Sigmatropic Rearrangement of 3-(Aryloxymethyl)coumarins: A Simple Synthesis of Hydroxylated 3-Benzylcoumarins

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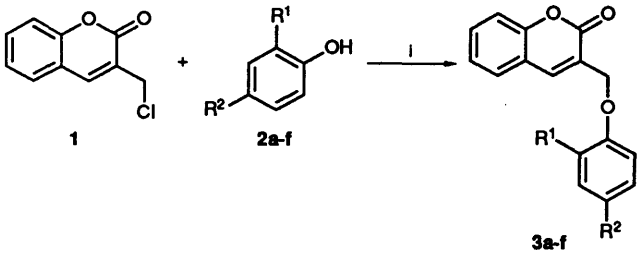
3-Aryloxymethyl[1]benzopyran-2-ones **3a–e**, when heated in diphenyl ether for 4 h, gave high yields of hydroxylated 3-benzyl[1]benzopyran-2-ones **4a–e**, whereas 3-[(*ortho*-substituted)aryloxymethyl][1]benzopyran-2-ones **3a, e** in refluxing quinoline furnished 4-(hydroxyphenyl)-3-methyl-[1]benzopyran-2-ones **7a, e** in 60–62% yield, these products being expected from [3,3]sigmatropic rearrangement, together with compounds **4a, e** in 35% yield. Compounds **3b–d** on refluxing in quinoline furnished exclusively the hydroxylated 3-benzylcoumarins **4b–d**.

3-Alkyl- and 4-alkyl-coumarins are well known [1] for their anthelmintic, hypnotic, insecticidal and antifungal properties, as well as their anticoagulant effect on the blood. A number of syntheses [2] for these compounds have also been reported. Our recent success in the synthesis [3] of 3,4-fused pyrano- and furanocoumarins encouraged us to undertake a study of the thermal rearrangement of 3-aryloxymethyl[1]benzopyran-2-ones **3**. As the 3-alkyl- and 4-phenyl-coumarins are biologically active we also wanted to functionalise the phenyl ring with an OH group. We report the results of our work aimed at studying the sigmatropic rearrangement of compounds **3a–f**. 3-Aryloxymethyl[1]benzopyran-2-ones **3** were synthesized in 68–72% yield by reflux of 3-chloromethylcoumarin **1** with an appropriate phenol **2a–f** and anhydrous potassium carbonate in acetone for 20 h (Scheme 1).



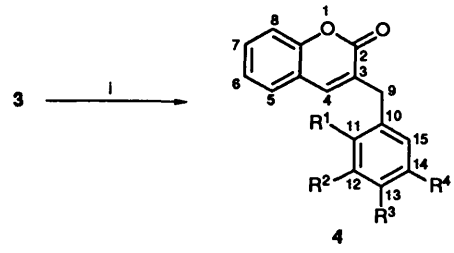
	R^1	R^2		R^1	R^2
a	Cl	H	**d**	H	H
b	H	Me	**e**	Me	H
c	H	Cl	**f**	NO_2	H

Scheme 1 *Reagents and conditions:* i, K_2CO_3, Me_2CO, reflux

Results and Discussion

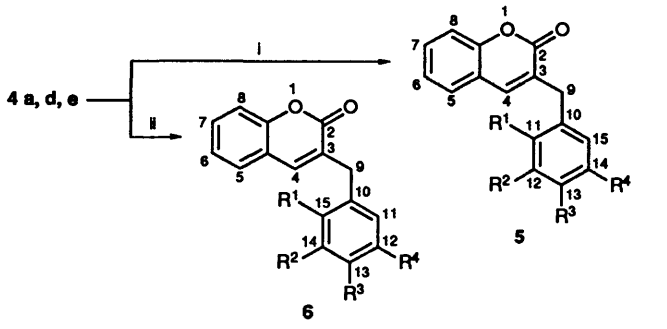
The compounds **3** remain unaffected when heated in refluxing *o*-dichlorobenzene, *N*,*N*-dimethylaniline, decalin, (perhydronaphthalene) hexamethylphosphoric triamide (HMPT) or *N*,*N*-diethylaniline. However, compound **3a**, when heated in diphenyl ether at 240 °C for 4 h, gave a solid, m.p. 178 °C, in 90% yield. The structure **4a** was assigned to this product from elemental analysis and spectral data, including a homodecoupling experiment. Compounds **3b–e** also underwent smooth conversion into products **4b–e** when heated in diphenyl ether at 240 °C for 4 h. Extensive charring occurred in the case of the ether **3f** and only a very low yield of the expected compound **4f** (~9%) was obtained (Scheme 2).

