

Reaction of 3-Halogeno-2*H*-1-benzopyran-2-ones with Organometallic Compounds. Synthesis of 4-Alkyl-2*H*-1-benzopyran-2-ones. X-Ray Molecular Structure of 3-Bromo-3,4-dihydro-4-isopropylcoumarin

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3-Halogeno-2*H*-1-benzopyran-2-ones react with magnesium, lithium, aluminium and copper derivatives to give 3,4-dihydrocoumarins and 3-(*o*-hydroxyphenyl)propenols as major products. The nature and the ratio of the products in the final mixture depend on the solvent and on the organometallic reagent. Grignard derivatives yield 1,4-monoalkylation compounds in tetrahydrofuran (THF) or 1,2-dialkylation derivatives in toluene. In some cases the dehalogenation competes with the 1,2-alkylation process in the reactions with alkylolithiums. The presence of the halogen at C-3 increases the reductive ability of organoaluminiums. In general, the reaction with lithium dialkylcuprates leads to complex mixtures of products. The 4-alkyl-3-halogeno-3,4-dihydrocoumarins obtained undergo dehydrohalogenation easily, and lead to 4-alkylcoumarins in good yields. The tandem alkylation–dehydrohalogenation of 3-halogeno-2*H*-1-benzopyran-2-ones constitutes a versatile synthesis of 4-alkylcoumarins.

The reaction of coumarins with organometallic compounds is a very well known synthetic method to 2*H*-1-benzopyrans. We have now studied the reactivity of 3-chloro- and 3-bromocoumarins towards magnesium, lithium, aluminium and copper derivatives in order to confirm the influence of the halogen on the behaviour of these substrates.

The Grignard derivatives react with 3-chlorocoumarin **1**, 3-bromocoumarin **2**, and 3-bromo-4-methylcoumarin **3** leading to dihydrocoumarins, chromen-2-ols, and open-chain compounds as a consequence of 1,4- and/or 1,2-addition or reduction processes (Scheme 1). The rate of reaction is intermediate between that with the organolithiums and that with organoaluminiums, and the solvent plays an important role in determining the ratio of the products in the final mixture (Table 1).

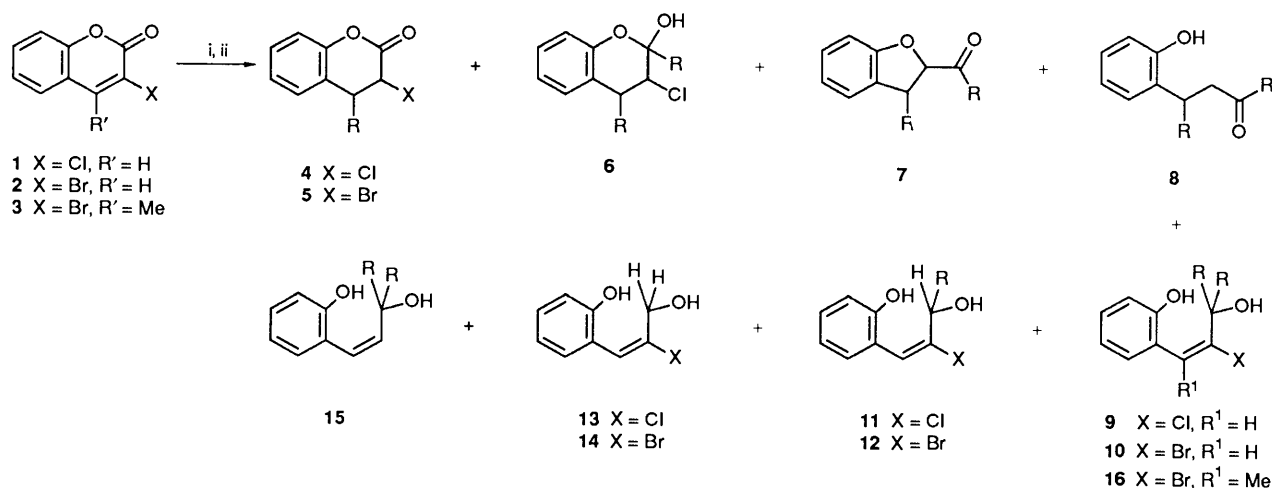
As previously described for 3-phenyl- and 3-ethoxycarbonylcoumarin,^{1–3} in our case the 1,4-addition process was favoured when the reactions were carried out in ether solvents (THF or diethyl ether) and with increasingly bulky groups R; the resulting 4-alkyl-3-halogeno-3,4-dihydrocoumarins **4** and **5** were obtained as a mixture of *cis* (80–90%) and *trans* (20–10%) isomers.

Indeed a double 1,2-addition was the major process for 3-bromo-4-methylcoumarin or when benzene or toluene was used as solvent.

The ratio of products in the final mixture also depends on the nature of the magnesium derivative; thus, EtMgI and EtMgBr led to the same mixture, but MeMgI did not produce 1,4-addition, and PrⁱMgBr gave reduction products (*E*)-2-bromo-1-(*o*-hydroxyphenyl)-4-methylpent-1-en-3-ol **12d** and (*E*)-2-chloro-1-(*o*-hydroxyphenyl)-4-methylpent-1-en-3-ol **11d** in 50–60% yield.

On the other hand, 3-chloro- and 3-bromo-coumarin behave in similar fashion towards organometallics. Only in the case of phenylmagnesium bromide did 3-bromocoumarin lead to phenyl 2,3-dihydro-3-phenylbenzofuranyl ketone **7f**, whereas 3-chlorocoumarin yielded 3-chloro-3,4-dihydro-2,4-diphenyl-2*H*-1-benzopyran-2-ol **6f**, but both products derive from a common hydroxy ketone (acyloin) intermediate **6'** that in the hydrolysis leads to the benzofuran **7** derivative—if X = Br—or to the chromanol—if X = Cl—(Scheme 2).

As an alternative to the preparation of compounds **4a**, **5a**, **4f** and **5f** we have tested the reactivity of compounds **1** and **2** with

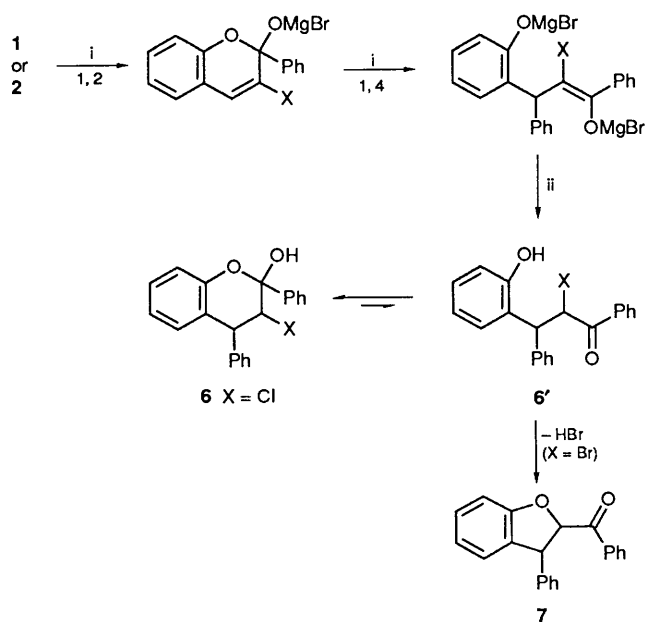


Scheme 1 a, R = Me; b, R = Et; c, R = Bu; d, R = Prⁱ; e, R = Bu^t; f, R = Ph. Reagents: i, organometallic compounds; ii, water

