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A Facile Synthetic Route to 2*H*-Chromenes: Reconsideration of the Mechanism of the DBU-Catalyzed Reaction between Salicylic Aldehydes and Ethyl 2-Methylbuta-2,3-dienoate**

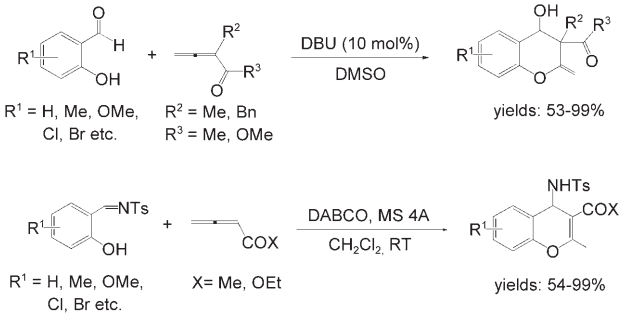
Lun-Zhi Dai, Yong-Ling Shi, Gui-Ling Zhao, and Min Shi*[a]

Abstract: Reactions of salicylaldehydes with ethyl buta-2,3-dienoate or penta-3,4-dien-2-one catalyzed by a catalytic amount of potassium carbonate produce the corresponding 2*H*-chromene products in moderate to good yields under mild conditions. A plausible reaction mechanism is discussed in the light of the results of an ^{18}O-labeling experiment. In addition, in view of these findings, the catalytic function of DBU in reactions of this kind is reconsidered.

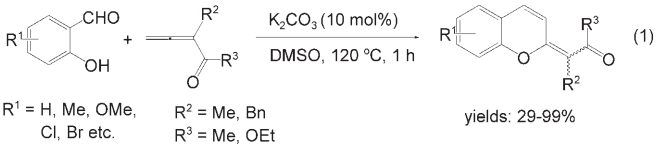
Keywords: chromenes · base-catalyzed condensation · heterocycles · reaction mechanisms · synthetic methods

Introduction

2*H*-Chromenes are key heterocyclic units in many natural and biologically relevant polyoxygenated active compounds.[1,2] The development of new efficient processes for the construction of important molecules using metal-free reagents has been the subject of increasing attention over the last couple of years. Recently, the base-catalyzed condensation of salicylic aldehydes with α,β-unsaturated carbonyl compounds, which yield tetrahydroxanthones and dihydrobenzopyrans, has been systematically investigated by Bräse et al.[3] On the other hand, our group has reported an efficient approach to functionalized 2*H*-1-benzopyrans by reactions of salicylic aldehydes or salicyl *N*-tosylimines with allenic esters or ketones in the presence of a variety of Lewis base catalysts (Scheme 1).[4,5] During our ongoing investigation into the mechanism of these reactions, we found that potassium carbonate (K_2CO_3) can also serve as an efficient catalyst, giving the corresponding functionalized 2*H*-chromenes in good yields in dimethyl sulfoxide (DMSO) at 120 °C [Eq. (1)].[6] Herein, we report the reactions of salicylic aldehydes with unsubstituted allenic esters or ketones catalyzed by K_2CO_3, which produce different types of 2*H*-chromenes under mild conditions. In addition, on the basis of our findings, the catalytic function of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) and K_2CO_3 in these reactions is discussed.



Scheme 1. Reactions of salicylic aldehydes or salicyl *N*-tosylimines with allenic esters or ketones in the presence of a variety of catalysts.



Results and Discussion

The reaction conditions have been optimized by reacting salicylaldehyde (**1a**; 1.0 equiv) with ethyl buta-2,3-dienoate

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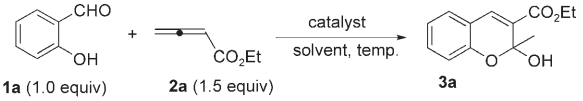
[**] DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene.

Supporting information for this article (detailed experimental procedures, data of all of the new compounds, and the X-ray crystal structure of **3b**) is available on the WWW under http://www.chemeurj.org/ or from the author.

