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A convenient general synthesis of 3-substituted 2*H*-chromene derivatives

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Received (in Cambridge, UK) 20th February 2002, Accepted 2nd April 2002
First published as an Advance Article on the web 26th April 2002

Reactions of 2-hydroxybenzaldehydes and 2-hydroxy-1-naphthaldehydes with various activated alkenes under Baylis–Hillman conditions have been shown to proceed with regioselective cyclisation to afford the corresponding 3-substituted chromene derivatives. In some cases competitive dimerisation of the alkene component was observed, and direct dimerisation in the absence of the aldehyde has been explored.

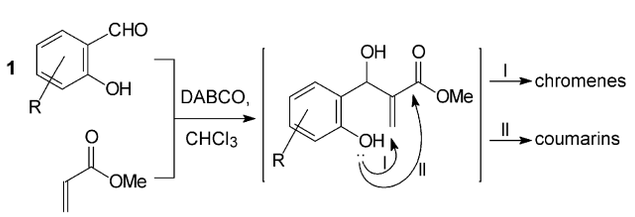
Introduction

Many naturally-occurring pharmacologically active compounds contain the 2*H*-1-benzopyran (2*H*-chromene) nucleus. Notable amongst these are the 2,2-dimethylchromene derivatives isolated from propolis, a resinous product known for over 2000 years for its healing properties.[1] Calonolide F, isolated from *Calophyllum tesymannii*,[2] also contains the 2,2-dimethylchromene moiety and exhibits anti-HIV activity, while synthetic analogues have been shown to possess antihypertensive[3] and anti-ischaemic[4] activity.

Various protocols have been developed for the synthesis of 2*H*-chromenes,[5] and new methods of accessing these important compounds continue to be reported. These include: the intramolecular cyclisation of Wittig intermediates;[6] the microwave-assisted reaction of salicylaldehyde with enamines;[7] the iodine-catalysed cyclocondensation of 2-hydroxybenzaldehydes with 2,2-dimethoxypropane[8] and ring-closing olefin metathesis.[9] In a preliminary communication[10] we recently described a novel and convenient synthesis of 3-acyl-2*H*-chromenes involving the Baylis–Hillman reaction of 2-hydroxybenzaldehydes with methyl vinyl ketone (MVK) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO). DeBoer[11] has prepared 2*H*-chromenes by reacting salicylaldehyde (as the phenoxide ion) with activated alkenes in an approach which presumably involves conjugate addition, followed by an aldol-type cyclisation. However, there is ample evidence, which will be reported elsewhere,[12] that the DABCO-catalysed reactions follow a Baylis–Hillman pathway.[13,14]

Results and discussion

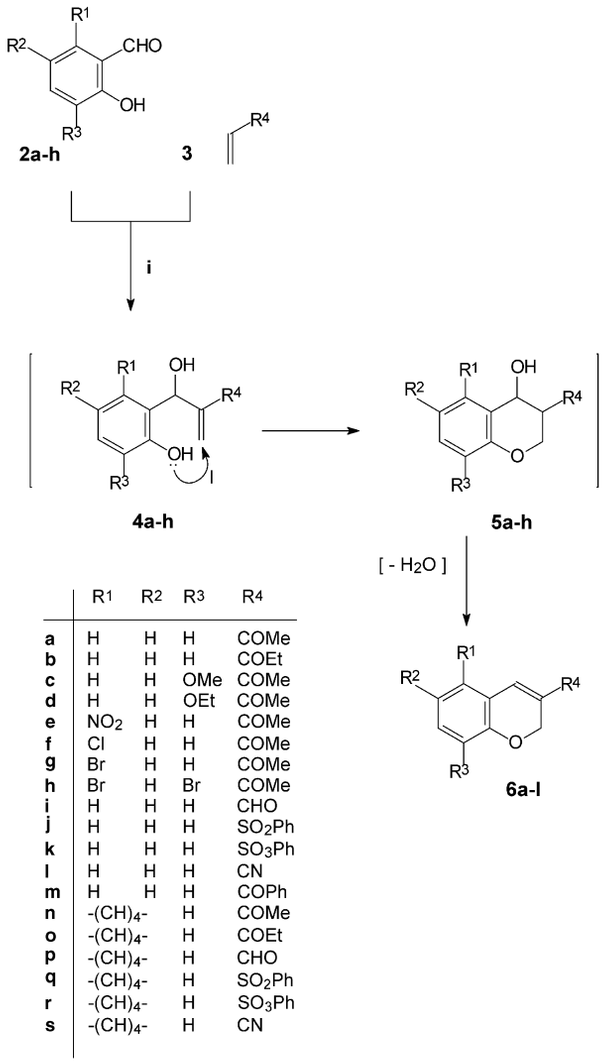
Previous attempts to prepare 2*H*-chromenes chemoselectively *via* the cyclisation of 2-hydroxybenzaldehyde-derived Baylis–Hillman products had proved unsuccessful affording, instead, complex mixtures of coumarin and chromene derivatives (Scheme 1).[15] Thus, while conjugate addition involving attack of the phenolic oxygen at the vinylic centre (path I) provides access to chromene derivatives, nucleophilic substitution at the acyl centre of the ester group (path II) leads to coumarin derivatives. Inhibition of the latter pathway was successfully achieved by replacing the acrylic esters used in the initial study[15] with vinyl ketones (R^4 = COMe, COEt; Scheme 2), while careful optimisation of the reaction conditions permitted isolation of chromene derivatives in up to 87% yield.[10] After examining various solvent systems for the reaction of salicylaldehyde with MVK, it was found that use of a vigorously stirred, heterogeneous mixture of chloroform and water, as the solvent system, and use of 0.8 equivalents of DABCO gave the best result; further improvement in the yield was achieved by adding more MVK at intervals during the course of the reaction.[10] The generality of the Baylis–Hillman approach to chromenes has subsequently been demonstrated by extending: i, the range of activated alkenes to include acrylaldehyde, acrylonitrile, phenyl vinyl sulfone and phenyl ethenesulfonate and ii, the range of 2-hydroxybenzaldehyde substrates to include 2-hydroxy-1-naphthaldehyde.



