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Chiral Activated Alkenes Induced Asymmetric Baylis–Hillman Reaction in Me_3N/H_2O/Solvent Medium

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ABSTRACT: *Chiral-activated alkenes,* L-*menthyl acrylate and (+)-N-α-phenylethyl acrylamide, induced asymmetric Baylis–Hillman reaction of aromatic aldehydes was realized at 25°C for 7 days in Me_3N/H_2O/solvent homogeneous medium. The corresponding Baylis–Hillman adducts were obtained in good chemical yield with moderate to excellent diastereoselectivity (up to 99% de).* Heteroatom Chem 17:317–321, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20209

INTRODUCTION

The Baylis–Hillman reaction was first documented in a German patent in 1972 [1]. This carbon–carbon bond-forming reaction allows the preparation of β-hydroxy-α-methylene carbonyl compounds under mild conditions. These densely functionalized adducts are versatile building blocks for the synthesis of a variety of natural or nonnatural target molecules [2]. Therefore, the Baylis–Hillman reaction, especially the asymmetric one has attracted much attention from the organic chemists and become one of the most challenging research area in modern organic chemistry during the past decade [3]. This tertiary amine (or phosphine) catalyzed coupling reaction involves the creation of a new chiral center accompanied with the formation of new carbon–carbon bond. Thus, there exist rich possibilities for realizing asymmetric transformation through the introduction of a chiral source into any of the three components (activated alkenes, aldehydes, and catalysts) of the Baylis–Hillman reaction. Among them, the reaction of chiral acrylic compound with an achiral aldehyde is a conventional strategy [4]. However, only a few examples lead to significant amounts of enantiopure β-hydroxy-α-methylene carbonyl compounds. For example, moderate diastereoselectivity was obtained using bornyl or sugar acrylate esters as the activated alkenes [4i, 4j]. The use of menthyl acrylate, in some cases, especially under high pressure resulted in high diastereomeric excesses [4d, 4f]. In addition, high stereoselectivity was observed employing Oppolzer's sultame [4g, 4h] and a novel camphor derivative [4k] as the chiral auxiliaries, respectively. Usually the reaction between these activated alkenes and aldehydes catalyzed by a tertiary amine took place with slow reaction rate; several days, even weeks were required for completion. Recently, we found that dramatic rate acceleration was observed by the addition of low-carbon alcohols or other polar solvents, such as THT, 1,4-dioxane, acetonitrile, etc. to transform the heterogeneous mixture of aqueous trimethylamine and the substrates into a clear

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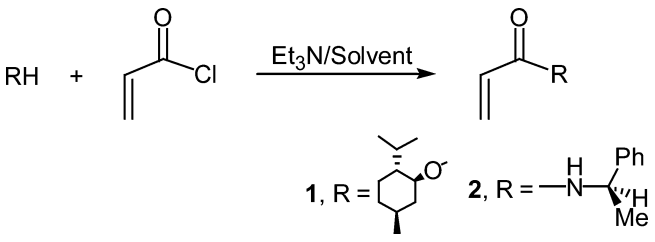
homogeneous solution. The corresponding Baylis–Hillman adducts were obtained in less time at low temperature with good to excellent chemical yield [5]. Based on this finding, in this context, the application of this new homogeneous medium to realize the asymmetric Baylis–Hillman reaction between the activated alkenes and aromatic aldehydes was investigated.

RESULTS AND DISCUSSION

According to the literature method [6], the reaction of acrylic chloride with L-menthol in the presence of triethylamine in THF led to L-menthyl acrylate **1**. Similarly, the condensation of (+)-α-phenylethylamine with acrylic chloride in the presence of triethylamine in methylene chloride from 0°C to room temperature provided (+)-*N*-α-phenylethyl acrylamide **2**.



First of all, a suitable solvent, which can form a homogeneous medium with trimethylamine and water, should be chosen for the reaction of aromatic aldehydes with **1**. Although excellent results were obtained using the corresponding low-carbon alcohol as the solvent in the reaction between aromatic aldehydes and acrylate esters of lower alcohols (C_1–C_4) [5], to avoid occurring transesterification between L-menthyl acrylate **1** and low-carbon alcohol only aprotic polar solvent, such as THF, 1,4-dioxane, DMF, acetonitrile etc., could be used as the solvent. A common substrate, 2,4-dichlorobenzaldehyde, was employed to study the effect of polar solvent on the Baylis–Hillman reaction of **1** and aromatic aldehydes. After evaluating a number of aprotic solvents as listed in Table 1, 1,4-dioxane was chosen as the best polar solvent in terms of both the chemical yield and the diastereoselectivity.