The phenolic nature of the products **4a–e** was also supported by their conversion with acetic anhydride and anhydrous sodium acetate into their acetates **5a–e**, and with *N*-bromosuccinimide (NBS) in tetrachloromethane into their bromo derivatives **6a–e** (Scheme 3). NBS effected nuclear bromination



	R^1	R^2	R^3	R^4
a	H	Cl	OH	H
b	OH	H	H	Me
c	OH	H	H	Cl
d	H	H	OH	H
e	H	Me	OH	H
f	H	No_2	OH	H

Scheme 2 *Reagents and conditions:* i, Ph_2O, reflux

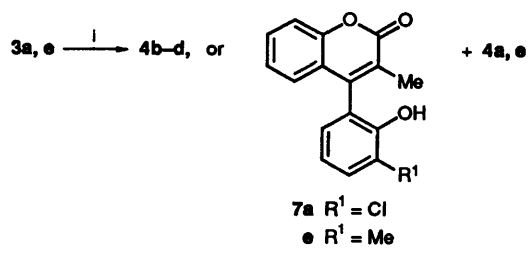


	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
5a	H	Cl	OAc	H	**6a**	H	Cl	OH	Br
b	OAc	H	H	Me	**b**	HO	Br	H	Me
c	OAc	H	H	Cl	**c**	HO	Br	H	Cl
d	H	H	OAc	H	**d**	H	H	OH	Br
e	H	Me	OAc	H	**e**	H	Me	OH	Br

Scheme 3 *Reagents:* i, Ac_2O, NaOAc; ii, NBS, CCl_4

of phenol in compounds **4** in preference to bromination/oxidation of the methylene which is benzylic with respect to the phenyl ring as well as allylic with respect to the coumarin ring system.

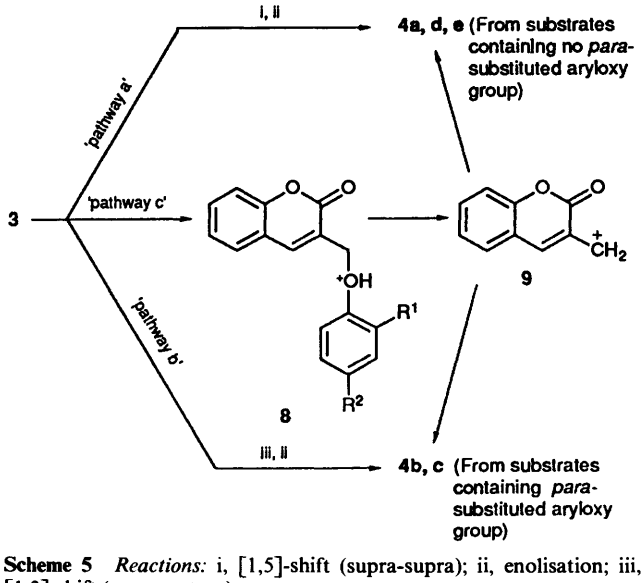
As unusual products **4** were obtained instead of those arising from [3,3]sigmatropic rearrangement, the substrates **3a–e** were heated in refluxing quinoline for 5 h. Two products were obtained in each case for substrates **3a** and **3e**, and these were separated by column chromatography over silica gel. Compound **3a** gave products **4a** (35%) and **7a** (60%). Compound **3e** gave products **4e** (35%) and **7e** (62%) (Scheme 4). Substrates **3b–**



Scheme 4 *Reagents and conditions:* i, Quinoline, reflux

d gave exclusively products **4b**, **4c** and **4d**, respectively. From the results it may be noted that only those substrates with an *ortho*-substituted aryloxy group furnish products arising from the initial [3,3]sigmatropic rearrangement. However, no tractable product was obtained when compound **3f** was refluxed in quinoline for 4 h. Nitroaryloxy-substituted butynes usually need a higher activation energy for thermal rearrangement and are known to decompose[4] at higher temperatures.

