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Does the DABCO-catalysed reaction of 2-hydroxybenzaldehydes with methyl acrylate follow a Baylis–Hillman pathway?

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Evidence is presented which supports the intermediacy of dipolar Baylis–Hillman-type adducts in the synthesis of coumarin and chromene derivatives from the reaction of 2-hydroxybenzaldehydes with methyl acrylate in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO).

The Baylis–Hillman reaction[1,2] continues to receive attention,[3] and has recently enjoyed the distinction of becoming a "textbook" reaction![4] Our research on this versatile transformation has been focused, largely, on its use in the construction of benzannulated heterocycles – an interest initially sparked by the isolation of a 2-substituted indolizine during distillation of a pyridine-2-carbaldehyde-derived Baylis–Hillman product.[5] Early attempts to extend the methodology to the synthesis of oxygenated analogues from 2-hydroxybenzaldehydes **1**, however, afforded complex mixtures of various chromene and coumarin derivatives (Scheme 1).[6–8] These observations prompted several questions. Could the regioselectivity of cyclisation be controlled to afford chromene or coumarin derivatives chemoselectively? Could the methodology be extended to the preparation of nitrogen- and sulfur-containing analogues? Are the Baylis–Hillman adducts **3** common intermediates (as suggested in Scheme 1) in the formation of the chromene and coumarin derivatives?

We have subsequently demonstrated *chemoselective* syntheses of chromene[9,10] and coumarin derivatives[11–13] under Baylis–Hillman conditions, and successfully extended the methodology to the preparation of quinoline[14] and thiochromene (benzothiopyran) derivatives.[15] In this communication, we address the remaining issue, *viz.*, the possible implication of Baylis–Hillman adducts **3** as common, pivotal intermediates in the formation of the chromene and coumarin derivatives.

Results and discussion

The reaction of 2-hydroxybenzaldehydes **1** with methyl acrylate **2** in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) could, in principle, proceed *via* a number of possible pathways, as illustrated for salicylaldehyde **1** (R^1 = H) in Scheme 2. An initial Baylis–Hillman reaction (Path A) would afford the adduct **3**, which could cyclise *via* conjugate addition–elimination or acyl substitution to give the chromene **4** or coumarin derivative **5**, respectively. Alternatively, initial conjugate addition (Path B) and subsequent aldol cyclisation of the resulting enolate **6** would give the chromene **4**,[16] while tandem acyl substitution and Baylis–Hillman reactions (Path C) would lead to the coumarin derivative **5**.[17] In our attempts to elucidate the mechanistic sequence in these transformations, several strategies have been explored, *viz.*,

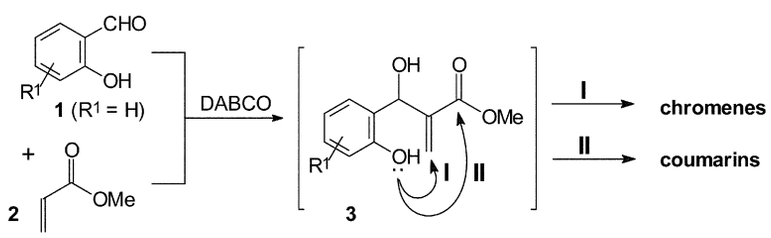
i, temporary protection of the phenolic hydroxy group of the 2-hydroxybenzaldehyde substrate **1** to permit isolation of a protected Baylis–Hillman adduct, subsequent deprotection and cyclisation being expected to afford chromene and coumarin derivatives;

ii, use of 4-hydroxybenzaldehyde as a model compound (for which intramolecular cyclisation is not possible) to explore the preferred initial reaction pathway (A, B or C); and

iii, the preparation and subsequent cyclisation of *unprotected* Baylis–Hillman products.