Scheme 1

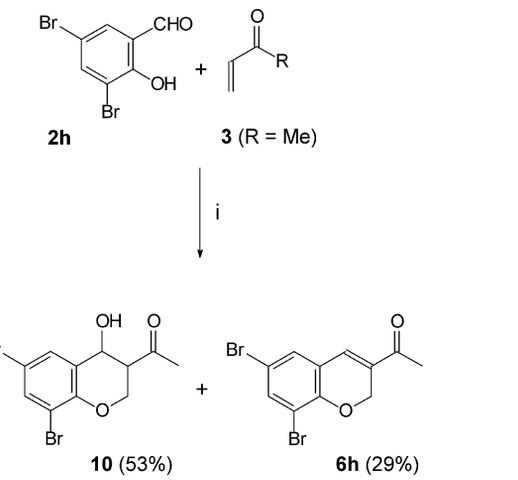
Treatment of salicylaldeyde **2a** (R^1 = R^2 = R^3 = H; Scheme 2) with acrylaldehyde, phenyl vinyl sulfone, phenyl ethenesulfonate and acrylonitrile under the established conditions afforded the 3-substituted chromenes **6i–l**, respectively, in yields ranging from 54 to 70%. Use of phenyl vinyl ketone **8**, however, gave 3-benzoyl-2*H*-chromene **6m** in disappointingly low yield (10%), the major product being the ketone dimer **9a** (Scheme 3), while reaction of 2-hydroxy-3,5-dinitrobenzaldehyde **2t** with MVK gave none of the expected chromene but afforded, instead, the MVK dimer **9b** as the sole product. Electron-withdrawing substituents are expected to activate the aldehyde to nucleophilic attack by a zwitterionic intermediate in the rate-determining step of the Baylis–Hillman reaction[16] but, in the case of 2-hydroxy-3,5-dinitrobenzaldehyde **2t**, none of the expected product was obtained. The *ortho*- and *para*-nitro substituents presumably enhance the acidity of the phenolic hydroxy group to the extent that protonation of DABCO occurs with consequent inhibition of its catalytic activity. In the reaction of 3,5-dibromo-2-hydroxybenzaldehyde **2h** with MVK, the chroman-4-ol **5h** was isolated in 53% yield together with the expected chromene **6h** (29%; Scheme 4), a result which is clearly consistent with the addition–elimination sequence proposed in Scheme 2. Although the chroman-4-ol **5h** contains two stereogenic centres, the apparent absence of signal doubling in both the ^{1}H- and ^{13}C NMR spectra suggests the presence of only one diastereomer (as an enantiomeric pair), formulated

 DOI: 10.1039/b201827f



	R1	R2	R3	R4
a	H	H	H	COMe
b	H	H	H	COEt
c	H	H	OMe	COMe
d	H	H	OEt	COMe
e	NO_2	H	H	COMe
f	Cl	H	H	COMe
g	Br	H	H	COMe
h	Br	H	Br	COMe
i	H	H	H	CHO
j	H	H	H	SO_2Ph
k	H	H	H	SO_3Ph
l	H	H	H	CN
m	H	H	H	COPh
n	-$(CH)_4$-		H	COMe
o	-$(CH)_4$-		H	COEt
p	-$(CH)_4$-		H	CHO
q	-$(CH)_4$-		H	SO_2Ph
r	-$(CH)_4$-		H	SO_3Ph
s	-$(CH)_4$-		H	CN

Scheme 2 *Reagents and conditions*: i, DABCO, $CHCl_3$–H_2O, rt.



Scheme 4 *Reagents and conditions*: i, DABCO, $CHCl_3$–H_2O, rt, 7 d.

