Supporting Informations

Decarbopalladations of π -Allylpalladium Intermediates Formed from Palladium-Catalyzed Arylations of 3-Allen-1-ols

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General

All reactions were carried out under an atmosphere of dry argon. Commercial reagents were used as received without further purification. All products were purified by flash column chromatography using silica gel 60 (70-230 mesh, Merck) and/or by a Young-Lin M930 HPLC employing a Nova-Pak silica preparative column and a UV detector. The products were identified with ^1H and ^{13}C NMR spectral data obtained from a Varian Mercury 400 MHz NMR spectrometer using tetramethylsilane as an internal standard and the new compounds were further characterized with FT-IR and HRMS.

Typical experimental procedure for the palladium-catalyzed arylation of 2,2-dimethyl-1-phenyl-3,4-pentadien-1-ol (**4a**)

In a 5 mL test tube were placed 2,2-dimethyl-1-phenyl-3,4-pentadien-1-ol **1a** (56.5 mg, 0.30 mmol), tetrakis(triphenylphosphine)palladium(0) (10.6 mg, 0.0091 mmol), K_2CO_3 (64.8 mg, 0.46 mmol), and a magnetic stirring bar. To the test tube was added iodobenzene **2a** (63.5 mg, 0.31 mmol) in dry 1,4-dioxane (1.0 mL) via cannula at 0 °C under argon atmosphere. The resulting mixture was stirred

for 10 min at room temperature and for 6 h at refluxing temperature in a preheated oil bath. The reaction mixture was cooled to room temperature and quenched by some water. The crude reaction mixture was diluted with 7 mL of water followed by addition of 10 mL diethyl ether. The ether extracts were combined and washed with a small portion of brine, dried over MgSO_4 and concentrated under reduced pressure. The crude product was separated by flash column chromatography (SiO_2 , *n*-hexane) afforded the 2-methyl-4-phenyl-2,4-pentadiene **4a** (41.3mg, 87 %) as a colorless oil. IR (neat) 2970, 2912, 2362, 1609, 1492, 1447, 1376, 1061, 1028, 895, 774, 703, 461 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.70 (d, 3H, $J = 0.8$ Hz), 1.87 (d, 3H, $J = 1.2$ Hz), 5.05 (t, 1H, $J = 1.4$ Hz), 5.50 (d, 1H, $J = 1.6$ Hz), 5.93 (q, 1H, $J = 1.6$ Hz), 7.22-7.40 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.21, 141.20, 136.80, 128.03, 127.22, 126.44, 124.84, 114.19, 26.47, 19.79. HRMS calcd. for $\text{C}_{12}\text{H}_{14}$: 158.1096. found: 158.1083.

2-Methyl-4-(*p*-methoxyphenyl)-2,4-pentadiene (**4b**)

IR (neat) 2932, 1608, 1510, 1450, 1377, 1301, 1248, 1177, 1036, 890, 839, 565 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.71 (d, 3H, $J = 1.6$ Hz), 1.86 (d, 3H, $J = 1.2$ Hz), 3.80 (s, 3H), 4.96 (t, 1H, $J = 1.6$ Hz), 5.43 (d, 1H, $J = 2.0$ Hz), 5.90 (q, 1H, $J = 1.6$ Hz), 6.83 (d, 2H, $J = 8.8$ Hz), 7.32 (d, 2H, $J = 8.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 158.88, 144.48, 136.60, 133.72, 127.53, 125.03, 113.41, 112.53, 55.33, 26.43, 19.77. HRMS calcd. for $\text{C}_{13}\text{H}_{16}\text{O}$: 188.1201. found: 188.1210.

2-Methyl-4-(*p*-nitrophenyl)-2,4-pentadiene (**4c**)

IR (neat) 2973, 2933, 2365, 1654, 1594, 1517, 1446, 1343, 1110, 1062, 1013, 908, 860, 765, 712 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.68 (d, 3H, $J = 1.2$ Hz), 1.89 (d, 3H, $J = 1.2$ Hz), 5.24 (s, 1H), 5.63 (d, 1H, $J = 0.8$ Hz), 5.91 (q, 1H, $J = 1.2$ Hz), 7.52 (d, 2H, $J = 8.8$ Hz), 8.15 (d, 2H, $J = 8.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 147.75, 146.85, 143.63, 138.45, 127.18, 123.54, 123.44, 117.66,

26.44, 19.93. HRMS calcd. for $C_{12}H_{13}NO_2$: 203.0946. found: 203.0947.