The reaction of *O*-acetylated 2-hydroxybenzaldehydes with methyl acrylate **2** in the presence of DABCO was shown[18] to afford chromene and coumarin derivatives of the type produced by *unprotected* analogues – an observation which indicated *in situ* de-acetylation but provided no information on the sequence of events. Attention was consequently turned to the use of *O*-*tert*-butyldimethylsilyl(TBDMS)-protected 2-hydroxybenzaldehydes, choice of the protecting group having been influenced by the expected stability of the resulting silyl ethers and their potential for selective removal using fluoride ion.[19,20] Treatment of salicylaldehyde **1** (R^1 = H) with *tert*-butyldimethylsilyl chloride in the presence of imidazole[20] failed to afford the required silyl ether **8** (Scheme 3); silylation was, however, effected in good yield by reacting the salicylaldehyde phenoxide ion with *tert*-butyldimethylsilyl chloride. The *O*-TBDMS-protected salicylaldehyde **8** was then treated with methyl acrylate **2** in the presence of DABCO in anticipation of obtaining the *O*-silylated Baylis–Hillman product **9**. In the event, starting material **8** was isolated together with salicylaldehyde **1** (R^1 = H), the chromene-3-carboxylic ester **4**, the coumarin derivatives **10** and **11**,[6–8] and the bis-silylated Baylis–Hillman product **12**!

A consolidated mechanistic sequence, which could account for the formation of all five of these compounds, is outlined in Scheme 4. Thus, the Baylis–Hillman adduct **14**, once formed



Scheme 1

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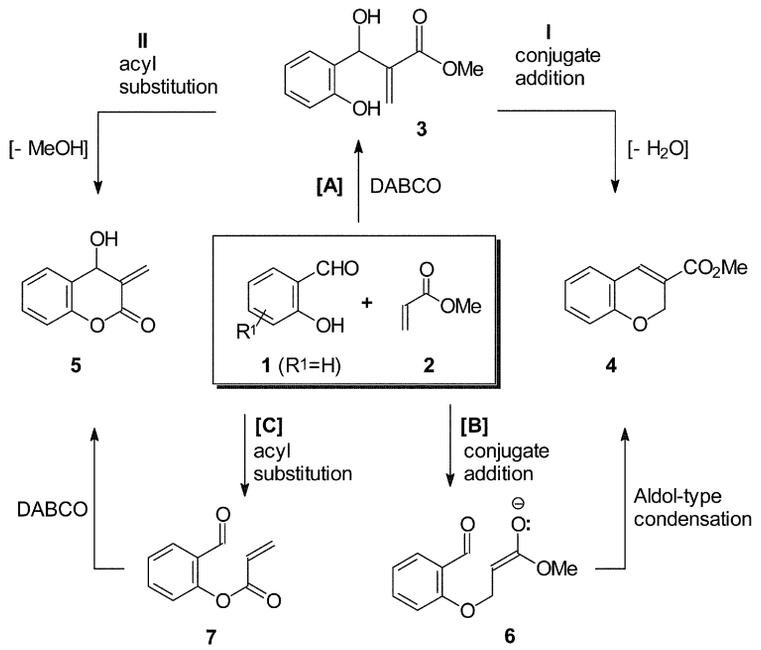
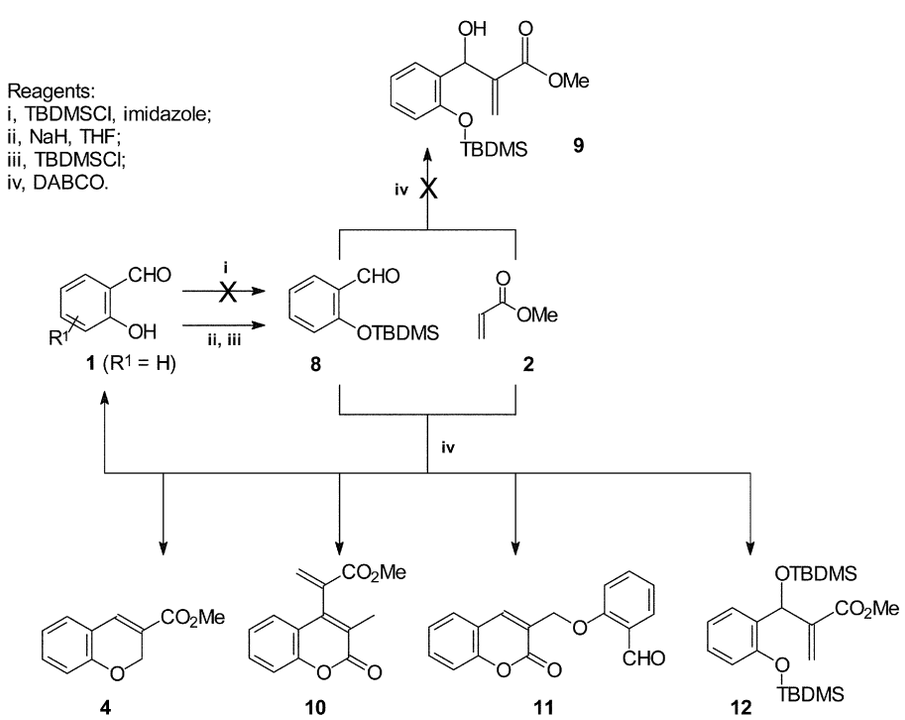


