

Indium and zinc-mediated Barbier-type addition reaction of 2,3-allenals with allyl bromide: an efficient synthesis of 1,5,6-alkatrien-4-ols†

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A zinc or indium-mediated Barbier-type addition reaction of 2,3-allenals with allyl bromide in a mixed medium of aqueous NH_4Cl and THF (5 : 2) was developed to provide an efficient route to 1,5,6-alkatrien-4-ols, which is synthetically very useful. No 1,4-addition reaction was observed. Depending on the substrates, both indium and activated zinc afforded the 1,2-addition products in moderate to excellent yields: for terminal allenals, activated zinc was better while in other cases the yields with indium were relatively higher.

Introduction

Recently, much attention has been paid to the transition metal-catalyzed or mediated reaction of functionalized allenes.^{1,2} In the case of 2,3-allenols, we and others have developed some methodologies for the synthesis of 2,5-dihydrofurans,³ α -methylene lactones,⁴ vinylic epoxides,⁵ and α - or β -amino alcohols⁶ starting from 2,3-allenols. A number of methods have been reported for the synthesis of 2,3-allenols: (1) the reactions of the mono-*O*-tetrahydropyran-2-yl derivatives of butyn-1,4-diols,⁷ allenic ketones,⁸ 4-chlorobut-2-yn-1-ol,⁹ or 2,3-allenoates¹⁰ with LiAlH_4 or DIBAL-H; (2) the Sn(II) -,¹¹ Cr(II) -,¹¹ or In -¹² mediated reaction of propargylic bromides with aldehydes or ketones; (3) the reaction of 1,2-allenyl lithium with aldehydes¹³ or ketones;¹³ (4) the Cu(I) -mediated homologation of terminal propargylic alcohols.¹⁴ On the other hand, the Barbier-type reaction between allyl halide and carbonyl compounds to afford homoallylic alcohols in aqueous media has become a very useful synthetic transformation. The metals that have been used in the aqueous Barbier-type reactions include aluminium,¹⁵ magnesium,¹⁶ manganese,¹⁷ zinc,¹⁸ antimony,¹⁹ gallium,²⁰ indium,²¹ bismuth,²² tin,²³ lead,²⁴ and cadmium,²⁵ *etc.* Of these metals, zinc offers the greatest potential for industrial application because of its relative low cost and ready availability. Indium²⁶ has the lowest first ionization potential relative to zinc, tin and magnesium. Therefore, it is facile to effect SET (single electron transfer) processes. In addition, it is not sensitive to boiling water or alkali and does not form oxides readily in air, which makes indium a promising metal for aqueous Barbier-type reactions. Herein, we wish to report our recent studies on Barbier-type allylations of 2,3-allenals with allyl bromide using indium and activated zinc in water.

Results and discussion

Synthesis of Starting Materials

4-Mono-substituted or 4,4-disubstituted 2,3-allenals were prepared from the reaction of 1,2-allenyl lithium with DMF by a modified procedure developed by us (Table 1).^{13b}

2-Substituted 2,3-allenals are easily available from 2,3-allenols by Swern oxidation (Table 2).²⁷

As a starting point, the Barbier-type addition reaction of 4,4-pentamethylenebutadienal **1a** was chosen to establish the protocol. Some representative results are listed in Table 3. From Table 3, it was observed that with 2 equiv. of indium the reaction of 2 equiv. of allyl bromide with **1a** in a mixed solvent of THF and water (2 : 5) at room temperature afforded 1,1-pentamethylene-1,2,6-heptatrien-4-ol **2a** in 59% yield (entry 1, Table 3). By using saturated aqueous NH_4Cl solution instead of water, the yield of the product was improved greatly to 95% (compare entry 6 with entries 1–3, Table 3). With a lesser or greater amount of saturated aqueous NH_4Cl solution, the yield dropped (entries 7 and 8, Table 3). We also observed that 2 equiv. of indium are necessary (compare entry 6 with entries 4 and 5, Table 3). Thus, conditions A (2 equiv. of allyl bromide, 2 equiv. of metal, NH_4Cl (sat. aq.) : THF = 5 : 2, rt) were established as the optimized reaction conditions. When indium was replaced with zinc powder, the reaction afforded **2a** in 37% (entry 9, Table 3). The isolated yield was improved to

Table 1 Preparation of 4,4-disubstituted or 4-mono-substituted 2,3-allenals

Entry	R ¹	R ²	Yield of 1 (%)
1	-(CH ₂) ₅ -		50 (1a)
2	<i>n</i> -C ₄ H ₉		23 (1b)
3	<i>c</i> -C ₆ H ₁₁	H	51 (1d)
4	<i>n</i> -C ₇ H ₁₅	H	36 (1e)
5	<i>n</i> -C ₁₀ H ₂₁	H	37 (1f)

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Table 2 Preparation of 2-substituted 2,3-allenals

Entry	R ¹	R ²	R ³	Yield of 1 (%)
1	<i>n</i> -C ₄ H ₉	H	CH ₃	80 (1c)
2	H	H	<i>n</i> -C ₁₀ H ₂₁	85 (1g)
3	H	H	<i>n</i> -C ₇ H ₁₅	75 (1h)
4	H	H	Allyl	54 (1i)
5	-(CH ₂) ₅ -		<i>n</i> -C ₃ H ₇	81 (1j)