2-Methyl-4-(*p*-tolyl)-2,4-pentadiene (4d)

IR (neat) 2969, 2925, 2363, 1608, 1511, 1448, 1376, 1185, 1061, 892, 834, 734 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, 3H, $J = 0.8$ Hz), 1.86 (d, 3H, $J = 1.6$ Hz), 2.34 (s, 3H), 5.00 (t, 1H, $J = 1.6$ Hz), 5.47 (d, 1H, $J = 2.0$ Hz), 5.91 (q, 1H, $J = 1.6$ Hz), 7.10 (d, 2H, $J = 8.4$ Hz), 7.28 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.97, 138.30, 136.95, 136.60, 128.72, 126.30, 124.98, 113.40, 26.45, 21.25, 19.79. HRMS calcd. for $C_{13}H_{16}$: 172.1252. found: 172.1263.

2-Methyl-4-(1-naphthyl)-2,4-pentadiene (4e)

IR (neat) 2928, 2361, 1648, 1505, 1454, 1059, 893, 799, 777, 640 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, 3H, $J = 0.4$ Hz), 1.79 (d, 3H, $J = 0.4$ Hz), 5.19 (d, 1H, $J = 2.4$ Hz), 5.40 (d, 1H, $J = 1.6$ Hz), 6.09 (q, 1H, $J = 1.2$ Hz), 7.29-8.00 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.93, 141.07, 135.75, 133.36, 131.47, 127.96, 127.18, 126.73, 125.93, 125.59, 125.49, 125.30, 118.21, 27.47, 19.23. HRMS calcd. for $C_{16}H_{16}$: 208.1252. found: 208.1256.

2-Methyl-4-(2-naphthyl)-2,4-pentadiene (4f)

IR (neat) 3056, 2910, 2362, 1606, 1505, 1446, 1133, 892, 858, 816, 749 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.73 (d, 3H, $J = 1.6$ Hz), 1.92 (d, 3H, $J = 1.6$ Hz), 5.15 (t, 1H, $J = 1.2$ Hz), 5.65 (d, 1H, J

= 1.2 Hz), 6.04 (q, 1H, J = 1.2 Hz), 7.39-7.83 (m, 7H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.08, 138.46, 137.05, 133.24, 132.67, 128.04, 127.55, 127.40, 125.90, 125.61, 125.32, 124.84, 124.71, 114.74, 26.51, 19.88. HRMS calcd. for $\text{C}_{16}\text{H}_{16}$: 208.1252. found: 208.1244.

2-Methyl-4-(*o*-tolyl)-2,4-pentadiene (4g)

4g

IR (neat) 3063, 3018, 2969, 2925, 1644, 1488, 1451, 1377, 1186, 1067, 1045, 983, 894, 768, 731, 620 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.42 (d, 3H, J = 1.2 Hz), 1.78 (d, 3H, 0.8 Hz), 2.23 (s, 3H), 4.98 (d, 1H, J = 2.8 Hz), 5.19 (d, 1H, J = 2.0 Hz), 5.90 (s, 1H, J = 1.2 Hz), 7.08-7.17 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.17, 142.65, 135.35, 135.23, 129.67, 128.69, 126.80, 125.99, 125.46, 116.85, 27.37, 19.98, 18.91. HRMS calcd. for $\text{C}_{13}\text{H}_{16}$: 172.1252. found: 172.1260.

2-(3,3-Dimethyl-1-butynyl)-3,3-dimethyl-5-*o*-tolyl-3,6-dihydro-2H-pyran (6g)

6g

IR (neat) 2967, 2929, 2868, 2362, 2244, 1667, 1493, 1461, 1362, 1328, 1266, 1198, 1115, 986, 947, 744 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.07 (s, 3H), 1.08 (s, 3H), 1.25 (s, 9H), 2.28 (s, 3H), 3.36 (ddd, 2H, J = 22.0, 16.4, 1.2 Hz), 4.27 (s, 1H), 4.65 (s, 1H), 7.09-7.18 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.52, 136.54, 135.58, 129.92, 129.50, 126.49, 125.73, 108.47, 97.33, 81.53, 73.84, 46.03, 32.50, 31.06, 27.65, 27.12, 24.61, 19.44. HRMS calcd. for $\text{C}_{20}\text{H}_{26}\text{O}$: 282.1984. found: 282.1986.

2-Phenyl-1,3-butadiene (7a)

7a

IR (neat) 2360, 2342, 1724, 1524, 1415, 680 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ , 5.19 (dd, 1H, J = 24.4, 0.8 Hz), 5.19 (d, 1H, J = 1.2 Hz), 5.24 (dd, 2H, J = 34.8, 0.8 Hz), 6.60 (dd, 1H, J = 17.2, 11.2 Hz), 7.26-7.35 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.06, 139.56, 137.98, 128.13, 127.97, 127.32, 117.03, 116.76.

References:

- (a) Suginome, M.; Nakamura, H.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4248. (b) Breu, J.; Hoecht, P.; Rohr, U.; Schatz, J.; Sauer, J. *Eur. J. Org. Chem.* **1998**, 2861. (c) Northrup, A. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 2458. (d) Jiang, P.; Gaspar, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 8622.

