The Baylis-Hillman Reaction: One-Pot Facile Synthesis of 2,4-Functionalized 1,4-Pentadienes

Deevi Basavaiah*, Duddu S. Sharada, Nagaswamy Kumaragurubaran and
Ravi Mallikarjuna Reddy

School of Chemistry, University of Hyderabad, Hyderabad-500 046, India

Supporting Information

Table of Contents

Characterization data for compounds 7-9, 12, 13, 15-18	S2-S4
¹³ C NMR spectra of the compounds 6-18	S5-S17

Characterization data for compounds 7, 8, 12, 13, 15-18.**Ethyl 2,4-dimethylidene-5-oxohexanoate (7):**

Colorless liquid. Yield: 78%; IR (neat): 1718, 1680, 1631 cm^{-1} ; ^1H NMR: δ 1.28 (t, 3H, $J=7.0$ Hz), 2.35 (s, 3H), 3.29 (s, 2H), 4.19 (q, 2H, $J=7.0$ Hz), 5.55 (d, 1H, $J=1.4$ Hz), 5.81 (s, 1H), 6.10 (s, 1H), 6.24 (s, 1H); ^{13}C NMR: δ 13.96, 25.55, 32.37, 60.51, 126.25, 126.41, 138.25, 146.30, 166.43, 198.41; Anal. calcd for $\text{C}_{10}\text{H}_{14}\text{O}_3$: C, 65.92; H, 7.74; found: C, 65.69; H, 7.70.

***n* Butyl 2,4-dimethylidene-5-oxohexanoate (8):**

Colorless liquid. Yield: 84%; IR (neat): 1718, 1680, 1631 cm^{-1} ; ^1H NMR: δ 0.93 (t, 3H, $J=7.1$ Hz), 1.24-1.50 (m, 2H), 1.53-1.73 (m, 2H), 2.34 (s, 3H), 3.29 (s, 2H), 4.13 (t, 2H, $J=6.8$ Hz), 5.55 (d, 1H, $J=2.0$ Hz), 5.80 (d, 1H, $J=1.6$ Hz), 6.10 (s, 1H), 6.24 (s, 1H); ^{13}C NMR: δ 13.47, 19.04, 25.55, 30.55, 32.45, 64.45, 126.06, 126.41, 138.34, 146.44, 166.53, 198.35; Anal. calcd for $\text{C}_{12}\text{H}_{18}\text{O}_3$: C, 68.55; H, 8.63; found: C, 68.29; H, 8.68.

Methyl 2,5-dimethylidene-6-oxoheptanoate (9):

Colorless liquid. Yield: 77%; IR (neat): 1724, 1680, 1631 cm^{-1} ; ^1H NMR: δ 1.10 (t, 3H, $J=7.2$ Hz), 2.72 (q, 2H, $J=7.2$ Hz), 3.31 (s, 2H), 3.74 (s, 3H), 5.57 (d, 1H, $J=1.2$ Hz), 5.75 (d, 1H, $J=1.2$ Hz), 6.09 (s, 1H), 6.23 (s, 1H); ^{13}C NMR: δ 8.14, 30.69, 32.75, 51.64, 125.02, 126.70, 137.98, 145.67, 166.93, 201.17; Anal. calcd for $\text{C}_{10}\text{H}_{14}\text{O}_3$: C, 65.92; H, 7.74; found: C, 66.22; H, 7.71.

Ethyl 2-methylidene-4-cyanopent-4-enoate (12):

Colorless liquid. Yield: 83%; IR (neat): 2226, 1718, 1633 cm^{-1} ; ^1H NMR: δ 1.31 (t, 3H, $J=7.3$ Hz), 3.25 (s, 2H), 4.22 (q, 2H, $J=7.3$ Hz), 5.75 (s, 1H), 5.83 (s, 1H), 5.96 (s, 1H), 6.38 (s, 1H); ^{13}C NMR: δ 13.92, 36.49, 60.92, 117.92, 120.38, 128.02, 132.08, 135.51, 165.51; Anal. calcd for $\text{C}_9\text{H}_{11}\text{NO}_2$: C, 65.44; H, 6.71; N, 8.48; found: C, 65.17; H, 6.67; N, 8.53.