Table 3 Effect of metals and solvents on the allylation of 4,4-pentamethylene butadienal (**1a**)

Entry	Metal	Solvent	Time/h	Yield of 2a (%) ^a
1	In	H ₂ O : THF = 5 : 2	45.5	59
2	In	NH ₄ Cl (2 M) : THF = 5 : 2	16	64
3	In	NH ₄ Cl (4 M) : THF = 5 : 2	14	84
4	In ^b	NH ₄ Cl (sat. aq.) : THF = 5 : 2	72	45
5	In ^c	NH ₄ Cl (sat. aq.) : THF = 5 : 2	48	64
6	In	NH ₄ Cl (sat. aq.) : THF = 5 : 2	4.3	95
7	In	NH ₄ Cl (sat. aq.) : THF = 1 : 2	17	54
8	In	NH ₄ Cl (sat. aq.) : THF = 10 : 1	27	40
9	Zn	NH ₄ Cl (sat. aq.) : THF = 5 : 2	17.5	37
10	Zn ^d	NH ₄ Cl (sat. aq.) : THF = 5 : 2	16	80

^a Isolated yield. ^b 1.1 equiv. of indium were used. ^c 1.5 equiv. of indium were used. ^d Activated Zn powder.

80% when activated zinc powder^{13b} was applied (entry 10, Table 3, conditions B).

Subsequently, the scope of the allylation of different 2,3-allenals was studied with some typical results summarized in Table 4. Various differently substituted 2,3-allenals were successfully used to afford 1,5,6-alkatrien-4-ols in moderate to good yields. 4,4-Disubstituted (entries 1–4, Table 4), 2,4-disubstituted (entries 5 and 6, Table 4), 4-mono-substituted (entries 7–12, Table 4), 2-mono-substituted (entries 13–18, Table 4), and fully substituted 2,3-allenals (entries 19 and 20, Table 4) all afforded the expected products smoothly, indicating the wide scope of this reaction. In most cases, the yields of 2,3-allenols with indium were higher than those with activated zinc (entries 1–12 and 19–20, Table 4), however, the reaction of terminal allenals with allyl bromide and activated zinc afforded the corresponding products in higher yields (entries 13–18, Table 4). In addition, it should be noted that in all the cases, 1,4-addition reaction to the conjugated C=C bond in the allenals was not observed, indicating the excellent chemoselectivity.

Conclusions

In conclusion, we have developed a convenient aqueous allylation reaction of 2,3-allenals with allyl bromide by using zinc or indium

in a mixed solvent of saturated aqueous NH₄Cl solution and THF, providing an efficient route to 1,5,6-alkatrien-4-ols. Due to the synthetic potential of the products, easy availability of the starting materials, and mild reaction conditions, this method may be useful in organic synthesis. Further studies on the scope and synthetic applications of this reaction are being carried out in our laboratory.

Experimental section

Synthesis of 2-substituted-2,3-allenals via the reaction of 1,2-allenyl lithium with DMF

(1) Synthesis of 4,4-pentamethylenebutadienal (**1a**).

Typical procedure

To a solution of vinylidenecyclohexane (3.21 g, 29.7 mmol) and THF (30 mL) was slowly added dropwise *n*-butyl lithium (11.1 mL, 2.5 M in hexane, 27.75 mmol) at –60 °C with stirring under a nitrogen atmosphere. After being stirred for 1.2 h at –55 °C, the mixture was cooled to –70 °C and a solution of anhydrous dimethylformamide (3.5 mL, *d* = 0.947, 3.31 g, 45.0 mmol) in anhydrous THF (10 mL) was added dropwise at this temperature. After being stirred at –70 °C for an additional 2.0 h, the mixture was poured into 500 mL of HCl (0.1 M, 0 °C) with vigorous stirring. The mixture was extracted with diethyl ether (50 mL × 3) after returning to room temperature. The combined organic extract was washed with ice-water (40 mL × 3) and dried over anhydrous Na₂SO₄. Evaporation and column chromatography on silica gel (petroleum ether–ethyl acetate = 200 : 1) afforded **1a**^{13b} (1.90 g, 50%); liquid, ¹H NMR (400 MHz, CDCl₃) δ 9.38 (d, *J* = 7.2 Hz, 1H), 5.70–5.61 (m, 1H), 2.30–2.15 (m, 4H), 1.68–1.59 (m, 4H), 1.58–1.50 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 214.3, 192.9, 107.7, 96.8, 30.0, 26.9, 25.5.

The following compounds were prepared according to this procedure.

(2) Synthesis of 4-butyl-2,3-octadienal (**1b**)

The reaction of *n*-butyl lithium (3.4 mL, 2.5 M in hexane, 8.5 mmol), 3-butyl-1,2-heptadiene (1.41 g, 9.3 mmol), dimethylformamide (1.06 mL, *d* = 0.947, 1.00 g, 13.8 mmol), and anhydrous THF (29 mL) afforded **1b**²⁸ (0.35 g, 23%); liquid, ¹H NMR (300 MHz, CDCl₃) δ 9.42 (d, *J* = 7.5 Hz, 1H), 5.83–5.75 (m, 1H), 2.17–2.05 (m, 4H), 1.49–1.20 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 6H).