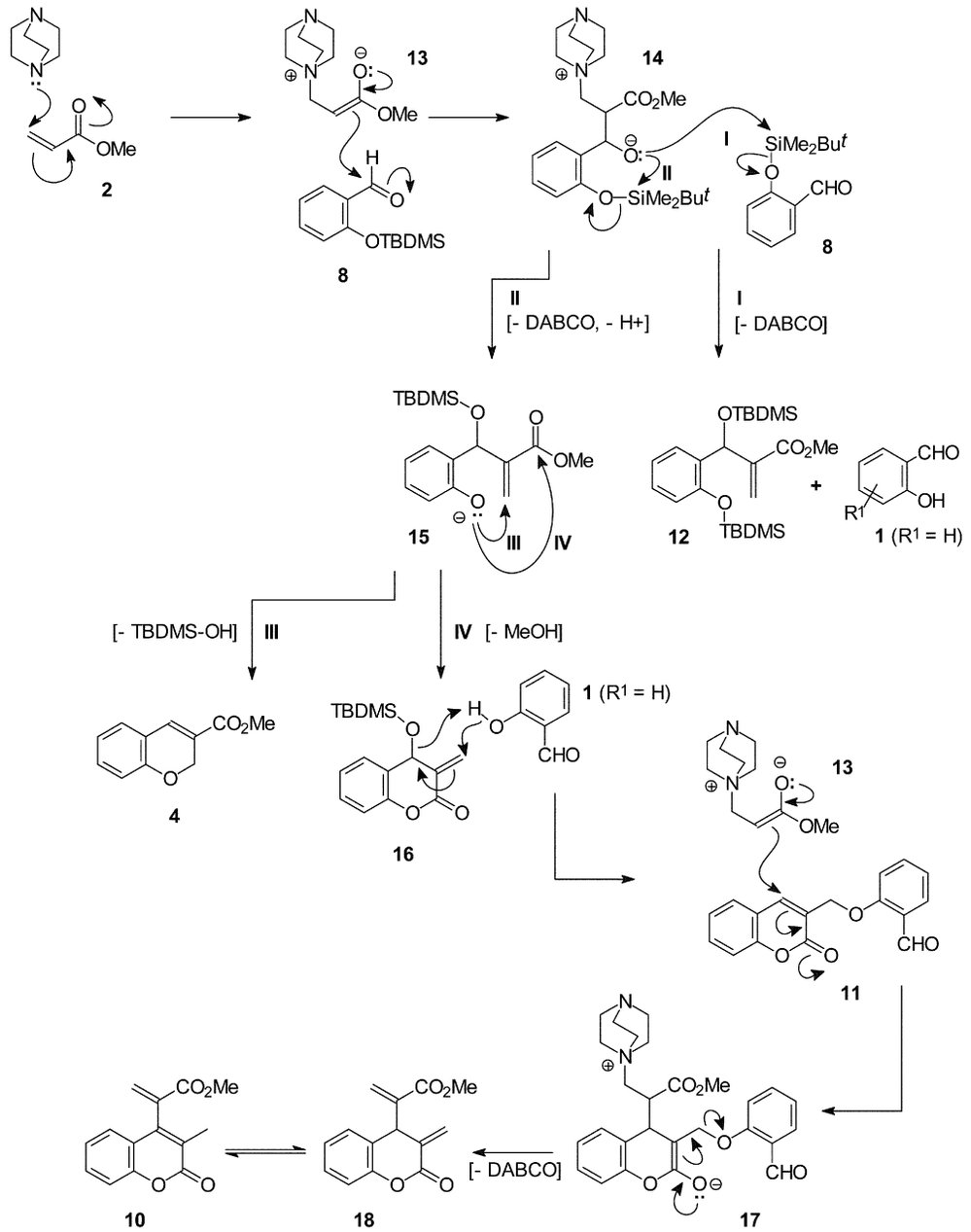
Scheme 2



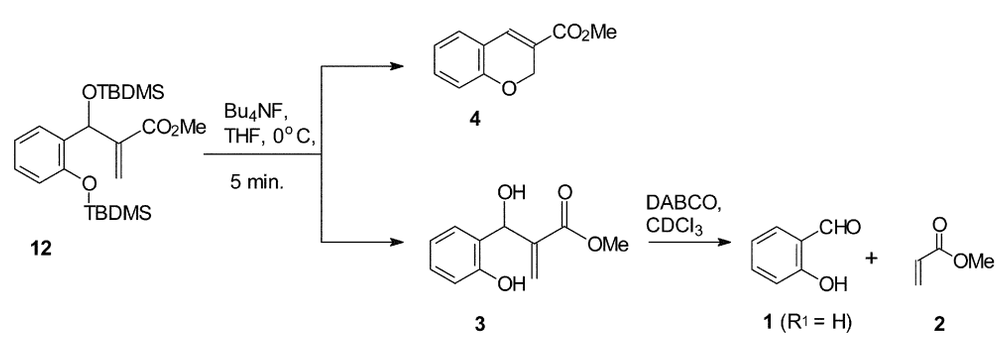
Scheme 3

by addition of the "Baylis–Hillman zwitterion" **13** to the *O*-silylated salicylaldehyde **8**, may attack another substrate molecule **8**. Nucleophilic displacement of salicylaldehyde **1** (R^1 = H) and elimination of DABCO would then afford the bis-silylated derivative **12** (Path I; Scheme 4). Concomitant intramolecular attack (Path II) would lead, following loss of DABCO, to the phenoxide ion **15**; subsequent cyclisation, *via* conjugate addition (Path III) or acyl substitution (Path IV), would then afford the chromene **4** or the intermediate coumarin derivative **16**, respectively. Allylic displacement of TBDMS-OH from the intermediate **16** (*via* a 6-centred transition-state complex) would then explain the formation of the coumarin derivative **11**. Subsequent addition of the Baylis–Hillman zwitterion **13a**, elimination of salicylaldehyde and DABCO from the intermediate adduct **17** and, finally, tautomerism would then account for the formation of the 4-substituted chromene **10**.

In order to demonstrate the ability of *unprotected* Baylis–Hillman products to undergo intramolecular cyclisation, the disilylated derivative **12** was treated with tetrabutylammonium fluoride in THF at 0 °C (Scheme 5).[20] Preparative layer chromatography of the resulting mixture afforded the chromene-3-carboxylic ester **4** and, as the major product, the hitherto somewhat elusive Baylis–Hillman product **3**.[21,22] The latter compound, which was fully characterised, was then dissolved in $CDCl_3$ and the resulting solution subjected to periodic ^{1}H NMR analysis. After one week, there was no evidence of cyclisation, and DABCO was added to the solution on the assumption that the cyclisation might well be DABCO-catalysed. ^{1}H NMR analysis of the resulting mixture, however, indicated substantial formation of salicylaldehyde **1** (R^1 = H) and methyl acrylate **2**. This result supports the proposed[23] reversibility of the Baylis–Hillman reaction, but clearly fails to demonstrate



