Synthesis of 3-allylchromones, homoisoflavones and bischromones from (*E*)-1-(2-hydroxyphenyl)-3-(*N,N*-dimethylamino)prop-2-en-1-one

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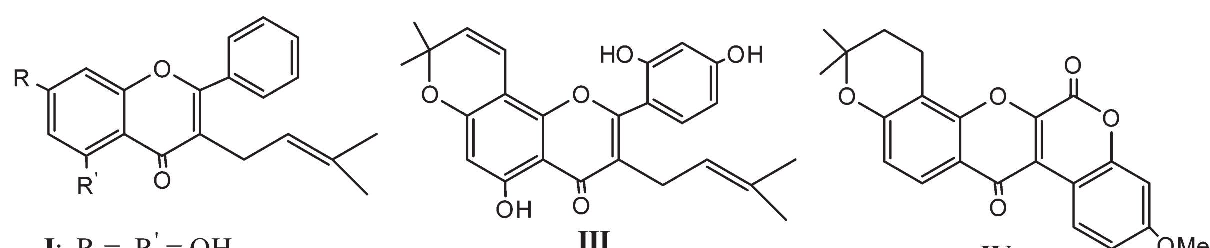
(*E*)-1-(2-Hydroxyphenyl)-3-(*N,N*-dimethylamino)prop-2-en-1-one reacts with allyl bromide, prenyl bromide, benzyl bromide and α,α′-dibromo-*p*-xylene in DMF to produce 3-allyl-, 3-prenyl-chromones, homoisoflavones and bischromones, respectively. Similar compounds were also obtained by deformylative allylation or benzylation of 3-formylchromone.

Keywords: 3-formylchromone, bischromone, enaminone, deformylative allylation, homoisoflavone

Prenylated flavones and chromones are widely distributed in the plant kingdom and many of them are pharmaceutically important.[1,2] Screening of many naturally occurring prenylated flavonoids on cyclooxygenase (COX-1), COX-2 and on 5-lipoxygenase (5-LOX) and 12-LOX showed that inhibitory activities of prenylated flavonoids are much stronger towards 5-LOX than on 12-LOX.[3] 3-Prenylflavones **I** and **II** (Fig. 1) isolated from *Sida cordifolia*, which is commonly used as a traditional medicine against chronic dysentery, asthma and gonorrhoea, are reported to have analgesic and antiinflamatory activities in animal models.[4] Morusin (**III**) (Fig. 1) isolated from a Chinese crude drug (Morus root bark) exhibited specific inhibition of 5-LOX than that of COX-2. Morusin also inhibited proliferation of MDA-MB-231 and MCF-7 breast tumour cells and A549 lung cancer cell.[5]

Although prenylation in the benzenoid moiety of a chromone system is commonly achieved by prenylation of a phenolic hydroxyl group followed by Claisen rearrangement, prenylation in the pyran ring is not straightforward. 3-Allyl-2-methoxychromone was obtained along with 3-allyl-4-methoxycoumarin from the reaction of diazomethane on 3-allyl-4-hydroxycoumarin, which was synthesised by allylation of 4-hydroxycoumarin followed by controlled Claisen rearrangement in NaOAc/Ac_2O and then hydrolysis.[6] Therefore an easy route for the allylation of the chromone ring especially at the 3-position is of great interest. In connection to our recent report on the isocyanide-induced coupling of chromone-3-carbaldehyde,[7] we attempted the synthesis of 6-oxodehydrodeguelin (**IV**), a rotenone analogue, which required prenylation of the hydroxyl group in 7-hydroxychromone-3-carbaldehyde (**1**). Surprisingly, on heating **1** with **2** (R^2 = Me, H) in acetone in the presence of K_2CO_3, the reaction mixture afforded **3** (~10%) and **4** (R^2 = H) (12%) (Scheme 1). We have recently reported the deformylative Mannich reaction of **5**[8] and 2-arylaminochromone-3-carbaldehyde[9] for the synthesis of different bischromones. The defromylative alkenylation reaction in the formation of **3** from **1** encouraged us to study this allylation reaction on **5**. We report here the syntheses of 3-allylchromone, 3-isoprenylchromone, homoisoflavone and a bischromone derivative.

