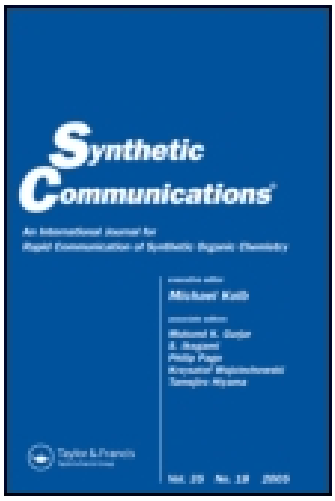

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In-MEDIATED ALLYLATION OF α-KETO ESTERS WITH ALLYL HALIDES*

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In-MEDIATED ALLYLATION OF α-KETO ESTERS WITH ALLYL HALIDES*

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ABSTRACT

The chemoselective reaction of α-keto esters with allyl halides, propargyl bromides, and allenyl bromide using indium metal afforded α-hydroxy-γ,δ-unsaturated esters in good to excellent yields under mild conditions.

Metal-mediated addition of allyl halides to aldehydes or ketones is one of the fundamental reactions in carbon-carbon bond formations, and has become a well established method for the synthesis of homoallylic alcohols.[1] The reactions of carbonyl compounds with allyl- and crotyl-metal reagents

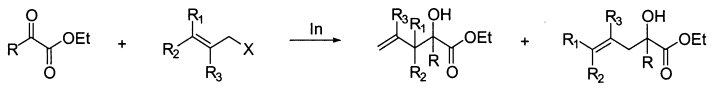
*This paper is dedicated to Professor Chang Hwan Rhee on the occasion of his 60th birthday.
†Corresponding author.

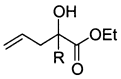
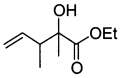
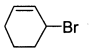
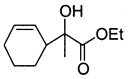
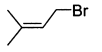
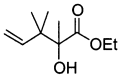
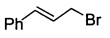
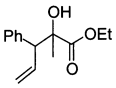
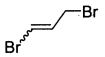
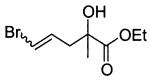
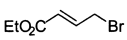
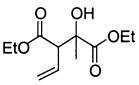
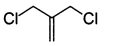
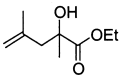
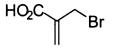
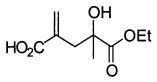
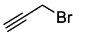
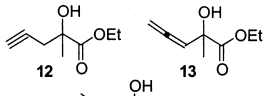
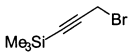
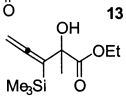
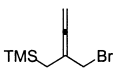
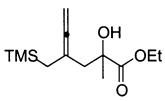
derived from a variety of metals, in particular, have been widely investigated.[2] Recently, it has been reported that indium-mediated allylation of carbonyl compounds in aqueous media afforded the corresponding homoallylic alcohols.[3] Those reactions in aqueous media are of special interest because they offer the possibility of environmentally benign reaction conditions by reducing the burden of organic solvent disposal. Although lots of examples on the indium-mediated allylation in aqueous media of simple aldehydes and ketones have been reported,[4] as far as we are aware, no systematic studies of the chemoselective allylation into α-keto esters have been published. As part of our continuing effort to expand the synthetic utility of indium, we now report that indium metal is highly effective for the chemoselective allylation of α-keto esters to afford α-hydroxy-γ,δ-unsaturated esters.

To find optimum conditions for indium-mediated allylation, ethyl pyruvate was chosen as a standard substrate and it was reacted with allyl bromide in the presence of indium in various solvents. Of the solvents tested, the best results were obtained in MeOH/0.1N HCl(1:4). The indium-mediated reaction of ethyl pyruvate with allyl bromide in MeOH/0.1 N HCl(1:4) afforded ethyl 2-hydroxy-2-methyl-4-pentenoate in 90% yield (Table 1, entry 1). However, the yields were decreased in other solvent systems under the identical conditions despite longer reaction times. Also, ethyl 3-methyl-2-oxobutyrate (entry 2) and ethyl benzoylformate (entry 3) were reacted with allyl bromide under the identical conditions to produce the desired compound **2** and **3**, respectively. The reactions are completely chemoselective and no addition to the ester group is observed by ^{1}H NMR spectroscopy of the crude reaction mixture.

