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 alkyllithiums. 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).

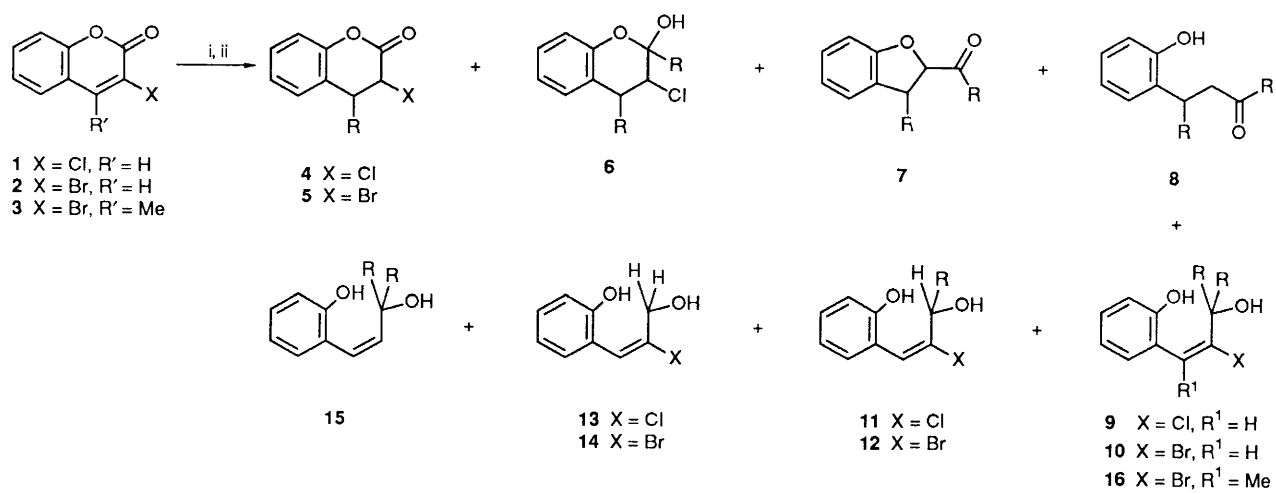
As previously described for 3-phenyl- and 3-ethoxycarbonylcoumarin,[1–3] in our case the 1,4-addition process was favoured when the reactions were carried out in ether solvents (THF or diethyl ether) and with increasingly bulky groups R; the resulting 4-alkyl-3-halogeno-3,4-dihydrocoumarins **4** and **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 Pr^{i}MgBr 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

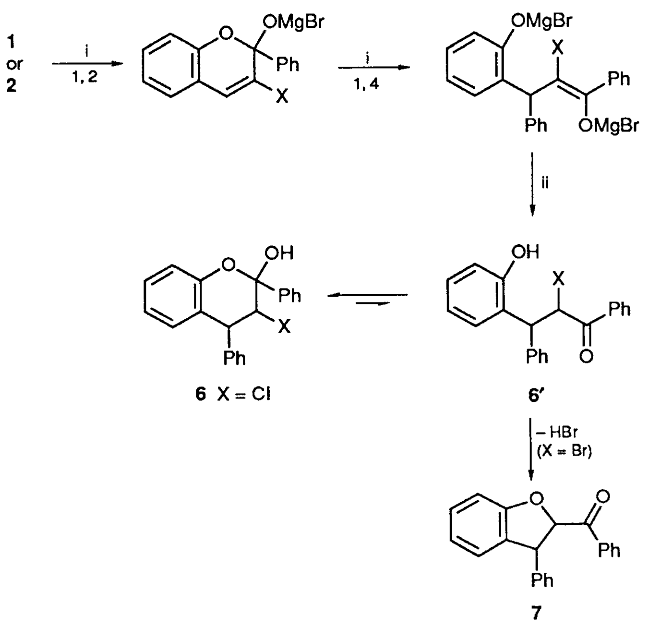


Scheme 1 **a**, R = Me; **b**, R = Et; **c**, R = Bu; **d**, R = Pr^i; **e**, R = Bu^i; **f**, R = Ph. *Reagents:* i, organometallic compounds; ii, water