(**2a**; 1.5 equiv) under catalysis by various bases (10 mol%), including K_2CO_3, ethyldiisopropylamine (iPr_2NEt), DBU, PPh_3, 1,4-diazabicyclo[2.2.2]octane (DABCO), and 4-(*N*,*N*-dimethylamino)pyridine (DMAP), in a variety of solvents at room temperature (25°C) to 120°C. The results obtained are summarized in Table 1. In the presence of K_2CO_3 (10 mol%), the corresponding 2*H*-chromene product **3a** was obtained in good yields in polar solvents such as DMSO and protonic solvents such as ethanol at room temperature (Table 1, entries 2 and 5). When the reaction was catalyzed by DBU in ethanol, the corresponding 2*H*-chromene product **3a** was obtained in moderate yields (Table 1, entries 6 and 14). Reducing the amount of **2a** used from 1.5 equivalents to 1.0 equivalent resulted in lower yields (Table 1, entries 4 and 14). Solvents of low polarity, such as tetrahydrofuran (THF) and toluene (PhMe), proved to be poor choices for the reaction (Table 1, entries 3, 8, and 12). Other nucleophilic promoters, such as DABCO, DMAP, and PPh_3, proved to be less effective in this reaction under otherwise identical conditions (Table 1, entries 15–18). Thus, we found DMSO or ethanol to be the solvent of choice and K_2CO_3 to be the best base promoter for this reaction at 25°C. However, for salicylaldehydes with electron-withdrawing groups on the benzene ring, we found that no reaction occurred with ethanol as the solvent. Therefore, we chose DMSO as the solvent so as to extend the range of applicable substrates.

Table 1. Reactions of salicylaldehyde (**1a**; 0.5 mmol) with ethyl buta-2,3-dienoate (**2a**; 0.75 mmol) in the presence of various bases and in a variety of solvents.



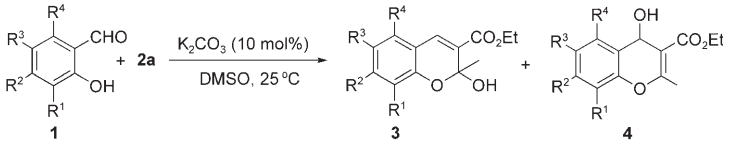
1a (1.0 equiv) **2a** (1.5 equiv) **3a**

Entry	Solvent	Catalyst (mol%)	Temp. [°C]	Time [h]	Yield [%][a]
1	DMSO	K_2CO_3 (10)	120	0.75	52
2	DMSO	K_2CO_3 (10)	25	4	64
3	THF	K_2CO_3 (10)	25	72	complex
4[b]	DMSO	K_2CO_3 (10)	25	4	54
5	EtOH	K_2CO_3 (10)	25	48	68
6	EtOH	DBU (20)	25	24	52
7	DMF	DBU (20)	25	5	50
8	THF	DBU (20)	25	48	complex
9	DMSO	DBU (20)	25	3	56
10	*t*BuOH	DBU (20)	25	48	55
11	CH_3CN	DBU (20)	25	24	59
12	PhMe	DBU (20)	25	12	complex
13	H_2O/EtOH (4:1)	DBU (20)	25	36	37
14[b]	EtOH	DBU (20)	25	24	50
15	EtOH	DABCO (20)	25	96	30
16	DMSO	DABCO (20)	25	3	48
17	DMSO	PPh_3 (20)	25	6	15
18	EtOH	DMAP (20)	25	72	29

[a] Yield of isolated product. [b] One equivalent of ethyl buta-2,3-dienoate was used.

Several other salicylic aldehydes also react with ethyl buta-2,3-dienoate under these optimized reaction conditions, affording the corresponding chromenes **3** in moderate yields. The results are summarized in Table 2. The structures of the products were determined on the basis of their spectroscopic and analytical data. The structure of **3b** was confirmed by X-ray diffraction analysis.[7] The range of applicable substrates includes both electron-rich (Table 2, entries 1–5) and electron-poor (Table 2, entries 6–8) salicylaldehydes. As can be seen in Table 2, the work-up procedure strongly influences the structure of the product (Table 2, entries 1, 7, and 8). If the reaction mixture was purified by column chromatography on silica gel, product **3** was obtained, whereas purification on a column of neutral Al_2O_3 led exclusively to product **4** instead. Interestingly, **4i** could be converted to **3i** in moderate yield under acidic conditions. These results suggest that silicic acids in silica gel facilitate migration of the hydroxy group. Furthermore, neat **4i** was also completely transformed to **3i** after two days in the absence of other agents (Scheme 2).