On heating a mixture of **5**, allyl bromide (**2**, R^2 = H), anhydrous $AlCl_3$ in benzene, no change in **5** was observed (Table 1, entry 1). No identifiable compound was isolated when a mixture of **5**, allyl bromide, K_2CO_3 and NaI was heated in THF (entry 2). Microwave irradiation of the same mixture for 5 mins showed no change when monitored by TLC (entry 3).

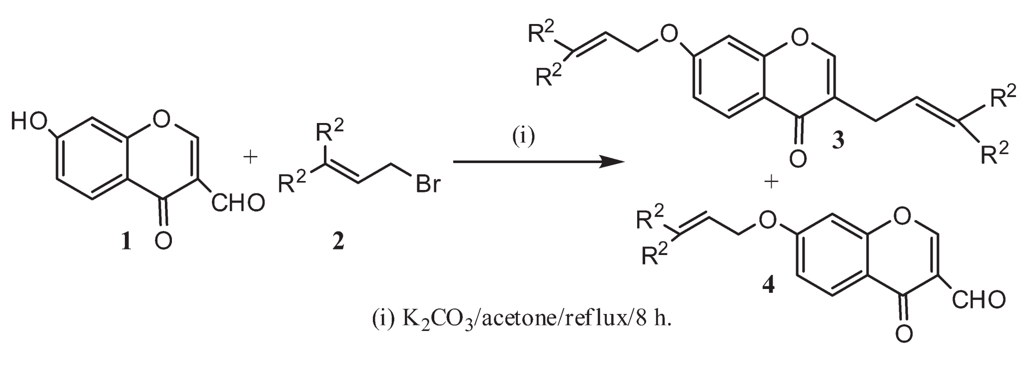


I: R = R' = OH
II: R = H; R' = OH

III
(Morusin)

IV

Fig. 1



Scheme 1

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Table 1 Reactions of **5** with **2** (R^2 = H) under different conditions

Entry	R^1	Reaction conditions		Time	Product	Yield /%	M. p. /°C
		Reagent	Solvent				
1	Me	Anhyd. $AlCl_3$	Benzene	6 h	N. R	–	–
2	Me	K_2CO_3, NaI	THF	6 h	Product could not be isolated		
3	Me	K_2CO_3, NaI, MW		5 min	N. R.	–	–
4	Me	K_2CO_3, NaI	CH_3CN	10 h	**6b**	10	80-82
5	Me	K_2CO_3, NaI	CH_3COCH_3	10 h	**6b**	25	80-82
6	H	K_2CO_3, NaI	CH_3COCH_3	10 h	**6a**	23	Thick oil
7	Cl	K_2CO_3, NaI	CH_3COCH_3	10 h	**6c**	25	78-80
8	Me	K_2CO_3, NaI	DMF	5 h	**6b**	22	80-82
9	Me	K_2CO_3, NaI, CH_3CN/sonication		12 h	Very slow progress		
10	Me	K_2CO_3, NaI, DMF/sonication		12 h	Very slow progress		

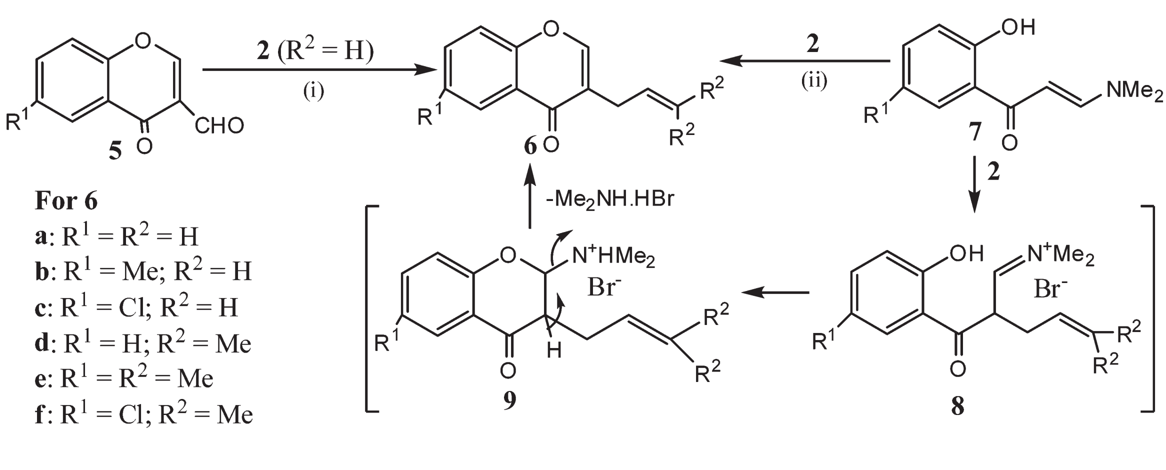
NR, No reaction; MW, microwave irradiation.