2-(*p*-Methoxyphenyl)-1,3-butadiene (7b)

IR (neat) 2836, 1610, 1511, 1463, 1287, 1247, 1178, 1034, 992, 896, 836, 583 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 3.81 (s, 3H), 5.15 (d, 1H, J = 1.2 Hz), 5.18 (s, 1H), 5.21 (d, 1H, J = 6.0 Hz), 5.22 (d, 1H, J = 2.0 Hz), 6.59 (dd, 1H, J = 17.6, 10.4 Hz), 6.87 (d, 2H, J = 8.8 Hz), 7.24 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 158.88, 147.46, 138.22, 132.00, 129.18, 116.84, 115.85, 113.43, 55.32. HRMS calcd. for $\text{C}_{11}\text{H}_{12}\text{O}$: 160.0888. found: 160.0874.

2-(*p*-Nitrophenyl)-1,3-butadiene (7c)

IR (neat) 2920, 2361, 2341, 1595, 1516, 1344, 1110, 997, 919, 853, 748, 699 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 5.12 (d, 1H, J = 17.2 Hz), 5.27 (d, 1H, J = 10.0 Hz), 5.28 (s, 1H), 5.42 (s, 1H), 6.61 (dd, 1H, J = 17.6, 11.0 Hz), 7.46 (d, 2H, J = 8.8 Hz), 8.20 (d, 2H, J = 8.8 Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 194.46, 146.31, 136.98, 129.00, 123.38, 118.79, 117.90, 94.44. HRMS calcd. for $\text{C}_{10}\text{H}_9\text{NO}_2$: 175.0633. found: 175.0625.

2-(1-Naphthyl)-1,3-butadiene (7e)

IR (neat) 3044, 2360, 1590, 1506, 1402, 1255, 987, 903, 801, 777 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 4.67 (d, 1H, $J = 17.2$ Hz), 5.11 (d, 1H, $J = 9.6$ Hz), 5.24 (s, 1H), 5.58 (s, 1H), 6.75 (dd, 1H, $J = 17.2, 10.8$ Hz), 7.29 (dd, 1H, $J = 7.2, 1.6$ Hz), 7.38-7.46 (m, 3H), 7.78-7.88 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.22, 138.96, 137.59, 133.34, 131.70, 127.94, 127.47, 126.48, 126.17, 125.57, 125.52, 125.17, 119.48, 117.60. HRMS calcd. for $\text{C}_{14}\text{H}_{12}$: 180.0939. found: 180.0926.

2,3-Dimethyl-4-phenyl-2,4-pentadiene (9a)

IR (neat) 3082, 2988, 2916, 2859, 1613, 1492, 1446, 1372, 1140, 1028, 898, 780, 711 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.68 (d, 3H, $J = 1.6$ Hz), 1.72 (d, 3H, $J = 1.2$ Hz), 1.79 (s, 3H), 4.94 (d, 1H, $J = 2.0$ Hz), 5.50 (d, 1H, $J = 1.6$ Hz), 7.20-7.36 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.91, 139.64, 129.51, 128.15, 127.98, 127.21, 126.17, 112.21, 22.09, 20.15, 19.33.

Reference: Nakayama, J.; Machida, H.; Saito, R.; Akimoto, K.; Hoshino, M. *Chem. Lett.* **1985**, 1173.

E/Z-2-Methyl-4-phenyl-2,4-hexadiene (9b)

IR (neat) 2968, 2912, 2857, 1492, 1442, 1376, 1073, 868, 750, 701 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) for *E*-isomer δ 1.51 (d, 3H, $J = 0.8$ Hz), 1.73 (dd, 3H, $J = 7.2, 1.2$ Hz), 1.88 (d, 3H, $J = 1.2$ Hz), 5.80 (p, 1H, $J = 1.2$ Hz), 5.93 (qd, 1H, $J = 7.2, 1.2$ Hz), 7.13-7.33 (m, 5H). ^1H NMR (400 MHz, CDCl_3) for *Z*-isomer δ 1.49 (s, 3H), 1.67 (d, 3H, 6.8 Hz), 1.77 (s, 3H), 5.62 (q, 1H, $J = 7.2$ Hz), 5.84 (p, 1H, $J = 1.2$ Hz), 7.13-7.33 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) for *E/Z* mixture δ 142.10, 140.47, 139.59, 138.36, 136.37, 133.40, 128.92, 127.97, 127.83, 127.59, 126.35, 126.24, 125.17,

123.81, 122.00, 26.93, 25.61, 19.84, 19.49, 15.64, 14.99.

Reference: Baldwin, J. E.; Bennett, P. A. R.; Forrest, A. K. *J. Chem. Soc., Chem. Commun.* **1987**, 250.

4a

4c

6g

7e

9a