Table 2. Reactions of salicylic aldehydes (0.5 mmol) with ethyl buta-2,3-dienoate (**2a**; 0.75 mmol) in the presence of K_2CO_3 (10 mol%) in DMSO at 25°C.

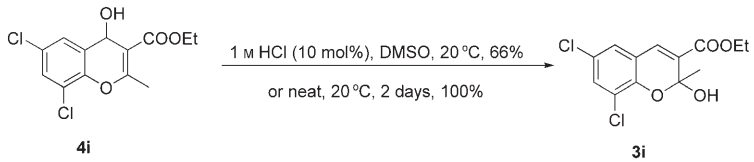


1 **3** **4**

Entry	R^1	R^2	R^3	R^4	Product	Yield [%][a]
1	OMe	H	H	H	**3b**	66
					4b	57[b]
2	H	OMe	H	H	**3c**	67
3	H	H	OMe	H	**3d**	71
4	H	H	Me	H	**3e**	50
5	H			H	**3f**	29
6	H	H	Cl	H	**3g**	85
7	H	H	Br	H	**3h**	60
					4h	68[b]
8	Cl	H	Cl	H	**3i**	58
					4i	63[b]

[a] Yield of isolated product. [b] After purification by column chromatography on Al_2O_3.

However, when the above optimized conditions were applied to the reaction of salicylic aldehyde with penta-3,4-dien-2-one, many by-products were produced, presumably

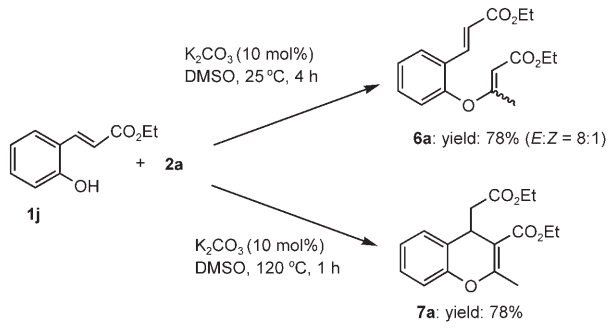


4i **3i**

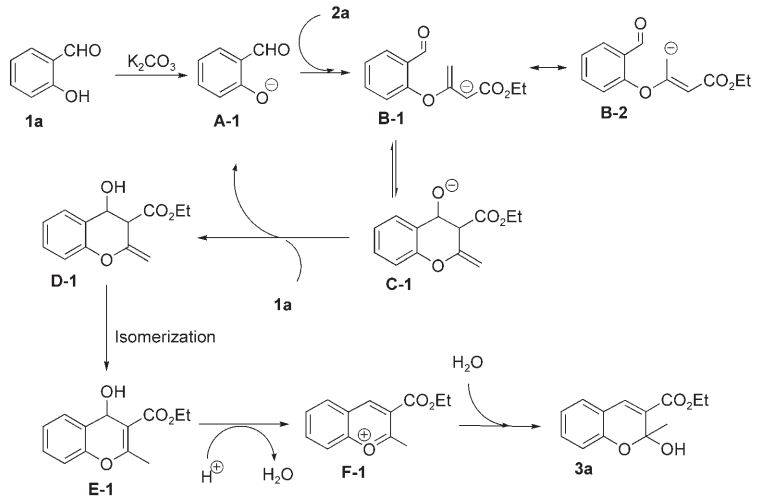
Scheme 2. Transformation of **4i** to **3i** under different conditions.

due to the higher reactivity of penta-3,4-dien-2-one compared to that of ethyl buta-2,3-dienoate in the presence of K_2CO_3. Therefore, we explored the use of other organic solvents in this reaction. To our delight, performing the reactions in ethanol at 25 °C afforded the desired products **5** in moderate yields, albeit with the formation of a small amount of unidentified by-products. The results are summarized in Table 3.