Table 1 Reaction of compounds **1**, **2** and **3** with Grignard derivatives

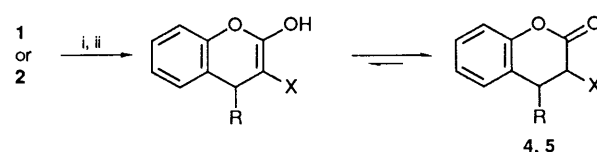
Coumarin	RMgX	Solvent ^a	Yield (%)								
			4	5	6	7	9	10	11	12	
1	MeMgI	Et ₂ O-PhMe						9a	85		
1	EtMgBr	Et ₂ O-PhMe	4b	55				9b	40		
1	EtMgBr	PhMe	4b	25				9b	70		
1	EtMgBr	Et ₂ O	4b	70				9b	25		
1	EtMgI	Et ₂ O	4b	75				9b	20		
1	BuMgBr	PhMe	4c	5				9c	85		
1	BuMgBr	Et ₂ O	4c	40				9c	50	11c	5
1	BuMgBr	THF	4c	65				9c	20	11c	15
1	Pr ⁱ MgBr	Et ₂ O-PhMe	4d	65				9d	15	11c	15
1	Pr ⁱ MgBr	PhMe	4d	20				9d	20	11d	57
1	Pr ⁱ MgBr	Et ₂ O	4d	25				9d	42	11d	30
1	PhMgBr	Et ₂ O-PhMe			6f	20		9f	60		b
2	MeMgI	Et ₂ O-PhMe						10a	80		
2	EtMgBr	Et ₂ O-PhMe			5b	40		10b	52		b
2	EtMgBr	PhMe			5b	27		10b	65		b
2	EtMgBr	THF			5b	66		10b	30		b
2	EtMgBr	Et ₂ O			5b	40		10b	52		b
2	BuMgBr	PhMe			5c	12		10c	70		12c
2	BuMgBr	THF			5c	72		10c	20		
2	Pr ⁱ MgBr	Et ₂ O-PhMe			5d	60		10d	22		12d
2	Pr ⁱ MgBr	PhMe			5d	24		10d	16		12d
2	Pr ⁱ MgBr	Et ₂ O			5d	70		10d	12		12d
2	PhMgBr	Et ₂ O-PhMe					7f	60	10f	20	c
3	EtMgBr	Et ₂ O									d

^a The reactions were carried out at 0 °C for 30 min. ^b Compounds **15** (4–10%) were also isolated. ^c Compound **8f** (15%) was isolated. ^d 4-Bromo-3-ethyl-5-(*o*-hydroxyphenyl)hex-4-en-3-ol **16b** (70%) was isolated.

**Scheme 2** Reagents: i, PhMgBr; ii, water

lithium dimethylcuprate and lithium diphenylcuprate; the reactions led to a complex mixture of compounds except for 3-chlorocoumarin and lithium dimethylcuprate which yielded compound **4a** (65%) as a mixture of *cis* (60%) and *trans* (40%) isomers. The difference in the ratio of isomers when lithium dimethylcuprate and Grignard derivatives were used is a consequence not of the organometallic reagent's nature but of the stereochemical interactions in the kinetically controlled tautomerization of the 4-alkyl-3-halogeno-4*H*-1-benzopyran-2-ol to afford the final product (Scheme 3).

Lithium derivatives react with 3-halogenocoumarins to afford 1,2-addition compounds as major products **9** or **10**, but in

**Scheme 3** Ratio of *cis:trans* isomers: R = Me, 60:40; R = Et, 80:20; R = Bu, 85:15; R = Prⁱ, 90:10; Reagents: i, organometallic compound; ii, water

the reaction of compound **1** with butyllithium, the chromanone **4c** can be isolated in 30% yield (Table 2). From the reaction mixtures when butyllithium was used as reagent, important amounts of dehalogenation compounds could be obtained; this behaviour was also observed with magnesium and copper derivatives.

It has previously been shown that coumarins suffer a double 1,2-addition towards trialkylaluminiums in hexane, benzene, or toluene.^{4,5} In the present case, the halogen at C-3 increases the reduction ability of organoaluminiums, with the 1,2-alkylation and 1,2-reduction products **11** or **12** being the major products of the reactions; in the case of triisobutylaluminium, double 1,2-reduction is the most important process (compounds **13** or **14**) (Scheme 4). On the other hand, trimethylaluminium is less reactive than other organoaluminiums, and it requires higher concentrations and reaction times to give moderate yields of dialkylated diols **9a** and **10a** (Table 3).

The reactivity of organoaluminiums diminished when diethyl ether or THF were used as the solvent, whereas these solvents increased the reductive power; as an example, with the system Et₃Al-THF compound **13** was obtained 60% yield (Table 3).

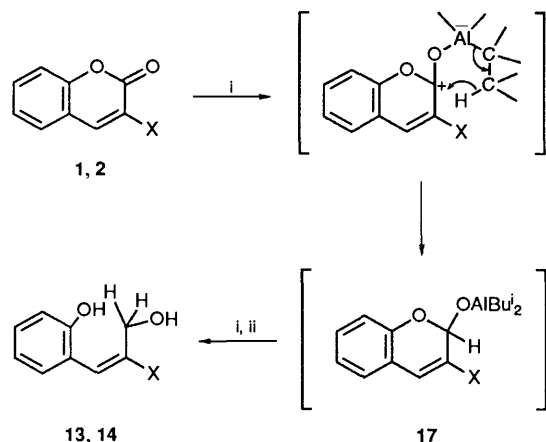
The reduction of 3-chloro- and 3-bromo-coumarin with DIBAL-H is not a satisfactory method to obtain compounds **13** and **14**. The first step to the hemiacetal intermediate **17** is a fast process, but its transformation to the final product is very slow at 0 °C. Nevertheless this intermediate is transformed to

Table 2 Reaction of compounds 1 and 2 with lithium derivatives

Coumarin	RLi	Solvent	Yield (%)			
			4	9	10	15
1	MeLi	Et ₂ O ^a		9a 80		
1	BuLi	PhMe ^b	4c 10	9c 80		
1	BuLi	Et ₂ O ^a	4c 20	9c 70		
2	MeLi	Et ₂ O ^a			10a 60	15a 25
2	BuLi	PhMe ^b			10c 60	15c 35

^a The reactions were carried out at 0 °C. ^b The reactions were carried out at -40 °C.

the monoalkylated derivatives 11 and 12, by addition of one equivalent of organolithium or a Grignard derivative (Scheme 5, Table 4).

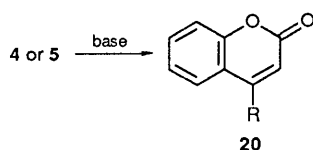


Scheme 4 Reagents: i, Buⁱ₃Al; ii, water

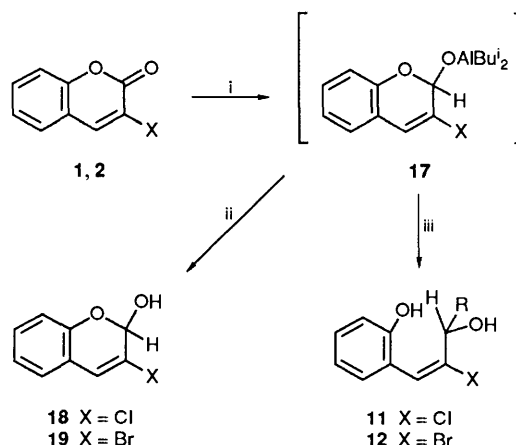
The described monoalkylation process could be achieved from the corresponding coumarin and organoaluminium as previously reported,^{4,5} but the methodology presented here is advantageous because lithium and magnesium derivatives are more easily accessible than are the aluminium ones, and because some of the last substrates showed only reductive (Buⁱ₃Al) or alkylation (Me₃Al) properties.

