 134.28, 126.25, 125.76, 123.45, 117.70, 117.49 and 20.60. The ^1H and ^{13}C NMR spectra for this isomer were identical with those obtained for an authentic sample: [δ_H 8.23 (1 H, d), 7.98 (1 H, s), 7.57 (1 H, m), 7.20–7.40 (4 H, m) and 2.35 (3 H, s); δ_C(DEPT) 135.74, 134.32, 126.39, 125.69, 123.40, 117.67, 117.46 and 20.57].

A series of small-scale pyrolyses was carried out at various furnace temperatures. For the peaks observed at δ_C 177.10 and 176.82 in the ^{13}C NMR spectrum of the crude pyrolysate, attributed to the carbonyl group in each isomer, the ratio of 2-methylxanthone:3-methylxanthone was obtained at each temperature and from the GLC traces of the crude pyrolysate the ratio of dibenzofuran:xanthone isomers was also obtained (see the Discussion section): (0.054 g, 0.214 mmol), 130–160 °C, 750 °C, 1×10^{-3} Torr, 30 min; (0.048 g, 0.19 mmol), 130–140 °C, 850 °C, 1×10^{-3} Torr, 40 min; (0.099 g, 0.393 mmol), 140–150 °C, 950 °C, 1×10^{-3} Torr, 40 min.

Xanthone (0.040 g, 0.206 mmol), 130–140 °C, 950 °C, 1×10^{-3} Torr, 35 min. The only product of the pyrolysis was recovered xanthone. No dibenzofuran was present (from GLC).

2-(Allyloxy)diphenyl[$^2H_2$]methane **12** (0.108 g, 0.478 mmol), 100–120 °C, 750 °C, 1×10^{-3} Torr, 35 min. The entire pyrolysate was dissolved in deuteriochloroform and analysed, by ^1H and ^{13}C NMR spectroscopy, for its fluorenol content. The ^1H NMR spectrum showed a triplet at δ_H 3.85, indicating that one of the deuterium labels had been replaced by hydrogen, and a singlet at δ_H 3.86 corresponding to the methylene peak of fluoren-1-ol (authentic fluoren-1-ol showed a methylene peak at δ_H 3.84). The ^{13}C NMR spectrum showed a triplet at δ_C 33.15, again indicating that a deuterium label had been replaced, and a methylene peak at δ_C 33.45 corresponding to fluoren-1-ol (authentic fluoren-1-ol showed a methylene peak at δ_C 33.41). From these spectra it was not possible to determine if any [9-$^2H_2$]fluoren-1-ol was present in the pyrolysate.

The relative amounts of the fluorenol components were obtained from a 360 MHz ^1H NMR spectrum, sharpened by ^2H-irradiation. By accurate integration of the observed peaks for the unlabelled fluorene and the [9-^1H]fluoren-1-ol components relative to a doublet at δ_H 6.72, known to correspond to one aromatic proton of fluoren-1-ol, the relative amount of the [9-$^2H_2$]fluoren-1-ol was obtained by difference. A ^2H NMR spectrum showed no peaks at δ_H 6.72 in the region of the doublet. The relative amounts of [9-$^2H_2$]fluoren-1-ol: [9-^1H][9-^2H]fluoren-1-ol:[9-$^1H_2$]fluoren-1-ol were found to be 4.6:4.4:1.

[9,9-$^2H_2$]*Fluorene.*—A sample of labelled fluorene[32] containing 94% ^2H in the 9-position was pyrolysed at 750 °C (5×10^{-3} Torr) (inlet temperature 50–70 °C, pyrolysis time 15 min). The ^2H NMR spectrum of the entire pyrolysate showed no evidence of scrambling of the label into the aromatic positions.

Acknowledgements

We are most grateful to British Petroleum plc for a research studentship (to H. S. H.) and to Dr. J. T. Sharp for helpful discussions.

