Supporting Information

Novel Synthesis of Conjugated Dienes Directly Attached to a Quaternary Carbon Center via Pd(0)-Catalyzed Deconjugative Allylation of Alkenylidenemalonates

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General.
All manipulations were performed under an argon atmosphere unless otherwise mentioned. All solvents and reagents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70-230 mesh), and flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh).
Preparation of Malonates.

Diethyl ethylidenemalonate 1a \([17041-60-0]\), dimethyl 2-((\(E\))-but-2-enyldiene)malonate 4a, and dimethyl 2-((\(E\))-pent-2-enyldiene)malonate 4b were prepared by Knoevenagel condensation.\(^1\)

**Dimethyl 2-((\(E\))-but-2-enyldiene)-malonate (4a)**

IR (neat) 1723, 1639, 1602, 1436 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.92 (dd, \(J = 7.1, 1.6\) Hz, 3 H), 3.79 (s, 3 H), 3.85 (s, 3 H), 6.35 (dq, \(J = 15.1, 7.1\) Hz, 1 H), 6.54 (ddq, \(J = 15.1, 11.5, 1.6\) Hz, 1 H), 7.37 (d, \(J = 11.5\) Hz, 1 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 19.4, 52.4, 52.4, 122.4, 127.0, 144.8, 146.0, 164.9, 165.5; LRMS (EI) \(m/z\) 184 (M\(^+\)), 169, 152, 137, 124, 121, 109, 93, 79, 65. Anal. Calcd for C\(_9\)H\(_{12}\)O\(_4\): C, 58.69; H, 6.57. Found: C, 58.90; H, 6.50.

**Diethyl 2-((\(E\))-pent-2-enyldiene)malonate (4b)**

IR (neat) 1724, 1636, 1436 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.07 (t, \(J = 7.0\) Hz, 3 H), 2.25 (qdd, \(J = 7.0, 7.0, 1.3\) Hz, 2 H), 3.79 (s, 3 H), 3.85 (s, 3 H), 6.38 (dt, \(J = 15.3, 7.0\) Hz, 1 H), 6.52 (ddt, \(J = 15.3, 11.3, 1.3\) Hz, 1 H), 7.38 (d, \(J = 11.3\) Hz, 1 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 12.9, 26.7, 52.4, 52.4, 112.6, 124.7, 146.3, 151.1, 164.9, 165.5; LRMS (EI) \(m/z\) 198 (M\(^+\)), 169, 138, 123, 110, 107, 79; HRMS (EI) calcd for C\(_{10}\)H\(_{14}\)O\(_4\): 198.0892, found 198.0879. Anal. Calcd for C\(_{10}\)H\(_{14}\)O\(_4\): C, 60.59; H, 7.12. Found: C, 60.79; H, 7.09.

Preparation of Allylic Acetates.

Allylic acetates 5b, 5c and 5e are known in the literature and were prepared by reaction of the corresponding alcohols with acetic anhydride and pyridine [5b,\(^2\) 5c,\(^2\) 5e\(^3\)]. Allylic acetate 5d was also prepared from (\(E\))-4-(tert-butyldimethylsilyl)oxybut-2-en-1-ol\(^4\) by the similar manner.

**\((E)\)-Acetic acid 4-(tert-butyldimethylsilyloxy)but-2-enyl ester (5d).**

IR (neat) 1744, 1252 cm\(^{-1}\); \(^1\)H NMR (400 MHz, benzene-\(d_6\)) \(\delta\) 0.01 (s, 6 H), 0.95 (s, 9 H), 1.64 (s, 3 H), 3.93 (m, 1 H), 4.46 (dd, \(J = 6.2, 1.1\) Hz, 2 H), 5.63 (dtt, \(J = 15.5, 4.4, 1.1\) Hz, 1 H), 5.77-5.85 (m, 1 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) -4.9, 18.6, 21.2, 26.1, 62.9, 64.5, 123.4, 133.9, 170.4; LRMS (EI) \(m/z\) 185 (M\(^+\)-OAc), 149, 135, 127, 117; HRMS (EI) calcd for C\(_{10}\)H\(_{21}\)O\(_4\)Si (M\(^+\)-OAc) 185.1362, found 185.1375. Anal. Calcd for C\(_{12}\)H\(_{25}\)O\(_3\)Si: C, 58.97; H, 9.90. Found: C, 58.83; H, 9.72.

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\(^1\) Jones, G. *Org. React.* 1967, 15, 204.
Determination of the Stereochemistry of \( \text{6ba} \) (Scheme 3).

