Palladium-Catalyzed Cyclization Reaction of Allylic Bromides with 1,2-Dienyl Ketones. An Efficient Synthesis of 3-Allylic Polysubstituted Furans

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Supporting Information

Experimental Section

Allyl chloride and allyl bromide are commercially available and used as it is. 3-Bromo-2-phenyl-1-propene (**3c**),[1,2] cinnamyl bromide (**3d**),[3] 3-butyl-3,4-pentadien-2-one (**1a**),[4] 3-methyl-3,4-pentadien-2-one (**1b**),[4] 3-allyl-3,4-pentadien-2-one (**1c**),[4] 3,4-dodecadien-2-one (**1d**),[4] were prepared according to the published procedures. ^{1}H NMR spectra were measured using $CDCl_3$ as the solvent and Me_4Si as the internal standard. MS spectra (EI) were measured at a ionization voltage of 70 eV.

Reaction of 3-Butyl-3,4-pentadien-2-one with Allyl Chloride or Bromide (Table 1). To a solution of 1.0 mmol of 3-butyl-3,4-pentadien-2-one (**1a**) and allyl halide (**3**) (for the equivalents see Table 1) in acetonitrile (2 mL) were added 1 equiv of K_2CO_3 and 5 mol % of the catalyst. The reaction mixture was stirred at 25 ^{o}C for the time specified in **Table 1**. Upon the completion of the reaction as monitored by TLC (eluent: hexanes), the mixture was quenched with water and extracted with ether. Dring over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane) afforded 4-allyl-3-butyl-2-methylfuran **4a** and 3-butyl-2-methylfuran **5a**.

Reaction of 1-Substituted 1,2-Allenyl Ketones with Allyl Bromides (Table 2).

To a solution of 1.0 mmol of allyl bromide (**3**) and 1.5 equiv of 1,2-allenketone (**1**) in acetonitrile (2 mL) were added 1 equiv of K_2CO_3 and 5 mol % of $PdCl_2(PhCN)_2$. The reaction mixture was stirred at 25 ^oC for the time specified in **Table 2**. Upon the completion of the reaction as monitored by TLC (eluent: hexanes), the mixture was quenched with water and extracted with ether. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane) afforded polysubstituted furans **4**.

3-Butyl-2-methylfuran (5a):[5] liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (s, 1 H), 6.19 (s, 1 H), 2.30 (t, *J* = 7.4 Hz, 2 H), 2.19 (s, 3 H), 1.15 - 1.54 (m, 4 H), 0.90 (t, *J* = 7.3 Hz, 3 H); MS (m/e) 138 (M^+, 24), 95 (100); IR (neat) 1624, 1559 cm^{-1}.

4-Allyl-3-butyl-2-methylfuran (4a): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 1 H), 5.32-5.99 (m, 1 H), 4.98 - 5.16 (m, 2 H), 3.08 (d, *J* = 6.4Hz, 2 H), 2.27 (t, *J* = 7.8 Hz, 2 H), 2.18 (s, 3 H), 1.18 - 1.52 (m, 4 H), 0.90 (t, *J* = 7.1 Hz, 3 H); MS (m/e) 178 (M^+, 46), 43 (100); IR (neat) 1637, 1559 cm^{-1}; HRMS calcd for $C_{12}H_{18}O$ 178.1358. Found 178.1368.

3-Butyl-2-methyl-4-(2-phenyl-2-propenyl) furan (4b): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25-7.52 (m, 5 H), 7.01 (s, 1 H), 5.46 (s, 1 H), 5.09 (s, 1 H), 3.55 (s, 2 H), 2.33 (t, *J* = 7.4 Hz, 2 H), 2.23 (s, 3 H), 1.26-1.58 (m, 4 H), 0.94 (t, *J* = 6.9 Hz, 3 H); MS (m/e) 254 (M^+, 62), 43 (100); IR (neat) 1626, 1559 cm^{-1}; HRMS calcd for $C_{18}H_{22}O$ 254.1671. Found 254.1679.

(*E*)-3-Butyl-2-methyl-4-(3-phenyl-2-propenyl) furan (4c): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.08-7.31 (m, 5 H), 6.99 (s, 1 H), 6.38 (d, *J* = 15.8, 1 H), 6.21 (dt, *J* = 15.8, 6.5 Hz, 1 H), 3.18 (d, *J* = 6.5 Hz, 2 H), 2.23 (t, *J* = 7.5 Hz, 2 H), 2.15 (s, 3 H), 1.13-1.33 (m, 4 H), 0.82 (t, *J* = 7.2 Hz, 3 H); MS (m/e) 254 (M^+, 72), 43 (100); IR (neat) 1628, 1597, 1558 cm^{-1}; HRMS calcd for $C_{18}H_{22}O$ 254.1671. Found

254.1672.