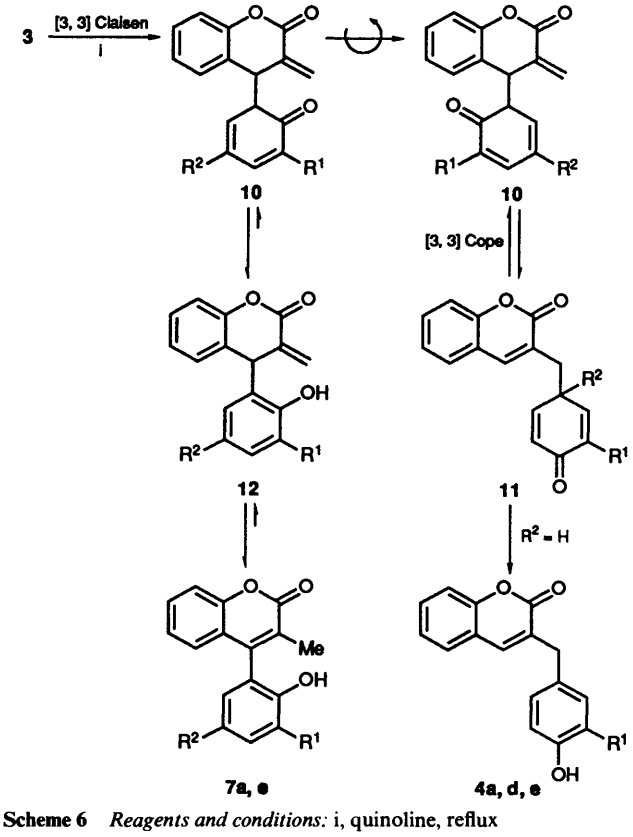
The formation of products **4a**, **d**, **e** and **4b**, **c** from substrates **3a–e** may be explained *via* [1,5]- and [1,3]-sigmatropic shifts, respectively, followed by enolisation. This mechanism is likely to operate at least in diphenyl ether (Scheme 5). Thermal [1,3]-shifts occur by a supra-antara pathway since a supra-supra process is symmetry forbidden. Steric effects are likely to limit the generality of the [1,3]-shifts; examples of [1,3]-shifts are rare[5] in the literature but it is interesting to note that compounds **4b**, **c** are obtained in excellent yield. For substrates **3a**, **d**, **e** the *para* position of the aryloxy moiety is free and [1,5]-shifts can easily occur, but in case of substrates **3b**, **c** the *para* position of the aryloxy moiety is blocked, [1,5]-shifts cannot occur, and, perhaps due to this, [1,3]-shifts occur at the *ortho* position of the aryloxy moiety to give compounds, **4b**, **c**. An alternative route (pathway c) was also considered. Acid catalysis (kinetic acidity) might be coming into play at high temperatures, possible with diphenyl ether as solvent, and formation of products **4** from substrates **3** may reasonably be rationalised by protonation of the ether oxygen of compounds of **3** to give intermediates **8**, loss of the phenol **2** to give a stabilised cation **9** and the reattachment of the aryl moiety at the primary centre *via* an electrophilic substitution process at the *para* or *ortho* position of the activated aromatic ring ('pathway c', Scheme 5). However, we could not obtain any evidence in



Scheme 5 *Reactions:* i, [1,5]-shift (supra-supra); ii, enolisation; iii, [1,3]-shift (supra-antara)

favour of this pathway. When compound **3a** was refluxed in *o*-dichlorobenzene (b.p. 180 °C) in the presence of catalytic amount of toluene-4-sulfonic acid no tractable product was obtained. When compound **3f** was heated in diphenyl ether with excess of phenol at 240 °C for 6 h, compound **4f** was obtained in only 9% yield, extensive charring took place, and we failed to get any of the cross-product **4d**.