The reaction of \( \text{4b} \) with \( \text{5a} \) gave the product \( \text{6ba} \) as an inseparable mixture of 3E-isomer and 3Z-isomer (3E/3Z=1/2), whose ratio was estimated by \(^1\)H-NMR spectrum of \( \text{6ba} \). In order to separate the mixture and to elucidate the stereochemistry of each product, conversion of \( \text{6ba} \) into \( \text{Z-7} \) and \( \text{E-7} \) was carried out as follows:

To a suspension of LiAlH\(_4\) (29 mg, 0.75 mmol) in Et\(_2\)O (1.0 mL) was added a solution of \( \text{6ba} \) (60 mg, 0.25 mmol) in Et\(_2\)O (1 mL) at 0 °C, and the mixture was stirred at room temperature for 5 hours. To the mixture was added Na\(_2\)SO\(_4\)·10H\(_2\)O, and the mixture was stirred for several hours. The mixture was filtered through a pad of Celite, and the filtrate was concentrated. The residual crude material was treated with Ac\(_2\)O (0.07 mL, 0.75 mmol) and pyridine (1 mL) at room temperature for overnight. After usual work-up, the residue was purified by column chromatography on AgNO\(_3\)-coated silica gel (CH\(_2\)Cl\(_2\)·Et\(_2\)O, 5/1) to afford \( \text{Z-7} \) (39 mg, 57%) and \( \text{E-7} \) (18 mg, 27%).

\((5\text{E},7\text{Z})\)-4,4-Diacetoxymethylnona-1,5,7-triene ((Z)-7).

IR (neat) 1744, 1439, 1377, 1234 cm\(^{-1}\); \(^1\)H NMR (400 MHz, acetonitrile-\(d_3\)) \(\delta\) 1.73 (dd, \(J = 6.9, 1.0\) Hz, 3 H), 1.98 (s, 6 H), 2.28 (ddd, \(J = 7.2, 1.2, 1.2\) Hz, 2 H), 4.02 (d, \(J = 11.1\) Hz, 2 H), 4.05 (d, \(J = 11.1\) Hz, 2 H), 5.04-5.11 (m, 2 H), 5.43-5.52 (m, 1 H), 5.57 (d, \(J = 16.0\) Hz, 1 H), 5.76 (ddd, \(J = 16.7, 10.5, 7.2\) Hz, 1 H), 5.96 (ddq, \(J = 10.7, 10.7, 1.0\) Hz, 1 H), 6.42 (ddd, \(J = 16.0, 10.7, 1.0\) Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.8, 21.2, 38.2, 42.9, 66.1, 118.7, 125.8, 126.3, 129.1, 132.5, 132.8, 170.6; LRMS (EI) \(m/z\) 266 (M\(^+\)), 225, 206, 183, 165, 123, 105; HRMS (EI) calcd for C\(_{15}\)H\(_{22}\)O\(_4\) 266.1518, found 266.1507.

Anal. Calcd for C\(_{15}\)H\(_{22}\)O\(_4\): C, 67.64; H, 8.33. Found: C, 67.46; H, 8.41.

\((5\text{E},7\text{E})\)-4,4-Diacetoxymethylnona-1,5,7-triene ((E)-7).

IR (neat) 1743, 1438, 1378, 1232 cm\(^{-1}\); \(^1\)H NMR (400 MHz, benzene-\(d_6\)) \(\delta\) 1.55 (d, \(J = 6.9\) Hz, 3 H), 1.63 (s, 6 H), 2.11 (dd, \(J = 7.3, 0.9\) Hz, 2 H), 4.10 (d, \(J = 10.4\) Hz, 2 H), 4.17 (d, \(J = 10.4\) Hz, 2 H), 4.95-4.99 (m, 2 H), 5.34 (d, \(J = 15.7\) Hz, 1 H), 5.45 (dq, \(J = 15.3, 6.9\) Hz, 1 H), 5.59-5.70 (m, 1 H), 5.89-5.96 (m, 1 H), 6.02 (dd, \(J = 15.7, 10.3\) Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 18.3, 21.1, 38.1, 42.6, 66.1, 118.5, 129.3, 130.3, 130.9, 131.2, 132.5, 170.5; LRMS (EI) \(m/z\) 266 (M\(^+\)), 225, 206, 183, 165, 123, 105; HRMS (EI) calcd for C\(_{15}\)H\(_{22}\)O\(_4\) 266.1518, found 266.1506. Anal. Calcd for C\(_{15}\)H\(_{22}\)O\(_4\): C, 67.64; H, 8.33. Found: C, 67.53; H, 8.32.