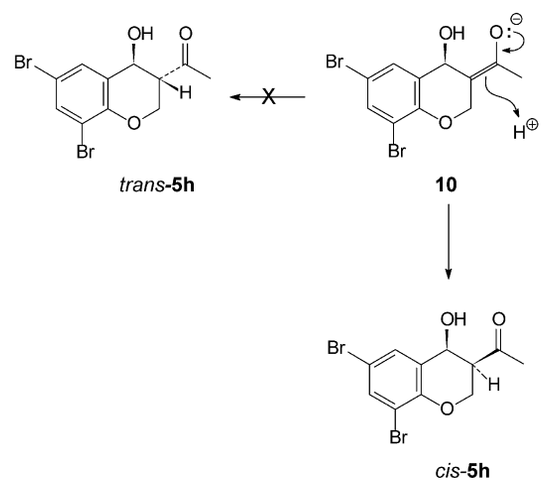
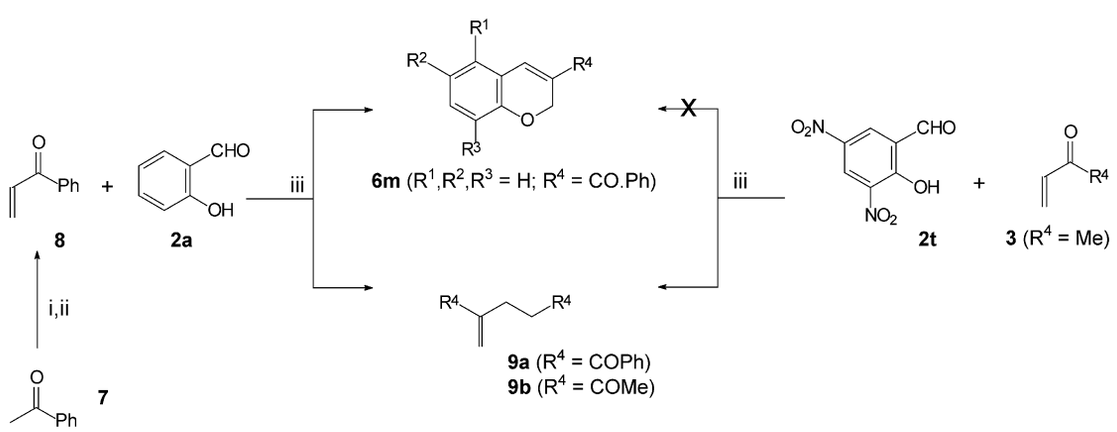


Fig. 1 Diastereofacial selectivity during enolate protonation (showing one enantiomeric series).

as the cis-isomer ***cis*-5h** (Fig. 1) on the basis of the small vicinal coupling ($J_{3,4}$ = 3.5 Hz) between the 3- and 4-methine protons. In a *trans*-diequatorial arrangement of the 3- and 4-substituents, the methine protons would be diaxial and could be expected to exhibit much larger coupling constants. The observed stereochemistry is attributed to protonation at the less hindered face of the enolate intermediate **10**.

Reaction of 2-hydroxy-1-naphthaldehyde **2n** (instead of salicylaldehyde) with the series of activated alkenes **3** afforded the corresponding 3-substituted benzo[*f*]chromenes **6n–s** in yields ranging from 17 to 67% (Table 1); in some cases, the benzochromanol precursors **5q–s** were isolated in low yields (2–4%) together with the corresponding benzo[*f*]chromenes **6**.

In an earlier study in our laboratories, Robinson[13,15] had isolated the 4-substituted chromane **13** (Scheme 5) from a reaction between salicylaldeyde and methyl acrylate under Baylis–Hillman conditions. The formation of this product was attributed to *in situ* conjugate addition of the "Baylis–Hillman

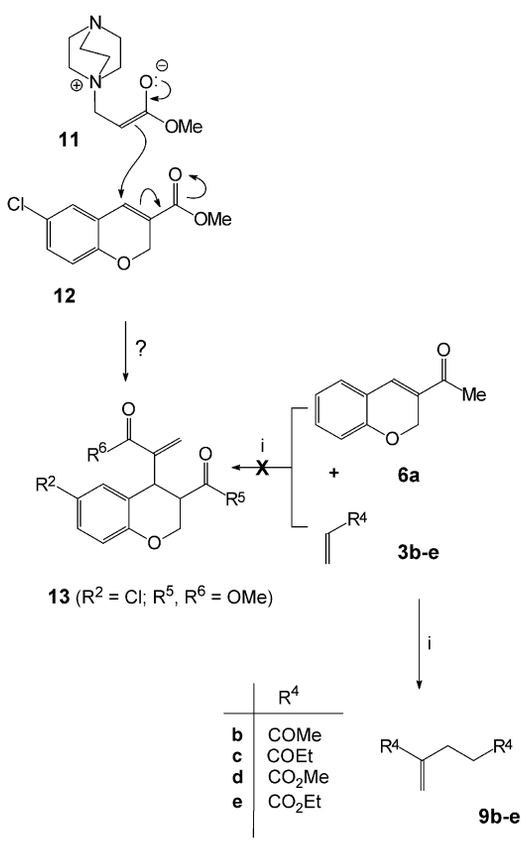


Scheme 3 *Reagents and conditions*: i, HCHO, Me_2NH_2Cl, HCl, EtOH, reflux, 2 h; ii, heat; iii, DABCO, $CHCl_3$–H_2O, rt, 7 d.

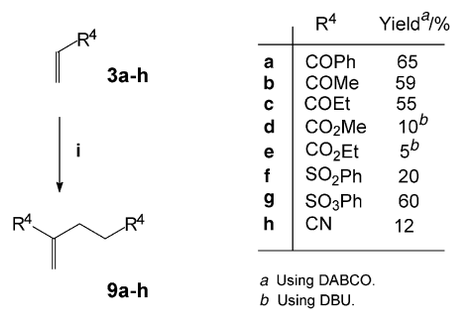
Table 1 Data for 3-substituted chromene derivatives **6a**–**s** (Scheme 2)