Table 1 summarizes the experimental results and illustrates the efficiency and scope of the present method.[5] For the allyl bromides, the presence of various substituents at the β position, such as methyl (entry 4), dimethyl (entry 6), phenyl (entry 7), bromo (entry 8) or ethoxycarbonyl (entry 9) exhibited little effects on both the reaction rates and product yields. Good to excellent yields were obtained in reactions of various α-substituted allyl bromides as well. In case of methallyl dichloride (entry 10), the desired allylation occurred followed by reduction of allyl chloride to produce the dechlorinated compound **10**. It is especially noteworthy that a substrate having an acidic hydrogen such as 2-(bromomethyl)acrylic acid was also reacted to provide the corresponding α-hydroxy-γ,δ-unsaturated esters **11** in good yield (entry 11). In case of propargyl bromide (entry 12), regioisomeric products were produced. However, 3-bromo-1-(trimethylsilyl)-1-propyne gave the allenylated compound **14** as a sole product (entry 13). The protocol developed here could also be applied to a reaction with allenyl bromide. For example, ethyl pyruvate was reacted with

Table 1. Reaction of α-Keto Esters with a Variety of Allyl Halides Using Indium Metal



Entry	R	Allyl halide	Product		Isolated Yield,%
1[a]	CH_3			**1**	90
2[a]	$(CH_3)_2CH$			**2**	94
3[a]	Ph			**3**	92
4[b]	CH_3			**4**	79(1.2:1)[e]
5[c]	CH_3			**5**	68(4.5:1)[e]
6[b]	CH_3			**6**	68
7[c]	CH_3			**7**	85(100:0)[e]
8[a]	CH_3			**8**	61(1.2:1)[f]
9[c]	CH_3			**9**	85(100:0)[e]
10[c]	CH_3			**10**	72
11[d]	CH_3			**11**	67
12[c]	CH_3			**12** **13**	71(2.7:1)[g]
13[b]	CH_3			**14**	72
14[b]	CH_3			**15**	77

[a]solvent: MeOH/0.1N HCl. [b]solvent: THF/H_2O. [c]solvent: MeOH/0.2N HCl. [d]solvent: H_2O. [e]diastereomeric ratio. [f]cis / trans ratio and configuration of 1,3-dibromo-1-propene was retained. [g]regioisomeric ratio.

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4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene[6] under the identical conditions to give the desired compound **15** in 77% yield (entry 14).

In conclusion, the reaction of α-keto esters with allyl halides, propargyl bromides, and allenyl bromide with indium metal afforded α-hydroxy-γ,δ-unsaturated esters in MeOH/0.1N HCl at room temperature in good to excellent yields. It offers a complementary approach to the aldol reaction. The present method may serve as an alternative to the existing synthetic methods because of mild reaction condition and some advantages of indium metal such as ease of handling, high reactivity and selectivity, low toxicity and operational simplicity. Further studies on the enantioselective synthesis of α-hydroxy-γ,δ-unsaturated esters and other 1,n-dicarbonyl compounds using indium catalyst are now in progress.

EXPERIMENTAL SECTION

Ethyl 2-hydroxy-2-methyl-4-pentenoate (1) To a solution of ethyl pyruvate (116.0 mg, 1.0 mmol) and allyl bromide (181.0 mg, 1.5 mmol) in 5 mL of MeOH/0.1N HCl (1:4) was added indium (115.0 mg, 1.0 mmol: indium power (99.99%) purchased from Aldrich Chem Co.) in one portion. The reaction mixture was stirred vigorously at room temperature for 2 hr. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ether (3×25 mL) and the combined organic layer washed with water (20 mL), brine (20 mL), dried with $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1) leading to ethyl 2-hydroxy-2-methyl-4-pentenoate (142.0 mg, 90%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.79 (m, 1H), 5.14 (m, 2H), 4.22 (q, $J = 7.32$ Hz, 2H), 2.99 (s, 1H), 2.30 (m, 2H), 1.41 (s, 3H), 1.29 (t, $J = 7.02$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.61, 132.52, 119.07, 74.30, 61.86, 44.71, 25.54, 14.26; IR (film) 3490, 3010, 2960, 1700, 1430, 1360, 1240, 1200, 1150 cm^{-1}; HRMS(CI) calcd for $C_8H_{15}O_3$ $[M+H]^+$ 159.1022, found 159.1035.