Moreover, the reaction of (*E*)-ethyl 3-(2-hydroxyphenyl)-acrylate (**1j**; 0.5 mmol) with ethyl buta-2,3-dienoate (0.75 mmol) under identical conditions afforded 3-[2-(2-ethoxycarbonylvinyl)phenoxy]but-2-enoic acid ethyl ester (**6a**) in 78% yield as a mixture of *E* and *Z* isomers (*E*:*Z* = 8:1, as determined by NOE spectroscopy; see the Supporting Information). On the other hand, at 120 °C under otherwise identical conditions, ethyl 4-(2-ethoxy-2-oxoethyl)-2-methyl-4*H*-chromene-3-carboxylate (**7a**) was formed in 78% yield, suggesting that the reaction involves an oxo-Michael addition/Michael addition sequence (Scheme 3).

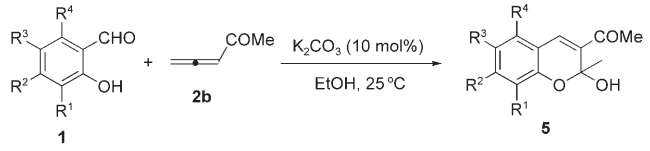


Scheme 3. Reaction of (*E*)-ethyl 3-(2-hydroxyphenyl)acrylate (**1j**) with ethyl buta-2,3-dienoate (**2a**).



Scheme 4. A plausible pathway for the reaction of salicylaldehyde (**1a**) with ethyl buta-2,3-dienoate (**2a**).

Table 3. Reactions of salicylic aldehydes (0.5 mmol) with penta-3,4-dien-2-one (**2b**; 0.75 mmol) in the presence of K_2CO_3 (10 mol%) at 25 °C.

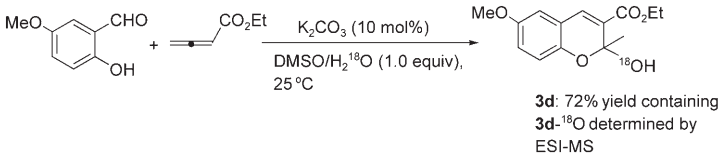


Entry	R^1	R^2	R^3	R^4	Product	Yield [%][a]
1	H	H	H	H	**5a**	67
2	OMe	H	H	H	**5b**	68
3	H	H	Me	H	**5c**	68
4	H	H	Cl	H	**5d**	64
5	H	H	Br	H	**5e**	74
6	Cl	H	Cl	H	**5f**	67

[a] Yield of isolated product.

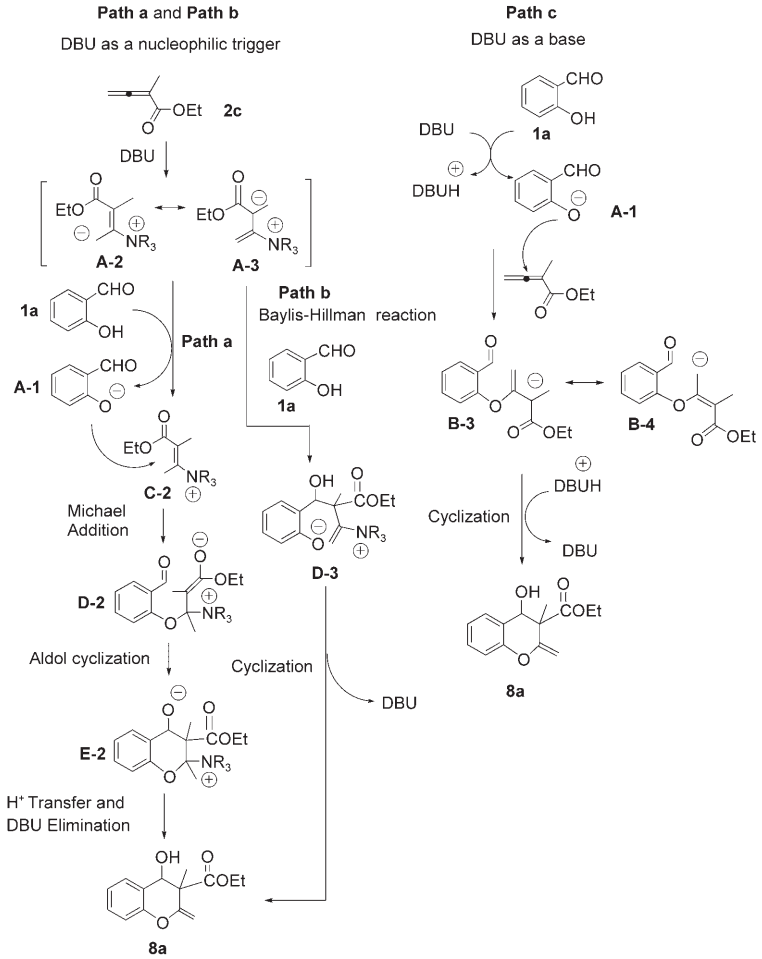
A mechanism for the reaction of salicylaldehyde with ethyl buta-2,3-dienoate catalyzed by K_2CO_3 has been proposed on the basis of previous investigations (Scheme 4).[4–6,8] Initially, the non-nucleophilic inorganic base potassium carbonate abstracts a proton from salicylaldehyde to produce oxy-anionic intermediate **A-1**. Subsequent conjugate addition of **A-1** to ethyl buta-2,3-dienoate (**2a**) generates the resonance-stabilized intermediates **B-1** and **B-2**. An intramolecular aldol reaction then produces the cyclized intermediate **C-1**, which abstracts a proton from salicylaldehyde **1a** to afford compound **D-1**, in the process regenerating intermediate **A-1**. Product **D-1** is easily isomerized to intermediate **E-1**. Dehydration of **E-1** gives intermediate **F-1**, which is attacked by ambient water to give product **3a**.