However, on heating the above mixture in acetonitrile under reflux for 10 h subsequent work up and chromatographic separation yielded 3-allylchromone (**6b**) in poor yield (10%) (entry 4). Use of acetone in place of acetonitrile improved the yield to 23–25% (entries 5–7) (Scheme 2), whereas, use of DMF as solvent in the above reaction did not improve the yield but shortened the reaction time (entry 8). The above reaction was performed under sonication using acetonitrile or DMF as solvent at room temperature, but the progress of reaction was found to be very slow (entries 9 and 10). None of the above procedures can be considered as a satisfactory preparative route for the synthesis of 3-allylchromone because of their poor yields.

(*E*)-1-(2-Hydroxyphenyl)-3-(*N*,*N*-dimethylamino)prop-2-en-1-one (**7**), which can be synthesised readily by the reaction of *o*-hydroxyacetophenone with *N*,*N*-dimethylformamide dimethyl acetal (DMFDMA),[10] is a versatile reagent for the synthesis of different heterocycles and many naturally occurring compounds.[11] Compound **7** has been utilised in the synthesis of 3,3′-bichromone by anodic oxidation in the presence of $Et_4N^+ClO_4^-$ in acetonitrile[12] or by using $POCl_3$ followed by oxidation,[13] 3-acetylchromone,[14] 3-bromochromone,[10,15] chromone-3-sulfinic acid.[16] Compound **7** has also been used for the synthesis of 5-(2-hydroxyphenyl)isoxazole, which was utilised for the synthesis of 2-aminochromone.[17] In an attempt to utilise this versatile reagent **7** for the synthesis of 3-allylchromone, enaminone **7** was heated with **2** (R^2 = H) in DMF at 80–100 °C for 10 h. After the usual work-up and chromatographic separation, compounds **6a–c** were obtained with improved yield (40–45%). Addition of K_2CO_3 into the reaction mixture of **7** and **2** in DMF showed an adverse effect. Formation of **6** may be rationalised as follows: enamine **7** reacts with **2** (R^2 = H) to form **8**, which subsequently cyclises to **9** and eliminates $Me_2NH.HBr$ to form **6** (Scheme 2). 3-Prenylchromones (**6d–f**) were similarly obtained by using prenyl bromide (**2**: R^2 = Me) in place of allyl bromide.

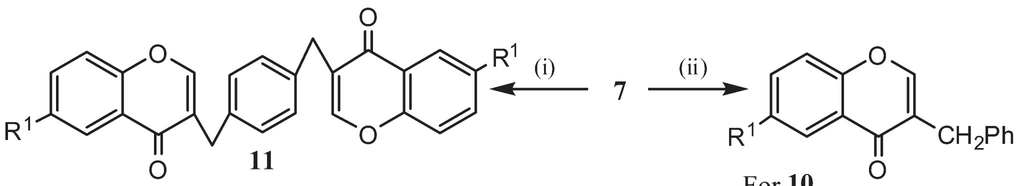
Homoisoflavones are naturally occurring compounds[18,19] and act as antioxidants and antifungal agents,[20] some members also exhibit immunomodulatory activity.[19] 3-Benzylchromones were prepared earlier by isomerisation of 3-benzylidenechromanone or from 1-(2-hydroxyphenyl)-3-phenylpropane-1-one by reaction with HCO_2Et/Na or CH_3SO_2Cl/DMF or $HC(OEt)_3$/70% $HClO_4$.[20] In an attempt to synthesise homoisoflavone from **7**, an equimolar mixture of **7** and benzyl bromide was heated in DMF at 80–100 °C for 4 h. After the usual work-up and chromatographic separation, the reaction mixture yielded homoisoflavones (**10a–c**) (Scheme 3).