Ethyl 2-hydroxy-2-isopropyl-4-pentenoate (2) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (m, 1H), 5.10 (d, $J = 7.82$ Hz, 1H), 5.06 (s, 1H), 4.23 (q, $J = 7.13$ Hz, 2H), 3.17 (s, 1H), 2.53, 2.50 (dd, $J = 6.34$, 13.79 Hz, 1H), 2.40, 2.36 (dd, $J = 8.19$, 13.70 Hz, 1H), 1.99 (m, 1H), 1.29 (t, $J = 7.14$ Hz, 3H), 0.97 (d, $J = 6.83$ Hz, 3H), 0.85 (d, $J = 6.83$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.33, 133.08, 118.47, 79.68, 61.75, 41.55, 35.09, 17.42, 15.91, 14.31; IR (film) 3500, 3020, 2940, 1700, 1420, 1400, 1240 cm^{-1}; HRMS(CI) calcd for $C_{10}H_{19}O_3$ $[M+H]^+$ 187.1335, found 187.1315.

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Ethyl 2-hydroxy-2-phenyl-4-pentenoate (3) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, $J = 7.72$ Hz, 2H), 7.36 (t, $J = 7.08$ Hz, 2H), 7.35 (m, 1H), 5.81 (m, 1H), 5.17, 5.14 (dd, $J = 17.08$, 9.76 Hz, 2H), 4.21 (m, 2H), 3.77 (s, 1H), 2.99, 2.96 (dd, $J = 7.76$, 13.99 Hz, 1H), 2.78, 2.74 (dd, $J = 6.49$, 14 Hz, 1H), 1.27 (t, $J = 7.16$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.62, 141.42, 132.40, 128.25, 127.78, 125.35, 119.30, 77.89, 62.50, 44.17, 14.10; IR (film) 3480, 3020, 2960, 1710, 1430, 1410, 1240 cm^{-1}; HRMS(CI) calcd for $C_{13}H_{17}O_3$ $[M + H]^+$ 221.1179, found 221.1148.

Ethyl 2-hydroxy-2,3-dimethyl-4-pentenoate (4) ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.78 (m, 1H), 5.14–4.99 (m, 2H), 4.24 (m, 2H), 3.15 (s, 1H), 2.46 (m, 1H), 1.32 (t, $J = 3.66$ Hz, 3H), 1.08 (d, $J = 6.72$ Hz, 3H), 0.96 (d, $J = 6.72$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.18, 177.06, 139.34, 138.60, 116.87, 116.09, 76.41, 76.14, 65.98, 61.99, 61.93, 46.32, 46.16, 24.37, 23.59, 15.36, 15.30, 14.30, 13.58; IR (film) 3520, 3020, 2960, 1700, 1430, 1410, 1240 cm^{-1}; HRMS(CI) calcd for $C_9H_{17}O_3$ $[M + H]^+$ 173.1179, found 173.1185.

Ethyl 2-(2′-cyclohexenyl)-2-hydroxy-2-methylpropanoate (5) ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.90–5.85 (m, 1H), 5.83–5.37 (m, 1H), 4.26 (q, $J = 7.02$ Hz, 2H), 2.68 (s, 1H), 1.99 (m, 1H), 1.89–1.82 (m, 2H), 1.52–1.41 (m, 2H), 1.39 (s, 3H), 1.31 (t, $J = 7.02$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.12, 176.93, 130.97, 130.36, 126.35, 125.29, 76.48, 61.92, 61.80, 43.88, 43.81, 25.02, 24.11, 23.59, 22.95, 22.44, 21.97, 21.84, 14.28; IR (film) 3520, 3030, 2960, 2940, 1710, 1440, 1420, 1250 cm^{-1}; HRMS(CI) calcd for $C_{11}H_{19}O_3$ $[M + H]^+$ 199.1335, found 199.1325.

Ethyl 2-hydroxy-2,3,3-trimethyl-4-pentenoate (6) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94, 5.90 (dd, $J = 10.96$, 16.00 Hz, 1H), 5.00 (d, $J = 3.35$ Hz, 1H), 4.96 (d, $J = 9.71$ Hz, 1H), 4.17 (m, 2H), 3.41 (s, 1H), 1.28 (s, 3H), 1.24 (t, $J = 7.19$, 3H), 1.02 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.80, 144.22, 113.56, 78.80, 62.20, 43.82, 22.79, 22.33, 21.11, 14.62; IR (film) 3490, 3020, 2950, 1690, 1410, 1360, 1240, 1120 cm^{-1}; HRMS(CI) calcd for $C_{10}H_{19}O_3$ $[M + H]^+$ 187.1335, found 187.1321.