To test the plausibility of this proposed mechanism, we designed an ^{18}O isotopic labeling experiment by employing $H_2{}^{18}O$ (^{18}O content = 94.1%), which was run under identical conditions (Scheme 5). When $H_2{}^{18}O$ was deployed under the standard reaction conditions, chromene **3d** containing [^{18}O]-**3d**, determined by ESI-MS (see Supporting Information), was obtained in 72% yield, suggesting that ambient water does indeed participate in the addition to intermediate **F-1** to give the corresponding hydroxy-group-migrated product (Scheme 5). This result is consistent with the mechanism proposed in Scheme 4.



Scheme 5. ^{18}O-Labeling experiment to probe the mechanism of the reaction of 2-hydroxy-5-methoxybenzaldehyde with ethyl buta-2,3-dienoate (**2a**) under identical conditions.

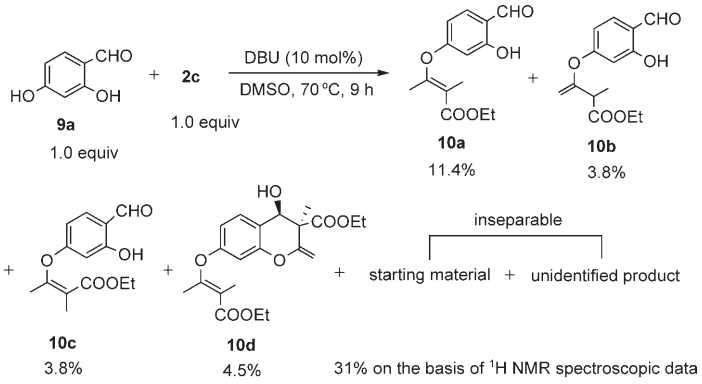
The above results allow us to reconsider the mechanism of the reaction of salicylaldehyde with ethyl 2-methylbuta-



Scheme 6. Plausible reaction mechanism.

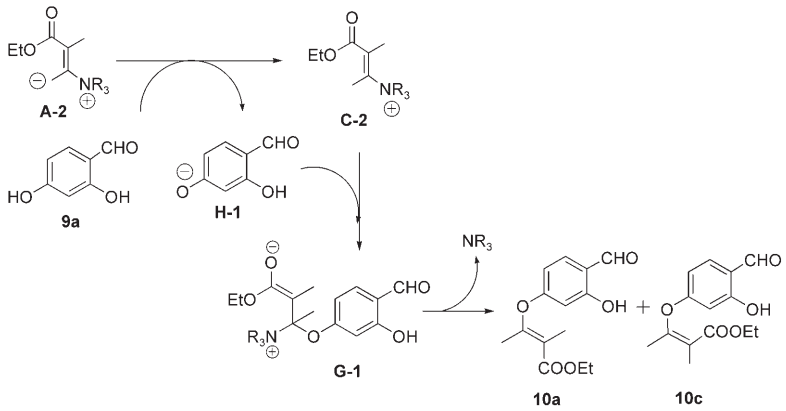
2,3-dienoate or 3-methylpenta-3,4-dien-2-one under catalysis by DBU to give the corresponding product **8a**.[4] In our previous report, we proposed three different mechanisms (Scheme 6). As can be seen in Scheme 6, in paths a and b, DBU acts as a nucleophilic trigger, while in path c, it serves as a base.