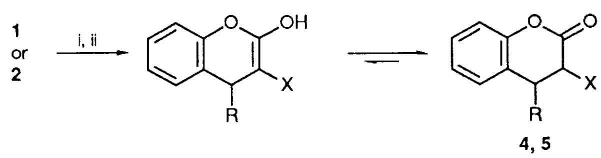
Table 1 Reaction of compounds **1**, **2** and **3** with Grignard derivatives

			Yield (%)							
Coumarin	RMgX	Solvent[a]	4	5	6	7	9	10	11	12
1	MeMgI	Et_2O–PhMe					**9a** 85			
1	EtMgBr	Et_2O–PhMe	**4b** 55				**9b** 40			
1	EtMgBr	PhMe	**4b** 25				**9b** 70			
1	EtMgBr	Et_2O	**4b** 70				**9b** 25			
1	EtMgI	Et_2O	**4b** 75				**9b** 20			
1	BuMgBr	PhMe	**4c** 5				**9c** 85			
1	BuMgBr	Et_2O	**4c** 40				**9c** 50		**11c** 5	
1	BuMgBr	THF	**4c** 65				**9c** 20		**11c** 15	
1	Pr^iMgBr	Et_2O–PhMe	**4d** 65				**9d** 15		**11c** 15	
1	Pr^iMgBr	PhMe	**4d** 20				**9d** 20		**11d** 57	
1	Pr^iMgBr	Et_2O	**4d** 25				**9d** 42		**11d** 30	
1	PhMgBr	Et_2O–PhMe			**6f** 20		**9f** 60			*b*
2	MeMgI	Et_2O–PhMe						**10a** 80		
2	EtMgBr	Et_2O–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_2O		**5b** 40				**10b** 52		*b*
2	BuMgBr	PhMe		**5c** 12				**10c** 70		**12c** 14
2	BuMgBr	THF		**5c** 72				**10c** 20		
2	Pr^iMgBr	Et_2O–PhMe		**5d** 60				**10d** 22		**12d** 16
2	Pr^iMgBr	PhMe		**5d** 24				**10d** 16		**12d** 56
2	Pr^iMgBr	Et_2O		**5d** 70				**10d** 12		**12d** 10
2	PhMgBr	Et_2O–PhMe				**7f** 60		**10f** 20		*c*
3	EtMgBr	Et_2O								*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



Scheme 3 Ratio of *cis*:*trans* isomers: R = Me, 60:40; R = Et, 80:20; R = Bu, 85:15; R = Pr^i, 90:10; *Reagents:* i, organometallic compound; 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 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 Et_3Al–THF compound **13** was obtained 60% yield (Table 3).

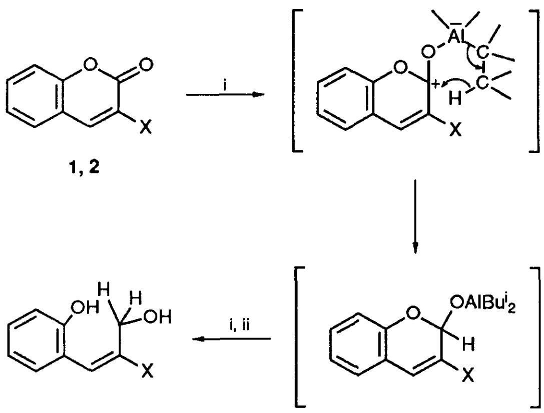
The reduction of 3-chloro- and 3-bromo-coumarin with DIBAL-H is not a satisfactory method to obtain compounds **13** and **14**. The first step to the hemiacetal intermediate **17** is a fast process, but its transformation to the final product is very slow at 0 °C. Nevertheless this intermediate is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

Table 2 Reaction of compounds **1** and **2** with lithium derivatives

			Yield (%)			
Coumarin	RLi	Solvent	4	9	10	15
1	MeLi	Et_2O[a]		**9a** 80		
1	BuLi	PhMe[b]	**4c** 10	**9c** 80		
1	BuLi	Et_2O[a]	**4c** 20	**9c** 70		
2	MeLi	Et_2O[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).