An alternative mechanism may be possible in quinoline. It should be noted that there is a remarkable difference between substrates containing *para*-substituted and those containing *ortho*-substituted groups. Compounds **3** may undergo a [3,3]Claisen rearrangement followed by a [3,3]Cope rearrangement to give dienone **11**. When $R^2 \neq H$, the dienones **11** cannot re-aromatise and go back to Claisen product **7a**, **e**, *etc.*, *via* *exo*-methylene compound and so the ethers **3** may undergo a [1,3]-shift followed by enolisation to give compounds **4b**, **c**. When $R^2 = H$, the dienones **11** re-aromatise to the phenols **4a**, **d**, **e**. Presumably, in quinoline, proton transfer is assisted and so the Claisen intermediate **10** aromatises rapidly before further Cope rearrangement can occur (Scheme 6).



Scheme 6 *Reagents and conditions:* i, quinoline, reflux

It is relevant to mention here that the corresponding 4-(aryloxymethyl)[1]benzopyran-2-one failed to undergo any such rearrangement.[6] Recently there has been increased interest in the synthesis of 3-benzylcoumarins[7–11] due to their well known biological activities. Some of them are used as central nervous system stimulants[12] while others are effective against intestinal nematodes.[13] They are also known to possess rodenticidal,[14] analgesic,[15,16] and plant-growth-regulating activities.[17] It is interesting to note that the simple methodology described here is general for a range of 3-(substituted aryloxymethyl)[1]benzopyran-2-ones as substrates for the preparation of hydroxylated 3-benzylcoumarins in high yield. The introduction of an OH group in the benzyl moiety provides an effective handle for further modification of the benzyl part of the molecule. To our knowledge this is the first report on the synthesis of hydroxylated 3-benzylcoumarins.

Experimental

M.p.s were determined in a sulfuric acid-bath and are uncorrected. UV absorption spectra were recorded on a Hitachi 200–20 spectrometer for solutions in 95% ethanol. IR spectra were run for KBr discs on a Perkin-Elmer 1330 apparatus. ^{1}H NMR spectra were determined for solutions in deuteriochloroform with $SiMe_4$ as internal standard on a Jeol FX-100 (100 MHz) spectrometer at the Indian Institute of Chemical Biology, Calcutta and a Bruker WH-400 (400 MHz) spectrometer at the University of Alberta, Edmonton, Canada. *J*-Values are given in Hz. ^{13}C NMR spectra were determined for solutions in deuteriochloroform with $SiMe_4$ as internal standard on a Jeol FX-100 (100 MHz) spectrometer. Elemental analyses and recording of mass spectra (EI) were carried out by RSIC (CDRI), Lucknow. Silica gel (60–120 mesh) was obtained from BDH. Extracts were dried over anhydrous sodium sulfate. Light petroleum fractions LP1 and LP2 refer to the fractions boiling in the range 40–60 and 60–80 °C, respectively.

General Procedure for the Preparation of 3-(*Aryloxymethyl*)-[1]*benzopyran-2-ones* **3a–f**.—A mixture of 3-(chloromethyl)-coumarin[18] **1** (1 g, 6 mmol), an appropriate phenol **2** (5 mmol) and anhydrous potassium carbonate (2 g) in dry acetone (75 cm^3) was refluxed for 14 h. The reaction mixture was cooled and filtered, and the solvent was removed from the filtrate under reduced pressure. The residual mass was extracted with chloroform (3 × 20 cm^3), and the extract was washed with saturated brine (3 × 20 cm^3) and dried (Na_2SO_4). Removal of solvent gave a crude solid, which was purified by column chromatography over silica gel using benzene–LP2 (1 : 1) as eluent.