Compd.	R^1	R^2	R^3	R^4	Yield[a](%)	HRMS data: *m/z*, M^+		
						Found	Mol. formula	Required
6a	H	H	H	COMe	81	174.0671	$C_{11}H_{10}O_2$	174.0681
6b	H	H	H	COEt	83	188.0835	$C_{12}H_{12}O_2$	188.0837
6c	H	H	OMe	COMe	79	204.0788	$C_{12}H_{12}O_3$	204.0786
6d	H	H	OEt	COMe	84	218.0945	$C_{13}H_{14}O_3$	218.0943
6e	H	NO_2	H	COMe	54	219.0516	$C_{11}H_9NO_4$	219.0532
6f	H	Cl	H	COMe	56	208.0296	$C_{11}H_9{}^{35}ClO_2$	208.0291
6g	H	Br	H	COMe	87	251.9795	$C_{11}H_9{}^{79}BrO_2$	251.9786
6h	H	Br	Br	COMe	29(53)[b]	329.8881	$C_{11}H_8O_2{}^{79}Br_2$	329.8891
6i	H	H	H	CHO	54	160.0532	$C_{10}H_8O_2$	160.0524
6j	H	H	H	SO_2Ph	70	272.0510	$C_{15}H_{12}O_3S$	272.0506
6k	H	H	H	SO_3Ph	60	288.0444	$C_{15}H_{12}O_4S$	288.0455
6l	H	H	H	CN	65	157.0520	$C_{10}H_7NO$	157.0527
6m	H	H	H	COPh	10[c]	236.0835	$C_{16}H_{12}O_2$	236.0837
6n	–(CH)$_4$–		H	COMe	67	224.0832	$C_{15}H_{12}O_2$	224.0837
6o	–(CH)$_4$–		H	COEt	58	238.0994	$C_{16}H_{14}O_2$	238.1005
6p	–(CH)$_4$–		H	CHO	17	210.0678	$C_{14}H_{10}O_2$	210.0681
6q	–(CH)$_4$–		H	SO_2Ph	20(2)[b]	322.0674	$C_{19}H_{14}O_3S$	322.0664
6r	–(CH)$_4$–		H	SO_3Ph	61(4)[b]	338.0617	$C_{19}H_{14}O_4S$	338.0613
6s	–(CH)$_4$–		H	CN	50(2)[b]	207.0675	$C_{14}H_9NO$	207.0684

[a] Chromatographed material. [b] Yield of corresponding chroman-4-ol intermediate. [c] The dimer **9a** was isolated as the major product (65%; see Scheme 3).



Scheme 5 *Reagents and conditions*: i, DABCO, $CHCl_3$, rt.



Scheme 6 *Reagents and conditions*: i, DABCO or DBU, $CHCl_3$.

zwitterion" **11** to methyl 6-chlorochromene-3-carboxylate **12**, the latter acting as a Michael acceptor. In an attempt to demonstrate such transformations, 3-acetyl-2*H*-chromene **6a** was treated with several activated alkenes **3b**–**e** in the presence of DABCO but, in each case, the sole product was the corresponding alkene dimer **9** (Scheme 5). Dimerisation of activated alkenes in the presence of DABCO has been reported by Drewes *et al.*[17] and Basavaia *et al.*,[18] while other researchers have effected similar dimerisation using phosphine[19] and rhodium complex[20] catalysts. The formation of such dimers as competition products in our own studies prompted further examination of this reaction using the activated alkenes **3a**–**h** as substrates (Scheme 6). The dimeric products **9a**–**h** were obtained in low to moderate yields, methyl and ethyl acrylate requiring the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[21] to effect dimerisation, albeit in very low yield (10% and 5% respectively).

In summary, it is evident that the application of Baylis–Hillman methodology provides convenient, general and relatively efficient access to 3-substituted 2*H*-chromenes, and that the alkene dimers, observed in some cases as competition products, can generally be obtained by direct dimerisation using an appropriate catalyst.

Experimental

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. NMR spectra were recorded on Bruker AMX400 or AVANCE 400 MHz spectrometers at 303 K in $CDCl_3$ or DMSO-d_6, and calibrated using solvent signals. Infrared spectra were recorded on a Perkin Elmer FT-IR spectrum 2000 spectrometer, using hexachlorobutadiene or nujol mulls, thin films or NaCl discs. Low-resolution (EI) mass spectra were obtained on a Finnigan-Mat GCQ mass spectrometer and high-resolution (EI) mass spectra on a VG70-SEQ double-focusing magnetic sector spectrometer (Cape Technikon Mass Spectrometry unit). Elemental (HRMS) analytical and other data for the chromene derivatives **6a**–**s** are detailed in Table 1. The general synthetic procedures are illustrated by the following examples.

3-Acetyl-2*H*-chromene 6a

A mixture of salicylaldehyde **2a** (1.0 cm^3, 9.6 mmol), methyl vinyl ketone (1.2 cm^3, 14 mmol) and DABCO (0.86 g, 7.7 mmol)