As an extension of this work, we intended to synthesise bischromones linked through 3,3′-positions of chromone rings. A literature survey revealed that 3,3′-bischromones having methylene,[9] arylmethylene, piperazine-*N*,*N*′-dimethylene[21] or glycine-*N*,*N*-dimethylene[8] linkers have been synthesised. Some 3,3′-bis(1-benzopyrans) exhibit HIV antiviral activity.[22] 3,3′-Bis(3,4-dihydro-4-hydroxy-6-methoxy-2*H*-1-benzopyran) was isolated from the stem bark of *Kalopanax septemlobus*.[23] We report the synthesis of 3,3′-bischromones having a *p*-xylyl tether. Heating a mixture of **5** and α,α′-dibromo-*p*-xylene in a 2:1 molar ratio in acetone in the presence of K_2CO_3 for 20 h yielded **11** (10–15%) and **12** (10%) (Scheme 4). However, when a mixture of enaminoketone **7** and α,α′-dibromo-*p*-xylene in a 2:1 molar ratio was heated in DMF for 4 h at 80–100 °C, the reaction mixtures yielded **11** (45–48%) (Scheme 3).



(i) K_2CO_3/acetone/reflux/10 h; (ii) DMF, 80-100 °C, 8 h.

Scheme 2

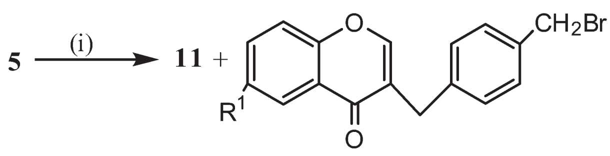


For **11-12**
a: R^1 = H
b: R^1 = Me

For **10**
a: R^1 = H
b: R^1 = Me
c: R^1 = Cl

(i) p-$C_6H_4(CH_2Br)_2$, DMF/80-100 °C, 6 h; (ii) $PhCH_2Br$, DMF, 80-100 °C, 4 h.

Scheme 3



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(i) p-$C_6H_4(CH_2Br)_2$, K_2CO_3, Acetone, reflux, 20 h.

Scheme 4

Thus, we have achieved the synthesis of 3-allyl-, 3-prenyl- and 3-benzyl substituted chromones from enaminoketone **7**. This methodology was then utilised for the synthesis of bischromones. The deformylative allylation reaction on chromone-3-carbaldehyde has also been achieved.

Experimental

The recorded melting points are uncorrected. IR spectra were recorded in KBr on a Beckman IR 20A, ^{1}H NMR spectra on a Bruker 300 MHz spectrometer and mass spectra on Qtof Micro YA 263 instrument and elemental analysis on a Perkin Elmer 240c elemental analyzer. Light petroleum refers to the fraction with distillation range 60–80 °C. Column chromatography was performed using silica gel (100–200 mesh).

*Reaction of 7-hydroxy-4-oxo-4H-1-benzopyran-3-carbaldehyde (**1**) with **2***

A mixture of **1** (380 mg, 2 mmol), **2** (R^2 = Me) (375 mg, 2.5 mmol) and K_2CO_3 (550 mg, 4 mmol) in acetone (25 mL) was heated under reflux for 8 h. The reaction mixture was filtered and residue was washed with acetone. All the washings and the filtrate were mixed together and solvent was removed from the mixture under reduced pressure. Crushed ice (30 g) was added to the concentrate to afford a semisolid mass, which was extracted with $CHCl_3$. The organic layer was washed with water, dried over Na_2SO_4 and chromatographed using 20% benzene in petroleum ether to afford **3** (R^2 = Me). A similar procedure using allyl bromide **2** (R^2 = H) in place of prenyl bromide **2** (R^2 = Me) produced **3** (R^2 = H) from the first few fractions of the eluent and the latter fractions afforded **4** (R^2 = H).