Ethyl 2-hydroxy-2-methyl-3-phenyl-4-pentenoate (7) ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28 (m, 5H), 6.32 (m, 1H), 5.28 (d, $J = 3.97$, 1H), 5.24 (d, $J = 11.60$, 1H), 4.04 (m, 2H), 3.58 (d, $J = 9.77$, 1H), 3.29 (s, 1H), 1.50 (s, 3H), 1.20 (t, $J = 6.71$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.25, 140.12, 136.23, 128.62, 128.42, 127.22, 118.40, 76.74, 61.97, 58.10, 24.77, 14.11; IR (film) 3500, 3020, 2940, 1700, 1440, 1410, 1240, 1140 cm^{-1}; HRMS(CI) calcd for $C_{14}H_{19}O_3$ $[M + H]^+$ 235.1335, found 235.1328.

***trans*-Ethyl 5-bromo-2-hydroxy-2-methyl-4-pentenoate (8-*trans*)** ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.77 (m, 1H), 5.16 (m, 1H), 4.60 (d, $J = 10.07$ Hz, 1H), 4.25 (m, 2H), 2.45 (m, 2H), 1.43 (s, 3H), 1.31 (t, $J = 7.33$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.64, 132.52, 119.14,

74.32, 61.91, 44.73, 25.58, 14.29; IR (film) 3500, 3020, 2960, 1720, 1420, 1400, 1240 cm^{-1}; HRMS(CI) calcd for $C_8H_{14}Br_1O_3$ $[M+H]^+$ 237.0128, found 237.0126.

***cis*-Ethyl 5-bromo-2-hydroxy-2-methyl-4-pentenoate (8-*cis*)** ^1H NMR (200 MHz, $CDCl_3$) δ 6.15 (m, 1H), 5.24 (d, $J=27.45$ Hz, 1H), 5.16 (m, 1H), 4.25 (m, 2H), 2.45 (m, 2H), 1.53 (s, 3H), 1.33 (t, $J=7.33$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.42, 135.02, 119.02, 74.32, 61.54, 44.73, 24.88, 14.22; IR (film) 3500, 3020, 2960, 1720, 1420, 1400, 1240 cm^{-1}; HRMS(CI) calcd for $C_8H_{14}Br_1O_3$ $[M+H]^+$ 237.0128, found 237.0126.

Diethyl 2-hydroxy-2-methyl-3-vinylsuccinate (9) ^1H NMR (200 MHz, $CDCl_3$) δ 5.94 (m, 1H), 5.38 (d, $J=10.07$ Hz, 1H), 5.30 (d, $J=17.09$ Hz, 1H), 4.26 (q, $J=7.33$ Hz, 2H), 4.16 (q, $J=7.02$ Hz, 2H), 3.47 (d, $J=9.77$ Hz, 1H), 1.35 (s, 3H), 1.31 (t, $J=7.33$ Hz, 3H), 1.26 (t, $J=7.32$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.84, 172.49, 130.85, 121.61, 74.94, 61.97, 61.30, 57.35, 23.91, 14.15, 14.08; IR (film) 3500, 3020, 2960, 1710, 1430, 1410, 1240 cm^{-1}; HRMS(CI) calcd for $C_{11}H_{19}O_5$ $[M+H]^+$ 231.1234, found 231.1222.

Ethyl 2-hydroxy-2,4-dimethyl-4-pentenoate (10) ^1H NMR (400 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.68 (s, 1H), 4.15 (m, 2H), 2.55 (d, $J=13.72$ Hz, 1H), 2.39 (d, $J=13.57$ Hz, 1H), 1.69 (s, 3H), 1.36 (s, 3H), 1.24 (t, $J=7.22$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.18, 141.67, 115.36, 74.89, 62.18, 48.19, 26.86, 24.27, 14.56; IR (film) 3500, 3020, 2940, 1700, 1430, 1350, 1440 cm^{-1}; HRMS(CI) calcd for $C_9H_{17}O_3$ $[M+H]^+$ 173.1179, found 173.1185.