The yields summarized in Tables 1–4 were determined by ¹H NMR spectroscopy on the reaction mixtures. In the Experimental section, the yields refer to pure, isolated compounds in optimized experiments.

The isomeric mixture of 4-alkyl-3-halogeno-3,4-dihydrocoumarins 4 and 5 was transformed into 4-alkylcoumarins 20 by a base-promoted dehydrohalogenation and the yields and the experimental conditions are summarized in Table 5. The major isomer of the 3-bromo derivatives 5 is easily dehydrohalogenated in pyridine at 50 °C, whereas the minor component is recovered unchanged. Otherwise, 3-chloro derivatives 4 were recovered unchanged after treatment with pyridine in refluxing benzene. Moreover we have been unable to epimerize the mixture to the most stable compound by reaction with Ac₂O–AcONa; ¹ 4-alkylcoumarins are obtained from both 3-chloro and 3-bromo derivatives, dehydrohalogenation of the major isomer being easier than that of the minor one.



The *cis*-configuration of the 3-bromo-3,4-dihydro-4-isopropylcoumarin 5d, determined by X-ray crystallography (Fig. 1), was extended for all the major isomers of the 3-halogeno



Scheme 5 Reagents: i, DIBAL-H; ii, water; iii, RMgX or RLi

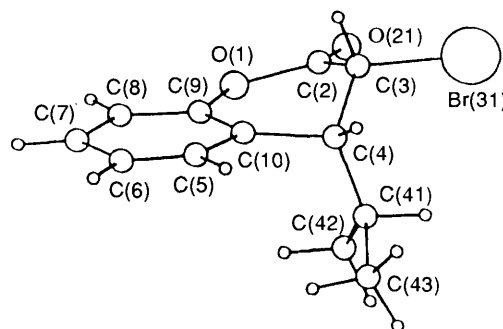


Fig. 1 X-Ray structure and crystallographic numbering for compound 5d (hydrogen atoms omitted)

derivatives 4 and 5 because of the observed systematic behaviour of their chemical shifts for H^a (Table 6), and their behaviour towards Ac₂O–AcNa (Table 5). The *cis*-configuration of the major isomers was corroborated by NOE experiments between H^a and H^b, and by the observed anisotropy for methylene protons in 4b and the methyl protons in 4d in their ¹H NMR spectra (this anisotropy is higher in 3-chloro than in 3-bromo derivatives).

On the other hand, our results are in agreement with those previously described by Ivanov and Bojilova¹ for 3-phenylcoumarin, leading to the less stable *cis*-isomer assigned by a study on epimerization with Ac₂O–AcNa and the coupling constants.

Experimental

M.p.s were measured on a Leitz Laborlux D microscope with a heating device and are uncorrected. NMR spectra were recorded on either Bruker AC80 or Bruker WP200 SY spectrometers and chemical shifts are given downfield from SiMe₄ as internal standard. Mass spectra were measured on a Hewlett-Packard 5988A mass spectrometer.

Table 3 Reaction of compounds **1** and **2** with R₃Al^a

Coumarin	R ₃ Al	Solvent	Yield (%)					
			9	10	11	12	13	14
1	Me ₃ Al	PhMe	9a 75					
1	Et ₃ Al	PhMe	9b 40		11b 55			
1	Et ₃ Al	THF					13 65	
1	Bu ₃ Al	PhMe	9c 7		11c 85			
1	Bu ⁱ ₃ Al	PhMe			11c 40		13 50	
2	Me ₃ Al	PhMe		10a 70				
2	Et ₃ Al	PhMe		10b 17		12b 75		
2	Bu ₃ Al	PhMe		10c 5		12c 85		
2	Bu ⁱ ₃ Al	PhMe				12c 15		14 80

^a The reactions were carried out at 0 °C for 10 h.**Table 4** Reaction of compound **1** and **2** with DIBAL-H/RM

Coumarin	RM	Yield (%)					
		11	12	13	14	18	19
1				13 7		18 85	
1	MeMgI	11a 85		13 9			
1	Pr ⁱ MgBr	11d 49		13 19			<i>a</i>
1	BuLi	11c 70		13 2			<i>b</i>
2							19 90
2	EtMgBr		12b 90		14 7		
2	PhMgBr		12f 80				

^a Compound **9d** (25%) was isolated. ^b Compound **9c** (20%) was isolated.**Table 5** Dehydrohalogenation of the isomeric mixture of compound **4** or compound **5**

Substrate	Method	Time (h)	Yield (%) of compound 20	Recovery (%) of unchanged substrate
4a	a	2	3 20a	92 <i>cis/trans</i>
4b	a	2	2 20b	95 <i>cis/trans</i>
4c	a	2	5 20c	90 <i>cis/trans</i>
4d	a	2	3 20d	95 <i>cis/trans</i>
5b	a	2	80 20b	10 <i>trans</i>
5c	a	2	92 20c	5 <i>trans</i>
5d	a	2	93 20d	5 <i>trans</i>
4a	b	2		95 <i>cis/trans</i>
4b	b	10	2 20b	90 <i>cis/trans</i>
4c	b	10	5 20c	90 <i>cis/trans</i>
5b	b	10	2 20b	90 <i>cis/trans</i>
4a	c	0.2	33 20a	27 <i>cis/37 trans</i>
5b	c	3	80 20b	
4c	c	3	85 20c	
5b	c	0.2	40 20b	40 <i>cis/10 trans</i>
5b	c	3	75 20b	
5c	c	3	80 20c	

Method ^a Boiling benzene with a few drop of pyridine. ^b 0.1 mol dm⁻³ NaOAc in Ac₂O at room temperature. ^c 0.1 mol dm⁻³ NaOAc in Ac₂O at reflux.

Starting materials 3-chlorocoumarin,⁶ 3-bromocoumarin⁷ and 3-bromo-4-methylcoumarin⁸ were prepared as previously described.

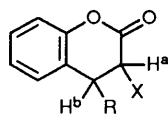
Reaction of Compound 1 with Me₂CuLi. Synthesis of 3-Chloro-3,4-dihydro-4-methyl-2H-1-benzopyran-2-one 4a.—To a stirred suspension of CuI (0.31 g, 1.6 mmol) in dry diethyl ether (20 cm³) under N₂ at -10 °C was added a solution of MeLi in diethyl ether (2 cm³; 3.2 mmol). The colourless solution was cooled to -40 °C and a solution of compound **1** (0.2 g, 1.1 mmol) in diethyl ether (20 cm³) was added dropwise. The mixture was stirred at between -40 and -30 °C for 30 min, and quenched with saturated aq. NH₄Cl (15 cm³). The product was extracted with EtOAc (3 × 20 cm³) and the extract was washed sequentially with water and brine. The organic layer was dried over anhydrous MgSO₄, the solvent was evaporated off, and the

residue was flash chromatographed on silica gel with methylene dichloride as eluant, to yield *title compound 4a* (0.2 g, 60%) as a mixture of *cis/trans* (3/2) isomers; b.p. 45–46 °C/0.5 mmHg (Found: C, 61.2; H, 4.7. C₁₀H₉ClO₂ requires C, 61.0; H, 4.6%).

cis-4a, δ_H(200 MHz; CDCl₃) 1.43 (3 H, d, *J* 7 Hz), 3.44 (1 H, dq, *J* 4, 7 Hz), 4.71 (1 H, d, *J* 4 Hz) and 6.9–7.4 (4 H, m); *m/z* 198 (M⁺ + 2, 24%), 196 (M⁺, 78) and 133 (100).

trans-4a, δ_H(200 MHz; CDCl₃) 1.37 (3 H, d, *J* 7 Hz), 3.32 (1 H, dq, *J* 5, 7 Hz), 4.43 (1 H, d, *J* 5 Hz) and 6.91–7.32 (4 H, m); *m/z* 198 (M⁺ + 2, 24%), 196 (M⁺, 75) and 133 (100).