TABLE 1 Effect of Solvent on the Baylis–Hillman Reaction

Solvent	*THF*	*1,4-dioxane*	*DMF*	*CH_3CN*
Yield (%)[a]	61	86	79	52
De (%)[b]	40	39	40	23

[a]Isolated yield based on aldehyde.
[b]De value was determined by HPLC.

Second, the influence of the reaction temperature on the reaction was examined using the coupling of **1** and 2,4-dichlorobenzaldehyde as the model reaction. By comparison of the reaction carried out at different temperature (0, 25, 40, and 60°C, respectively), it was found that the reaction temperature had little influence on the Baylis–Hillman reaction under our conditions. So we chose 25°C (room temperature) as the convenient reaction temperature.

Moreover, the molar ratio of aldehydes to **1** was also an important factor to the reaction. The reaction with a 1:1, 1:2, and 1:3 molar ratio of 3-nitrobenaldehyde to **1** was conducted under the same conditions, respectively. The diastereomeric excess value was slightly influenced by this variation, whereas the yield of the product was improved remarkably with the increase of the molar ratio of aldehydes to **1** (48, 61, and 82%, respectively). Hence, we prefer to run the reaction with a 1:3 molar ratio of aldehyde to the activated alkene.

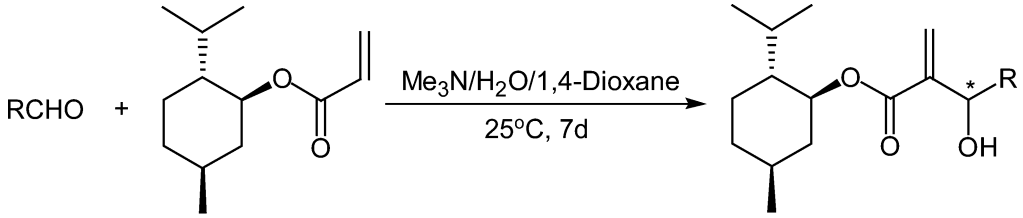
Different aromatic aldehydes were employed to couple with **1** under the aforementioned optimal reaction conditions. The experimental results were listed in Table 2.

As shown in Table 2, the nature of the aldehyde was found to be an essential factor to the reaction. For example, better yield was obtained for the aldehyde substituted with electron withdrawing group(s), such as nitro, fluoro, trifluoromethyl, etc., on the benzene ring. While benzaldehyde, *p*-methylbenzaldehyde and aliphatic aldehydes, such as isobutyraldehyde, isovaleraldehyde, failed to produce any of desired products. In terms of diastereoselectivity, the existence of electron-withdrawing groups at the 3 or 4 positions of the benzene ring was also favored to improve the de values, while the electron donating hydroxyl group substituted aromatic aldehyde and 5-methylfuraldehyde resulted in dramatic decrease in diastereoselectivity.

Since no methanolysis phenomenon was observed upon the treatment of chiral acrylamide **2** with methanol, it is feasible to conduct the asymmetric Baylis–Hillman reaction of **2** with aromatic aldehydes in Me_3N/H_2O/methanol system. The experimental results were listed in the Table 3.

As shown in Table 3, compared with **1** chiral acrylamide **2** exhibited much lower reactivity. Only using 3-nitrobenzaldehyde and 4-nitrobenzaldehyde as the substrate was the corresponding adduct obtained with low chemical yield (54 and 47%, respectively) in Me_3N/H_2O/methanol system. Under the same conditions, other aromatic aldehydes failed to

TABLE 2 Experimental Data of Adducts **3** Prepared from the Reaction of Aromatic Aldehydes with **1**

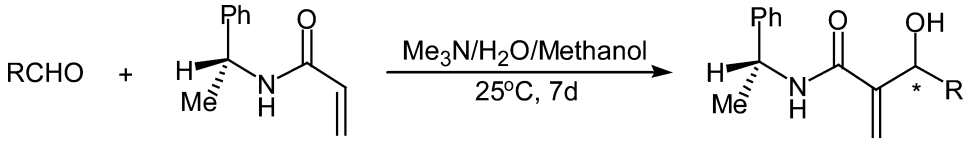


1 **3**

Product **3**	*R*	*mp (°C)*	*yield (%)*[a]	*de (%)*[b]
a	4-$O_2NC_6H_4$	Viscous liquid	88	83
b	3-$O_2NC_6H_4$	Viscous liquid	82	99
c	2,4-$(O_2N)_2C_6H_3$	Viscous liquid	79	78
d	4-$F_3CC_6H_4$	Viscous liquid	91	67
e	4-FC_6H_4	99-101	72	95
f	2,4-$Cl_2C_6H_3$	Viscous liquid	86	39
g	3-ClC_6H_4	Viscous liquid	70	98
h	4-HOC_6H_4	87-88	57	71
i	5-Me-2-furan	Viscous liquid	59	12

[a]Isolated yield based on aldehyde.
[b]De value was determined by HPLC.