(3) Synthesis of 4-cyclohexylbutadienal (**1d**)

The reaction of *n*-butyl lithium (8.5 mL, 2.5 M in hexane, 21.25 mmol), cyclohexyl-1,2-propadiene (2.76 g, 22.6 mmol), dimethylformamide (2.8 mL, *d* = 0.947, 2.65 g, 36.3 mmol), and anhydrous THF (60 mL) afforded **1d** (1.62 g, 51%); liquid, ¹H NMR (300 MHz, CDCl₃) δ 9.46 (d, *J* = 7.5 Hz, 1H), 5.89–5.81 (m, 1H), 5.75 (t, *J* = 6.0 Hz, 1H), 2.28–2.13 (m, 1H), 1.89–1.59 (m, 5H), 1.40–1.08 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 218.6, 192.4, 102.0, 99.5, 36.6, 32.84, 32.80, 25.7; IR (neat), *ν* (cm^{–1}) 2926, 2852, 1941, 1692, 1449, 1112, 1091; MS (70 ev, EI) *m/z* (%) 150 (M⁺, 5.33), 107 (M⁺ – C₃H₇, 100); elemental

Table 4 Allylation of 2,3-allenals mediated by In or Zn

Entry	1 R ¹	R ²	R ³	Metal	Time/h	Yield of 2 (%) ^a
1	-(CH ₂) ₅ -		H (1a)	In	4.3	95 (2a)
2	-(CH ₂) ₅ -		H (1a)	Zn	16	80 (2a)
3	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H (1b)	In	7.5	84 (2b)
4	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H (1b)	Zn	13	77 (2b)
5	<i>n</i> -C ₄ H ₉	H	CH ₃ (1c)	In	12	65 (2c)
6	<i>n</i> -C ₄ H ₉	H	CH ₃ (1c)	Zn	17	57 (2c)
7	<i>c</i> -C ₆ H ₁₁	H	H (1d)	In	26.3	86 (2d)
8	<i>c</i> -C ₆ H ₁₁	H	H (1d)	Zn	27	74 (2d)
9	<i>n</i> -C ₇ H ₁₅	H	H (1e)	In	12	89 (2e)
10	<i>n</i> -C ₇ H ₁₅	H	H (1e)	Zn	10.4	81 (2e)
11	<i>n</i> -C ₁₀ H ₂₁	H	H (1f)	In	10	85 (2f)
12	<i>n</i> -C ₁₀ H ₂₁	H	H (1f)	Zn	10	80 (2f)
13	H	H	<i>n</i> -C ₁₀ H ₂₁ (1g)	In	11	84 (2g)
14	H	H	<i>n</i> -C ₁₀ H ₂₁ (1g)	Zn	10	84 (2g)
15	H	H	<i>n</i> -C ₇ H ₁₅ (1h)	In	10.3	82 (2h)
16	H	H	<i>n</i> -C ₇ H ₁₅ (1h)	Zn	12	88 (2h)
17	H	H	Allyl (1i)	In	9.5	73 (2i)
18	H	H	Allyl (1i)	Zn	17	75 (2i)
19	-(CH ₂) ₅ -		<i>n</i> -C ₃ H ₇ (1j)	In	9.2	72 (2j)
20	-(CH ₂) ₅ -		<i>n</i> -C ₃ H ₇ (1j)	Zn	11	69 (2j)

^a Isolated yield.

analysis: calcd for C₁₀H₁₄O: C, 79.96; H, 9.39; found: C, 79.97; H, 9.39.

(4) Synthesis of 2,3-undecadienal (**1e**)

The reaction of *n*-butyl lithium (8.0 mL, 2.5 M in hexane, 20.0 mmol), 1,2-decadiene (3.04 g, 22.0 mmol), dimethylformamide (3.0 mL, *d* = 0.947, 2.85 g, 38.9 mmol), and anhydrous THF (60 mL) afforded **1e** (1.20 g, 36%): liquid, ¹H NMR (300 MHz, CDCl₃) δ 9.46 (d, *J* = 7.2 Hz, 1H), 5.82–5.69 (m, 2H), 2.16 (qd, *J* = 7.1, 3.0 Hz, 2H), 1.52–1.40 (m, 2H), 1.38–1.18 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 219.1, 192.3, 98.5, 96.3, 31.7, 28.9, 28.8, 28.7, 27.4, 22.5, 14.0; IR (neat), ν (cm⁻¹) 2956, 2927, 2856, 2798, 1944, 1693, 1466, 1378, 1107, 1080; MS (70 ev, EI) *m/z* (%) 166 (M⁺, 6.81), 81 (100); elemental analysis: calcd for C₁₁H₁₈O: C, 79.46; H, 10.91; found: C, 79.47; H, 10.94.