Reaction of Compounds 1, 2 and 3 with Organometallic Compounds. General Procedure.—(a) *With organomagnesium, organolithium, and organoaluminium compounds.* To a magnetically stirred solution of compound **1**, **2** or **3** (0.022 mol) in the appropriate solvent (Tables 1–3) (100 cm³) was added

Table 6 Chemical shifts and coupling constants (J^{ab} in Hz) for H^a in compounds **4** and **5**

R	(X = Cl)		(X = Br)	
	Major	Minor	Major	Minor
Me	4.71 (4.3)	4.43 (4.6)		
Et	4.86 (4.6)	4.56 (2.7)	4.80 (3.8)	4.57 (2.2)
Bu	4.81 (4.6)	4.52 (2.6)	4.76 (3.8)	4.56 (2.3)
Pr ⁱ	4.91 (6.3)	4.65 (2.1)	4.87 (5.5)	4.76 (1.9)

Table 7 Fractional positional parameters (with esd's) for compound **5d**

Atom	x	y	z
Br(31)	0.589 7(4)	0.032 9(7)	0.125 8(2)
O(1)	0.377(2)	0.583(4)	0.191(1)
O(21)	0.602(2)	0.486(3)	0.186 7(8)
C(2)	0.490(4)	0.423(6)	0.179(1)
C(3)	0.436(3)	0.194(6)	0.155(2)
C(4)	0.290(3)	0.187(5)	0.106(2)
C(5)	0.035(3)	0.283(8)	0.132(2)
C(6)	-0.057(3)	0.406(7)	0.153(2)
C(7)	-0.008(3)	0.607(7)	0.190(2)
C(8)	0.140(3)	0.653(7)	0.201(2)
C(9)	0.231(3)	0.513(7)	0.176(2)
C(10)	0.186(3)	0.325(6)	0.139(2)
C(41)	0.302(3)	0.293(7)	0.040(1)
C(42)	0.346(3)	0.527(6)	0.032(2)
C(43)	0.171(3)	0.192(7)	-0.011(2)

Table 8 Bond lengths (Å) and bond angles (°) (with esd's) for compound **5d**

Br(31)-C(3)	1.912(4)	C(5)-C(6)	1.261(5)
O(1)-C(2)	1.470(4)	C(5)-C(10)	1.423(4)
O(1)-C(9)	1.418(3)	C(6)-C(7)	1.436(5)
O(21)-C(2)	1.099(4)	C(7)-C(8)	1.401(4)
C(2)-C(3)	1.490(5)	C(8)-C(9)	1.356(5)
C(3)-C(4)	1.584(4)	C(9)-C(10)	1.368(5)
C(4)-C(10)	1.534(4)	C(41)-C(42)	1.450(5)
C(4)-C(41)	1.534(5)	C(41)-C(43)	1.614(4)
C(2)-O(1)-C(9)	118.8(3)	C(6)-C(7)-C(8)	117.8(3)
O(1)-C(2)-O(21)	117.8(3)	C(7)-C(8)-C(9)	119.6(4)
O(1)-C(2)-C(3)	114.3(3)	O(1)-C(9)-C(8)	112.9(3)
O(21)-C(2)-C(3)	127.8(4)	O(1)-C(9)-C(10)	123.9(3)
Br(31)-C(3)-C(2)	108.5(2)	C(8)-C(9)-C(10)	123.2(3)
Br(31)-C(3)-C(4)	113.0(3)	C(4)-C(10)-C(5)	124.4(3)
C(2)-C(3)-C(4)	117.0(3)	C(4)-C(10)-C(9)	121.1(3)
C(3)-C(4)-C(10)	103.5(3)	C(5)-C(10)-C(9)	114.2(3)
C(3)-C(4)-C(41)	114.0(2)	C(4)-C(41)-C(42)	123.4(3)
C(10)-C(4)-C(41)	110.7(3)	C(4)-C(41)-C(43)	107.5(3)
C(6)-C(5)-C(10)	126.3(4)	C(42)-C(41)-C(43)	118.0(3)
C(5)-C(6)-C(7)	118.8(3)		

dropwise (30 min) the organometallic compound (0.083 mol) under nitrogen (see Tables 1–5). At the end of the reaction (monitored by TLC) the solution was poured into ice-water and acidified. The organic layer was decanted, washed with saturated aq. NaHCO_3 , and dried (MgSO_4). The mixture (after

removal of the solvent) was chromatographed on silica gel with methylene dichloride (for compounds **4–10**) or methylene dichloride-diethyl ether (20:1) (for compounds **11–14**) as eluant, and the products were purified by distillation under reduced pressure or recrystallization from hexane-benzene.

(b) *Reaction of 3-halogenocoumarin 1 or 2 with DIBAL-H/organometallic compounds. One-pot synthesis of compounds 11 and 12.* To a stirred solution of compound **1** or **2** (2.2 mmol) in toluene (50 cm^3) under nitrogen at 40 °C was dropped a solution of DIBAL-H in hexane (2.3 cm^3 ; 2.3 mmol). The temperature was allowed to rise to 0 °C for 15 min and then a solution of the appropriate Grignard reagent in diethyl ether (4.4 mmol) or butyllithium (in hexane) was syringed into the reaction mixture, and the mixture was stirred at 0 °C for 30 min. After hydrolysis, the solution was worked up as described above.

The physical and spectral characteristics of the products **4–18**, and the optimized experimental conditions and chemical yields are given below.

3-Chloro-4-ethyl-3,4-dihydro-2H-1-benzopyran-2-one **4b**.

[EtMgBr, Et₂O; 0 °C; 66% as a mixture of *cis/trans*-isomers (85:15)]; b.p. 46–47 °C/0.2 mmHg (Found: C, 62.6; H, 5.2. $\text{C}_{11}\text{H}_{11}\text{ClO}_2$ requires C, 62.7; H, 5.3%); m/z 212 ($M^+ + 2$, 24%), 210 (M^+ , 76) and 181 (100). *cis-4c* δ_{H} (200 MHz; CDCl_3) 0.97 (3 H, t, J 7 Hz), 1.63 (1 H, m), 2.01 (1 H, m), 3.16 (1 H, ddd, J 5, 9, 5 Hz), 4.86 (1 H, d, J 5 Hz) and 7.0–7.43 (4 H, m). *trans-4a* δ_{H} 4.56 (1 H, d, J 3 Hz).

4-Butyl-3-chloro-3,4-dihydro-2H-1-benzopyran-2-one **4c**.

[BuMgBr, THF; 0 °C; 60% as a mixture of *cis/trans* isomers (90:10)]; b.p. 100–101 °C/0.4 mmHg (Found: C, 65.6; H, 6.15. $\text{C}_{13}\text{H}_{15}\text{ClO}_2$ requires C, 65.4; H, 6.3%); m/z 240 ($M^+ + 2$, 23%), 238 (M^+ , 68) and 181 (100). *cis-4c* δ_{H} (80 MHz; CDCl_3) 0.91 (3 H, t, J 6 Hz), 1.40 (4 H, m), 1.69 (1 H, m), 1.95 (1 H, m), 3.20 (1 H, ddd, J 5, 8, 5 Hz), 4.81 (1 H, d, J 5 Hz) and 7.0–7.4 (4 H, m). *trans-4c* δ_{H} 4.52 (1 H, d, J 3 Hz).

