

# Dramatic Solvent Effect in the Reduction of 2,3-Allenic Acid Esters. A Simple Synthesis of 2,3-Allenols from 2,3-Allenates

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2,3-Allenols were prepared conveniently from the reduction reaction of 2,3-allenoates with DIBAL-H (Diisobutylaluminum hydride) in toluene. A dramatic solvent effect was observed for this reaction.

**Keywords** 2,3-allenoates, reduction, 2,3-allenols

## Introduction

2,3-Allenols are an important class of functionalized allenes, which can be used as the starting materials for the synthesis of oxiranes,<sup>1</sup> 2,5-dihydrofurans,<sup>2</sup>  $\alpha$ -methylene lactone,<sup>3</sup>  $\alpha$ - or  $\gamma$ -amino alcohols,<sup>4</sup> and  $\alpha$ ,  $\beta$ -unsaturated ketones.<sup>5</sup> These compounds were usually prepared by reductive elimination of mono-*O*-tetrahydropyran-2-yl or alkoxy derivatives of butyne-1,4-diols,<sup>6</sup> transition metal-mediated or -catalyzed reaction of 1-alkynyl epoxides,<sup>7</sup> the reaction of Grignard reagents with 4-hydroxy-2-alkynyl chlorides,<sup>8</sup> hydrolysis of 2,3-allenyl bromides,<sup>9</sup> treatment of allylic alcohols with :CBr<sub>2</sub> and RLi,<sup>10</sup> electrochemical reaction of aldehydes or ketones with propargylic bromides,<sup>11</sup> CrCl<sub>2</sub>-mediated reaction of aldehydes or ketones with propargylic bromides,<sup>12</sup> and CuBr-mediated reaction of terminal propargylic alcohols with paraformaldehyde.<sup>13</sup> In this paper we wish to report a facile synthesis of substituted 2,3-allenols via the reduction of 2,3-allenoates.

Treatment of ethyl 2-methyl-4-phenyl-2,3-but-

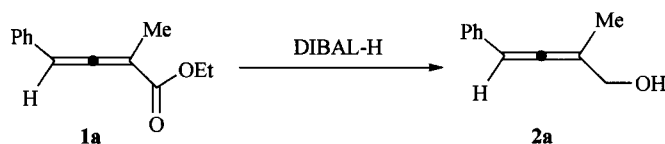
dienoate (**1a**) with 4.0 equiv. of DIBAL-H solution in cyclohexane at room temperature afforded a complicated mixture (Entry 1, Table 1). The reaction carried out in anhydrous ether using 2 equiv. of DIBAL-H (solution in cyclohexane) at -78 °C afforded **2a** in 15% yield. With 3.0 equiv. of DIBAL-H in cyclohexane, the reaction in ether at -90—-140 °C afforded a complicated mixture (Entry 2, Table 1). However, it is interesting to note that the corresponding reaction using the DIBAL-H solution in toluene afforded **2a** cleanly in 83% yield (Entry 4, Table 1), indicating that an interesting dramatic solvent effect occurred in this reduction. Some typical results of the reduction of 2,3-allenoates with DIBAL-H in toluene are summarized in Table 2. From Table 2 it can be seen that R<sup>1</sup> can be aromatic, alkyl and H groups and R<sup>2</sup> can be aromatic, benzyl, allyl and alkyl groups and the yields range from 53% to 85%. However, with a carbon-carbon bond in the R<sup>2</sup> substituent, the reaction afforded 2,3-allenol **2c** in 42% yield together with an unidentified product (Entry 3, Table 2)

In conclusion, we have observed a dramatic solvent effect in the reduction reaction of 2,3-allenoates using DIBAL-H as the reductant. So far the reason for this is not clear yet. With the convenient synthesis of 2,3-allenoates,<sup>14-19</sup> this method provides a facile route to 2,3-allenols. With our recent advances in the resolution of racemic 2,3-allenoic acids, this method may provide a

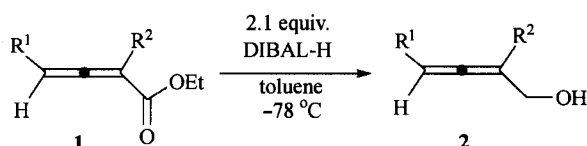
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Received February 7, 2002; revised and accepted April 16, 2002.