References

1 Preliminary communication, J. I. G. Cadogan, C. L. Hickson, H. S. Hutchison and H. McNab, *J. Chem. Soc., Chem. Commun.*, 1985, 643.
2 J. I. G. Cadogan, H. S. Hutchison and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1407.
3 J. I. G. Cadogan, H. S. Hutchison and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2875.
4 J. I. G. Cadogan, C. L. Hickson, H. S. Hutchison and H. McNab, preceding paper.
5 W. S. Trahanovsky and C. C. Ong, *J. Am. Chem. Soc.*, 1970, **92**, 7174.
6 J. I. G. Cadogan, C. L. Hickson and H. McNab, *Tetrahedron*, 1986, **42**, 2135.
7 F. Ullmann and I. Goldberg, *Ber. Dtsch. Chem. Ges.*, 1902, **35**, 2811.
8 H. J. Schiefele, Jr., and D. F. DeTar, *Org. Synth.*, 1952, **32**, 8.
9 R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, 1958, **80**, 2896.
10 V. Seidlova, K. Pelz, E. Adlerova, I. Jirkovsky, J. Metysova and M. Protiva, *Collect. Czech. Chem. Commun.*, 1969, **34**, 2258.
11 F. Ullmann and M. Zlokasoff, *Ber. Dtsch. Chem. Ges.*, 1905, **38**, 2111.
12 E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, 1953, **18**, 864.
13 F. E. Ray and C. F. Hull, *J. Org. Chem.*, 1949, **14**, 394.
14 W. C. Lothrop, *J. Am. Chem. Soc.*, 1939, **61**, 2115.
15 P. H. Graham, E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, 1961, **26**, 1008.
16 W. D. Crow and H. McNab, *J. Chem. Res.*, 1988, (*S*) 26.
17 T. Jogima, H. Takeshiba and T. Konotsune, *Chem. Pharm. Bull.*, 1972, **20**, 2191.
18 G. C. Levy, R. L. Lichter and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, Wiley Interscience, New York, 1980, 2nd edn, p. 111.
19 T.-L. Ho, *Tetrahedron*, 1985, **41**, 3, and references therein.
20 H. McNab and M. E.-A. Murray, *J. Chem. Soc., Perkin Trans. 1*, 1989, 589.
21 J. I. G. Cadogan, H. S. Hutchison and H. McNab, unpublished work.
22 I. Agranat and Y. Tapuhi, *J. Am. Chem. Soc.*, 1979, **101**, 665.
23 P. W. Westerman, S. P. Gunasekera, M. Uvais, S. Sultanbawa and R. Kazlauskas, *Org. Magn. Reson.*, 1977, **9**, 631, quoted by E. Breitmaier and W. Voelter, *^{13}C N.m.r. Spectroscopy*, Verlag Chemie, Weinheim, 1978, 2nd edn, p. 297.
24 J. I. G. Cadogan, C. L. Hickson and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1885.
25 W. F. Short and M. L. Stewart, *J. Chem. Soc.*, 1929, 553.
26 W. S. Trahanovsky, C. C. Ong and J. A. Lawson, *J. Am. Chem. Soc.*, 1968, **90**, 2839.
27 A. Kanala and S. Kovac, *Chem. Zvesti*, 1975, **29**, 215.

28 P. Billon, *Ann. Chim. (Paris)*, 1927, **7**, 339.
29 G. Goldschmiedt, *Monatsh. Chem.*, 1902, **23**, 886.
30 A. Luttringhaus and K. Hauschild, *Ber. Dtsch. Chem. Ges.*, 1940, **73**, 145.
31 W. Lawson, W. H. Perkin, Jr., and R. Robinson, *J. Chem. Soc.*, 1924, **125**, 652.
32 R. J. Bailey, P. J. Card and H. Shechter, *J. Am. Chem. Soc.*, 1983, **105**, 6096.

Paper 0/02568B
Received 8*th June* 1990
Accepted 20*th July* 1990