***n*-Butyl 2-methylidene-4-cyanopent-4-enoate (13):**

Colorless liquid. Yield: 85%; IR (neat): 2226, 1718, 1633 cm^{-1} ; ^1H NMR: δ 0.94 (t, 3H, 7.3 Hz), 1.24-1.52 (m, 2H), 1.54-1.77 (m, 2H), 3.25 (s, 2H), 4.17 (t, 2H, $J=6.9$ Hz), 5.75 (s, 1H), 5.83 (s, 1H), 5.96 (s, 1H), 6.38 (s, 1H); ^{13}C NMR: δ 13.47, 19.04, 30.50, 36.57, 64.85, 117.91, 120.54, 127.98, 131.93, 135.62, 165.61; MS (m/z): 193 (M^+); Anal. calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_2$: C, 68.37; H, 7.82; N, 7.25; found: C, 68.13; H, 7.86; N, 7.19.

2-Ethoxycarbonyl-4-methoxycarbonylpenta-1,4-diene (15):

Colorless liquid. Yield: 84%; IR (neat): 1722, 1631 cm^{-1} ; ^1H NMR: δ 1.28 (t, 3H, $J=7.3$ Hz), 3.33 (s, 2H), 3.75 (s, 3H), 4.20 (q, 2H, $J=7.3$ Hz), 5.59 (m, 2H), 6.25 (s, 2H); ^{13}C NMR: δ 14.03, 33.68, 51.73, 60.64, 126.38, 126.62, 137.83, 138.04, 166.42, 166.94; Anal. calcd for $\text{C}_{10}\text{H}_{14}\text{O}_4$: C, 60.59; H, 7.12; found: C, 60.42; H, 7.15.

2-(*n*-Butoxycarbonyl)-4-methoxycarbonylpenta-1,4-diene (16):

Colorless liquid. Yield: 85%; IR (neat): 1722, 1631 cm^{-1} ; ^1H NMR: δ 0.94 (t, 3H, $J=7.0$ Hz), 1.24-1.52 (m, 2H), 1.54-1.75 (m, 2H), 3.33 (s, 2H), 3.75 (s, 3H), 4.15 (t, 2H, $J=6.4$ Hz).

Hz), 5.59 (m, 2H), 6.26 (s, 2H); ^{13}C NMR: δ 13.51, 19.06, 30.55, 33.66, 51.67, 64.50, 126.32, 126.49, 137.84, 138.06, 166.45, 166.88; MS (m/z): 226 (M^+); Anal. calcd for $\text{C}_{12}\text{H}_{18}\text{O}_4$: C, 63.70; H, 8.02; found: C, 63.62; H, 8.04.

2-Ethoxycarbonyl-4-methoxycarbonylpenta-1,4-diene (15):

[from ethyl acrylate and methyl 2-(bromomethyl)prop-2-enoate (5a)]

Colorless liquid. Yield: 81%. Spectral data (IR, ^1H and ^{13}C NMR) of this molecule are identical with that of the molecule prepared from ethyl 2-(bromomethyl)prop-2-enoate (**5b**) and methyl acrylate.

2,4-Diethoxycarbonylpenta-1,4-diene (17):

Colorless liquid. Yield: 82%; IR (neat): 1720, 1631 cm^{-1} ; ^1H NMR: δ 1.28 (t, 6H, $J=7.2$ Hz), 3.33 (s, 2H), 4.20 (q, 4H, $J=7.2$ Hz), 5.57 (s, 2H), 6.24 (s, 2H); ^{13}C NMR: δ 14.02, 33.64, 60.60, 126.29, 138.13, 166.44; Anal. calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4$: C, 62.25; H, 7.60; found: C, 62.48; H, 7.56.

2-(*n*-Butoxycarbonyl)-4-ethoxycarbonylpenta-1,4-diene (18):

Colorless liquid. Yield: 78%; IR (neat): 1720, 1633 cm^{-1} ; ^1H NMR: δ 0.93 (t, 3H, $J=7.3$ Hz), 1.20-1.52 (m, 5H), 1.54-1.76 (m, 2H), 3.33 (s, 2H), 4.09-4.29 (m, 4H), 5.58 (s, 2H), 6.25 (s, 2H); ^{13}C NMR: δ 13.56, 14.06, 19.11, 30.60, 33.69, 60.63, 64.54, 126.31, 138.18, 166.47, 166.53; Anal. calcd for $\text{C}_{13}\text{H}_{20}\text{O}_4$: C, 64.98; H, 8.39; found: C, 65.14; H, 8.35.