(5) Synthesis of 2,3-tetradecadienal (**1f**)

The reaction of *n*-butyl lithium (7.0 mL, 2.5 M in hexane, 17.5 mmol), 1,2-tridecadiene (3.40 g, 18.9 mmol), dimethylformamide (2.3 mL, *d* = 0.95, 2.19 g, 29.8 mmol), and anhydrous THF (60 mL) afforded **1f** (1.35 g, 37%): liquid, ¹H NMR (300 MHz, CDCl₃) δ 9.48 (d, *J* = 7.2 Hz, 1H), 5.85–5.70 (m, 2H), 2.18 (qd, *J* = 7.2, 3.0 Hz, 2H), 1.53–1.40 (m, 2H), 1.39–1.19 (m, 14H), 0.87 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 219.1, 192.4, 98.6, 96.3, 31.9, 29.55, 29.53, 29.3, 28.9, 28.8, 27.5, 22.7, 14.1; IR (neat), ν (cm⁻¹) 2925, 2855, 1943, 1695, 1465, 1107, 1086; MS (70 ev, EI) *m/z* (%) 208 (M⁺, 3.40), 81 (100); elemental

analysis: calcd for C₁₄H₂₄O: C, 80.71; H, 11.61; found: C, 80.74; H, 11.55.

Synthesis of 2-substituted-2,3-allenals *via* the oxidation of 2,3-allenols

(1) Synthesis of 2-methyl-2,3-octadienal (**1c**).²⁷ Typical procedure

To a solution of oxalyl chloride (1.7 mL, *d* = 1.49, 2.53 g, 20.0 mmol) in anhydrous CH₂Cl₂ (35 mL) was slowly added dropwise anhydrous DMSO (2.7 mL, *d* = 1.10, 2.97 g, 38.1 mmol) at –78 °C with stirring under a nitrogen atmosphere. After being stirred for 20 min at this temperature, a solution of 2-methyl-2,3-octadienol (2.1 g, 15.0 mmol) in anhydrous CH₂Cl₂ (15 mL) was added dropwise at –78 °C. After being stirred at –78 °C for an additional 1.3 h, Et₃N (10 mL, *d* = 0.73, 7.3 g, 72.3 mmol) was added at this temperature. After removing the cooling bath, the mixture was diluted with ether (40 mL) and washed with water (30 mL × 3). The ether layer was dried over anhydrous Na₂SO₄. Evaporation and column chromatography on silica gel (petroleum ether–ethyl acetate = 80 : 1 to 40 : 1) afforded **1c** (1.66 g, 80%): liquid, ¹H NMR (300 MHz, CDCl₃) δ 9.50 (s, 1H), 5.71–5.61 (m, 1H), 2.15 (q, *J* = 7.2 Hz, 2H), 1.75 (d, *J* = 2.7 Hz, 3H), 1.50–1.29 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 218.4, 192.9, 106.3, 95.5, 30.9, 27.5, 21.9, 13.7, 10.8; IR (neat), ν (cm⁻¹) 2958, 2931, 2860, 1949, 1720, 1671, 1627, 1465, 1378, 1260, 1224; MS (70 ev, EI) *m/z* (%) 138 (M⁺, 1.05), 123 (M⁺ – CH₃, 5.71), 95 (100); elemental analysis: calcd for C₉H₁₄O: C, 78.21; H, 10.21; found: C, 78.22; H, 10.20.

The following compounds were prepared according to this procedure.

(2) Synthesis of 2-decyl-2,3-butadienal (1g)

The reaction of oxalyl chloride (1.05 mL, $d = 1.49$, 1.64 g, 12.4 mmol), anhydrous DMSO (1.8 mL, $d = 1.10$, 1.98 g, 25.4 mmol), 2-decyl-2,3-butadienol (1.60 g, 7.6 mmol), and Et_3N (7.0 mL, $d = 0.73$, 5.11 g, 50.6 mmol) in anhydrous CH_2Cl_2 (45 mL) afforded **1g** (1.35 g, 85%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 9.55 (s, 1H), 5.29 (t, $J = 2.7$ Hz, 2H), 2.20–2.10 (m, 2H), 1.48–1.35 (m, 2H), 1.34–1.17 (m, 14H), 0.86 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 222.3, 192.3, 110.9, 80.1, 31.9, 29.5, 29.32, 29.28, 29.2, 27.5, 24.1, 22.6, 14.1; IR (neat), ν (cm^{-1}) 2926, 2855, 2721, 1960, 1931, 1688, 1466, 1374, 1227, 1158; MS (70 ev, EI) m/z (%) 208 (M^+ , 3.23), 109 (100); elemental analysis: calcd for $\text{C}_{14}\text{H}_{24}\text{O}$: C, 80.71; H, 11.61; found: C, 80.68; H, 11.62.