Compound **3a** (70%), m.p. 148 °C; λ_{max}/nm 310 (log ε 4.23), 273 (4.01) and 260 (3.91); ν_{max}/cm^{-1} 1730 (C=O) and 1235; δ 5.03 (2 H, s), 6.84–7.72 (8 H, m) and 8.00–8.20 (1 H, m) (Found: C, 67.1; H, 3.7. $C_{16}H_{11}ClO_3$ requires C, 67.0; H, 3.8%).

Compound **3b** (68%), m.p. 120 °C; λ_{max}/nm 312 (4.28) and 275 (3.98); ν_{max}/cm^{-1} 1740 (C=O) and 1280; δ 2.32 (3 H, s), 5.02 (2 H, s), 6.88–7.68 (8 H, m) and 7.88–8.04 (1 H, m) (Found: C, 76.5; H, 5.4. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%).

Compound **3c** (70%), m.p. 175 °C; λ_{max}/nm 315 (4.31), 276 (3.93) and 260 (3.79); ν_{max}/cm^{-1} 1730 (C=O) and 1270; δ 5.02 (2 H, s), 6.88–7.76 (8 H, m) and 7.84–7.96 (1 H, m) (Found: C, 67.1; H, 3.7. $C_{16}H_{11}ClO_3$ requires C, 67.0; H, 3.8%).

Compound **3d** (72%), m.p. 131 °C; λ_{max}/nm 312 (4.21) and 275 (3.99); ν_{max}/cm^{-1} 1745 (C=O) and 1260; δ 5.02 (2 H, s), 6.92–7.60 (9 H, m) and 7.84–8.00 (1 H, m) (Found: C, 76.1; H, 4.8. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8%).

Compound **3e** (70%), m.p. 140 °C; λ_{max}/nm 312 (4.28) and 275 (3.98); ν_{max}/cm^{-1} 1740 (C=O) and 1255; δ 2.40 (3 H, s), 5.10 (2 H, s) and 6.92–7.93 (9 H, m) (Found: C, 76.6; H, 5.3. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%).

Compound **3f** (70%), m.p. 185 °C; λ_{max}/nm 312 (4.29) and 262 (3.82); ν_{max}/cm^{-1} 1750 and 1240; δ 5.01 (2 H, s) and 7.02–8.07 (9 H, m) (Found: C, 64.7; H, 3.8. $C_{16}H_{11}NO_5$ requires C, 64.6; H, 3.7%).

General Procedure for the Synthesis of Hydroxylated 3-*Benzyl*[1]*benzopyran-2-ones* **4a–e**.—A 3-(aryloxymethyl)coumarin **3** (0.5 g) was heated in diphenyl ether (5 cm^3) on an oil-bath at 240 °C for 4 h. Diphenyl ether was removed under reduced pressure and the residue was chromatographed over silica gel. Elution of the column with LP2 removed the residual diphenyl ether and then a solid was obtained by elution of the column with benzene–LP2 (3 : 1).

Compound **4a** (90%), m.p. 178 °C; λ_{max}/nm 310 (4.78) and 280 (3.87); ν_{max}/cm^{-1} 3300 and 1700 (C=O); δ_H 3.82 (2 H, s, CH_2), 5.54 (1 H, s, OH, D_2O exchangeable), 6.96–7.02 (1 H, d, *J* 8, 14-H), 7.08–7.12 (1 H, dd, *J* 8 and 1.8, 15-H), 7.26 (1 H, d, *J* 1.8, 11-H), 7.22–7.28 (1 H, dt, *J* 8, 6-H), 7.34 (1 H, s, 4-H), 7.32–7.36 (1 H, m, 5-H), 7.38–7.42 (1 H, dd, *J* 8 and 1.3, 8-H) and 7.46–7.50 (1 H, m, 7-H); δ_C 35.00, 116.30, 117.18, 119.93, 120.18, 124.83, 128.30, 128.77, 129.12, 130.41, 130.65, 131.42, 140.18, 152.24, 153.12 and 161.30; *m/z* 288 and 286 (M$^+$), 252 (base peak), 238, 223, 175 (Found: C, 67.0; H, 3.8. $C_{16}H_{11}ClO_3$ requires C, 67.0; H, 3.8%).