TABLE 3 Experimental Data of the Adducts **4** Prepared from the Reaction between Aromatic Aldehydes and **2**



2 **4**

Product **4**	*R*	*mp (°C)*	*Yield (%)*[a]	*de (%)*[b]
a	4-$O_2NC_6H_4$	135–137	47	94
b	3-$O_2NC_6H_4$	118–119	54	97

[a]Isolated yield based on aldehyde.
[b]De value was determined by HPLC.

form the Baylis–Hillman adduct. However, it was gratifying that both of the two substrates had an excellent diastereoselectivity (97% de and 94% de, respectively).

In conclusion, the asymmetric Baylis–Hillman reaction of two chiral activated alkenes, L-menthyl acrylate and (+)-*N*-α-phenylethyl acrylamide, with aromatic aldehydes was realized in the Me_3N/H_2O/solvent homogeneous medium. The corresponding Baylis–Hillman adducts were obtained in good chemical yield with moderate to excellent diastereoselectivity. Compared with other tertiary amine catalytic systems, this medium demonstrated a significant rate acceleration effect on the Baylis–Hillman reaction. This dramatic rate acceleration was observed not only for achiral activated alkenes [5] but also for chiral activated alkenes.

EXPERIMENTAL SECTION

General Methods

^1H NMR was recorded in $CDCl_3$ on a Bruker AC-P300 instrument using TMS as an internal standard. Specific rotations were measured on a Perkin-Elmer 341MC polarimeter. de value was determined on a HP-1100 instrument (silica column: 250 mm × 4.6 mm, dp 5 μm; mobile phase: hexane/*i*-PrOH). Elemental analyses were conducted on a Yanaco CHN Corder MT-3 automatic analyzer. Melting points were determined on a T-3 melting point apparatus. All temperatures and pressures were uncorrected. All of the solvent was dried according standard method and used after fresh distillation. Acrylic chloride was purchased from Aldrich and used after fresh distillation.

L-*Menthyl Acrylate* **1**. Following the modified literature method [6], the reaction of L-menthol (7.81 g, 0.05 mol), acrylic chloride (9.05 g, 0.1 mol) in the presence of triethylamine (6.07 g, 0.06 mol) provided 7.15 g of **1** as a colorless liquid, yield 68%; bp 104–106°C/1.3 Kpa; n_D^{20} 1.4416; $[\alpha]_{578}$ −8.2 (c 1, $CHCl_3$); ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.69–2.21 (m, 18H), 4.69 (dt, $J = 10.02$ Hz, 4.01 Hz, 1H), 5.72 (d, $J = 10.40$ Hz, 1H), 6.04 (dd, $J = 10.40$ Hz, 15.87 Hz, 1H), 6.32 (dd, $J = 1.56$ Hz, 15.87 Hz, 1H).

N-(+)-α-Phenylethyl Acrylamide **2**. To a stirring mixture of (+)-α-Phenylethylamine (3.03 g, 25 mmol), triethylamine (6.06 g, 60 mmol) and methylene chloride (60 mL) was added dropwise acrylic chloride (2.35 g, 26 mmol) below 0°C. The resulting mixture was slowly warmed to room temperature and stirred for 24 h and then washed successively with water, brine. The organic phase was separated and dried over anhydrous magnesium sulfate. After removal of solvent, the crude product was purified by column chromatography on silica gel (200–300 mesh, gradient eluted with petroleum ether/ethyl acetate) to afford 2.74 g of **2** as a white solid, yield, 63%; mp 93–94°C; $[\alpha]_D$ + 180.6(c 1, $CHCl_3$); ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 1.51 (d, $J = 6.60$ Hz, 3H), 5.19 (m, 1H), 5.63 (dd, $J = 2.18$ Hz, 10.8 Hz, 1H), 5.80 (br., 1H), 6.09 (dd, $J = 10.08$ Hz, 16.7 Hz, 1H), 6.29 (dd, $J = 2.18$ Hz, 16.7 Hz, 1H), 7.25–7.34 (m, 5Harom); Anal. Calcd For $C_{11}H_{13}NO$: C, 75.43; H, 7.43; N, 8.00; Found: C, 75.35; H, 7.46; N, 8.11.