in $CHCl_3$ (1.0 cm^3) and H_2O (1.0 cm^3) was stirred vigorously under N_2 in a stoppered flask at room temperature. After stirring the reaction mixture for 24 hours, additional methyl vinyl ketone (0.4 cm^3, 5 mmol) and DABCO (0.29 g, 2.6 mmol) were added and stirring was continued for 24 hours before adding further quantities of methyl vinyl ketone (0.20 cm^3, 2.4 mmol) and DABCO (0.10 g, 0.85 mmol) and stirring for a further 72 hours. Flash chromatography of the resulting mixture [on silica; elution with hexane–EtOAc (4 : 1)] afforded, as yellow crystals, 3-acetyl-2*H*-chromene **6a**, mp 39–40 °C (lit.[11] 50–53 °C); ν_{max} (hexachlorobutadiene mull/cm^{-1}) 1655 (CO); δ_H (400 MHz; $CDCl_3$) 2.39 (3H, s, CH_3), 4.99 (2H, s, CH_2), 6.83 (1H, d, *J* 7.1, ArH), 6.95–7.23 (3H, series of multiplets, ArH) and 7.29 (1H, s, 4-H); δ_C (100 MHz; $CDCl_3$) 25.0 (CH_3), 64.2 (CH_2), 116.3, 120.7, 121.8, 129.1, 130.8, 132.4, 133.9 and 155.6 (ArC and C=CH) and 195.9 (CO); *m*/*z* 174 (M^+, 62%) and 131 (100).

3-Acetyl-6,8-dibromochroman-4-ol 5h and 3-acetyl-6,8-dibromo-2*H*-chromene 6h

3,5-Dibromo-2-hydroxybenzaldehyde **2h** (1.0 g, 3.6 mmol) was reacted with methyl vinyl ketone (0.44 cm^3, 5.4 mmol) and DABCO (0.32 g, 2.9 mmol) in chloroform (1.0 cm^3) and water (1.0 cm^3) following the general procedure. Work-up and flash chromatography gave two products:

i) 3-Acetyl-6,8-dibromo-2*H*-chromene 6h. Yellow crystals, mp 74–75 °C; ν_{max} (hexachlorobutadiene mull/cm^{-1}) 1666 (CO); δ_H (400 MHz; $CDCl_3$) 2.40 (3H, s, CH_3), 5.10 (2H, s, CH_2), 7.16 (1H, s, 4-H), 7.23 (1H, d, *J* 2.2, ArH) and 7.58 (1H, d, *J* 2.2, ArH); δ_C (100 MHz; $CDCl_3$) 25.2 (CH_3), 65.3 (CH_2), 111.2, 113.5, 123.2, 130.5, 131.5, 132.1, 137.4 and 151.4 (ArC and CH=C) and 195.3 (CO); *m*/*z* 332 (M^+, 64.3%) and 289 (100).

ii) 3-Acetyl-6,8-dibromochroman-4-ol 5h. Pale yellow crystals, mp 132–134 °C (Found: M^+, 347.8990. $C_{11}H_{10}O_3{}^{79}Br_2$ requires: *M*, 347.8997); ν_{max} (hexachlorobutadiene mull/cm^{-1}) 3444 (OH) and 1696 (CO); δ_H (400 MHz; $CDCl_3$), 2.34 (3H, s, CH_3), 3.02 (1H, d, *J* 5.3, OH), 3.04 (1H, m, 3-H), 4.43 (1H, dd, *J* 11.4 and 13.8, 2-H), 4.60 (1H, dd, *J* 3.5 and 11.4, 2-H), 5.04 (1H, m, 4-H), 7.44 (1H, s, ArH) and 7.60 (1H, s, ArH); δ_C (100 MHz; $CDCl_3$) 29.0 (CH_3), 50.6 (CH), 63.2 (CH_2), 64.2 (CH), 111.7, 112.9, 126.1, 131.8, 135.7 and 150.1 (ArC) and 206.8 (CO); *m*/*z* 350 (M^+, 30%) and 289 (100).

3-Benzoyl-2*H*-chromene 6m and 1,5-diphenyl-2-methylenepentane-1,5-dione 9a

Salicylaldehyde **2a** (1.0 cm^3, 9.6 mmol) was reacted with phenyl vinyl ketone **8**[22] (1.9 g, 14 mmol) and DABCO (0.86 g, 7.7 mmol) in chloroform (1.0 cm^3) and water (1.0 cm^3) following the general procedure. Work-up and flash chromatography gave two products:

i) 3-Benzoyl-2*H*-chromene 6m. Yellow oil; ν_{max} (hexachlorobutadiene mull/cm^{-1}) 1750 (CO); δ_H (400 MHz; $CDCl_3$) 5.16 (2H, s, CH_2), 6.91–7.73 (10H, series of multiplets, ArH and 4-H); δ_C (100 MHz; $CDCl_3$) 65.3 (CH_2), 116.4, 121.0, 121.8, 128.4, 129.0, 129.3, 129.8, 132.0, 132.5, 137.0, 137.6 and 155.6 (ArC and C=CH) and 194.1 (CO); *m*/*z* 236 (M^+, 24.0%) and 105 (100).

ii) 1,5-Diphenyl-2-methylenepentane-1,5-dione 9a. White crystals, mp 52 °C (lit.[24] 57–58 °C); ν_{max} (in chloroform/cm^{-1}) 1684 and 1650 (2 × CO); δ_H (400 MHz; $CDCl_3$) 2.91 (2H, t, *J* 7.2, CH_2), 3.24 (2H, t, *J* 2.2, CH_2), 5.67 and 5.96 (2H, 2 × s, C=CH_2) and 7.40–7.98 (10H, series of multiplets, ArH); δ_C (100 MHz; $CDCl_3$) 27.3 (CH_2), 37.2 (CH_2), 127.3, 128.1, 128.2, 128.6, 129.5, 132.2, 133.1, 136.7, 137.7 and 146.7 (ArC and C=CH_2), 198.1 (CO) and 199.2 (CO).