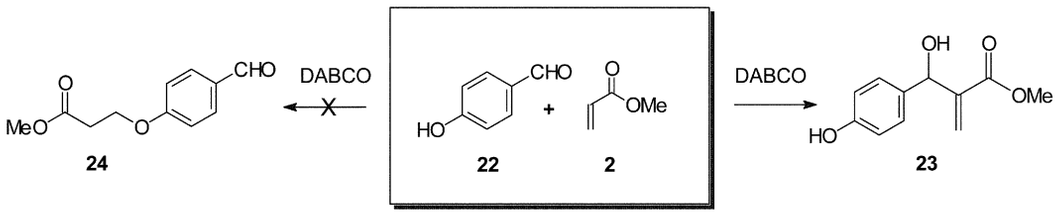
Scheme 4



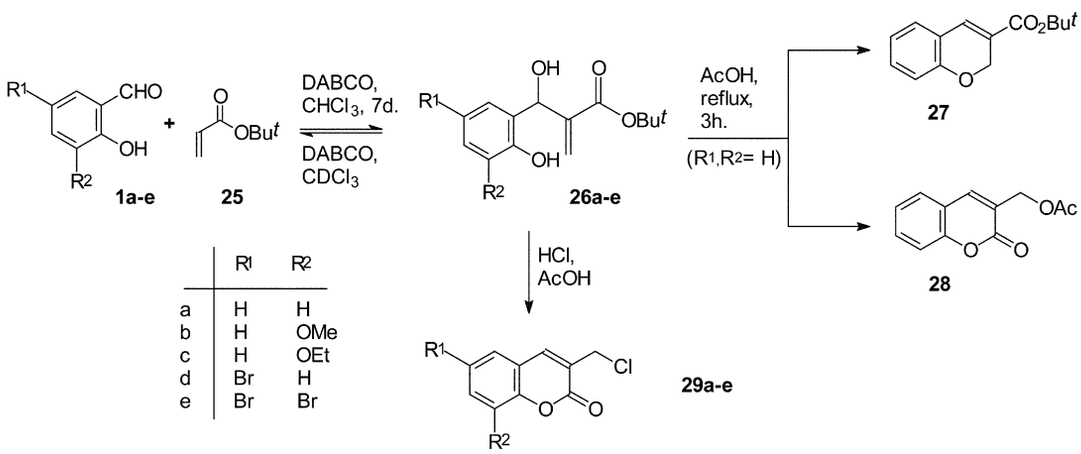
Scheme 5

implication of a Baylis–Hillman pathway in the formation of chromene and coumarin derivatives!

The competition between the Baylis–Hillman and conjugate-addition pathways (Scheme 2; Paths A and B, respectively) was investigated by treating 4-hydroxybenzaldehyde **22** with methyl vinyl ketone (MVK) in the presence of DABCO. Under these conditions, however, the only product to be isolated was the MVK dimer.[10] When methyl acrylate **2**, which exhibits little tendency to dimerise under Baylis–Hillman conditions, was used as the activated alkene, the only product to be isolated [together with starting material (60%)] was, in fact, the Baylis–Hillman adduct **23** (10%; Scheme 6). None of the conjugate-addition product **24** could be detected. Further support for an initial Baylis–Hillman step in the cyclisation reactions under



Scheme 6



Scheme 7

investigation is provided by the isolation of Baylis–Hillman adducts as intermediates in our reported syntheses of quinoline[14] and thiochromene[15] systems.

We have subsequently found that reaction of 2-hydroxybenzaldehydes **1a**–**e** (Scheme 7) with *tert*-butyl acrylate **25** in the presence of DABCO affords the *isolable* Baylis–Hillman products **26a**–**e**.[13] On treatment with DABCO in $CDCl_3$, the salicylaldehyde-derived adduct **26a** was shown to undergo a *retro*-Baylis–Hillman reaction. In refluxing acetic acid, however, the adduct **26a** was converted to the chromene and coumarin derivatives **27** and **28**,[13] respectively, demonstrating the capacity of Baylis–Hillman adducts to undergo intramolecular cyclisation, albeit under acidic conditions! In fact, treatment of the *tert*-butyl ester adducts **26a**–**e** with hydrochloric acid has been shown to provide convenient, efficient and chemoselective access to the corresponding 3-(chloromethyl)-coumarins **29a**–**e**.[13] The isolability of the adducts **26a**–**e** may be attributed to the steric and electronic effects of the *tert*-butyl group, which appear to inhibit spontaneous, intramolecular nucleophilic attack at both the vinylic and carbonyl centres.

While it is apparent that the 2-hydroxybenzaldehyde-derived Baylis–Hillman adducts (**3** and **26a**–**e**) cyclise in acidic media, their failure to undergo such cyclisation in the presence of DABCO was, initially, somewhat puzzling. A possible explanation lies in the interplay between the reversible and non-reversible transformations outlined in Scheme 8. Thus, reversible addition of the Baylis–Hillman zwitterions (**13** or **30**) to the 2-hydroxybenzaldehyde **1** (R^1 = H) produces the corresponding dipolar adducts **31** and **32**. In the case of the methyl ester **31**, proton transfer affords the more stable isomeric species **33**, which contains a nucleophilic phenoxide moiety and two highly electrophilic centres, C-1 (activated by intramolecular hydrogen-bonding) and C-3′ (activated by the adjacent quaternary nitrogen). Dipolar adducts of type **33** are, we suggest, the pivotal intermediates, which undergo slow but *irreversible* intramolecular (S_N) cyclisation and dehydration (*via* path I) or acyl substitution (*via* path II) to afford chromene or coumarin products, respectively. In the case of the *tert*-butyl ester **32**, cyclisation is inhibited and elimination of DABCO affords the relatively stable Baylis–Hillman product **26a**. Formation of the adduct **26a** is *reversible*, and conjugate addition by DABCO would initiate the observed *retro*-Baylis–Hillman process. Addition of HCl (Nu: = Cl^-) in strongly acidic medium, however, would afford the protonated species **35**, which could undergo rapid and *irreversible* cyclisation to the corresponding 3-(chloromethyl)coumarin **29a** (Scheme 7) *via* acid-catalysed acyl substitution (path II).