(3) Synthesis of 2-heptyl-2,3-butadienal (1h)

The reaction of oxalyl chloride (0.48 g, 3.8 mmol), anhydrous DMSO (0.55 mL, $d = 1.10$, 0.61 g, 7.5 mmol), 2-heptyl-2,3-butadienol (0.51 g, 3.0 mmol), and Et_3N (2.1 mL, $d = 0.73$, 1.53 g, 15.2 mmol) in anhydrous CH_2Cl_2 (18 mL) afforded **1h** (0.37 g, 75%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 9.54 (s, 1H), 5.29 (t, $J = 2.6$ Hz, 2H), 2.20–2.08 (m, 2H), 1.50–1.35 (m, 2H), 1.34–1.15 (m, 8H), 0.85 (t, $J = 6.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 222.2, 192.2, 110.9, 80.1, 31.7, 29.1, 29.0, 27.5, 24.1, 22.6, 14.0; IR (neat), ν (cm^{-1}) 2956, 2927, 2857, 2727, 1952, 1931, 1688, 1466, 1377, 1263, 1161, 1089, 1008; MS (70 ev, EI) m/z (%) 166 (M^+ , 0.65), 137 ($\text{M}^+ - \text{CHO}$, 18.06), 95.1 (100); elemental analysis: calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91; found: C, 79.50; H, 10.93.

(4) Synthesis of 2-allyl-butadienal (1i)

The reaction of oxalyl chloride (1.4 mL, $d = 1.49$, 2.09 g, 16.6 mmol), anhydrous DMSO (2.4 mL, $d = 1.10$, 2.64 g, 33.8 mmol), 2-allylbutadienol (1.15 g, 10.5 mmol), and Et_3N (9.0 mL, $d = 0.73$, 6.57 g, 65.0 mmol) in anhydrous CH_2Cl_2 (20 mL) afforded **1i** (0.61 g, 54%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 9.57 (s, 1H), 5.87–5.71 (m, 1H), 5.34 (t, $J = 2.9$ Hz, 2H), 5.14–5.01 (m, 2H), 2.97–2.89 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 222.1, 191.5, 134.0, 116.7, 109.1, 80.8, 28.8; IR (neat), ν (cm^{-1}) 3065, 2985, 2917, 2828, 2729, 1959, 1931, 1683, 1642, 1428, 1229, 1165, 993, 920; MS (70 ev, EI) m/z (%) 108 (M^+ , 2.72), 107 ($\text{M}^+ - \text{H}$, 25.17), 79 ($\text{M}^+ - \text{CHO}$, 100); elemental analysis: calcd for $\text{C}_7\text{H}_8\text{O}$: C, 77.75; H, 7.46; found: C, 77.60; H, 7.79.

(5) Synthesis of 2-propyl-4,4-pentamethylenebutadienal (1j)

The reaction of oxalyl chloride (0.445 g, 3.5 mmol), anhydrous DMSO (0.5 mL, $d = 1.10$, 0.550 g, 7.1 mmol), 2-propyl-4,4-pentamethylenebutadienol (0.502 g, 2.8 mmol), and Et_3N (1.9 mL, $d = 0.73$, 1.39 g, 13.7 mmol) in anhydrous CH_2Cl_2 (18 mL) afforded **1j** (0.404 g, 81%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 9.46 (s, 1H), 2.24 (t, $J = 6.0$ Hz, 4H), 2.13 (t, $J = 7.4$ Hz, 2H), 1.75–1.55 (m, 6H), 1.49–1.37 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 213.4, 193.1, 109.7, 108.1, 30.6, 27.4, 26.8, 25.8, 20.9, 13.6; IR (neat), ν (cm^{-1}) 2932, 2856, 1946, 1682, 1446, 1261, 1216, 1181, 1105, 1019; MS (70 ev, EI) m/z (%) 178 (M^+ , 7.71), 149 ($\text{M}^+ - \text{CHO}$, 73.17), 79 (100); elemental analysis: calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.85; H, 10.18; found: C, 80.71; H, 10.33.

Typical procedure for the zinc or indium mediated aqueous allylation of 2,3-allenals.

(1) Synthesis of 1,1-pentamethylene-1,2,6-heptatrien-4-ol (2a)

Typical procedure for the reaction with indium

To a reaction vessel were added sequentially **1a** (40 mg, 0.29 mmol), an indium particle (with a size of ~ 0.5 mm (radius), 75 mg, 0.65 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl (2.0 mL). To this mixture was then added allyl bromide (75 mg, 0.63 mmol) with vigorous stirring at rt. After 4.3 h with stirring the reaction was complete as monitored by TLC. The mixture was quenched with 10 mL of H_2O , extracted with diethyl ether (30 mL \times 2), washed with brine (20 mL), and dried over anhydrous Na_2SO_4 . Evaporation and column chromatography on silica gel (petroleum ether–ethyl acetate = 5 : 1) afforded **2a** (49.6 mg, 95%): liquid, ^1H NMR (400 MHz, CDCl_3) δ 5.89–5.76 (m, 1H), 5.20–5.03 (m, 3H), 4.14 (q, $J = 6.0$ Hz, 1H), 2.39–2.24 (m, 2H), 2.20–2.05 (m, 4H), 1.93 (s, 1H), 1.66–1.45 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 134.4, 117.7, 106.2, 92.9, 69.2, 41.8, 31.5, 27.3, 25.9; IR (neat), ν (cm^{-1}) 3354, 3076, 2927, 2854, 1966, 1641, 1447, 1436, 1345, 1264, 1058, 1024; MS (70 ev, EI) m/z (%) 178 (M^+ , 12.30), 67 (100); elemental analysis: calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.85; H, 10.18; found: C, 80.86; H, 10.22.

