

# Chloroprene as a Source of Fine Chemicals: Palladium-Catalyzed Synthesis of Terminal Allenes

Masamichi Ogasawara, Hisashi Ikeda, Takashi Nagano, and Tamio Hayashi\*  
*Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo,  
Kyoto 606-8502, Japan*

## Supporting Data

**General.** All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. Tetrahydrofuran was distilled from sodium benzophenone-ketyl under nitrogen prior to use. Dpbp,<sup>1</sup> DPEphos,<sup>2</sup> [PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub>,<sup>3</sup> Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>,<sup>4</sup> and PhCH=CCl<sub>2</sub><sup>5</sup> were prepared by reported methods. (Z)-2-Chloro-1-phenyl-1,3-butadiene **5** was prepared from PhCH=CCl<sub>2</sub> and CH<sub>2</sub>=CHMgBr in 79% isolated yield according to a procedure of Minato and Tamao<sup>6</sup> and its NMR data were consistent with those reported previously.<sup>7</sup> NaOMe, KO<sup>t</sup>Bu, MeCH(COOEt)(COMe), and CH<sub>2</sub>(COOMe)<sub>2</sub> were purchased from Wako Pure Chemical Industries and used as received. MeCH(COOMe)<sub>2</sub> and (CH<sub>2</sub>=CHCH<sub>2</sub>)CH(COOMe)<sub>2</sub> were purchased from Aldrich Chemical Co. and used as received. HN(COO<sup>t</sup>Bu)<sub>2</sub> was purchased from Tokyo Chemical Industry and used without further purification. Chloroprene (50% v/v in toluene with 0.5% of catechol) was a generous gift from Denki Kagaku Kogyo Co. Ltd. and used after distillation. The distilled chloroprene contained ca. 10 mol% of toluene (checked by NMR) but used for the following reactions without further purification. Reaction progress was monitored by analytical TLC using 0.25 mm Merck F-254 silica gel glass plates. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (<sup>1</sup>H, 500 MHz; <sup>13</sup>C, 125 MHz). <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm downfield of internal tetramethylsilane.

**Palladium-Catalyzed Synthesis of Allenes.** The reaction conditions and results are summarized in Table 1. A typical procedure is given for preparation of **3a**. The characterization data of the products are listed below.

**Dimethyl 2-(buta-2,3-dienyl)-2-methylpropane-1,3-dioate (3a).** To a mixture of Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (161 mg, 156  $\mu$ mol), DPEphos (170 mg, 316  $\mu$ mol), MeCH(COOMe)<sub>2</sub> (**2a**, 850 mg, 5.82 mmol), and NaOMe (345 mg, 639 mmol) in THF (10 mL) was added chloroprene **1** (with ca. 10% of toluene; ca. 3.0 g, ca. 30 mmol) by means of syringe under nitrogen. The mixture was warmed to 70 °C (bath temp.) and refluxed for 3 h. The mixture was diluted with hexane (ca. 100 mL) and the precipitate was removed by filtration. The mother liquor was concentrated using a rotary evaporator and the residue was passed through a short pad of silica gel using ether as eluent. Concentration of the solution followed by vacuum transfer of the residue gave the terminal allene **3a** as colorless liquid. Yield: 1.08 g (5.45 mmol, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.44 (s, 3H), 2.58 (dt, *J* = 7.9 and 2.4 Hz, 2H), 3.73 (s, 6H), 4.67 (dt, *J* = 6.7 and 2.4 Hz, 2H), 5.00 (tt, *J* = 7.9 and 6.7 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  19.78, 35.27, 52.52, 53.97, 74.55, 84.51, 172.19, 210.22. Anal. Calcd for C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>: C, 60.59; H, 7.12. Found: C, 60.62; H, 7.13.

**Dimethyl 2-(buta-2,3-dienyl)propane-1,3-dioate (3b).** <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.60 (ddt, *J* = 7.4, 6.7, and 3.1 Hz, 2H), 3.51 (t, *J* = 7.4 Hz, 1H), 3.74 (s, 6H), 4.72 (dt, *J* =

6.7 and 3.1 Hz, 2H), 5.14 (quint,  $J = 6.7$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  27.40, 51.27, 52.53, 76.23, 86.63, 169.24, 208.72. Anal. Calcd for  $\text{C}_9\text{H}_{12}\text{O}_4$ : C, 58.69; H, 6.57. Found: C, 58.78; H, 6.86.