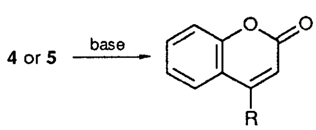


Scheme 4 *Reagents:* i, Bu^i_3Al; ii, water

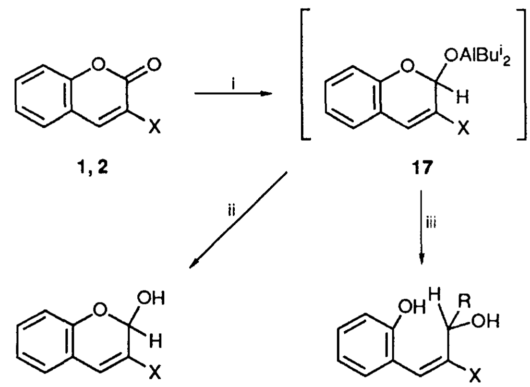
The described monoalkylation process could be achieved from the corresponding coumarin and organoaluminium as previously reported,[4,5] but the methodology presented here is advantageous because lithium and magnesium derivatives are more easily accessible than are the aluminium ones, and because some of the last substrates showed only reductive (Bu^i_3Al) or alkylation (Me_3Al) 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 Ac_2O–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 derivatives **4** and **5** because of the observed systematic behaviour of their chemical shifts for H[a] (Table 6), and their behaviour towards Ac_2O–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).



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

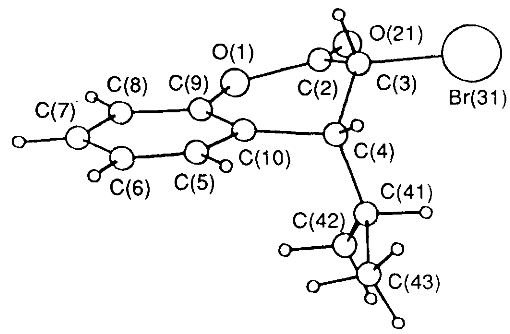


Fig. 1 X-Ray structure and crystallographic numbering for compound **5d** (hydrogen atoms omitted)

On the other hand, our results are in agreement with those previously described by Ivanov and Bojilova[1] for 3-phenylcoumarin, leading to the less stable *cis*-isomer assigned by a study on epimerization with Ac_2O–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 $SiMe_4$ as internal standard. Mass spectra were measured on a Hewlett-Packard 5988A mass spectrometer.

Table 3 Reaction of compounds **1** and **2** with R_3Al[a]

Coumarin	R_3Al	Solvent	Yield (%) 9	10	11	12	13	14
1	Me_3Al	PhMe	**9a** 75					
1	Et_3Al	PhMe	**9b** 40		**11b** 55			
1	Et_3Al	THF					**13** 65	
1	Bu_3Al	PhMe	**9c** 7		**11c** 85			
1	$Bu^i{}_3Al$	PhMe			**11c** 40		**13** 50	
2	Me_3Al	PhMe		**10a** 70				
2	Et_3Al	PhMe		**10b** 17		**12b** 75		
2	Bu_3Al	PhMe		**10c** 5		**12c** 85		
2	$Bu^i{}_3Al$	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^iMgBr	**11d** 49		**13** 19			*a*
1	BuLi	**11c** 70		**13** 2			*b*
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 *cis*/*trans*
4b	a	2	2 **20b**	95 *cis*/*trans*
4c	a	2	5 **20c**	90 *cis*/*trans*
4d	a	2	3 **20d**	95 *cis*/*trans*
5b	a	2	80 **20b**	10 *trans*
5c	a	2	92 **20c**	5 *trans*
5d	a	2	93 **20d**	5 *trans*
4a	b	2		95 *cis*/*trans*
4b	b	10	2 **20b**	90 *cis*/*trans*
4c	b	10	5 **20c**	90 *cis*/*trans*
5b	b	10	2 **20b**	90 *cis*/*trans*
4a	c	0.2	33 **20a**	27 *cis*/37 *trans*
5b	c	3	80 **20b**	
4c	c	3	85 **20c**	
5b	c	0.2	40 **20b**	40 *cis*/10 *trans*
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 Ac_2O at room temperature. [c] 0.1 mol dm^{-3} NaOAc in Ac_2O at reflux.