The reaction of activated zinc powder (45 mg, 0.69 mmol), **1a** (41 mg, 0.30 mmol), allyl bromide (91 mg, 0.76 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl (2.0 mL) at rt for 16 h afforded **2a** (43 mg, 80%).

The following compounds were prepared according to this procedure.

(2) Synthesis of 7-butyl-1,5,6-undecatrien-4-ol (2b)

The reaction of an indium particle (60 mg, 0.52 mmol), **1b** (32 mg, 0.18 mmol), allyl bromide (49 mg, 0.41 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 7.5 h afforded **2b** (33.1 mg, 84%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 5.94–5.78 (m, 1H), 5.28–5.20 (m, 1H), 5.19–5.09 (m, 2H), 4.16 (q, $J = 6.0$ Hz, 1H), 2.42–2.24 (m, 2H), 2.02–1.90 (m, 4H), 1.70 (bs, 1H), 1.46–1.23 (m, 8H), 0.90 (t, $J = 6.9$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 198.6, 134.5, 117.8, 108.6, 96.0, 69.3, 42.1, 32.2, 29.8, 22.4, 14.0; IR (neat), ν (cm^{-1}) 3384, 3077, 2958, 2930, 2860, 1962, 1641, 1466, 1378, 1026, 913; MS (70 ev, EI) m/z (%) 222 (M^+ , 14.60), 193 ($\text{M}^+ - \text{C}_2\text{H}_5$, 10.97), 179 ($\text{M}^+ - \text{C}_3\text{H}_7$, 64.17), 95 (100); elemental analysis: calcd for $\text{C}_{15}\text{H}_{26}\text{O}$: C, 81.02; H, 11.79; found: C, 81.01; H, 11.80.

The reaction of zinc powder (59 mg, 0.91 mmol), **1b** (72 mg, 0.40 mmol), allyl bromide (144 mg, 1.20 mmol), THF (1.0 mL), and saturated aqueous NH_4Cl solution (2.6 mL) at rt for 13 h afforded **2b** (68.1 mg, 77%).

(3) Synthesis of 5-methyl-1,5,6-undecatrien-4-ol (2c)

The reaction of an indium particle (119 mg, 1.03 mmol), **1c** (55 mg, 0.40 mmol), allyl bromide (100 mg, 0.83 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 12 h afforded **2c** (46.8 mg, 65%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 5.90–5.73 (m, 1H), 5.28–5.17 (m, 1H), 5.16–5.05 (m, 2H), 4.09–3.98 (m, 1H), 2.46–2.35 (m, 1H), 2.32–2.19 (m, 1H), 1.98 (q,

$J = 6.9$ Hz, 2H), 1.83 (bs, 1H), 1.70 (d, $J = 2.7$ Hz, 3H), 1.43–1.26 (m, 4H), 0.93–0.84 (m, 3H); IR (neat), ν (cm^{-1}) 3364, 3077, 2958, 2928, 2859, 1964, 1641, 1459, 1438, 1378, 1290, 1261, 1221, 1101, 1013, 992, 913; MS (70 ev, EI) m/z (%) 180 (M^+ , 0.23), 165 ($M^+ - \text{CH}_3$, 8.19), 137 ($M^+ - \text{C}_3\text{H}_7$, 24.99), 43 (100); elemental analysis: calcd for $\text{C}_{12}\text{H}_{20}\text{O}$: C, 79.94; H, 11.18; found: C, 79.94; H, 11.17.

The reaction of zinc powder (55 mg, 0.84 mmol), **1c** (55 mg, 0.40 mmol), allyl bromide (100 mg, 0.83 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 17 h afforded **2c** (41 mg, 57%).

(4) Synthesis of 1-cyclohexyl-1,2,6-heptatrien-4-ol (**2d**)

The reaction of an indium particle (113 mg, 0.98 mmol), **1d** (74.5 mg, 0.50 mmol), allyl bromide (150 mg, 1.25 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 26.3 h afforded **2d** (82 mg, 86%): liquid, ^1H NMR (400 MHz, CDCl_3) δ 5.89–5.77 (m, 1H), 5.32–5.23 (m, 2H), 5.17–5.07 (m, 2H), 4.21–4.13 (m, 1H), 2.39–2.26 (m, 2H), 2.04–1.89 (m, 2H), 1.78–1.58 (m, 5H), 1.33–1.00 (m, 5H); IR (neat), ν (cm^{-1}) 3358, 3076, 2925, 2851, 1961, 1641, 1449, 1030, 994, 913; MS (70 ev, EI) m/z (%) 192 (M^+ , 1.07), 151 ($M^+ - \text{C}_3\text{H}_5$, 50.63), 91 (100); elemental analysis: calcd for $\text{C}_{13}\text{H}_{20}\text{O}$: C, 81.20; H, 10.48; found: C, 81.24; H, 10.44.