3-Phenylsulfonyl-3,4-dihydro-2*H*-benzo[*f*]chromen-4-ol 5q and 3-phenylsulfonyl-2*H*-benzo[*f*]-chromene 6q

A mixture of 2-hydroxy-1-naphthaldehyde **2n** (1.0 g, 5.8 mmol), phenyl vinyl sulfone (1.5 g, 8.7 mmol) and DABCO (0.52 g, 4.7 mmol) in $CHCl_3$ (1.0 cm^3) and water (1.0 cm^3) was stirred vigorously at room temperature under N_2. After stirring for 24 hours, phenyl vinyl sulfone (0.5 g, 2.9 mmol) and DABCO (0.17 g, 1.6 mmol) were added and stirring was continued for 72 hours; thereafter, additional phenyl vinyl sulfone (0.25 g, 1.5 mmol) and DABCO (0.06 g, 0.5 mmol) were added and stirring was continued for a further 72 hours. Flash chromatography of the resulting mixture [on silica; elution with hexane–EtOAc (4 : 1)] afforded two products:

i) 3-Phenylsulfonyl-2*H*-benzo[*f*]chromene 6q. Dark yellow crystals, mp 186–188 °C; ν_{max} (chloroform/cm^{-1}) 3020 (C=C–H) and 2918 (CH_2); δ_H (400 MHz; $CDCl_3$) 4.97 (2H, d, *J* 0.8, CH_2), 7.10 (1H, d, *J* 8.8, ArH), 7.21–7.80 (10H, series of multiplets, ArH) and 7.88 (1H, s, 4-H); δ_C (100 MHz; $CDCl_3$) 63.1 (CH_2), 113.4, 117.2, 121.3, 124.8, 127.8, 128.1, 128.3, 128.8, 129.3, 129.5, 130.7, 133.6, 133.7, 139.7 and 153.6 (ArC and C=CH); *m*/*z* 322 (M^+, 66%) and 180 (100).

ii) 3-Phenylsulfonyl-3,4-dihydro-2*H*-benzo[*f*]chromen-4-ol 5q. An oil, (Found: M^+, 340.0769. $C_{19}H_{16}O_4S$ requires: *M*, 340.0779); ν_{max} (hexachlorobutadiene mull/cm^{-1}) 3023 (OH); δ_H (400 MHz; $CDCl_3$) 3.28 (1H, d, *J* 3.5, OH), 3.63 (1H, dt, *J* 3.0 and 11.8, 3-H), 4.55 (1H, m, 2-H), 4.65 (1H, t, *J* 11.8, 2-H), 5.83 (1H, s, 4-H), 7.00 (1H, d, *J* 9.0, ArH), 7.37–8.07 (10H, series of multiplets, ArH); δ_C (100 MHz; $CDCl_3$) 59.0 (CH_2), 59.5 (CH), 63.2 (CH), 113.5, 118.2, 121.8, 124.2, 127.6, 128.5, 128.6, 129.3, 129.6, 131.3, 132.3, 134.5, 138.6 and 151.5 (ArC); *m*/*z* 340 (M^+, 90%) and 169 (100).

3-Methyleneheptane-2,6-dione 9b

A mixture of methyl vinyl ketone (1.0 cm^3, 12 mmol) and DABCO (0.45 g, 4.0 mmol) in chloroform (1.0 cm^3) was stirred at room temperature in a stoppered reaction flask for 7 days. The resulting mixture was purified by flash chromatography [elution with hexane–EtOAc (3 : 2)] to afford, as a dark yellow oil, 3-methyleneheptane-2,6-dione **9b**, ν_{max} (thin film/cm^{-1}) 1709 and 1670 (CO); δ_H (400 MHz; $CDCl_3$) 2.02 (3H, s, CH_3), 2.22 (3H, s, CH_3), 2.43 (2H, m, CH_2), 2.47 (2H, m, CH_2), 5.73 and 5.93 (2H, 2 × s, C=CH_2); δ_C (100 MHz; $CDCl_3$) 25.0 (CH_3), 25.6 (CH_2), 29.6 (CH_2), 42.2 (CH_3), 125.9 (C=*C*H_2), 147.5 (*C*=CH_2), 199.2 (CO) and 207.5 (CO).

Compounds **6a**, **6c**, **6f** and **6g**,[23] **6i**,[11] **6l**,[23] **6m**,[11] **9a**,[24] **9b**,[25] **9c**,[26] **9d** and **9e**[27] and **9h**[18] have also been reported by other researchers; compounds **6b**, **6d**, **6e** and **6h** were reported in our preliminary communication.[10] Analytical data for the other, new chromene derivatives **6** and dimeric products **9** are as follows.

3-Phenylsulfonyl-2*H*-chromene 6j

White crystals, mp 122–123 °C; ν_{max} (hexachlorobutadiene mull/cm^{-1}) 3077 and 3058 (C=C–H) and 1311 (S=O); δ_H (400 MHz; $CDCl_3$) 4.85 (2H, s, CH_2), 6.68 (1H, d, *J* 16.6, ArH) and 6.81–7.92 (9H, series of multiplets, ArH and 4-H); δ_C (100 MHz; $CDCl_3$) 63.11 (CH_2), 116.3, 119.9, 122.3, 127.9, 129.4, 129.5, 131.1, 132.6, 132.8, 133.8, 139.3 and 154.1 (ArC and CH=C); *m*/*z* 272 (M^+, 91%) and 131 (100).