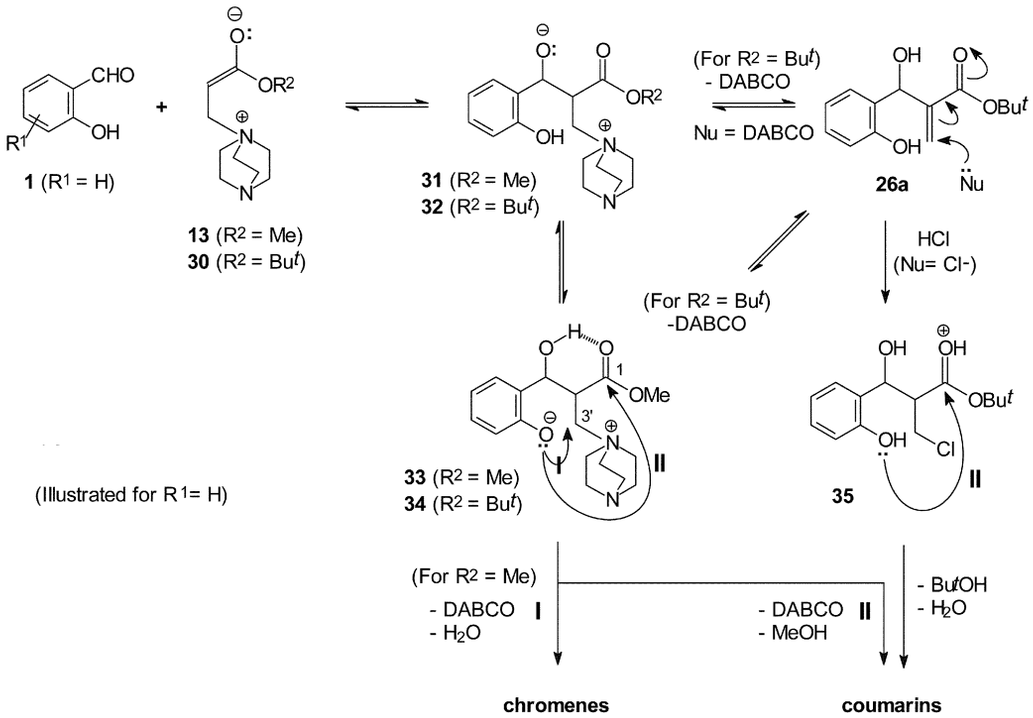
In the light of the cumulative evidence, we conclude that in the formation of chromene and coumarin derivatives from DABCO-catalysed reactions of 2-hydroxybenzaldehydes **1** with methyl acrylate **2**: i) the Baylis–Hillman reaction *precedes* conjugate addition or acyl substitution; and ii) the pivotal intermediates are, in fact, highly activated dipolar adducts of type **33**, rather than the Baylis–Hillman products *per se*.

Experimental

NMR spectra were recorded on Bruker AMX400 or AVANCE 400 MHz spectrometers at 303 K in $CDCl_3$ and calibrated using solvent signals. Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrum 2000 spectrometer. Low-resolution (EI) mass spectra were obtained on a Finnigan-Mat GCQ mass spectrometer and high-resolution (EI) mass spectra on a VG70-SEQ Micromass double-focusing magnetic sector spectrometer (Cape Technikon Mass Spectrometry unit). The preparation and characterisation of compounds **4**,**10**,**11**,**26a**–**e**,**27**,**28** and **29a**–**e** have been reported previously.[6–8,13,18,21]

2-(*tert*-Butyldimethylsilyloxy)benzaldehyde 8

Salicylaldehyde (1.9 ml, 18 mmol) was added dropwise to a stirred suspension of washed NaH (50% dispersion in oil; 0.94 g, 20 mmol) in dry THF (50 ml) under N_2. The mixture was stirred at room temperature for 30 min, *tert*-butyldimethylsilyl chloride (3.0 g, 20 mmol) in dry THF was then added and the resulting mixture was stirred at room temperature for 12 h. The reaction was quenched by the addition of aq. $NaHCO_3$ (20 ml) and the resulting mixture extracted into diethyl ether (3 × 20 ml). The ethereal extracts were washed with saturated brine (50 ml) and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to give the crude product (6.4 g), which was purified by flash chromatography [elution with hexane–EtOAc