Compound **4b** (85%), m.p. 171 °C; λ_{max}/nm 312 (4.62) and 282 (3.69); ν_{max}/cm^{-1} 3325 and 1700 (C=O); δ 2.25 (3 H, s), 3.84 (2 H, s), 5.52 (1 H, s, D_2O exchangeable) and 6.84–7.60 (8 H, m); *m/z* 266 (M$^+$, base peak), 248, 237 and 159 (Found: C, 76.6; H, 5.3. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%).

Compound **4c** (70%), m.p. 198 °C; λ_{max}/nm 312 (4.76) and 284 (3.80); ν_{max}/cm^{-1} 3310 and 1710 (C=O); δ 3.80 (2 H, s), 5.48 (1 H, s, D_2O exchangeable) and 6.96–7.56 (8 H, m); *m/z* 288, 286, 252 (base peak), 238 and 223 (Found: C, 67.0; H, 3.9. $C_{16}H_{11}ClO_3$ requires C, 67.0; H, 3.8%).

Compound **4d** (88%), m.p. 164 °C; λ_{max}/nm 310 (4.79) and 278 (3.92); ν_{max}/cm^{-1} 3340 and 1730 (C=O); δ 3.82 (2 H, s), 4.86 (1 H, s, D_2O exchangeable) and 6.80–7.64 (9 H, m); *m/z* 252 (M$^+$, base peak), 235, 224 and 207 (Found: C, 76.1; H, 4.8. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8%).

Compound **4e** (87%), m.p. 160 °C; λ_{max}/nm 310 (4.57) and 282 (3.68); ν_{max}/cm^{-1} 3320 and 1710 (C=O); δ 2.32 (3 H, s), 3.83 (2 H, s), 5.01 (1 H, s, D_2O exchangeable) and 6.77–7.50 (8 H, m) (Found: C, 76.7; H, 5.3. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%).

Compound **4f** (9%), m.p. 135 °C; λ_{max}/nm 310 (4.72) and 282 (3.85); ν_{max}/cm^{-1} 3300 and 1705; δ 4.02 (2 H, s), 5.12 (1 H, s) and 7.04–8.01 (8 H, m) (Found: C, 64.5; H, 3.8. $C_{16}H_{11}NO_5$ requires C, 64.6; H, 3.7%).

Preparation of Acetate Derivatives of Phenolic Compounds **4a–e**.—A phenolic compound **4** (0.2 g) was heated with anhydrous sodium acetate (0.2 g) and acetic anhydride (2 cm^3) on a water-bath for 6 h and was then left overnight. The reaction mixture was poured into crushed ice and scratched with a glass rod before being extracted with diethyl ether (2 × 25 cm^3). The extract was washed successively with 5% aq. sodium hydrogen carbonate and saturated brine and dried. Removal of solvent gave a viscous oil, which was then purified by column chromatography over silica gel. Elution of the column with benzene–LP2 (1 : 1) furnished the desired acetate derivative **5a–e**.

Compound **5a** (95%), viscous liquid; λ_{max}/nm 315 (4.10), 272 (4.00) and 240 (3.72); ν_{max}/cm^{-1} 1780, 1750 and 1240; δ 2.30 (3 H, s, OAc), 3.90 (2 H, s, 9-H), 7.05–7.09 (2 H, m, 14- and 15-H), 7.24 (1 H, ddd, *J* 8 and 1.3, 6-H), 7.29–7.34 (3 H, m, 4-, 5- and 11-H), 7.38 (1 H, dd *J* 8 and 1.8, 8-H) and 7.47 (1 H, ddd, *J* 8 and 1.8, 7-H); *m/z* 330 and 328 (M$^+$) (Found: C, 65.7; H, 4.0. $C_{18}H_{13}ClO_4$ requires C, 65.8; H, 3.9%).