Phenyl 2*H*-chromene-3-sulfonate 6k

White crystals, mp 82–84 °C; ν_{max} (hexachlorobutadiene mull/cm^{-1}) 3065 (C=C–H), 2922 (CH_2) and 1487 (S=O); δ_H (400 MHz; $CDCl_3$) 5.21 (2H, d, *J* 1.0, CH_2), 6.92 (1H, d, *J* 8.1, ArH) and 6.97–7.37 (9H, series of multiplets, ArH and 4-H); δ_C (100 MHz; $CDCl_3$) 63.3 (CH_2), 116.7, 119.7, 122.3, 122.5,

125.1, 127.4, 129.6, 129.9, 133.3, 135.8, 149.4 and 154.7 (ArC and C=CH); *m*/*z* 288 (M^+, 69%) and 131 (100).

3-Acetyl-2*H*-benzo[*f*]chromene 6n

Yellow crystals, mp 122–124 °C; ν_{max} (hexachlorobutadiene mull/cm^{-1}) 1660 (CO); δ_H (400 MHz; $CDCl_3$) 2.51 (3H, s, CH_3), 5.09 (2H, s, CH_2), 7.10 (1H, d, *J* 8.6, ArH), 7.41–7.99 (6H, series of multiplets, ArH) and 8.01 (1H, s, 4-H); δ_C (100 MHz; $CDCl_3$) 25.1 (CH_3), 64.0 (CH_2), 113.9, 117.6, 120.9, 124.4, 127.7, 128.4, 128.9, 129.4, 130.1, 130.8, 133.2 and 155.2 (ArC and C=C) and 195.6 (CO); *m*/*z* 224 (M^+, 63%) and 181 (100).

3-Propanoyl-2*H*-benzo[*f*]chromene 6o

Yellow crystals, mp 88–90 °C; ν_{max} (chloroform/cm^{-1}) 1654 (CO); δ_H (400 MHz; $CDCl_3$) 1.22 (3H, t, *J* 7.2, CH_3), 2.89 (2H, q, *J* 7.2, CH_2), 5.10 (2H, s, CH_2), 7.10 (1H, d, *J* 8.8, ArH), 7.42–7.99 (5H, series of multiplets, ArH) and 8.02 (1H, s, 4-H); δ_C (100 MHz; $CDCl_3$) 8.6 (CH_3), 30.4 (CH_2), 64.3 (CH_2), 114.0, 117.6, 120.9, 124.3, 127.6, 127.9, 128.8, 128.9, 129.4, 130.8, 133.0 and 155.1 (ArC and C=CH) and 198.6 (CO); *m*/*z* 238 (M^+, 95%) and 181 (100).

2*H*-Benzo[*f*]chromene-3-carbaldehyde 6p

Yellow crystals, mp 144–146 °C; ν_{max} (chloroform/cm^{-1}) 1630 (CO); δ_H (400 MHz; $CDCl_3$) 5.1 (2H, s, CH_2) 7.10 (1H, d, *J* 8.6, ArH), 7.41–7.80 (4H, series of multiplets, ArH), 7.95 (1H, s, 4-H), 8.00 (1H, d, *J* 8.6, ArH) and 9.7 (1H, s, CHO); δ_C (100 MHz; $CDCl_3$) 63.2 (CH_2), 114.0, 117.7, 121.0, 124.6, 128.1, 129.0, 129.4, 129.5, 131.1, 130.7, 134.2 and 137.6 (ArC and C=CH) and 189.5 (CO); *m*/*z* 210 (M^+, 65.5%) and 181 (100).

Phenyl 4-hydroxy-3,4-dihydro-2*H*-benzo[*f*]chromene-3-sulfonate 5r and phenyl 2*H*-benzo[*f*]chromene-3-sulfonate 6r

2-Hydroxy-1-naphthaldehyde (0.5 g, 2.9 mmol) was reacted with phenyl ethenesulfonate (0.80 g, 4.4 mmol) and DABCO (0.26 g, 2.3 mmol) in $CHCl_3$ (1.0 cm^3) and water (1.0 cm^3) following the general procedure. Work-up and flash chromatography gave two products:

i) Phenyl 2*H*-benzo[*f*]chromene-3-sulfonate 6r. Yellow crystals, mp 164–166 °C; ν_{max} (chloroform/cm^{-1}) 3022 (C=C–H) and 2923 (CH_2); δ_H (400 MHz; $CDCl_3$) 5.06 (2H, s, CH_2), 7.10 (1H, d, *J* 8.8, ArH), 7.21–7.80 (10H, series of multiplets, ArH) and 7.88 (1H, s, 4-H); δ_C (100 MHz; $CDCl_3$) 63.2 (CH_2), 113.2, 117.3, 121.3, 122.0, 122.3, 124.9, 127.4, 128.2, 128.8, 129.5, 129.9, 130.6, 132.4, 134.2, 149.4 and 154.4 (ArC and C=CH); *m*/*z* 338 (M^+, 100%) and 181 (91.7).