Starting materials 3-chlorocoumarin,[6] 3-bromocoumarin[7] and 3-bromo-4-methylcoumarin[8] were prepared as previously described.

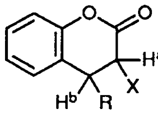
Reaction of Compound **1** *with* Me_2CuLi. *Synthesis of* 3-*Chloro*-3,4-*dihydro*-4-*methyl*-2H-1-*benzopyran*-2-*one* **4a**.—To a stirred suspension of CuI (0.31 g, 1.6 mmol) in dry diethyl ether (20 cm^3) under N_2 at −10 °C was added a solution of MeLi in diethyl ether (2 cm^3; 3.2 mmol). The colourless solution was cooled to −40 °C and a solution of compound **1** (0.2 g, 1.1 mmol) in diethyl ether (20 cm^3) was added dropwise. The mixture was stirred at between −40 and −30 °C for 30 min, and quenched with saturated aq. NH_4Cl (15 cm^3). The product was extracted with EtOAc (3 × 20 cm^3) and the extract was washed sequentially with water and brine. The organic layer was dried over anhydrous $MgSO_4$, 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. $C_{10}H_9ClO_2$ requires C, 61.0; H, 4.6%).

cis **4a**, δ_H(200 MHz; $CDCl_3$) 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; $CDCl_3$) 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 organomaluminium compounds*. To a magnetically stirred solution of compound **1**, **2** or **3** (0.022 mol) in the appropriate solvent (Tables 1–3) (100 cm^3) was added

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



R	(X = Cl) Major	(X = Cl) Minor	(X = Br) Major	(X = Br) 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 cf 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, Et_2O; 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. $C_{11}H_{11}ClO_2$ 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. $C_{13}H_{15}ClO_2$ 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**, [Pr^iMgBr, Et_2O–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. $C_{12}H_{13}ClO_2$ 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. $C_{11}H_{11}BrO_2$ 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 H) 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. $C_{13}H_{15}BrO_2$ 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**. [Pr^iMgBr, Et_2O; 0 °C; 64% as mixture of *cis*/*trans* isomers (95:5)] (Found: C, 53.4; H, 4.8. $C_{12}H_{13}BrO_2$ requires C, 53.55; H, 4.9%); *m*/*z* 270 (M^+ + 2, 6%), 268 (M^+, 6) and 147 (100). cis-**5b** 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, Et_2O–PhMe; 0 °C; 15%); m.p. 187–188 °C (Found: C, 74.8; H, 4.95. $C_{21}H_{17}ClO_2$ 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 (M^+ + 2, 2%), 336 (M^+, 4) and 105 (100).

Phenyl-2,3-*dihydro*-3-*phenylbenzofuran*-2-*yl ketone* **7f**. (PhMgBr, Et_2O–PhMe; 0 °C; 54%); m.p. 125–126 °C (Found: C, 83.9; H, 5.25. $C_{21}H_{16}O_2$ 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 (M^+, 52%) 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 $C_{21}H_{18}O_2$: 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 (M^+, 26%) and 105 (100).

(E)-3-*Chloro*-4-(o-*hydroxyphenyl*)-2-*methylbut*-3-*en*-2-*ol* (**9a**). (MeMgI, Et_2O–PhMe; 0 °C; 79%); m.p. 105–106 °C (Found: C, 62.2; H, 6.05. $C_{11}H_{13}ClO_2$ 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 (M^+ + 2, 2%), 212 (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. $C_{13}H_{17}ClO_2$ 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 (M^+ + 2, 1%), 240 (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. $C_{17}H_{25}ClO_2$ 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 (M^+ + 2, 1%), 296 (M^+, 3) and 221 (100).