To investigate the mechanism of the reaction, a control experiment was carried out by reacting 2,4-dihydroxybenzaldehyde (**9a**) with ethyl 2-methylbuta-2,3-dienoate (**2c**) under catalysis by DBU in DMSO at 70°C. Interestingly, four products, **10a**, **10b**, **10c**, and **10d**, were obtained, along with the starting material **9a** (31% recovery on the basis of ^{1}H NMR spectroscopic data) and an unidentified product, which proved inseparable from **9a** (Scheme 7). If the reaction were to follow path a, attack of the 4-OH group of **9a** on intermediate **C-2** would generate intermediate **G-1**, subsequent elimination from which would yield products **10a** and **10c** as a mixture of *E* and *Z* isomers. However, the pathway depicted in Scheme 8 cannot explain the formation of product **10b**. In path b (Scheme 6), salicylaldehyde **1a** is first attacked by the "Baylis–Hillman zwitterions" **A-3**, that is to say, conjugate addition at 2-OH or 4-OH is less competitive so that the chromene derivative should be the predominant product, which is at variance with the distribution of products shown in Scheme 7. In addition, the reaction between salicylaldehyde **1a** and allenic ester **2d** in the presence of the non-nucleophilic catalyst K_2CO_3 at room temperature also gave **12a** as the major product, along with **11a** (Scheme 9).[6] The transformation of **12a** to **11a** has been observed at 120°C in DMSO in the presence of K_2CO_3.[6] Moreover, no reaction occurred on attempting to use 2-hydroxy-5-nitrobenzaldehyde as a substrate, probably due to the lower nucleophilicity of the corresponding oxy-anionic intermediate because of the presence of the strongly electron-withdrawing nitro group on its benzene ring.[4] Considering all of the collected evidence, path b seems to be unreasonable. Since the reaction seems unlikely to proceed according to path a or path b, we believe that path c is a more reasonable process for reactions of this kind.

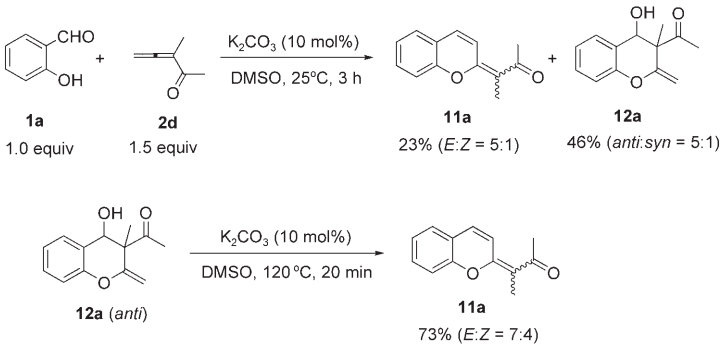


Scheme 7. Reaction of 2,4-dihydroxybenzaldehyde (**9a**) and ethyl 2-methylbuta-2,3-dienoate (**2c**) catalyzed by DBU in DMSO at 70°C.

Furthermore, if the reaction does indeed follow path c, changing the basicity of the amine should have a significant effect on the reaction.[9] To test this hypothesis, different amines were employed in the reaction in order to assess whether more basic catalysts were more effective. We found that amines such as DBU, DMAP, or pyridine with an sp^2 nitrogen atom were effective in promoting the reaction,



Scheme 8. Reaction mechanism of the formation of compounds **10a** and **10c**.