3-Chloro-3,4-dihydro-4-isopropyl-2H-1-benzopyran-2-one **4d**,

[PrⁱMgBr, Et₂O-PhMe; 0 °C; 61% as a mixture of *cis/trans* isomers (90:10)]; b.p. 95–97 °C/0.5 mmHg (Found: C, 64.2; H, 5.7. $\text{C}_{12}\text{H}_{13}\text{ClO}_2$ requires C, 64.15; H, 5.8%); m/z 226 ($M^+ + 2$, 5%), 224 (M^+ , 15) and 147 (100). *cis-4d* m.p. 70–71 °C; δ_{H} (80 MHz; CDCl_3) 0.75 (3 H, d, J 7 Hz), 1.03 (3 H, d, J 7 Hz), 2.55 (1 H, m), 3.20 (1 H, dd, J 7, 4 Hz), 4.91 (1 H, d, J 6 Hz) and 7.0–7.45 (4 H, m). *trans-4d* δ_{H} 4.65 (1 H, d, J 2 Hz).

3-Bromo-4-ethyl-3,4-dihydro-2H-1-benzopyran-2-one **5b**.

[EtMgBr, THF; 0 °C; 59% as a mixture of *cis/trans* isomers (80:15)] (Found: C, 51.7; H, 4.2. $\text{C}_{11}\text{H}_{11}\text{BrO}_2$ requires C, 51.8; H, 4.35%); m/z 256 ($M^+ + 2$, 1%), 254 (M^+ , 2) and 131 (100). *cis-5b* m.p. 67–68 °C; δ_{H} (200 MHz; CDCl_3) 1.00 (3 H, t, J 7 Hz), 1.60–2.10 (2 H, m), 3.10 (1 H, dt, J 4, 7 Hz), 4.80 (1 H, d, J 4 Hz) and 6.70–7.40 (4 H, m). *trans-5b* δ_{H} 4.57 (1 H, d, J 2 Hz).

3-Bromo-4-butyl-3,4-dihydro-2H-1-benzopyran-2-one **5c**.

[BuMgBr, THF; 0 °C; 70% as a mixture of *cis/trans* isomers (91:9)] (Found: C, 55.0; H, 5.4. $\text{C}_{13}\text{H}_{15}\text{BrO}_2$ requires C, 55.1; H, 5.3%); m/z 284 ($M^+ + 2$, 20%), 282 (M^+ , 19) and 107 (100); *cis-5c* m.p. 75–76 °C; δ_{H} (80 MHz; CDCl_3) 0.96 (3 H, t, J 6 Hz), 1.41 (4 H, m), 1.85 (2 H, m), 3.13 (1 H, dt, J 4, 7 Hz), 4.76 (1 H, d, J 4 Hz) and 6.70–7.38 (4 H, m). *trans-5c* δ_{H} 4.56 (1 H, d, J 2 Hz).

3-Bromo-3,4-dihydro-4-isopropyl-2H-1-benzopyran-2-one **5d**.

[PrⁱMgBr, Et₂O; 0 °C; 64% as mixture of *cis/trans* isomers (95:5)] (Found: C, 53.4; H, 4.8. $\text{C}_{12}\text{H}_{13}\text{BrO}_2$ requires C, 53.55; H, 4.9%); m/z 270 ($M^+ + 2$, 6%), 268 (M^+ , 6) and 147 (100). *cis-5d* m.p. 57–58 °C; δ_{H} (80 MHz; CDCl_3) 0.84 (3 H, d, J 7 Hz), 1.06 (3 H, d, J 7 Hz), 2.50 (1 H, m), 3.10 (1 H, dd, J 5, 6 Hz), 4.87 (1 H, d, J 6 Hz) and 6.90–7.30 (4 H, m). *trans-5d* δ_{H} 4.76 (1 H, d, J 2 Hz).

3-Chloro-3,4-dihydro-2,4-diphenyl-2H-1-benzopyran-2-ol **6f**.

(PhMgBr, Et₂O-PhMe; 0 °C; 15%); m.p. 187–188 °C (Found: C, 74.8; H, 4.95. $\text{C}_{21}\text{H}_{17}\text{ClO}_2$ requires C, 74.9; H, 5.1%); δ_{H} (80

MHz; CDCl_3 -(CD_3)₂SO] 4.3 (1 H, q, *J* 11 Hz) and 6.65–7.70 (14 H, m); *m/z* 338 ($\text{M}^+ + 2$, 2%), 336 ($\text{M}^+ + 4$) and 105 (100).

Phenyl-2,3-dihydro-3-phenylbenzofuran-2-yl ketone 7f. (PhMgBr, Et₂O–PhMe; 0 °C; 54%); m.p. 125–126 °C (Found: C, 83.9; H, 5.25. C₂₁H₁₆O₂ requires C, 84.0; H, 5.4%); δ_{H} [80 MHz; CDCl_3 -(CD_3)₂SO] 5.02 (1 H, d, *J* 7 Hz), 5.77 (1 H, d, *J* 7 Hz), 6.80–7.70 (12 H, m) and 7.85–8.10 (2 H, m); *m/z* 300 ($\text{M}^+ + 2$, 1%), 198 ($\text{M}^+ + 4$) and 167 (100).

3-(o-Hydroxyphenyl)-1,3-diphenylpropan-1-one 8f. (PhMgBr, PhMe; 0 °C; 10%); m.p. 167–168 °C (lit.^{9,10} 166 °C) (Found: C, 83.55; H, 6.1. Calc. for C₂₁H₁₈O₂: C, 83.4; H, 6.0%); δ_{H} [80 MHz; CDCl_3 -(CD_3)₂SO] 3.81 (1 H, d, *J* 4 Hz), 5.21 (1 H, t, *J* 8 Hz), 6.61–7.38 (12 H, m), 7.71–8.00 (2 H, m) and 8.18 (1 H, s); *m/z* 302 ($\text{M}^+ + 2$, 26%) and 105 (100).

(E)-3-Chloro-4-(o-hydroxyphenyl)-2-methylbut-3-en-2-ol (9a). (MeMgI, Et₂O–PhMe; 0 °C; 79%); m.p. 105–106 °C (Found: C, 62.2; H, 6.05. C₁₁H₁₃ClO₂ requires C, 62.1; H, 6.2%); δ_{H} (80 MHz; CDCl_3) 1.46 (6 H, s), 6.69–7.24 (4 H, m) and 7.04 (1 H, s); *m/z* 214 ($\text{M}^+ + 2$, 2%), 212 ($\text{M}^+ + 5$) and 179 (100).

(E)-2-Chloro-3-ethyl-1-(o-hydroxyphenyl)pent-1-en-3-ol 9b. (EtMgBr, PhMe; 0 °C; 63%); m.p. 95–96 °C (Found: C, 64.8; H, 7.2. C₁₃H₁₇ClO₂ requires C, 64.9; H, 7.1%); δ_{H} (80 MHz; CDCl_3) 0.94 (6 H, t, *J* 7 Hz), 1.30–2.11 (4 H, m), 6.50–7.23 (4 H, m) and 7.03 (1 H, s); *m/z* 242 ($\text{M}^+ + 2$, 1%), 240 ($\text{M}^+ + 2$) and 165 (100).