(E)-2-*Chloro*-1-(o-*hydroxyphenyl*)-3-*isopropyl*-4-*methylpent*-1-*en*-3-*ol* **9d**. (Pr^iMgBr, Et_2O; 0 °C; 36%); m.p. 122–123 °C (Found: C, 67.1; H, 7.7. $C_{15}H_{21}ClO_2$ 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 (M^+ + 2, 1%), 268 (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. $C_{21}H_{17}ClO_2$ 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 (M^+ + 2, 2%), 336 (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. $C_{11}H_{13}BrO_2$ 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 (M^+ + 2, 2%), 256 (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. $C_{13}H_{17}BrO_2$ 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 (M^+ + 2, 14%), 284 (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. $C_{17}H_{25}BrO_2$ 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 (M^+ + 2, 1%), 340 (M^+, 1) and 85 (100).

(E)-2-*Bromo*-1-(o-*hydroxyphenyl*)-3-*isopropyl*-4-*methylprop*-1-*en*-3-*ol* **10d**. (Pr^iMgBr, PhMe; 0 °C; 20%); m.p. 119–120 °C (Found: C, 57.45; H, 6.7. $C_{15}H_{21}BrO_2$ 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 (M^+ + 2, 1%), 312 (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. $C_{21}H_{17}BrO_2$ 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 (M^+ + 2 − H_2O, 2%), 362 (M^+ − H_2O, 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. $C_{10}H_{11}ClO_2$ 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 (M^+ + 2, 1%), 198 (M^+, 4) and 165 (100).

(E)-2-*Chloro*-1-(o-*hydroxyphenyl*)*pent*-1-*en*-3-*ol* **11b**. (Et_3Al, PhMe; 0 °C; 50%); m.p. 74–75 °C (Found: C, 62.15; H, 6.1. $C_{11}H_{13}ClO_2$ 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, 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 (M^+ + 2, 1%), 212 (M^+, 4) and 165 (100).

(E)-2-*Chloro*-1-(o-*hydroxyphenyl*)*hept*-1-*en*-3-*ol* **11c**. (Bu_3Al, PhMe; 0 °C; 78%); m.p. 78–79 °C (Found: C, 64.8; H, 7.2. $C_{13}H_{17}ClO_2$ 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 (M^+ + 2, 1%), 240 (M^+, 2) and 165 (100).

(E)-2-*Chloro*-1-(o-*hydroxyphenyl*)-4-*methylpent*-1-*en*-3-*ol* **11d**. (Pr^iMgBr, PhMe; 0 °C; 49%); m.p. 100–101 °C (Found: C, 63.6; H, 6.5. $C_{12}H_{15}ClO_2$ 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 (M^+ + 2, 1%), 226 (M^+, 4) and 165 (100).

(E)-2-*Chloro*-1-(o-*hydroxyphenyl*)-5-*methylhex*-1-*en*-3-*ol* **11e**. (Bu_3^iAl, PhMe; 0 °C; 34%); m.p. 84–85 °C (Found: C, 65.0; H, 7.2. $C_{13}H_{17}ClO_2$ 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 (M^+ + 2, 1%), 240 (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. $C_{11}H_{13}BrO_2$ 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 (M^+ +2, 9%), 256 (M^+, 9) and 209 (100).

(E)-2-*Bromo*-1-(o-*hydroxyphenyl*)*hept*-1-*en*-3-*ol* **12c**. (Bu_3Al, PhMe; 0 °C; 78%); m.p. 79–80 °C (Found: C, 54.9; H, 5.9. $C_{13}H_{17}BrO_2$ 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 (M^+ + 2, 23%), 284 (M^+, 24) and 209 (100).

(E)-2-*Bromo*-1-(o-*hydroxyphenyl*)-4-*methylpent*-1-*en*-3-*ol* **12d**. (Pr^iMgBr, PhMe; 0 °C; 50%); m.p. 122–123 °C (Found: C, 55.1; H, 5.5. $C_{12}H_{15}BrO_2$ requires C, 53.15; 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 (M^+ + 2, 6%), 270 (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. $C_{15}H_{13}BrO_2$ 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 (M^+ + 2, 1%), 304 (M^+, 1) and 207 (100).