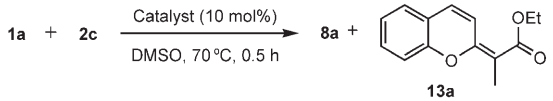


Scheme 9. Reaction of **1a** with **2d** in the presence of K_2CO_3 at 25 °C and transformation of compound **12a** at high temperature.

whereas amines such as *i*Pr_2NEt, DABCO, or NEt_3 with an sp^3 nitrogen atom showed no catalytic activity (Table 4). Thus, the typical Baylis–Hillman catalyst DABCO proved ineffective in this reaction, further suggesting that DBU acts as a base rather than as a nucleophilic trigger.[10] The reason why pyridine is less effective is presumably because it is a weaker base than DBU and DMAP on the basis of pK_a value (Table 4). These failures of *i*Pr_2NEt, DABCO, and NEt_3 as catalysts, taken together with the successful use of DBU, DMAP, and pyridine, indicate that the imine double bond can be assumed to play an important role in this reaction.[11]

In conclusion, we have presented an efficient, K_2CO_3-catalyzed reaction of salicylaldehydes with unsubstituted allenic ketones or esters that provides easy access to functionalized 2*H*-1-chromenes.[12] Moreover, the mechanism of the DBU-catalyzed reaction between salicylic aldehydes and ethyl 2-methylbuta-2,3-dienoate has been discussed. Based on the results of control experiments, we believe that DBU most likely serves as a base rather than as a nucleophilic trigger in reactions of this kind.

Table 4. Examination the influences of different amine catalysts on the reaction between **1a** and **2c**.



Catalyst	pK_a[a]	Conversion [%]	Product	Yield [%][b]
DBU	>12	100	**8a**	57 (*anti*/*syn* = 4.6:1)
			13a	19
DMAP	9.7	100	**8a**	56 (*anti*/*syn* = 7.8:1)
			13a	5
iPr_2NEt[c]	11.4	0	–	–
DABCO[c]	8.8	0	–	–
NEt_3[c]	10.9	0	–	–
Pyridine	8.8	18	**8a**	11 (*anti*/*syn* = 6:1)
			13a	trace

[a] Measured in R_3N^+H, H_2O, 25 °C; from reference [9]. [b] Yield of isolated product. [c] No desired products could be obtained even when the reaction time was extended to 3 h.

Experimental Section

General remarks: Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer from solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants (*J*) are given in Hz. Mass spectra were recorded on an HP-5989 instrument. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses, obtained with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All of the reactions were monitored by TLC on Huanghai GF_{254} silica-gel-coated plates. Flash column chromatography was carried out on 200–300 mesh silica gel at medium pressure.

Typical procedure for the reaction of salicylaldehyde with ethyl buta-2,3-dienoate in the presence of K_2CO_3 in DMSO at room temperature: Salicylaldehyde (**1a**; 61 mg, 0.5 mmol), ethyl buta-2,3-dienoate (**2a**; 84 mg, 0.75 mmol), and K_2CO_3 (7.0 mg, 0.05 mmol) were added to DMSO (1.0 mL) in a Schlenk tube. The solution was stirred for 4 h at room temperature (25 °C). The reaction mixture was then diluted with ethyl acetate (20 mL) and washed with water (3×15 mL). The DMSO was extracted into the aqueous phase. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: EtOAc/petroleum ether, 1:4) to give the corresponding product **3a** (74 mg, 64% yield) as a yellow solid, which was suitable for analytical purposes.

Ethyl 2-hydroxy-2-methyl-2*H*-chromene-3-carboxylate (3a): This compound was obtained as a pale yellow solid; m.p. 88–90 °C; IR (CH_2Cl_2): $\tilde{\nu}$ = 3429, 2984, 2939, 1712, 1629, 1486, 1458, 1214 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.37 (t, 3H, *J* = 7.1 Hz; CH_3), 1.96 (s, 3H; CH_3), 3.93 (s, 1H; OH), 4.24–4.35 (m, 2H; CH_2), 6.95–7.00 (m, 2H; ArH), 7.22–7.35 (m, 2H; ArH), 7.57 ppm (s, 1H; =CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 27.6, 61.0, 97.7, 116.6, 118.7, 121.5, 125.5, 128.6, 132.2, 134.2, 152.5, 165.1 ppm; MS (EI): *m*/*z*: 216 (49) [M^+−18], 187 (32) [M^+−47], 173 (54) [M^+−61], 144 (100) [M^+−90], 115 (73) [M^+−119], 89 (40) [M^+−145], 63 (29) [M^+−171], 43 (40) [M^+−191]; HRMS: calcd for $C_{13}H_{14}O_4$ (−H_2O) 216.0786; found: 216.0796

Acknowledgements

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