Project supported by the Major State Basic Research Development Program (No. G2000077500), the National Natural Science Foundation of China, and Shanghai Municipal Committee of Science and Technology.

**Table 1** Reduction of ethyl 2-methyl-4-phenyl-2,3-butadienoates with DIBAL-H

Entry	Solvent for DIBAL-H	DIBAL-H (equiv.)	Solvent	Temp. (°C)	Time (h)	Yield (%)
1	cyclohexane	4.0	–	r. t.	1.5	complicated
2	cyclohexane	2.0	ether	–78	3.0	15
3	cyclohexane	3.0	ether	–90 – –140	3.5	complicated
4	toluene	2.1	toluene	–78	5.0	83

**Table 2** Synthesis of substituted 2,3-allenols via the reduction of 2,3-allenoates with DIBAL-H

Entry	1		Time (h)	Yield of 2 (%)	
	R <sup>1</sup>	R <sup>2</sup>			
1	Ph	Me	(1a)	5	83 (2a)
2	C <sub>6</sub> H <sub>13</sub>	Me	(1b)	3	71 (2b)
3	Ph	Allyl	(1c)	6	42 (2c) <sup>a</sup>
4	C <sub>4</sub> H <sub>9</sub>	Me	(1d)	2	76 (2d)
5	1-Naphthyl	Me	(1e)	5	57 (2e)
6	H	Bn	(1f)	3	85 (2f)
7	H	C <sub>3</sub> H <sub>7</sub>	(1g)	3	53 (2g)
8	C <sub>3</sub> H <sub>7</sub>	Me	(1h)	3	63 (2h)

<sup>a</sup> An unknown product was also formed.

facile synthesis of optically active 2,3-allenols with the axial chirality.<sup>20</sup>

## Experimental

The starting materials 2,3-allenoates **1a**–**1h** were prepared according to the known procedure.<sup>14–19</sup> **1c** and **1f** are new compounds. The spectral data are listed as follows:

Ethyl 2-allyl-4-phenylbuta-2,3-dienoate (**1c**)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.16–7.27 (m, 5H), 6.47 (t,  $J$  = 3.0 Hz, 1H), 5.75–5.84 (m, 1H), 4.95–5.10 (m, 2H), 4.09–4.17 (m, 2H), 3.03–3.08 (m, 2H), 1.17 (t,  $J$  = 6.9 Hz, 3H); <sup>13</sup>C NMR

(75.4 MHz, CDCl<sub>3</sub>)  $\delta$ : 212.58, 166.55, 135.01, 132.55, 129.05 (2C), 128.00, 127.53 (2C), 116.90, 103.23, 98.87, 61.46, 33.70, 14.52; IR (neat)  $\nu$ : 1945, 1713, 1256 cm<sup>–1</sup>; MS  $m/z$  (%): 228 (M<sup>+</sup>, 16.47), 155 (100); HRMS calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub> 228.1150, found 228.1135.

Ethyl 2-benzylbuta-2,3-dienoate (**1f**) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.20–7.30 (m, 5H), 5.11 (t,  $J$  = 2.5 Hz, 2H), 4.20 (q,  $J$  = 7.2 Hz, 2H), 3.59 (t,  $J$  = 2.5 Hz, 2H), 1.28 (t,  $J$  = 6.9 Hz, 3H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$ : 214.65, 167.10, 139.31, 129.15 (2C), 128.52 (2C), 126.60, 100.53, 79.49, 61.40, 35.14, 14.48; MS  $m/z$  (%): 202 (M<sup>+</sup>, 2.27), 129 (100); IR (neat)  $\nu$ : 1967, 1942, 1712, 1602, 1259 cm<sup>–1</sup>; HRMS calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub> 202.0994, found 202.0996.