**Dimethyl 2,2-bis(buta-2,3-dienyl)propane-1,3-dioate (3b').**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.65 (dt,  $J = 8.1$  and  $2.4$  Hz, 4H), 3.73 (s, 6H), 4.67 (dt,  $J = 6.6$  and  $2.4$  Hz, 4H), 4.94 (tt,  $J = 8.1$  and  $6.6$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  31.96, 52.47, 57.91, 74.66, 84.10, 170.94, 210.13. Anal. Calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_4$ : C, 66.09; H, 6.83. Found: C, 65.98; H, 6.82.

**Dimethyl 2-(2-propenyl)-2-(buta-2,3-dienyl)propane-1,3-dioate (3c).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.61 (dt,  $J = 7.9$  and  $2.4$  Hz, 2H), 2.69 (dt,  $J = 7.4$  and  $1.1$  Hz, 2H), 3.72 (s, 6H), 4.66 (dt,  $J = 6.6$  and  $2.4$  Hz, 2H), 4.95 (tt,  $J = 7.9$  and  $6.6$  Hz, 1H), 5.09-5.14 (m, 2H), 5.65 (ddt,  $J = 16.7$ ,  $10.3$ , and  $7.4$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  31.94, 36.90, 52.39, 57.93, 74.63, 84.17, 119.33, 132.27, 171.04, 210.15. Anal. Calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_4$ : C, 64.27; H, 7.19. Found: C, 64.32; H, 7.17.

**Ethyl 2-acetyl-2-methylhexa-4,5-dienoate (3d).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.27 (t,  $J = 7.1$  Hz, 3H), 1.37 (s, 3H), 2.16 (s, 3H), 2.49 (ddt,  $J = 14.2$ ,  $8.2$ , and  $2.4$  Hz, 1H), 2.60 (ddt,  $J = 14.2$ ,  $7.6$ , and  $2.8$  Hz), 4.19 (dq,  $J = 10.8$  and  $7.1$  Hz, 1H), 4.21 (dq,  $J = 10.8$  and  $7.1$  Hz, 1H), 4.66 (ddd,  $J = 6.7$ ,  $2.8$ , and  $2.4$  Hz, 2H), 4.97 (ddt,  $J = 8.2$ ,  $7.6$ , and  $6.7$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.09, 18.89, 26.29, 34.42, 59.79, 61.43, 74.68, 84.63, 172.41, 205.00, 210.06. Anal. Calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_3$ : C, 67.32; H, 8.22. Found: C, 67.05; H, 8.06.

**Di-tert-butyl N-(buta-2,3-dienyl)iminodicarboxylate (3e).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.51 (s, 18H), 4.18 (dt,  $J = 6.2$  and  $2.9$  Hz, 2H), 4.78 (dt,  $J = 6.6$  and  $2.9$  Hz, 1H), 5.21 (tt,  $J = 6.6$  and  $6.2$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  28.12, 44.73, 76.64, 82.35, 87.58, 152.21, 208.82. Anal. Calcd for  $\text{C}_{14}\text{H}_{23}\text{O}_4\text{N}$ : C, 62.43; H, 8.61; N, 5.20. Found: C, 62.28; H, 8.37; N, 5.12.

**tert-Butyl 2-(tert-butoxycarbonylamino)hexa-4,5-dienoate (3f).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.45 (s, 9H), 1.47 (s, 9H), 2.44 (br, 1H), 2.51 (br, 1H), 4.28 (br, 1H), 4.70 (d,  $J = 5.6$  Hz, 2H), 5.01 (m, 1H), 5.13 (br d,  $J = 7.0$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  28.02, 28.36, 32.15, 53.62, 75.12, 79.69, 82.01, 84.59, 155.19, 170.96, 209.68. Anal. Calcd for  $\text{C}_{15}\text{H}_{25}\text{O}_4\text{N}$ : C, 63.58; H, 8.89; N, 4.94. Found: C, 63.54; H, 8.83; N, 4.83.

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