*3-(3-Methyl-2-buten-1-yl)-7-(3-methyl-2-buten-1-yloxy)-4*H*-1-benzopyran-4-one* [**3** (R^2 = Me)]: White crystalline solid, (60 mg, 10%); m.p. 92–94 °C; IR: ν_{max} 2950, 1655, 1635, 1460, 1410 cm^{-1}; ^{1}H NMR: δ($CDCl_3$) 1.70 (3H, s, CH_3), 1.77 (6H, s, 2 x CH_3), 1.82 (3H, s, CH_3), 3.17 (2H, d, J = 6.6 Hz, CH_2), 4.58 (2H, d, J = 6.3 Hz, CH_2), 5.27 (1H, t, J = 6.6 Hz, =CH), 5.49 (1H, t, J = 6.3 Hz, =CH), 6.80 (1H, br.s, 8-H), 6.95 (1H, br.d, J = 8.7 Hz, 6-H), 7.61 (1H, s, 2-H), 8.12 (1H, br.d, J = 8.7 Hz, 5-H). Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found:C, 76.62; H, 7.52%.

*3-(2-Propen-1-yl)-7-(2-propen-1-yloxy)-4*H*-1-benzopyran-4-one* [**3** (R^2 = H)]: White crystalline solid, (55 mg, 11%); m.p. 68–70 °C; IR: ν_{max} 2935, 1650, 1615, 1450, 1414 cm^{-1}; ^{1}H NMR: δ($CDCl_3$) 3.22 (2H, d, J = 6.0 Hz, CH_2), 4.62 (2H, d, J = 5.3 Hz, CH_2), 5.13 (1H, d, J = 9.0 Hz, =CH_2), 5.17 (1H, d, J = 16.2 Hz, =CH_2), 5.34 (1H, d, J = 10.5 Hz, =CH_2), 5.45 (1H, d, J = 17.1 Hz, =CH_2), 5.89–6.11 (2H, m, 2 x =CH), 6.81 (1H, br.s, 8-H), 6.97 (1H, br.d, J = 8.7 Hz, 6-H), 7.67 (1H, s, 2-H), 8.13 (1H, d, J = 8.7 Hz, 5-H). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.52; H, 5.72%.

*7-(2-Propen-1-yloxy)-4-oxo-4*H*-1-benzopyran-3-carbaldehyde* [**4** (R^2 = H)]: White crystalline solid, (55 mg, 12%); m.p. 150–152 °C; IR: ν_{max} 2928, 1700, 1656, 1624, 1440 cm^{-1}; ^{1}H NMR: δ($CDCl_3$) 4.66 (2H, d, J = 5.0 Hz, CH_2), 5.37 (1H, d, J = 10.2 Hz, =CH_2), 5.46 (1H, d, J = 17.4 Hz, =CH_2), 6.00–6.12 (1H, m, =CH), 6.93 (1H, br.s, 8-H), 7.06 (1H, br.d, J = 9.0 Hz, 6-H), 8.18 (1H, d, J = 9.0 Hz, 5-H), 8.48 (1H, s, 2-H), 10.38 (1H, s, CHO). Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.64; H, 4.47%.

*Reaction of 4-oxo-4H-1-benzopyran-3-carbaldehyde (**5**) with allyl bromide(**2**, R^2 = H)*

A mixture of **5** (2 mmol), allyl bromide **2** (R^2 = H) (300 mg, 2.5 mmol) and K_2CO_3 (550 mg, 4 mmol) in acetone (25 mL) was heated under reflux with stirring for 10 h. The resultant reaction mixture was filtered and washed with acetone. The filtrate and washings were mixed together and solvent was removed under reduced pressure. Ice-water (20 g) was added to the concentrate when an oily mass appeared. It was extracted with $CHCl_3$ and the organic layer was washed with water, dried over Na_2SO_4 and chromatographed. Compound **6** was obtained by eluting with 20% benzene in light petroleum.