4-Ethoxycarbonyl-4-hydroxy-2-methylenylpentanoic acid (11) ^1H NMR (200 MHz, $CDCl_3$) δ 6.44 (s, 1H), 5.82 (s, 1H), 4.21 (m, 2H), 2.86 (d, $J=14.04$ Hz, 1H), 2.69 (d, $J=14.04$ Hz, 1H) 1.47 (s, 3H), 1.30 (t, $J=7.02$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.10, 172.37, 135.03, 131.67, 74.30, 62.14, 41.20, 25.56, 14.13; IR (film) 3010, 3940, 1700, 1670, 1610, 1420, 1400, 1140, 950 cm^{-1}; HRMS(CI) calcd for $C_9H_{15}O_5$ $[M+H]^+$ 203.0921, found 203.0938.

Ethyl 2-hydroxy-2-methyl-4-pentynoate (12) ^1H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, $J=3.58$, 2H), 3.16 (s, 1H), 2.63 (d, $J=16.59$ Hz, 1H), 2.52 (d, $J=16.59$ Hz, 1H) 2.03 (m, 1H), 1.43 (s, 3H), 1.28 (t, $J=5.04$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.55, 79.34, 73.93, 71.71, 62.50, 31.21, 25.44, 14.51; HRMS(CI) calcd for $C_8H_{13}O_3$ $[M+H]^+$ 157.0866, found 157.0877.

Ethyl 2-hydroxy-2-methyl-3,4-pentadienoate (13) ^1H NMR (400 MHz, $CDCl_3$) δ 5.32 (t, $J=6.79$, 1H), 4.92 (m, 2H), 4.23 (q, $J=3.58$, 2H), 3.16 (s, 1H), 1.49 (s, 3H), 1.26 (t, $J=7.36$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.91, 175.48, 96.36, 79.34, 72.87, 62.54, 25.24, 14.51; HRMS(CI) calcd for $C_8H_{13}O_3$ $[M+H]^+$ 157.0866, found 157.0854.

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Ethyl 2-hydroxy-2-methyl-3-trimethylsilyl-3,4-pentadienoate (14) ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 (s, 2H), 4.26 (q, $J = 6.83$ Hz, 2H), 1.56 (s, 3H), 1.31 (t, $J = 7.19$, 3H), 0.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.03, 176.21, 101.42, 75.31, 71.82, 62.12, 26.65, 14.28, 0.03; IR (film) 3480, 3020, 2940, 1910, 1700, 1430, 1400, 1240, 1120 cm^{-1}; HRMS(CI) calcd for $C_{11}H_{21}O_3Si_1$ $[M + H]^+$ 229.1261, found 229.1251.

Ethyl 2-hydroxy-2-methyl-4-[(trimethylsilyl)methyl]-4,5-hexadienoate (15) ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.65 (m, 2H), 4.21 (m, 2H), 3.33 (s, 1H), 2.52–2.21 (m, 2H), 1.43 (s, 3H), 1.35 (s, 2H), 1.30 (t, $J = 7.02$ Hz, 3H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.18, 176.43, 143.04, 96.37, 75.75, 74.93, 61.67, 44.51, 26.67, 26.13, 22.58, 14.20, −1.16; IR (film) 3450, 3020, 2940, 1700, 1400, 1260, 1140 cm^{-1}; HRMS(CI) calcd for $C_{13}H_{25}O_3Si_1$ $[M + H]^+$ 257.1574, found 257.1561.

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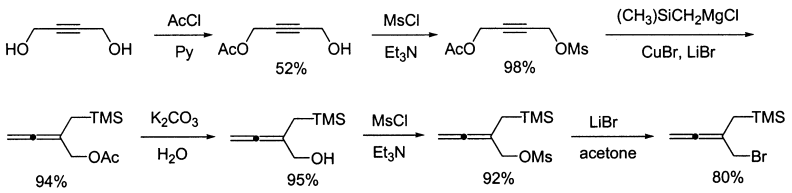
5. All new compounds have satisfactory analytical data including ^{1}H, ^{13}C-NMR, MS, and IR spectroscopy.
6. 4-Bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene was prepared from 2-butyn-1,4-diol according to the following scheme.



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