### Synthesis of 2-methyl-4-phenylbuta-2,3-dienol (**2a**)

#### Typical procedure

DIBAL-H (2.1 mL, 1.0 mol/L solution in toluene, 2.1 mmol) was added dropwise to a solution of **1a** (202 mg, 1.0 mmol) in dry toluene (1 mL). After the reaction was complete as monitored by TLC (eluent: hexane/ethyl acetate = 6:1,  $V:V$ ), the mixture was quenched with 0.5 mL of methanol, washed with 25 mL of aqueous HCl solution (5%). The organic layer was separated and the aqueous layer was extracted by ether. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 6:1,  $V:V$ ) to give 133 mg (83%) of **2a**:<sup>7a</sup> white solid, m. p.

57—58 °C (petroleum ether);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.21—7.32 (m, 5H), 6.27 (q,  $J = 2.7$  Hz, 1H), 4.14—4.17 (m, 2H), 2.01 (s, 1H), 1.85 (d,  $J = 2.7$  Hz, 3H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.07, 134.98, 128.86 (2C), 127.29, 127.02 (2C), 104.95, 97.27, 64.09, 15.69; IR (KBr)  $\nu$ : 3244, 1951  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 161 ( $\text{M}^+ + 1$ , 4.36), 160 ( $\text{M}^+$ , 33.18), 128 (100).

#### 2-Methyldeca-2,3-dien-1-ol (**2b**)

Starting from **1b** (210 mg, 1.0 mmol) in toluene (1 mL) and DIBAL-H in toluene (2.1 mL, 1.0 mol/L, 2.1 mmol) to afford 119 mg (71%) of **2b**: yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.25—5.28 (m, 1H), 3.98 (s, 2H), 2.00 (q,  $J = 6.7$  Hz, 2H), 1.69 (d,  $J = 2.7$  Hz, 3H), 1.50 (brs, 1H), 1.28—1.40 (m, 8H), 0.88 (t,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.25, 100.17, 93.96, 63.85, 31.60, 29.06, 29.04, 28.66, 22.57, 15.56, 14.00; IR (neat)  $\nu$ : 3333, 2927, 1968  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 168 ( $\text{M}^+$ , 3), 43 (100); HRMS calcd for  $\text{C}_{11}\text{H}_{20}\text{O}$  168.1514, found 168.1534.

#### 2-Allyl-4-phenylbuta-2,3-dien-1-ol (**2c**)

Starting from **1c** (228 mg, 1.0 mmol) in toluene (1 mL) and DIBAL-H in toluene (2.1 mL, 1.0 mol/L, 2.1 mmol) to afford 75 mg (42%) of **2c**: yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.22—7.34 (m, 5H), 6.35—6.37 (m, 1H), 5.87—5.96 (m, 1H), 5.20 (d,  $J = 17.0$  Hz, 1H), 5.10 (d,  $J = 9.0$  Hz, 1H), 4.19—4.22 (m, 2H), 2.95 (d,  $J = 6.6$  Hz, 2H), 1.95 (brs, 1H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.52, 135.32, 134.82, 128.92 (2C), 127.39 (2C), 126.99, 116.93, 108.17, 98.24, 62.96, 34.55; IR (neat)  $\nu$ : 3352, 2926, 1952  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 186 ( $\text{M}^+$ , 31.68), 187 ( $\text{M}^+ + 1$ , 4.67), 155 (100); HRMS calcd for  $\text{C}_{13}\text{H}_{14}\text{O}$  186.1044, found 186.1013.