*3-(2-Propen-1-yl)-4*H*-1-benzopyran-4-one* (**6a**): Thick oil, (90 mg, 24%); IR: ν_{max} 2928, 1645, 1480, 1406 cm^{-1}; ^{1}H NMR: δ($CDCl_3$) 3.25 (2H, d, J = 6.3 Hz, CH_2), 5.13 (1H, d, J = 8.7 Hz, =CH_2), 5.17 (1H, d, J = 16.5 Hz, =CH_2), 5.88–6.03 (1H, m, =CH), 7.35–7.44 (2H, m, 6-H and 8-H), 7.61–7.67 (1H, m, 7-H), 7.75 (1H, s, 2-H), 8.23 (1H, br.d, J = 7.8 Hz, 5-H). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.59; H, 5.49%.

*6-Methyl-3-(2-propen-1-yl)-4*H*-1-benzopyran-4-one* (**6b**): White crystalline solid, (90 mg, 23%); m.p. 80–82 °C; IR: ν_{max} 2919, 1637, 1484, 1324 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 2.45 (3H, s, 6-CH_3), 3.24 (2H, d, J = 6.0 Hz, CH_2), 5.13 (1H, d, J = 8.7 Hz, =CH_2), 5.17 (1H, d, J = 16.5 Hz, =CH_2), 5.90–6.13 (1H, m, =CH), 7.32 (1H, d, J = 8.4 Hz, 8-H), 7.45 (1H, br.d, J = 8.4 Hz, 7-H), 7.73 (1H, s, 2-H), 8.01 (1H, br.s, 5-H). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.10; H, 5.98%.

*6-Chloro-3-(2-propen-1-yl)-4*H*-1-benzopyran-4-one* (**6c**): White crystalline solid, (110 mg, 25%); m.p. 78–80 °C; IR: ν_{max} 2930, 1642, 1485, 1400 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 3.24 (2H, d, J = 6.0 Hz, CH_2), 5.15 (1H, d, J = 10.2 Hz, =CH_2), 5.17 (1H, d, J = 16.8 Hz, =CH_2), 5.90–5.98 (1H, m, =CH), 7.40 (1H, d, J = 8.7 Hz, 8-H), 7.59 (1H, br.d, J = 8.7 Hz, 7-H), 7.75 (1H, s, 2-H), 8.18 (1H, br.s, 5-H). Anal. Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11. Found: C, 65.21; H, 4.17%.

*Reaction of (E)-1-(2-hydroxyphenyl)-3-(N,N-dimethylamino)prop-2-en-1-one (**7**) with alkenyl bromides **2***

Alkenyl bromide **2** (2.2 mmol) was added to a solution of **7** (2 mmol) in dry DMF (5 mL) and the resultant mixture was heated in an oil bath at 80–100 °C for 8 h. The reaction mixture was then poured into ice-water (50 g) when an oily mass appeared. It was extracted with $CHCl_3$, the organic layer was washed with water, dried over Na_2SO_4 and chromatographed using 20% benzene in light petroleum as eluent to afford **6a–f**. **6a** (42%), **6b** (40%) and **6c** (45%) are identical in all respected with those obtained by deformylative allylation of **5**.

*3-(3-Methyl-2-buten-1-yl)-4*H*-1-benzopyran-4-one* (**6d**): Thick oil, (210 mg, 49%); IR: ν_{max} 2920, 1642, 1633, 1490 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 1.70 (3H, s, CH_3), 1.77 (3H, s, CH_3), 3.19 (2H, d, J = 6.9 Hz, CH_2), 5.28 (1H, t, J = 6.9 Hz, =CH), 7.35–7.43 (2H, m, 6-H and 8-H), 7.61–7.66 (1H, m, 7-H), 7.70 (1H, s, 2-H), 8.23 (1H, br.d, J = 7.2 Hz, 5-H). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.60; H, 6.48%.