The reaction of zinc powder (50 mg, 0.77 mmol), **1d** (45.5 mg, 0.30 mmol), allyl bromide (80 mg, 0.67 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 27 h afforded **2d** (43 mg, 74%).

(5) Synthesis of 1,5,6-tetradecatrien-4-ol (**2e**)

The reaction of an indium particle (100 mg, 0.87 mmol), **1e** (67 mg, 0.40 mmol), allyl bromide (98 mg, 0.82 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 12 h afforded **2e** (74.3 mg, 89%): liquid, ^1H NMR (400 MHz, CDCl_3) δ 5.89–5.78 (m, 1H), 5.33–5.26 (m, 1H), 5.25–5.19 (m, 1H), 5.17–5.08 (m, 2H), 4.22–4.14 (m, 1H), 2.40–2.26 (m, 2H), 2.05–1.96 (m, 2H), 1.96–1.86 (m, 1H), 1.45–1.35 (m, 2H), 1.34–1.19 (m, 8H), 0.87 (t, $J = 6.6$ Hz, 3H); IR (neat), ν (cm^{-1}) 3353, 3077, 2957, 2926, 2855, 1963, 1641, 1467, 1437, 1378, 1029, 995, 913; MS (70 ev, EI) m/z (%) 208 (M^+ , 0.49), 167 ($M^+ - \text{C}_3\text{H}_5$, 11.57), 83 (100); elemental analysis: calcd for $\text{C}_{14}\text{H}_{24}\text{O}$: C, 80.71; H, 11.61; found: C, 80.72; H, 11.61.

The reaction of zinc powder (50 mg, 0.77 mmol), **1e** (49 mg, 0.30 mmol), allyl bromide (80 mg, 0.67 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 10.4 h afforded **2e** (50 mg, 81%).

(6) Synthesis of 1,5,6-heptadecatrien-4-ol (**2f**)

The reaction of an indium particle (72 mg, 0.63 mmol), **1f** (60.9 mg, 0.29 mmol), allyl bromide (90 mg, 0.75 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 10 h afforded **2f** (62.4 mg, 85%): liquid, ^1H NMR (400 MHz, CDCl_3) δ 5.91–5.78 (m, 1H), 5.35–5.27 (m, 1H), 5.26–5.20 (m, 1H), 5.19–5.10 (m, 2H), 4.22–4.15 (m, 1H), 2.43–2.27 (m, 2H), 2.06–1.97 (m, 2H), 1.82 (bs, 1H), 1.45–1.36 (m, 2H), 1.35–1.19 (m, 14H), 0.87 (t, $J = 7.0$ Hz, 3H); IR (neat), ν (cm^{-1}) 3361, 3077, 2925, 2854, 1963, 1647, 1467, 1027, 913; MS (70 ev, EI) m/z (%) 250 (M^+ , 14.6), 235 ($M^+ - \text{CH}_3$,

30.7), 209 ($M^+ - \text{C}_3\text{H}_5$, 24.8), 95 (100); elemental analysis: calcd for $\text{C}_{17}\text{H}_{30}\text{O}$: C, 81.54; H, 12.08; found: C, 81.52; H, 12.13.

The reaction of zinc powder (60 mg, 0.92 mmol), **1f** (61 mg, 0.29 mmol), allyl bromide (97 mg, 0.81 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 10 h afforded **2f** (58.6 mg, 80%).

(7) Synthesis of 3-decyl-1,2,6-heptatrien-4-ol (**2g**)

The reaction of an indium particle (80 mg, 0.69 mmol), **1g** (62 mg, 0.30 mmol), allyl bromide (80 mg, 0.67 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 11 h afforded **2g** (62.9 mg, 84%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 5.92–5.75 (m, 1H), 5.20–5.08 (m, 2H), 4.92–4.81 (m, 2H), 4.12–4.02 (m, 1H), 2.49–2.37 (m, 1H), 2.36–2.24 (m, 1H), 2.08–1.89 (m, 2H), 1.75 (d, $J = 5.7$ Hz, 1H), 1.51–1.38 (m, 2H), 1.37–1.19 (m, 14H), 0.88 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 204.4, 134.4, 117.9, 107.1, 78.8, 70.7, 40.1, 31.9, 29.6, 29.5, 29.4, 29.3, 28.2, 27.6, 22.7, 14.1; IR (neat), ν (cm^{-1}) 3374, 3077, 2925, 2854, 1955, 1641, 1466, 1378, 1035, 992, 913; MS (70 ev, EI) m/z (%) 250 (M^+ , 1.2), 235 ($M^+ - \text{CH}_3$, 10.81), 221 ($M^+ - \text{CHO}$, 6.04), 209 ($M^+ - \text{C}_3\text{H}_5$, 17.96), 109 (100); elemental analysis: calcd for $\text{C}_{17}\text{H}_{30}\text{O}$: C, 81.54; H, 12.08; found: C, 81.56; H, 12.09.

The reaction of zinc powder (40 mg, 0.61 mmol), **1g** (62.1 mg, 0.30 mmol), allyl bromide (72.5 mg, 0.60 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 10 h afforded **2g** (39 mg, 84%).