#### 2-Methylocta-2,3-dien-1-ol (**2d**)<sup>7b</sup>

Starting from **1d** (151 mg, 0.83 mmol) and DIBAL in toluene (2.1 mL, 1.0 mol/L, 2.1 mmol) to afford 88 mg (76%) of **2d**: yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.26—5.28 (m, 1H), 3.98 (s, 2H), 2.00

(q,  $J = 6.9$  Hz, 2H), 1.69 (d,  $J = 2.7$  Hz, 3H), 1.50 (brs, 1H), 1.32—1.39 (m, 4H), 0.89 (t,  $J = 5.4$  Hz, 3H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.09, 100.35, 94.21, 63.81, 31.26, 28.77, 22.07, 15.70, 13.85; IR (neat)  $\nu$ : 3332, 2928, 1968, 1012  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 140 ( $\text{M}^+$ , 0.34), 98 (100), 107 (11.61), 83 (77.21).

#### 2-Methyl-4-(1'-naphthyl)buta-2,3-dien-1-ol (**2e**)

Starting from **1e** (133 mg, 0.5 mmol) and DIBAL in toluene (1.08 mL, 1.0 mol/L, 1.08 mmol) to afford 65 mg (57%) of **2e**: white solid, m. p.: 56—57 °C (petroleum ether);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.23 (d,  $J = 9.0$  Hz, 1H), 7.87 (d,  $J = 9.6$  Hz, 1H), 7.75 (d,  $J = 8.4$  Hz, 1H), 7.42—7.57 (m, 4H), 6.96—6.98 (m, 1H), 4.20—4.22 (m, 2H), 1.93 (d,  $J = 2.7$  Hz, 3H), 1.85 (brs, 1H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.75, 134.14, 131.22, 131.04, 128.93, 127.87, 126.35, 125.98, 125.84, 125.72, 123.78, 103.65, 93.82, 64.23, 15.80; IR (KBr)  $\nu$ : 3354, 2923, 1954, 1013, 790, 774  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 210 ( $\text{M}^+$ , 17.88), 192 (100), 178 (93.45), 152 (60.64); HRMS calcd for  $\text{C}_{15}\text{H}_{14}\text{O}$  210.1045, found 210.1015.

#### 2-Benzylbuta-2,3-dien-1-ol (**2f**)<sup>21</sup>

Starting from **1f** (5.05 g, 25 mmol) in toluene (70 mL) and DIBAL-H in toluene (52.5 mL, 1.0 mol/L, 52.5 mmol) to afford 3.42 g (85%) of **2f**: yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.05—7.50 (m, 5H), 4.65—5.05 (m, 2H), 4.03 (s, 2H), 3.39 (s, 2H), 1.70 (brs, 1H); IR (neat)  $\nu$ : 3347, 2912, 1951, 1599, 1491  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 160 ( $\text{M}^+$ , 59), 115 (100).

#### 2-Propylbuta-2,3-dien-1-ol (**2g**)<sup>7b</sup>

Starting from **1g** (7.70 g, 50 mmol) in toluene (150 mL) and DIBAL in toluene (2.1 equiv.) to afford 2.94 g (53%) of **2g**: yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.71—4.98 (m, 2H), 4.02—4.04 (m, 2H), 1.82—2.09 (m, 2H), 1.57 (brs, 1H), 1.32—1.55 (m, 2H), 0.98 (t,  $J = 7.3$  Hz, 3H); IR (neat)  $\nu$ : 3387, 2962, 1958  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 112 ( $\text{M}^+$ , 4), 95 (100).

**2-Methylhepta-2,3-dien-1-ol (2h)<sup>8,9</sup>**

Starting from **1h** (2.60 g, 16.8 mmol) to afford 1.34 g (63 %) of **2h**: yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 5.19—5.31 (m, 1H), 3.98 (s, 2H), 1.98 (q, *J* = 7.08 Hz, 2H), 1.70 (d, *J* = 2.9 Hz, 3H), 1.56 (brs, 1H), 1.31—1.54 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); IR (neat) ν: 3317, 2959, 1967 cm<sup>-1</sup>; MS *m/z* (%): 126 (M<sup>+</sup>, 7), 84 (100).

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(E0202076 PAN, B. F.; DONG, L. J.)