General Procedure for the Reaction of **1** *with Aromatic Aldehydes*

2 mmol of aromatic aldehyde, 1 mL (5 mmol) of 33% aqueous trimethylamine and 2 mL of 1,4-dioxane was mixed together and stirred for 5 min. To the resulting mixture was then added 1.26 g (6 mmol) of **1** and the whole stirred for 7 days at the room temperature. 5 mL of distilled water and 20 mL of chloroform was added, and the reaction mixture was stirred for 5 min. The organic layer was separated, and the aqueous phase was extracted with chloroform (2 × 10 mL). The combined organic phase was dried over anhydrous magnesium sulfate. After removal of solvent, the crude product was purified by column chromatography on silica gel (200–300 mesh, gradient eluted with petroleum ether/ethyl acetate) to afford the corresponding Baylis–Hillman adduct **3** (Table 2).

3a: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.58–1.98 (m, 18H), 3.33 (broad, 1H), 4.67 (dt, $J = 10.32$ Hz, 4.25 Hz, 1H), 5.57 (d, $J = 1.55$ Hz, 1H), 5.80 (d, $J = 1.55$ Hz, 1H), 6.34 (d, $J = 1.82$ Hz, 1H), 7.53 (d, $J = 8.52$ Hz, 2Harom), 8.16 (d, $J = 8.52$ Hz, 2H); Anal. Calcd for $C_{20}H_{27}NO_5$: C, 66.46; H, 7.53; N, 3.87. Found: C, 66.47; H, 7.40; N, 3.85; HPLC condition: hexane:*i*-PrOH = 98:2 (0.6 mL/min), $t_R = 13.0$ min and 14.5 min.

3b: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.57–1.91 (m,18H), 2.80 (broad, 1H), 4.70 (dt, $J = 10.10$ Hz, 4.03 Hz 1H), 5.58 (s, 1H), 5.84 (d, $J = 3.35$ Hz 1H), 6.36 (s, 1H), 7.50–8.23 (m, 4Harom); Anal. Calcd For $C_{20}H_{27}NO_5$: C, 66.46; H, 7.53; N, 3.87. Found: C, 66.26; H, 7.59; N, 3.90; HPLC condition: hexane:*i*-PrOH = 98:2 (0.6 mL/min), $t_R = 21.1$ and 22.3 min.

3c: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.51–2.01 (m, 18H), 3.48 (broad, 1H), 4.71 (dt, $J = 10.10$ Hz, 4.15 Hz, 1H), 5.75 (d, $J = 9.15$ Hz, 1H), 6.23 (d, $J = 4.15$ Hz, 1H), 6.37 (d, $J = 5.95$ Hz, 1H), 7.97–8.01 (m, 1Harom), 8.43–8.50 (m, 1Harom), 8.62–8.80 (m, 1Harom); Anal. Calcd for $C_{20}H_{26}N_2O_7$: C, 59.10; H, 6.45; N, 6.89. Found: C, 59.17; H, 6.66; N, 6.89; HPLC condition: hexane:*i*-PrOH = 98:2 (0.6 mL/min), $t_R = 5.8$ and 6.7 min.

3d: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.57–1.98 (m, 18H), 3.26 (broad, 1H), 4.70 (dt, $J = 10.11$ Hz, 4.14 Hz, 1H), 5.55 (s, 1H), 5.79 (d, $J = 6.99$ Hz, 1H), 6.34 (d, $J = 4.20$ Hz, 1H), 7.48–7.61 (m, 4Harom); Anal. Calcd for $C_{21}H_{27}F_3O_3$: C, 65.61; H, 7.08. Found: C, 65.56; H, 6.95; HPLC condition: hexane:*i*-PrOH = 98:2 (0.6 mL/min), $t_R = 9.8$ and 14.6 min.

3e: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.58–2.00 (m, 18H), 3.09 (broad, 1H), 4.67 (dt, $J = 10.12$ Hz, 4.14 Hz, 1H), 5.09 (s, 1H), 5.77 (d, $J = 8.45$ Hz, 1H), 6.29 (d, $J = 4.20$ Hz, 1H), 7.02 (m, 2Harom), 7.31 (m, 2Harom); Anal. Calcd for $C_{20}H_{27}FO_3$: C, 71.83; H, 8.14. Found: C, 71.65; H, 8.25; HPLC condition: hexane:*i*-PrOH = 98:2 (0.6 mL/min), $t_R = 4.1$ and 4.9 min.