(E)-3-Butyl-2-chloro-1-(o-hydroxyphenyl)hept-1-en-3-ol 9c. (BuMgBr, PhMe; 0 °C; 80%); m.p. 84–85 °C (Found: C, 68.8; H, 8.4. C₁₇H₂₅ClO₂ requires C, 68.8; H, 8.5%); δ_{H} (80 MHz; CDCl_3) 0.92 (6 H, m), 1.10–2.11 (12 H, m), 6.87 (1 H, s) and 6.90–7.26 (4 H, s); *m/z* 298 ($\text{M}^+ + 2$, 1%), 296 ($\text{M}^+ + 3$) and 221 (100).

(E)-2-Chloro-1-(o-hydroxyphenyl)-3-isopropyl-4-methylpent-1-en-3-ol 9d. (PrⁱMgBr, Et₂O; 0 °C; 36%); m.p. 122–123 °C (Found: C, 67.1; H, 7.7. C₁₅H₂₁ClO₂ requires C, 67.0; H, 7.9%); δ_{H} (80 MHz; CDCl_3) 0.71–1.62 (6 H, m), 1.82–2.51 (2 H, m), 6.71–7.47 (4 H, m) and 6.79 (1 H, s); *m/z* 270 ($\text{M}^+ + 2$, 1%), 268 ($\text{M}^+ + 4$) and 71 (100).

(E)-2-Chloro-3-(o-hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol 9f. (PhMgBr, PhMe; 0 °C; 54%); m.p. 146–147 °C (Found: C, 74.6; H, 5.2. C₂₁H₁₇ClO₂ requires C, 74.9; H, 5.1%); δ_{H} [80 MHz; CDCl_3 -(CD_3)₂SO] 6.75 (1 H, s) and 6.89–7.72 (14 H, m); *m/z* 338 ($\text{M}^+ + 2$, 2%), 336 ($\text{M}^+ + 2$) and 105 (100).

(E)-3-Bromo-4-(o-hydroxyphenyl)-2-methylbut-3-en-2-ol 10a. (MeMgI, PhMe; 0 °C; 70%); m.p. 89–99 °C (Found: C, 51.5; H, 5.15. C₁₁H₁₃BrO₂ requires C, 51.4; H, 5.1%); δ_{H} (80 MHz; CDCl_3) 1.47 (6 H, s), 6.74–7.25 (4 H, m) and 6.91 (1 H, s); *m/z* 258 ($\text{M}^+ + 2$, 2%), 256 ($\text{M}^+ + 2$) and 115 (100).

(E)-2-Bromo-3-ethyl-1-(o-hydroxyphenyl)pent-1-en-3-ol 10b. (EtMgBr, PhMe; 0 °C; 60%); m.p. 100–101 °C (Found: C, 54.9; H, 5.7. C₁₃H₁₇BrO₂ requires C, 54.75; H, 6.0%); δ_{H} (80 MHz; CDCl_3) 0.95 (6 H, t, *J* 7 Hz), 1.11–2.10 (4 H, m), 6.72–7.25 (4 H, m) and 7.06 (1 H, s); *m/z* 286 ($\text{M}^+ + 2$, 14%), 284 ($\text{M}^+ + 15$) and 128 (100).

(E)-2-Bromo-3-butyl-1-(o-hydroxyphenyl)hept-1-en-3-ol 10c. (BuMgBr, PhMe; 0 °C; 63%); m.p. 87.5–88.5 °C (Found: C, 59.65; H, 7.3. C₁₇H₂₅BrO₂ requires C, 59.8; H, 7.4%); δ_{H} (80 MHz; CDCl_3) 1.05 (6 H, m), 1.15–2.09 (8 H, m), 2.51–2.71 (4 H, m), 6.71–7.25 (4 H, m) and 7.05 (1 H, s); *m/z* 342 ($\text{M}^+ + 2$, 1%), 340 ($\text{M}^+ + 1$) and 85 (100).

(E)-2-Bromo-1-(o-hydroxyphenyl)-3-isopropyl-4-methylprop-1-en-3-ol 10d. (PrⁱMgBr, PhMe; 0 °C; 20%); m.p. 119–120 °C (Found: C, 57.45; H, 6.7. C₁₅H₂₁BrO₂ requires C, 57.5; H, 6.8%); δ_{H} (80 MHz; CDCl_3) 0.81–1.85 (12 H, m), 1.71–2.72 (2 H, m), 6.70–7.49 (4 H, m) and 7.01 (1 H, s); *m/z* 314 ($\text{M}^+ + 2$, 1%), 312 ($\text{M}^+ + 1$) and 91 (100).

2-Bromo-3-(o-hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol 10f. (PhMgBr, PhMe; 0 °C; 14%); m.p. 121–122 °C (Found: C, 66.3; H, 4.55. C₂₁H₁₇BrO₂ requires C, 66.2; H, 4.5%); δ_{H} (80 MHz;

CDCl_3) 6.52–7.53 (14 H, m) and 7.02 (1 H, s); *m/z* 364 ($\text{M}^+ + 2 - \text{H}_2\text{O}$, 2%), 362 ($\text{M}^+ - \text{H}_2\text{O}$, 2) and 283 (100).

(E)-3-Chloro-4-(o-hydroxyphenyl)but-3-en-2-ol 11a. (DIBAL-H/MeMgI, PhMe; 0 °C; 79%); m.p. 127.5–128.5 °C (Found: C, 60.4; H, 5.5. C₁₀H₁₁ClO₂ requires C, 60.5; H, 5.6%); δ_{H} (80 MHz; CDCl_3) 1.38 (3 H, d, *J* 6 Hz), 4.71 (1 H, q, *J* 6 Hz), 6.68 (1 H, s) and 6.71–7.23 (4 H, m); *m/z* 200 ($\text{M}^+ + 2$, 1%), 198 ($\text{M}^+ + 4$) and 165 (100).

(E)-2-Chloro-1-(o-hydroxyphenyl)pent-1-en-3-ol 11b. (Et₃Al, PhMe; 0 °C; 50%); m.p. 74–75 °C (Found: C, 62.15; H, 6.1. C₁₁H₁₃ClO₂ requires C, 62.1; H, 6.2%); δ_{H} (80 MHz; CDCl_3) 0.9 (3 H, t, *J* 7 Hz), 1.75 (2 H, qd, *J* 7 Hz), 4.34 (1 H, t, *J* 7 Hz), 6.93 (1 H, s) and 6.98–7.31 (4 H, m); *m/z* 214 ($\text{M}^+ + 2$, 1%), 212 ($\text{M}^+ + 4$) and 165 (100).

(E)-2-Chloro-1-(o-hydroxyphenyl)hept-1-en-3-ol 11c. (Bu₃Al, PhMe; 0 °C; 78%); m.p. 78–79 °C (Found: C, 64.8; H, 7.2. C₁₃H₁₇ClO₂ requires C, 64.9; H, 7.1%); δ_{H} (80 MHz; CDCl_3) 0.8 (3 H, t, *J* 5 Hz), 1.22 (4 H, m), 1.69 (2 H, m), 4.57 (1 H, t, *J* 7 Hz), 6.71 (1 H, s) and 6.81–7.22 (4 H, m); *m/z* 242 ($\text{M}^+ + 2$, 1%), 240 ($\text{M}^+ + 2$) and 165 (100).

(E)-2-Chloro-1-(o-hydroxyphenyl)-4-methylpent-1-en-3-ol 11d. (PrⁱMgBr, PhMe; 0 °C; 49%); m.p. 100–101 °C (Found: C, 63.6; H, 6.5. C₁₂H₁₅ClO₂ requires C, 63.6; H, 6.7%); δ_{H} (80 MHz; CDCl_3) 0.81 (3 H, d, *J* 7 Hz), 1.01 (3 H, d, *J* 7 Hz), 1.70–2.11 (1 H, m), 3.99 (1 H, d, *J* 9 Hz), 6.75 (1 H, s) and 6.81–7.28 (4 H, m); *m/z* 228 ($\text{M}^+ + 2$, 1%), 226 ($\text{M}^+ + 4$) and 165 (100).