Scheme 8

(9 : 1)] to afford *2-(tert-butyldimethylsilyloxy)benzaldehyde* **8** (2.7 g, 65%) (Found: **MH**$^+$, 237.1310. $C_{13}H_{20}SiO_2$ requires M+1, 237.1311); ν_{max} (hexachlorobutadiene mull/cm^{-1}) 1742 (CO); δ_H (400 MHz; $CDCl_3$) 0.26 [6H, s, $Si(CH_3)_2$], 1.02 [9H, s, $C(CH_3)_3$], 6.86 (1H, d, ArH), 7.01 (1H, t, ArH), 7.43 (1H, t, ArH), 7.80 (1H, d, ArH) and 10.46 (1H, s, CHO); δ_C (100 MHz; $CDCl_3$) −4.4 [$Si(CH_3)_2$], 18.3 [$SiC(CH_3)_3$], 25.6 [$SiC(CH_3)_3$], 120.2, 121.4, 127.3, 128.3, 135.6 and 158.8 (ArC) and 189.9 (CHO); *m/z* 236 (M$^+$, 0.9) and 179 (100%).

Attempted preparation of methyl 3-hydroxy-3-[2-(*tert*-butyldimethylsilyloxy)phenyl]-2-methylenepropanoate 9

A solution of 2-(*tert*-butyldimethylsilyloxy)benzaldehyde **8** (1.5 g, 6.4 mmol), methyl acrylate **2** (0.72 ml, 7.9 mmol) and DABCO (0.07 g, 0.6 mmol) in $CHCl_3$ (1.0 ml) was stirred in a stoppered flask under N_2 for 3 d. The crude mixture was purified by flash chromatography followed by preparative layer chromatography (elution with chloroform) to afford the following six compounds. i) Salicylaldehyde **1** (R^1 = H) (0.30 g, 39%). ii) Methyl 2*H*-1-chromene-3-carboxylate **4** (0.08 g, 6.6%). iii) 2-(*tert*-Butyldimethylsilyloxy)benzaldehyde **8** (0.22 g, 15%). iv) *Methyl 2-(3-methyl-1-benzopyran-2-on-4-yl)propenoate* **10**, as white crystals (0.03 g, 2%), mp 104–106 °C (Found: **M**$^+$, 244.0745. $C_{14}H_{12}O_4$ requires: M, 244.0736); ν_{max} (Nujol mull / cm^{-1}) 1707 and 1667 (2 × CO); δ_H (400 MHz; $CDCl_3$) 2.09 (3H, s, CH_3), 3.76 (3H, s, OCH_3), 5.82 and 6.87 (2H, 2 × s, $C=CH_2$), 7.21–7.46 (4H, m, ArH); δ_C (100 MHz; $CDCl_3$) 14.6 (CH_3), 52.7 (OCH_3), 116.8, 119.7, 123.9, 124.2, 125.6, 130.7, 131.4, 135.3, 145.8 and 152.4 (ArC, C=C and $C=CH_2$), 161.8 (CO_2CH_3) and 165.0 (CO). v) 3-[(2-Formylphenoxy)methyl]coumarin **11**, as white crystals, (0.05 g, 3%), mp 178–180 °C (lit.[*] 180–182 °C). vi) *Methyl 3-(tert-butyldimethylsilyloxy)-3-[2-(tert-butyldimethylsilyloxy)phenyl]-2-methylenepropanoate* **12** as a light yellow oil (0.33 g, 12%), (Found: **MH**$^+$, 437.2544. $C_{23}H_{40}Si_2O_4$ requires M+1, 437.2543); ν_{max} (hexachlorobutadiene mull /cm^{-1}) 1727 (CO); δ_H (400 MHz; $CDCl_3$) −0.020, 0.067, 0.23 and 0.26 [12H, 4 × s, 2 × $Si(CH_3)_2$], 0.86 and 0.99 [18H, 2 × s, 2 × $C(CH_3)_3$], 3.71 (3H, s, OCH_3), 5.44 and 6.14 (2H, 2 × s, $C=CH_2$), 6.05 (1H, s, OCH), 6.75 (1H, d, ArH), 6.93 (1H, t, ArH), 7.12 (1H, t, ArH) and 7.42 (1H, d, ArH); δ_C (100 MHz; $CDCl_3$) −4.76, −4.17, −4.11 and −4.12 [2 × $Si(CH_3)_2$], 18.2 [2 × $C(CH_3)_3$], 25.8 [2 × $C(CH_3)_3$], 51.5 (OCH_3), 66.7 (OCH), 117.8, 120.7, 124.8, 124.9, 128.1, 132.4, 143.9 and 152.3 (ArC and $C=CH_2$) and 166.9 (CO); *m/z* 436 (M$^+$, 0.05) and 179 (100%).