3f: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.54–2.22 (m, 18H), 3.17 (broad, 1H), 4.72 (dt, $J = 10.15$ Hz, 4.11 Hz, 1H), 5.61 (d, $J = 9.05$ Hz, 1H), 5.89 (s, 1H), 6.30 (d, $J = 5.88$ Hz, 1H), 7.24–7.41 (m, 3Harom); Anal. Calcd for $C_{20}H_{26}Cl_2O_3$: C, 62.34; H, 6.80. Found: C, 62.44; H, 6.66; HPLC condition: hexane:*i*-PrOH = 98:2 (0.6 mL/min), $t_R = 3.7$ and 4.2 min.

3g: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.59–1.98 (m, 18H), 3.15 (broad, 1H), 4.70 (dt, $J = 10.11$ Hz, 4.07 Hz, 1H), 5.47 (s, 1H), 5.79 (d, $J = 5.96$ Hz, 1H), 6.32 (s, 1H), 7.24–7.35 (m, 4Harom); Anal. Calcd for $C_{20}H_{27}ClO_3$: C, 68.46; H, 7.76. Found: C, 68.36; H, 7.80; HPLC condition: hexane:*i*-PrOH = 98:2 (0.6 mL/min), $t_R = 8.4$ and 10.1 min.

3h: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.58–2.21 (m, 18H), 3.39 (broad, 1H), 4.76 (m, 1H), 5.76 (d, $J = 5.88$ Hz, 1H), 6.08 (d, $J = 5.88$ Hz, 1H), 6.37 (d, $J = 9.09$ Hz, 1H), 7.38–8.21 (m, 4Harom), 10.01

(s, 1H, OH); Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.26; H, 8.48; HPLC condition: hexane:*i*-PrOH = 98:2 (0.9 mL/min), $t_R = 4.6$ and 6.1 min.

3i: ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 0.62–1.98 (m, 18H), 2.24 (s, 3H), 3.04 (broad, 1H), 4.72 (m, 1H), 5.50 (s, 1H), 5.87 (s, 2H), 6.04–6.31 (m, 2H); Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.21; H, 8.80. Found: C, 71.20; H, 8.75. HPLC condition: hexane:*i*-PrOH = 98:2 (0.7 mL/min), $t_R = 13.1$ and 13.9 min.

General Procedure of the Reaction of **2** *with Aromatic Aldehydes*

2 mmol of aromatic aldehyde, 1 mL (5 mmol) of 33% aqueous trimethylamine and 2 mL of methanol was mixed together and stirred for 5 min. To the resulting mixture was then added 1.26 g (6 mmol) of **2** and the whole stirred for 7 days at the room temperature. 5 mL of distilled water and 20 mL of chloroform was added, and the reaction mixture was stirred for 5 min. The organic layer was separated, and the aqueous phase was extracted with chloroform (2×10 mL). The combined organic phase was dried over anhydrous magnesium sulfate. After removal of solvent the crude product was purified by column chromatography on silica gel (200–300 mesh, gradient eluted with petroleum ether/ethyl acetate) to afford the corresponding Baylis-Hillman adduct **4** (Table 3).

4a: ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 1.42 (d, $J = 6.78$ Hz, 3H), 3.58 (broad, 1H), 5.02 (dq, $J = 7.10$ Hz, 6.78 Hz, 1H), 5.58 (d, $J = 5.85$ Hz, 2H), 5.86 (s, 1H), 6.52 (d, $J = 7.10$ Hz, 1H), 7.09–7.24 (m, 5Harom), 7.52 (d, $J = 8.70$ Hz, 2Harom), 8.14 (d, $J = 8.70$ Hz, 2Harom); Anal. Calcd For $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.33; H, 5.42; N, 8.76; HPLC condition: hexane:*i*-PrOH = 98:2 (0.7 mL/min), $t_R = 7.2$ and 7.6 min.

4b: ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 1.41 (d, $J = 6.78$ Hz, 3H), 3.58 (broad, 1H), 5.05 (dq, $J = 7.12$ Hz, 6.78 Hz, 1H), 5.54 (d, $J = 5.86$ Hz, 2H), 5.88 (s, 1H), 6.61 (d, $J = 7.12$ Hz, 1H), 6.98–7.33 (m, 5Harom), 7.44 (t, $J = 8.10$ Hz, 1Harom), 7.65 (d, $J = 8.10$ Hz, 1Harom), 8.07 (d, $J = 8.10$ Hz, 1Harom), 8.20 (s, 1Harom); Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35; H, 5.45; N, 8.56; HPLC condition: hexane:*i*-PrOH = 98:2 (0.6 mL/min), $t_R = 7.2$ and 8.5 min.

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