(E)-2-Chloro-1-(o-hydroxyphenyl)-5-methylhex-1-en-3-ol 11e. (Bu₃Al, PhMe; 0 °C; 34%); m.p. 84–85 °C (Found: C, 65.0; H, 7.2. C₁₃H₁₇ClO₂ requires C, 64.9; H, 7.1%); δ_{H} (80 MHz; CDCl_3) 0.74 (3 H, d, *J* 6 Hz), 0.85 (3 H, d, *J* 6 Hz), 1.12–1.20 (1 H, m), 1.51–1.62 (2 H, m), 3.5 (1 H, m), 6.75 (1 H, s) and 6.81–7.22 (4 H, m); *m/z* 242 ($\text{M}^+ + 2$, 1%), 240 ($\text{M}^+ + 2$) and 165 (100).

(E)-2-Bromo-1-(o-hydroxyphenyl)pent-1-en-3-ol 12b. (DIBAL-H/EtMgBr, PhMe; 0 °C; 79%); m.p. 94–95 °C (Found: C, 51.3; H, 5.15. C₁₁H₁₃BrO₂ requires C, 51.4; H, 5.1%); δ_{H} (80 MHz; CDCl_3) 0.84 (3 H, t, *J* 7 Hz), 1.79 (2 H, q, *J* 7 Hz), 4.24 (1 H, t, *J* 7 Hz), 6.71–7.31 (4 H, m) and 7.01 (1 H, s); *m/z* 258 ($\text{M}^+ + 2$, 9%), 256 ($\text{M}^+ + 9$) and 209 (100).

(E)-2-Bromo-1-(o-hydroxyphenyl)hept-1-en-3-ol 12c. (Bu₃Al, PhMe; 0 °C; 78%); m.p. 79–80 °C (Found: C, 54.9; H, 5.9. C₁₃H₁₇BrO₂ requires C, 54.75; H, 6.0%); δ_{H} (80 MHz; CDCl_3) 0.87 (3 H, t, *J* 5 Hz), 1.12–1.51 (4 H, m), 1.57–1.73 (2 H, m), 4.38 (1 H, t, *J* 6 Hz), 6.71–7.29 (4 H, m) and 7.01 (1 H, s); *m/z* 286 ($\text{M}^+ + 2$, 23%), 284 ($\text{M}^+ + 24$) and 209 (100).

(E)-2-Bromo-1-(o-hydroxyphenyl)-4-methylpent-1-en-3-ol 12d. (PrⁱMgBr, PhMe; 0 °C; 50%); m.p. 122–123 °C (Found: C, 55.1; H, 5.5. C₁₂H₁₅BrO₂ requires C, 55.15; H, 5.6%); δ_{H} (80 MHz; CDCl_3) 0.77 (3 H, d, *J* 7 Hz), 1.01 (3 H, d, *J* 7 Hz), 3.77 (1 H, d, *J* 9 Hz), 6.91–7.13 (4 H, m) and 7.03 (1 H, s); *m/z* 272 ($\text{M}^+ + 2$, 6%), 270 ($\text{M}^+ + 7$) and 211 (100).

(E)-2-Bromo-3-(o-hydroxyphenyl)-1-phenylprop-2-en-1-ol 12f. (DIBAL-H/PhMgBr, PhMe; 0 °C; 7%); m.p. 100–101 °C (Found: C, 59.2; H, 4.2. C₁₅H₁₃BrO₂ requires C, 59.0; H, 4.3%); δ_{H} (80 MHz; CDCl_3) 5.61 (1 H, s), 7.02 (1 H, s) and 6.73–7.41 (9 H, m); *m/z* 306 ($\text{M}^+ + 2$, 1%), 304 ($\text{M}^+ + 1$) and 207 (100).

(E)-2-Chloro-3-(o-hydroxyphenyl)prop-2-en-1-ol 13. (Bu₃Al, PhMe; 0 °C; 43%); m.p. 109–110 °C (Found: C, 58.4; H, 4.8. C₉H₉ClO₂ requires C, 58.55; H, 4.9%); δ_{H} (80 MHz; CDCl_3) 4.20 (2 H, s), 6.6 (1 H, s), 6.71–7.15 (4 H, m) and 7.02 (1 H, s); *m/z* 186 ($\text{M}^+ + 2$, 4%), 184 ($\text{M}^+ + 14$) and 131 (100).

2-Bromo-3-(o-hydroxyphenyl)prop-2-en-1-ol 14. (Bu₃Al, PhMe; 0 °C; 72%); m.p. 129–130 °C (Found: C, 47.3; H, 3.9. C₉H₉BrO₂ requires C, 47.2; H, 4.0%); δ_{H} [80 MHz; CDCl_3 -(CD_3)₂SO] 4.18 (2 H, s), 6.96 (1 H, s) and 6.75–7.25 (4 H, m); *m/z* 230 ($\text{M}^+ + 2$, 4%), 228 ($\text{M}^+ + 4$) and 131 (100).

(Z)-4-(o-Hydroxyphenyl)-2-methylbut-3-en-2-ol 15a. (2, MeLi, Et₂O; 0 °C; 23%); m.p. 53 °C (lit.¹¹ 53–55 °C); δ_{H} (80

MHz; CDCl₃) 1.33 (6 H, s), 5.93 (1 H, d, *J* 12 Hz), 6.36 (1 H, d, *J* 12 Hz) and 6.71–7.21 (4 H, m).

(*Z*)-3-Butyl-1-(*o*-hydroxyphenyl)hept-1-en-3-ol **15c**. (2, BuLi, PhMe; –40 °C; 32%); yellow oil; δ_H(80 MHz; CDCl₃) 0.86 (6 H, m), 0.93–1.71 (12 H, m), 5.71 (1 H, d, *J* 13 Hz), 6.36 (1 H, d, *J* 13 Hz) and 6.71–7.21 (4 H, m); *m/z* 263 (M⁺ + 1, 6%), 262 (M⁺, 30) and 205 (100); On distillation this compound was transformed into 2,2-dibutyl-2*H*-1-benzopyran. Yellow oil, b.p. 96 °C/1 mmHg (lit.,¹¹ 161–163 °C/15 mmHg); δ_H(80 MHz; CDCl₃) 0.87 (6 H, m), 0.94–1.80 (12 H, m), 5.44 (1 H, d, *J* 10 Hz), 6.34 (1 H, d, *J* 10 Hz) and 6.71–7.20 (4 H, m); *m/z* 245 (M⁺ + 1, 1%), 244 (M⁺, 4) and 187 (100).

(*E*)-4-Bromo-3-ethyl-5-(*o*-hydroxyphenyl)hex-4-en-3-ol **16b**. (EtMgBr, Et₂O; 0 °C; 65%); m.p. 84–85 °C (Found: C, 56.15; H, 6.3. C₁₄H₁₉BrO₂ requires C, 56.2; H, 6.4%); δ_H(80 MHz; CDCl₃) 0.89 (3 H, t, *J* 7 Hz), 0.95 (3 H, t, *J* 7 Hz), 1.61 (2 H, m), 2.01 (2 H, m), 2.19 (3 H, s), 6.71–7.17 (4 H, m) and 6.91 (1 H, s); *m/z* 300 (M⁺ + 2, 7%), 298 (M⁺, 8) and 57 (100).