*6-Methyl-3-(3-methyl-2-buten-1-yl)-4*H*-1-benzopyran-4-one* (**6e**): White crystalline solid, (200 mg, 44%); m.p. 86–88 °C; IR: ν_{max} 2925, 1642, 1635, 1487 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 1.70 (3H, s, CH_3), 1.76 (3H, s, CH_3), 2.45 (3H, s, 6-CH_3), 3.18 (2H, d, J = 6.9 Hz, CH_2), 5.27 (1H, t, J = 6.9 Hz, =CH), 7.31 (1H, d, J = 8.4 Hz, 8-H), 7.44 (1H, br.d, J = 8.4 Hz, 7-H), 7.67 (1H, s, 2-H), 8.01 (1H, br.s, 5-H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.01; H, 6.94%.

*6-Chloro-3-(3-methyl-2-buten-1-yl)-4*H*-1-benzopyran-4-one* (**6f**): White crystalline solid, (200 mg, 40%); m.p. 84–86 °C; IR: ν_{max} 2930, 1642, 1635, 1489 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 1.70 (3H, s, CH_3), 1.77 (3H, s, CH_3), 3.18 (2H, d, J = 6.9 Hz, CH_2), 5.26 (1H, t, J = 6.9 Hz, =CH), 7.38 (1H, d, J = 8.7 Hz, 8-H), 7.58 (1H, br.d, J = 8.7 Hz, 7-H), 7.69 (1H, s, 2-H), 8.19 (1H, br.s, 5-H). Anal. Calcd for $C_{14}H_{13}ClO_2$: C, 67.61; H, 5.27. Found: C, 67.51; H, 5.11%.

*Synthesis of homoisoflavones (***10a–c***)*

Benzyl bromide (340 mg, 2 mmol) was added to a solution of **7** (2 mmol) in DMF (5 mL). The reaction mixture was heated in an oil bath at 80–100 °C for 4 h and then poured into ice-water (50 g), when a semi solid mass appeared. It was extracted with $CHCl_3$, washed with water, dried over Na_2SO_4 and chromatographed to afford **10a–c** using 20% benzene in light-petroleum as eluent.

*3-Benzyl-4*H*-1-benzopyran-4-one* (**10a**): White crystalline compound; (190 mg, 40%); m.p. 108–110 °C (lit.[24] m.p. 110 °C); IR: ν_{max} 3050, 2910, 1636, 1628, 1486 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 3.82 (2H, s, CH_2), 7.21–7.31 (5H, m, ArH), 7.34–7.41 (2H, m, 6-H and 8-H), 7.60 (1H, s, 2-H), 7.62–7.65 (1H, m, 7-H), 8.23 (1H, br.d, J = 7.5 Hz, 5-H).

*3-Benzyl-6-methyl-4*H*-1-benzopyran-4-one* (**10b**): White crystalline compound; (200 mg, 40%); m.p.109 °C; IR: ν_{max} 3058, 2916, 1634, 1625, 1484 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 2.43 (3H, s, CH_3), 3.81 (2H, s, CH_2), 7.12–7.38 (6H, m, ArH), 7.43 (1H, br.d, J = 8.1 Hz, 7-H), 7.57 (1H, s, 2-H), 8.01 (1H, br.s, 5-H). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.37; H, 5.70%.

*3-Benzyl-6-chloro-4*H*-1-benzopyran-4-one* (**10c**): White crystalline compound; (270 mg, 50%); m.p.115 °C; IR: ν_{max} 3050, 2924, 1640, 1620, 1484 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 3.80 (2H, s, CH_2), 7.18–7.40 (6H, m, ArH), 7.55 (1H, dd, J = 9.0, 2.1 Hz, 7-H), 7.57 (1H, s, 2-H), 8.18 (1H, d, J = 2.1 Hz, 5-H). Anal. Calcd for $C_{16}H_{11}ClO_2$: C, 70.99; H, 4.10. Found: C, 71.10; H, 4.18%.