(8) Synthesis of 3-heptyl-1,2,6-heptatrien-4-ol (**2h**)

The reaction of an indium particle (76 mg, 0.66 mmol), **1h** (44 mg, 0.27 mmol), allyl bromide (80 mg, 0.67 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 10.3 h afforded **2h** (45 mg, 82%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 5.91–5.74 (m, 1H), 5.19–5.07 (m, 2H), 4.93–4.81 (m, 2H), 4.13–4.02 (m, 1H), 2.49–2.37 (m, 1H), 2.36–2.24 (m, 1H), 2.09–1.88 (m, 2H), 1.80 (bs, 1H), 1.53–1.38 (m, 2H), 1.37–1.17 (m, 8H), 0.87 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 204.4, 134.4, 117.9, 107.1, 78.8, 70.7, 40.1, 31.8, 29.3, 29.1, 28.2, 27.6, 22.6, 14.1; IR (neat), ν (cm^{-1}) 3355, 3077, 2927, 2856, 1956, 1641, 1466, 1435, 1374, 1206, 1028; MS (70 ev, EI) m/z (%) 208 (M^+ , 0.38), 207 ($M^+ - \text{H}$, 0.40), 193 ($M^+ - \text{CH}_3$, 5.83), 167 ($M^+ - \text{C}_3\text{H}_5$, 17.38), 83 (100); elemental analysis: calcd for $\text{C}_{14}\text{H}_{24}\text{O}$: C, 80.71; H, 11.61; found: C, 80.78; H, 11.61.

The reaction of zinc powder (40 mg, 0.61 mmol), **1h** (45 mg, 0.27 mmol), allyl bromide (80 mg, 0.67 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 12 h afforded **2h** (49.6 mg, 88%).

(9) Synthesis of 3-allyl-1,2,6-heptatrien-4-ol (**2i**)

The reaction of an indium particle (92 mg, 0.80 mmol), **1i** (43 mg, 0.40 mmol), allyl bromide (100 mg, 0.83 mmol), THF (1.0 mL), and saturated aqueous NH_4Cl solution (2.6 mL) at rt for 9.5 h afforded **2i** (43.6 mg, 73%): liquid, ^1H NMR (300 MHz, CDCl_3) δ 5.87–5.68 (m, 2H), 5.14–4.95 (m, 4H), 4.85–4.75 (m, 2H), 4.11–4.96 (m, 1H), 2.85–2.67 (m, 2H), 2.49 (s, 1H), 2.43–2.19 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.0, 135.5, 134.3, 118.0, 116.1, 105.1, 78.6, 70.4, 40.0, 33.3; IR (neat), ν (cm^{-1}) 3395, 3078, 2980, 2912, 1956, 1641, 1432, 1296, 1042; MS (70 ev, EI) m/z (%) 150

(M^+ , 0.29), 149 ($M^+ - H$, 2.38), 135 ($M^+ - CH_3$, 8.44), 109 ($M^+ - C_3H_5$, 77.94), 79 (100); elemental analysis: calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39; found: C, 79.94; H, 9.39.

The reaction of zinc powder (79.1 mg, 1.22 mmol), **1i** (64.7 mg, 0.6 mmol), allyl bromide (144.1 mg, 1.19 mmol), THF (1.6 mL), and saturated aqueous NH_4Cl solution (4.0 mL) at rt for 17 h afforded **2i** (67.5 mg, 75%).

(10) Synthesis of 1,1-pentamethylene-3-propyl-1,2,6-heptatrien-4-ol (**2j**)

The reaction of an indium particle (125 mg, 1.09 mmol), **1j** (61 mg, 0.34 mmol), allyl bromide (100 mg, 0.83 mmol), THF (1.0 mL), and saturated aqueous NH_4Cl solution (2.6 mL) at rt for 9.2 h afforded **2j** (54.3 mg, 72%): liquid, 1H NMR (300 MHz, $CDCl_3$) δ 5.90–5.72 (m, 1H), 5.16–5.04 (m, 2H), 4.04–3.96 (m, 1H), 2.47–2.33 (m, 1H), 2.32–2.18 (m, 1H), 2.17–2.04 (m, 4H), 1.93 (t, J = 7.0 Hz, 2H), 1.81 (s, 1H), 1.66–1.36 (m, 8H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 134.7, 117.2, 107.8, 105.5, 71.1, 40.2, 32.0, 31.9, 31.1, 27.84, 27.77, 26.1, 20.8, 13.8; IR (neat), ν (cm^{-1}) 3387, 3076, 2928, 2854, 1961, 1641, 1445, 1377, 1335, 1262, 1028; MS (70 ev, EI) m/z (%) 220 (M^+ , 3.84), 191 ($M^+ - C_2H_5$, 6.57), 177 ($M^+ - C_3H_7$, 100); elemental analysis: calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98; found: C, 81.75; H, 10.97.

The reaction of zinc powder (40 mg, 0.61 mmol), **1j** (52.9 mg, 0.30 mmol), allyl bromide (72.8 mg, 0.60 mmol), THF (0.8 mL), and saturated aqueous NH_4Cl solution (2.0 mL) at rt for 11 h afforded **2j** (45.2 mg, 69%).

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