3-Chloro-2*H*-1-benzopyran-2-ol **18**. (DIBAL-H, PhMe; –40 °C; 79%); m.p. 162–163 °C (Found: C, 59.4; H, 3.8. C₉H₇ClO₂ requires C, 59.2; H, 3.9%); δ_H(80 MHz; CDCl₃–(CD₃)₂SO) 6.06 (1 H, s), 6.75 (1 H, s) and 6.82–7.21 (4 H, m); *m/z* 184 (M⁺ + 2, 1%), 182 (M⁺, and M⁺ + 2 – H₂, 34) and 180 (M⁺ + H₂, 100).

3-Bromo-2*H*-1-benzopyran-2-ol **19**. (DIBAL-H, PhMe; –40 °C; 80%); m.p. 155–156 °C (Found: C, 47.7; H, 3.2. C₉H₇BrO₂ requires C, 47.6; H, 3.1%); δ_H(80 MHz; CDCl₃–(CD₃)₂SO) 5.78 (1 H, s), 6.82 (1 H, s) and 6.78–7.31 (4 H, m); *m/z* 228 (M⁺ + 2, 17%), 226 (M⁺, 17) and 147 (100).

Dehydrohalogenation of Compounds 4 and 5. Synthesis of 4-Alkylcoumarins 20.—A mixture *cis*- and *trans*-**4** or **5** (1.6 mmol) in the appropriate solvent (20 cm³) was refluxed with a base (Table 5) until the reaction was complete (TLC). The solution was cooled to room temperature and acidified with 6 mol dm^{–3} HCl. The organic layer was decanted, washed with aq. NaHCO₃ and dried over anhydrous MgSO₄. The solvent was eliminated and the residue was recrystallized from chloroform. The following compounds were thus prepared.

4-Methyl-2*H*-1-benzopyran-2-one **20a**. (Ac₂O–NaOAc; 52%); m.p. 81–82 °C (lit.,¹² 82 °C) (Found: C, 74.8; H, 4.9. Calc. for C₁₀H₈O₂: C, 75.0; H, 5.0%); δ_H(80 MHz; CDCl₃) 2.51 (3 H, d, *J* 1 Hz), 6.18 (1 H, q, *J* 1 Hz) and 6.85–7.61 (4 H, m).

4-Ethyl-2*H*-1-benzopyran-2-one **20b**. (C₆H₆–pyridine, **5b**; 75%); m.p. 69–70 °C (lit.,¹³ 70 °C) (Found: C, 75.9; H, 5.7. Calc. for C₁₁H₁₀O₂: C, 75.85; H, 5.9%); δ_H(80 MHz; CDCl₃) 1.36 (3 H, t, *J* 7 Hz), 2.81 (2 H, m), 6.29 (1 H, t, *J* 1 Hz) and 7.09–7.84 (4 H, m); *m/z* 174 (M⁺, 40%) and 131 (100).

4-Butyl-2*H*-1-benzopyran-2-one **20c**. (C₆H₆–pyridine, **5c**; 89%); m.p. 67–68 °C (Found: C, 77.1; H, 6.85. C₁₃H₁₄O₂ requires C, 77.2; H, 7.0%); δ_H(80 MHz; CDCl₃) 0.99 (3 H, td, *J* 6, 1 Hz), 1.09–1.98 (4 H, m), 2.77 (2 H, m), 6.26 (1 H, t, *J* 1 Hz) and 7.12–7.61 (4 H, m); *m/z* 203 (M⁺ + 1, 4%), 202 (M⁺, 20), and 160 (100).

4-Isopropyl-2*H*-1-benzopyran-2-one **20d**. (C₆H₆–pyridine, **5d**, 84%); b.p. 85–86 °C/1 mmHg (Found: C, 76.7; H, 6.35. C₁₂H₁₂O₂ requires C, 76.6; H, 6.4%); δ_H(80 MHz; CDCl₃) 1.31 (6 H, d, *J* 7 Hz), 3.30 (1 H, m), 6.27 (1 H, d, *J* 1 Hz) and 7.05–7.61 (4 H, m); *m/z* 189 (M⁺ + 1, 7%), 188 (M⁺, 51) and 145 (100).

X-Ray Crystallographic Structure Determination of Compound 5d.—Crystal data. The structure of compound **5d**,

C₁₂H₁₃BrO₂, was determined by X-ray diffraction. M_r = 269.14, monoclinic, space group *P*21/*c*, *a* = 9.411(2), *b* = 5.843(6), *c* = 21.100(5) Å, β = 99.47(2)°, *V* = 1 144(1) Å³, *Z* = 4, *D_x* = 1.56 g cm^{–3}. Mo-Kα radiation (graphite crystal monochromator, λ = 0.710 73 Å, μ(Mo-Kα) = 35.3 cm^{–1}, *F*(000) = 544, *T* = 293 K. Final conventional *R*-factor = 0.154 for 954 'observed' reflections and 125 variables.

Colourless crystal, 0.33 × 0.23 × 0.17 mm. Mo-Kα radiation with graphite crystal monochromator, Enraf-Nonius CAD4 single-crystal diffractometer. Unit-cell dimensions were determined from the angular settings of 25 reflections with 10° < θ < 15°. Space group was determined to be *P*21/*c* from systematic absences. 3694 Reflections measured, *hkl* range (–13, 0, 0) to (13, 8, 29), theta limits (0° < θ < 30°). ω–2θ Scan technique with a variable scan rate with a maximum scan time of 30 s per reflection. Intensity checked by monitoring three standard reflections every 60 min. Crystals were very unstable under X-rays and led to very high drift corrections. Because of this, neither good values of agreement factors nor accurate parameters were expected. Nevertheless, data collection and structure determination were carried out since the main interest of the work was to determine the molecular geometry. Final drift correction factors were between 1.00 and 2.29. Profile analysis was performed on all reflections.^{14,15} Some doubly measured reflections were averaged, *R*_{int} = Σ(|*I* – ⟨*I*⟩|)/Σ*I* = 0.095, 1009 unique reflections and 954 observed with *I* > 3σ(*I*). Lorentz and polarization corrections were applied and data reduced to |*F*|-values. Structure solved by direct methods, using the program SHELX86.¹⁶ Isotropic least-squares refinement, using SHELX,¹⁷ converged to *R* = 0.20. Anisotropic refinements followed by a difference Fourier synthesis allowed the location of some hydrogen atoms.

Positional parameters and anisotropic thermal parameters of the non-hydrogen atoms were refined, except those for O(21), C(4) and C(42) which were isotropically refined. All the hydrogen atoms were isotropically refined, with a common thermal parameters, riding, at constraining distances, on their parent atoms, except for H(31) and H(41), which co-ordinates were fixed. The final conventional agreement factor was *R* = 0.154 for the 954 'observed' reflections and 125 variables. Function minimized Σ*w*(*F*_o – *F*_c)², *w* = 1. Maximum shift-over-error ratio in the last full-matrix least-squares cycle was < 0.001. Final difference Fourier map showed no peaks > 1.32 e Å^{–3} nor < –2.56 e Å^{–3}. Fractional positional parameters for non-hydrogen atoms are given in Table 7, while Table 8 collects selected geometrical parameters.* Atomic scattering factors were taken from the International Tables for X-ray Crystallography.¹⁸ The plot was made with the PLUTO¹⁹ program. Geometrical calculations were made with PARST.²⁰ All calculations were made on an IBM 3090 Computer at the Computer Center of the University of Oviedo.

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* The fractional atomic co-ordinates, bond lengths and angles, torsion angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1991, issue 1, p. xviii).

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