*Reaction of 4-oxo-4H-1-benzopyran-3-carbaldehyde (***5***) with α,α′–dibromo-p-xylene*

A mixture of **5a** or **5b** (2 mmol), α,α′–dibromo-*p*-xylene (265 mg, 1 mmol) and K_2CO_3 (550 mg, 4 mmol) in acetone (25 mL) was heated under reflux with stirring for 20 h. The resultant reaction mixture was filtered and washed with acetone. The filtrate and washings were mixed together and concentrated under reduced pressure. Ice-water (20 g) was added to the concentrate when a semisolid mass appeared. It was extracted with $CHCl_3$, the organic layer was washed with water, dried over Na_2SO_4 and chromatographed using benzene as eluent. The first few fractions produced **11a** or **11b** and the latter fractions produced **12b**. Compound **12a** could not be isolated.

*3,3′-(*p*-Xylene-α,α′-diyl)bis(4*H*-1-benzopyran-4-one)* (**11a**): White crystalline solid (60 mg, 15%); m.p. 228–230 °C; IR: ν_{max} 3065, 2916, 1644, 1612, 1470 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 3.81 (4H, s, 2 x CH_2), 7.28 (4H, s, ArH), 7.37–7.44 [4H, m, 2 x (6-H + 8-H)], 7.63–7.68 (2H, m, ArH), 7.64 (2H, s, 2 x 2-H), 8.24 (2H, br.d, J = 7.5 Hz, 2 x 5-H). Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.99; H, 4.69%.

*3,3′-(*p*-Xylene-α,α′-diyl)bis(6-methyl-4*H*-1-benzopyran-4-one)* (**11b**): White crystalline solid (45 mg, 11%); m.p. 266–268 °C; IR: ν_{max} 3068, 2913, 1640, 1615, 1484 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 2.44 (6H, s, 2 x CH_3), 3.78 (4H, s, 2 x CH_2), 7.24 (4H, s, ArH), 7.30 (2H, d, J = 8.4 Hz, 2 x 8-H), 7.44 (2H, br.d, J = 8.4 Hz, 2 x 7-H), 7.59 (2H, s, 2 x 2-H), 8.00 (2H, br.s, 2 x 5-H); MS (positive ion electrospray): *m/z* 423 (M+H$^+$), 445 (M+Na$^+$). Anal. Calcd for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.44; H, 5.17%.

*3-(4-Bromomethyl)benzyl-6-methyl-4*H*-1-benzopyran-4-one* (**12b**): White crystalline solid (35 mg, 10%); m.p. 128–130 °C; IR: ν_{max} 3067, 2910, 1643, 1470, 1452 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 2.44 (3H, s, CH_3), 3.81 (2H, s, CH_2), 4.66 (2H, s, CH_2Br), 7.23–7.40 (5H, m, ArH), 7.45 (1H, br.d, J = 7.2 Hz, 7-H), 7.61 (1H, s, 2-H), 8.00 (1H, br.s, 5-H). Anal. Calcd for $C_{18}H_{15}BrO_2$: C, 62.99; H, 4.41. Found: C, 62.88; H, 4.32%.

*Reaction of (E)-1-(2-Hydroxyphenyl)-3-(N,N-dimethylamino)prop-2-en-1-one (***7***) with α,α′–dibromo-p-xylene*

A mixture of **7a** or **7b** (2 mmol) and α,α′–dibromo-*p*-xylene (265 mg, 1 mmol) in dry DMF (5 mL) was heated on an oil bath at 80–100 °C. The reaction mixture became turbid within half an hour. Heating was continued for 6 h. The reaction mixture was cooled and poured into ice-water (50 g), when a solid separated, which was crystallised from $CHCl_3$–light petroleum (40–60) to produce **11a** (190 mg, 48%) and **11b** (190 mg, 45%).

We gratefully acknowledge CSIR, New Delhi [project no. 01(2206)/07/EMR-II] for financial assistance; IICB and IACS, Jadavpur, R K M Residential College, Narendrapur for spectral analysis and finally the college authority for providing research facilities.

Received 30 June 2010; accepted 7 August 2010
Paper 1000234 doi: 10.3184/030823410X12862117705126
Published online: 22 October 2010

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