(E)-2-*Chloro*-3-(o-*hydroxyphenyl*)*prop*-2-*en*-1-*ol* **13**. (Bu^i_3Al, PhMe; 0 °C; 43%); m.p. 109–110 °C (Found: C, 58.4; H, 4.8. $C_9H_9ClO_2$ 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 (M^+ + 2, 4%), 184 (M^+, 14) and 131 (100).

2-*Bromo*-3-(o-*hydroxyphenyl*)*prop*-2-*en*-1-*ol* **14**. (Bu^i_3Al, PhMe; 0 °C; 72%); m.p. 129–130 °C (Found: C, 47.3; H, 3.9. $C_9H_9BrO_2$ 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 (M^+ + 2, 4%), 228 (M^+, 4) and 131 (100).

(Z)-4-(o-*Hydroxyphenyl*)-2-*methylbut*-3-*en*-2-*ol* **15a**. (**2**, MeLi, Et_2O; 0 °C; 23%); m.p. 53 °C (lit.,[11] 53–55 °C); δ_H(80

MHz; $CDCl_3$) 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; $CDCl_3$) 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; $CDCl_3$) 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, Et_2O; 0 °C; 65%); m.p. 84–85 °C (Found: C, 56.15; H, 6.3. $C_{14}H_{19}BrO_2$ requires C, 56.2; H, 6.4%); δ_H(80 MHz; $CDCl_3$) 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*-2H-1-*benzopyran*-2-*ol* **18**. (DIBAL-H. PhMe; −40 °C; 79%); m.p. 162–163 °C (Found: C, 59.4; H, 3.8. $C_9H_7ClO_2$ requires C, 59.2; H, 3.9%); δ_H[80 MHz; $CDCl_3$–$(CD_3)_2SO$] 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 − H_2, 34) and 180 (M^+ + H_2, 100).

3-*Bromo*-2H-1-*benzopyran*-2-*ol* **19**. (DIBAL-H, PhMe; −40 °C; 80%); m.p. 155–156 °C (Found: C, 47.7; H, 3.2. $C_9H_7BrO_2$ requires C, 47.6; H, 3.1%); δ_H[80 MHz; $CDCl_3$–$(CD_3)_2SO$] 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 cm^3) 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. $NaHCO_3$ and dried over anhydrous $MgSO_4$. The solvent was eliminated and the residue was recrystallized from chloroform. The following compounds were thus prepared.

4-*Methyl*-2H-1-*benzopyran*-2-*one* **20a**. (Ac_2O–NaOAc; 52%); m.p. 81–82 °C (lit.,[12] 82 °C) (Found: C, 74.8; H, 4.9. Calc. for $C_{10}H_8O_2$: C, 75.0; H, 5.0%); δ_H(80 MHz; $CDCl_3$) 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*-2H-1-*benzopyran*-2-*one* **20b**. (C_6H_6–pyridine, **5b**; 75%); m.p. 69–70 °C (lit.,[13] 70 °C) (Found: C, 75.9; H, 5.7. Calc. for $C_{11}H_{10}O_2$: C, 75.85; H, 5.9%); δ_H(80 MHz; $CDCl_3$) 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*-2H-1-*benzopyran*-2-*one* **20c**. (C_6H_6–pyridine **5c**; 89%); m.p. 67–68 °C (Found: C, 77.1; H, 6.85. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%); δ_H(80 MHz; $CDCl_3$) 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*-2H-1-*benzopyran*-2-*one* **20d**. (C_6H_6–pyridine, **5d**, 84%); b.p. 85–86 °C/1 mmHg (Found: C, 76.7; H, 6.35. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%); δ_H(80 MHz; $CDCl_3$) 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**, $C_{12}H_{13}BrO_2$, 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) $Å^3$, *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, $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$ = 0.095, 1009 unique reflections and 954 observed with $I > 3\sigma(I)$. 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 $\Sigma w(F_0 - F_0)^2$, *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 PLUTO[19] 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.

* 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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