Compound **5b** (90%), viscous liquid; λ_{max}/nm 312 (4.08), 275 (3.98) and 240 (3.70); ν_{max}/cm^{-1} 1780, 1740 and 1240; δ 2.24 (3 H, s), 2.36 (3 H, s), 3.83 (2 H, s) and 6.96–7.64 (8 H, m); *m/z* 308 (M$^+$) (Found: C, 74.0; H, 5.2. $C_{19}H_{16}O_4$ requires C, 74.0; H, 5.2%).

Compound **5c** (90%), viscous liquid; λ_{max}/nm 312 (4.10), 272 (3.92) and 238 (3.74); ν_{max}/cm^{-1} 1790, 1750 and 1250; δ 2.24 (3 H, s), 3.82 (2 H, s) and 7.00–7.60 (8 H, m) (Found: C, 65.7; H, 4.0. $C_{18}H_{13}ClO_4$ requires C, 65.8; H, 3.9%).

Compound **5d** (92%), viscous liquid; λ_{max}/nm 315 (4.02), 272 (3.85) and 240 (3.69); ν_{max}/cm^{-1} 1775, 1735 and 1260; δ 2.32 (3 H, s), 3.92 (2 H, s) and 7.02–7.64 (9 H, m) (Found: C, 73.4; H, 4.8. $C_{18}H_{14}O_4$ requires C, 73.5; H, 4.8%).

Compound **5e** (88%), viscous liquid; λ_{max}/nm 312 (4.10), 275 (3.98) and 238 (3.76); ν_{max}/cm^{-1} 1790 and 1735; δ 2.22 (3 H, s), 2.32 (3 H, s), 3.84 (2 H, s) and 7.00–7.67 (8 H, m) (Found: C, 74.0; H, 5.2. $C_{19}N_{16}O_4$ requires C, 74.0; H, 5.2%).

Preparation of Bromo Derivatives of Phenolic Compounds **4a–e**.—Compound **4** (5 mmol), NBS (0.9 g, 5 mmol) and benzoyl

peroxide (1 mg) were refluxed in tetrachloromethane (50 cm^3) for 10 h. The reaction mixture was filtered, chloroform (25 cm^3) was added, and the solution was washed successively with brine and water and dried. The solvent was removed under reduced pressure to give a viscous oil, which was then purified by column chromatography over silica gel using benzene–LP2 (1:3) as eluent.

Compound **6a** (91%), m.p. 192 °C; λ_{max}/nm 312 (4.29) and 280 (3.90); ν_{max}/cm^{-1} 3380 and 1730; δ_H 3.80 (2 H, s), 5.85 (1 H, s), and 7.22–7.60 (7 H, m); δ_C 35.00, 112.36, 116.36, 119.53, 122.24, 124.95, 128.06, 128.48, 129.94, 131.65, 132.36, 140.77, 149.07, 153.18 and 161.24 (Found: C, 52.5; H, 2.8. $C_{16}H_{10}BrClO_3$ requires C, 52.5; H, 2.7%).

Compound **6b** (90%), m.p. 182 °C; λ_{max}/nm 312 (4.23) and 282 (3.92); ν_{max}/cm^{-1} 3300 and 1700; δ 2.26 (3 H, s), 3.89 (2 H, s), 6.34 (1 H, s, D_2O exchangeable) and 7.00–7.72 7 H, m) (Found: C, 59.1; H, 3.8. $C_{17}H_{13}BrO_3$ requires C, 59.1; H, 3.8%).

Compound **6c** (85%), m.p. 207 °C; λ_{max}/nm 310 (4.31) and 280 (3.85); ν_{max}/cm^{-1} 3300 and 1700; δ 3.82 (2 H, s), 5.52 (1 H, s, D_2O exchangeable) and 6.94–7.72 (7 H, m) (Found: C, 52.5; H, 2.8. $C_{16}H_{10}BrClO_3$ requires C, 52.5; H, 2.7%).