ii) Phenyl 4-hydroxy-3,4-dihydro-2*H*-benzo[*f*]chromene-3-sulfonate 5r. An oil (Found: M^+, 356.0722. $C_{19}H_{16}O_5S$ requires: *M*, 356.0718); ν_{max} (chloroform/cm^{-1}) 3329 (OH); δ_H (400 MHz; $CDCl_3$) 2.74 (1H, d, *J* 4.4, OH), 4.02 (1H, q, *J* 3.5, 3-H), 4.60 (1H, dd, *J* 3.5 and 11.3, 2-H), 4.80 (1H, dd, *J* 3.5 and 11.3, 2-H), 5.93 (1H, m, 4-H), 7.11 (1H, d, *J* 9.2, ArH) and 7.19–8.12 (11H, series of multiplets, ArH); δ_C (100 MHz; $CDCl_3$) 60.6 (CH), 60.8 (CH_2), 61.3 (CH), 112.9, 118.5, 121.9, 122.3, 124.3, 127.4, 127.6, 128.9, 129.8, 130.0, 131.2, 132.2, 148.8 and 152.2 (ArC); *m*/*z* 356 (M^+, 59%) and 198 (100).

3-Cyano-3,4-dihydro-2*H*-benzo[*f*]chromen-4-ol 5s and 3-cyano-2*H*-benzo[*f*]chromene 6s

2-Hydroxy-1-naphthaldehyde (1.0 g, 5.8 mmol) was reacted with acrylonitrile (0.57 cm^3, 8.7 mmol) and DABCO (0.52 g, 4.7 mmol) in $CHCl_3$ (1.0 cm^3) and water (1.0 cm^3) following the general procedure. Work-up and flash chromatography afforded two products:

i) 3-Cyano-2*H*-benzo[*f*]chromene 6s. Yellow crystals, mp 120–122 °C; ν_{max} (hexachlorobutadiene mull/cm^{-1}) 2210 (CN); δ_H (400 MHz; $CDCl_3$) 4.88 (2H, s, CH_2), 7.09 (1H, d, *J* 8.8, ArH), 7.43–7.80 (4H, series of multiplets, ArH), 7.85 (1H, s, 4-H) and 7.86 (1H, d, *J* 8.8, ArH); δ_C (100 MHz; $CDCl_3$) 64.2 (CH_2), 100.3, 113.8, 117.0, 117.3, 121.0, 124.8, 128.2, 128.9, 129.5, 129.9, 133.5 and 135.3 (ArC) and 154.0 (CN); *m*/*z* 207 (M^+, 73%) and 206 (100).

ii) 3-Cyano-3,4-dihydro-2*H*-benzo[*f*]chroman-4-ol 5s. An oil (Found: M^+, 225.0788. $C_{14}H_{11}NO_2$ requires: *M*, 225.0790); ν_{max} (hexachlorobutadiene mull/cm^{-1}) 3421 (OH) and 2249 (CN); δ_H (400 MHz; $CDCl_3$) 2.75 (1H, br s, OH), 3.28 (1H, dt, *J* 11.8 and 3.6, 3-H), 4.42 (1H, m, 2-H), 4.53 (1H, dd, *J* 10.6 and 3.6, 2-H), 5.5 (1H, d, *J* 1.6, 4-H), 7.05 (1H, d, *J* 9.0, ArH), 7.41–7.79 (4H, series of multiplets, ArH) and 8.02 (1H, d, *J* 8.5, ArH); δ_C (100 MHz; $CDCl_3$) 32.3 (CH), 59.7 (CH), 60.7 (CH_2), 112.4, 116.8, 118.4, 121.6, 124.4, 127.8, 128.8, 129.4, 131.5 and 132.2 (ArC) and 151.6 (CN); *m*/*z* 225 (M^+, 66%) and 172 (100).

2,4-Bis(phenylsulfonyl)but-1-ene 9f

A colourless oil (Found: $M^+ - PhSO_2$, 195.04830. $C_{16}H_{16}O_4S_2$ requires: *M* − $PhSO_2$, 195.04798); ν_{max} (thin film/cm^{-1}) 3038 (C=C–*H*) and 2929 (CH_2); δ_H (400 MHz; $CDCl_3$) 2.64 (2H, m, CH_2), 3.32 (2H, m, CH_2), 5.80 and 6.38 (2H, 2 × s, C=CH_2) and 7.49–7.88 (10H, series of multiplets, ArH); δ_C (100 MHz; $CDCl_3$) 23.6 (CH_2), 54.4 (CH_2), 126.2, 128.1, 128.2, 129.4, 129.5, 133.9, 134.0, 137.8, 138.4 and 146.7 (ArC and C=CH_2).

Diphenyl but-1-ene-2,4-disulfonate 9g

A colourless oil (Found: M^+, 368.03881. $C_{16}H_{16}O_6S_2$ requires: *M*, 368.03883); ν_{max} (thin film/cm^{-1}) 2922 (CH_2) and 1588 (C=CH_2); δ_H (400 MHz; $CDCl_3$) 3.21 (2H, m, CH_2), 3.63 (2H, m, CH_2), 6.01 and 6.02 (2H, 2 × s, C=CH_2) and 7.18–7.43 (10H, series of multiplets, ArH); δ_C (100 MHz; $CDCl_3$) 25.8 (CH_2), 48.6 (CH_2), 121.8, 121.9, 127.5, 130.0, 130.1, 130.2, 130.3, 141.1, 148.9 and 149.1 (ArC and C=CH_2).

Acknowledgements

The authors thank the National Research Foundation (NRF) for a bursary (to X.W.N.) and both Rhodes University and the NRF for generous financial support.

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