Deprotection of methyl 3-(*tert*-butyldimethylsilyloxy)-3-[2-(*tert*-butyldimethylsilyloxy)phenyl]-2-methylenepropanoate 12

Tetrabutylammonium fluoride (1.0 g, 3.2 mmol) was added to a stirred solution of methyl 3-(*tert*-butyldimethylsilyloxy)-3-[2-(*tert*-butyldimethylsilyloxy)phenyl]-2-methylenepropanoate **12** (0.12 g, 0.27 mmol) in dry THF (1.0 ml) at 0 °C. After 5 minutes, water was added (0.2 ml), followed by dilute HCl until the solution was just acidic, and the mixture was then extracted with diethyl ether. The ethereal extracts were combined and dried (anhyd. $MgSO_4$), the solvent was removed *in vacuo* and the residue purified by preparative layer chromatography [elution with hexane–EtOAc (3 : 2)] to afford the following two products. i) *Methyl 3-hydroxy-3-(2-hydroxyphenyl)-2-methylenepropanoate* **3**, as a colourless oil (0.04 g, 71%), (Found: **M**$^+$, 208.0733. $C_{11}H_{12}O_4$ requires: M, 208.0736); δ_H (400 MHz; $CDCl_3$) 3.82 (3H, s, OCH_3), 4.12 (1H, br s, $CHOH$), 5.59 and 6.35 (2H, 2 × s, $C=CH_2$), 5.74 [1H, s, CH(OH)], 6.85 (1H, t, ArH), 6.93 (1H, d, ArH), 6.96 (1H, d, ArH), 7.21 (1H, t, ArH), 7.97 (1H, s, ArOH); δ_C (100 MHz; $CDCl_3$) 52.4 (OCH_3), 73.5 [CH(OH)], 117.6, 120.0, 123.8, 127.8, 128.0, 129.7, 139.4 and 155.9 (ArC and $C=CH_2$) and 167.7 (CO). ii) Methyl 2*H*-1-chromene-3-carboxylate **4** (0.01 g, 19%).

Methyl 3-hydroxy-3-(4-hydroxyphenyl)-2-methylenepropanoate 23

A mixture of 4-hydroxybenzaldehyde **22** (0.20 g, 1.6 mmol), methyl acrylate **2** (0.22 ml, 2.5 mmol) and DABCO (0.07 g, 0.7 mmol) in $CHCl_3$ (0.5 ml) was stirred in a stoppered flask under N_2 at room temperature for 7 d. The resulting mixture was purified by flash chromatography [elution with hexane–EtOAc (3 : 2)], to afford starting material (0.12 g, 60%) and, as colourless oil, *methyl 3-hydroxy-3-(4-hydroxyphenyl)-2-methylenepropanoate* **23** (0.03 g, 10%) (Found: **M**$^+$, 208.0743. $C_{11}H_{12}O_4$ requires: M, 208.0736; ν_{max} (hexachlorobutadiene mull /cm^{-1}) 3407 (br, OH) and 1710 (CO); δ_H (400 MHz;

$CDCl_3$) 3.13 [1H, br s, CH(O*H*)], 3.70 (3H, s, OCH_3), 5.49 [1H, s, C*H*(OH)], 5.85 and 6.31 (2H, 2 × s, C=CH_2), 6.10 (1H, br s, ArOH), 6.72 (2H, d, ArH) and 7.17 (2H, d, ArH); δ_C (100 MHz; $CDCl_3$) 52.0 (OCH_3), 72.8 [CH(OH)], 115.8, 125.8, 128.1, 133.0, 142.0 and 155.6 (ArC and C=CH_2) and 167.0 (CO).

Acknowledgements

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