Compound **6d** (87%), m.p. 182 °C; λ_{max}/nm 315 (4.21) and 280 (3.82); ν_{max}/cm^{-1} 3310 and 1700; δ 3.80 (2 H, s, CH_2), 5.50 (1 H, s, D_2O exchangeable, OH), 7.0 (1 H, d, *J* 8, 14-H), 7.16 (1 H, dd, *J* 8 and 1.8, 15-H), 7.24 (1 H, ddd, *J* 8 and 1.3, 6-H), 7.32 (1 H, dd, *J* 8 and 1.3, 5-H), 7.34 (1 H, s, 4-H), 7.39 (1 H, dd, *J* 8 and 1.8, 8-H), 7.41 (1 H, d, *J* 1.8, 11-H) and 7.48 (1 H, ddd, *J* 8 and 1.8, 7-H) (Found: C, 58.0; H, 3.3. $C_{16}H_{11}BrO_3$ requires C, 58.0; H, 3.3%).

Compound **6e** (86%), m.p. 180 °C; λ_{max}/nm 312 (4.28) and 282 (3.91); ν_{max}/cm^{-1} 3310 and 1705; δ 2.28 (3 H, s), 3.84 (2 H, s), 6.01 (1 H, s, D_2O exchangeable) and 6.97–7.51 (7 H, m) (Found: C, 59.1; H, 3.8. $C_{17}H_{13}BrO_3$ requires C, 59.1; H, 3.7%).

Rearrangement of 3-(*Aryloxymethyl*)*coumarins* **3a–e** *in Quinoline.*—A compound **3** (0.5 g) was refluxed in quinoline (5 cm^3) for 5 h. The reaction mixture was cooled and poured into ice-cold 6 mol dm^{-3} hydrochloric acid (5 cm^3). The crude mass was extracted with chloroform (3 × 25 cm^3) and the extract was washed successively with dil. HCl, brine and water, and was then dried. Removal of chloroform and column chromatography of the crude product over silica gel, using benzene as eluent, furnished the following products. Compounds **3b–d** gave exclusively products **4b–d**. Compounds **3a** and **3e** gave two products each (**4a**/**7a** and **4e**/**7e**).

Compound **7a** (60%) (along with 35% of **4a**), m.p. 186 °C; λ_{max}/nm 280 (3.98) and 240 (4.28); ν_{max}/cm^{-1} 3350 and 1715 (C=O); δ 2.02 (3 H, s), 5.94 (1 H, s, D_2O exchangeable) and 7.0–7.60 (7 H, m) (Found: C, 67.0; H, 3.9. $C_{16}H_{11}ClO_3$ requires C, 67.0; H, 3.8%).

Compound **7e** (62%) (along with 35% of **4e**), m.p. 176 °C; λ_{max}/nm 282 (3.92) and 240 4.29); ν_{max}/cm^{-1} 3340 and 1710 (C=O); δ 2.01 (3 H, s), 2.40 (3 H, s), 5.92 (1 H, s, D_2O exchangeable) and 6.91–7.76 (7 H, m) (Found: C, 76.6; H, 5.3. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%).

Rearrangement of Compound **3f** *in Diphenyl Ether in the Presence of Phenol; General Procedure.*—Compound **3f** (0.44 g, 2 mmol) was heated in diphenyl ether (5 cm^3) at 240 °C for 8 h with phenol (0.18 g, 2 mmol). TLC indicated the formation of product **4f** and gave no indication of the formation of cross-product **4d** with incorporation of phenol. Diphenyl ether was removed under reduced pressure and the residue was chromatographed over silica gel, using benzene as eluent, to give product **4f**, m.p. 135 °C (0.4 g, 9%).

Attempted Rearrangement of Compound **3a** *with Toluene-4-sulfonic acid in* o-*Dichlorobenzene; General Procedure.*—Compound **3a** (0.58 g, 2 mmol) was refluxed in *o*-dichlorobenzene (5 cm^3) with toluene-4-sulfonic acid (0.2 g) for 8 h. The reaction mixture was poured into crushed ice and extracted with diethyl ether (3 × 30 cm^3), and the extract was washed with saturated brine (2 × 25 cm^3) and finally dried. The solvent was removed and the residue was chromatographed over silica gel, using benzene–LP2 (3:1) as eluent, but gave no compound **4a**.

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