4-Allyl-2,3-dimethylfuran (4d): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 1 H), 5.78-5.96 (m, 1 H), 4.92-5.18 (m, 2 H), 3.08 (d, *J* = 6.1, 2 H), 2.18 (s, 3 H), 1.85 (s, 3 H); MS (m/e) 136 (M^+, 55), 81 (100); IR (neat) 1637, 1563 cm^{-1}; HRMS calcd for $C_9H_{12}O$ 136.0888. Found 136.0899.

(*E*)-2,3-Dimethyl-4-(3-phenyl-2-propenyl) furan (4e): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.45 (m, 5 H), 7.09 (s, 1 H), 6.44 (d, *J* = 15.9 Hz, 1 H), 6.30 (dt, *J* = 15.9, 6.1 Hz, 1 H), 3,25 (d, *J* = 6.1 Hz, 2 H), 2.21 (s, 2 H), 1.89 (s, 3 H); MS (m/e) 212 (M^+, 66), 43 (100); IR (neat) 1635, 1559 cm^{-1}; HRMS calcd for $C_{15}H_{16}O$ 212.1201. Found 212.1221.

2,3-Dimethyl-4-(2-phenyl-2-propenyl) furan (4f): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.52 (m, 5 H), 7.00 (s, 1 H), 5.42 (s, 1 H), 5.02 (s, 1 H), 3.50 (s, 2 H), 2.18 (s, 3 H),1.86 (s, 3 H); MS (m/e) 212 (M^+, 100); IR (neat) 1682, 1626, 1598, 1570 cm^{-1}; HRMS calcd for $C_{15}H_{16}O$ 212.1201. Found 212.1191.

3,4-Diallyl-2-methylfuran (4g): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 1 H), 5.74-5.98 (m, 2 H), 4.90-5.13 (m, 4 H), 2.96-3.16 (m, 4 H), 2.18 (s, 3 H); MS (m/e) 162 (M^+, 49), 43 (100); IR (neat) 1637, 1559, 1431 cm^{-1}; HRMS calcd for $C_{11}H_{14}O$ 162.1044. Found 162.1059.

(*E*)-3-Allyl-2-methyl-4-(3-phenyl-2-propenyl) furan (4h): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.42 (m, 5 H), 7.10 (s, 1 H), 6.44 (d, J = 15.86 Hz, 1 H), 6.30 (dt, J = 15.79, 6.25 Hz, 1 H), 5.78-5.94 (m, 1 H), 4.95-5.08 (m, 2 H), 3.25 (d, *J* = 6.44 Hz, 2 H), 3.10 (d, *J* = 5.86 Hz, 2H), 2.21 (s, 3 H); MS (m/e) 238 (M^+, 29), 117 (100); IR (neat) 1635, 1559, 1449 cm^{-1}; HRMS calcd for $C_{17}H_{18}O$ 238.1358. Found 238.1356.

3-Allyl-2-methyl-4-(2-phenyl-2-propenyl) furan (4i): liquid; ^{1}H NMR (300

MHz, $CDCl_3$) δ 7.24-7.52 (m, 5 H), 7.00 (s, 1 H), 5.75-5.95 (m, 1 H), 5.45 (s, 1 H), 4.94-5.13 (m, 3 H), 3.53 (s, 2 H), 3.09 (d, J = 5.8 Hz, 2H), 2.21 (s, 3 H); MS (m/e) 238 (M^+, 48), 43 (100); IR (neat) 1635, 1559, 1492 cm^{-1}; HRMS calcd for $C_{17}H_{18}O$ 238.1358. Found 238.1363.

Reaction of 3,4-Dodecadien-2-one (1d) with Allyl Bromide. To a solution of 0.5 mmol of 3,4-dodecadien-2-one (**1d**) and allyl bromide (**3b**) in solvent (1 mL) as specified in **Scheme 3**, 1 equiv of K_2CO_3 and 5 mol % of $PdCl_2(PhCN)_2$ were added. The reaction mixture was stirred at 25 ^oC. Upon the completion of the reaction as monitored by TLC (eluent: hexanes), the mixture was quenched with water and extracted with ether. Dring over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane) afforded a mixture of 3-allyl-2-heptyl-5-methylfuran **8** and 2-heptyl-5-methylfuran **9**. The ratio of **8** and **9** was determined by ^1H NMR analysis.

3-Allyl-2-heptyl-5-methylfuran (8): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.76-5.95 (m, 1 H), 5.75 (s, 1 H), 4.92-5.08 (m, 2 H), 3.02 (d, *J* = 6.3 Hz, 2 H), 2.48 (t, *J* = 7.4 Hz, 2 H), 2.21 (s, 3 H), 1.47-1.66 (m, 2 H), 1.12-1.40 (m, 8 H), 0.87 (t, *J* = 6.9 Hz, 3 H); MS (m/e) 220 (M^+, 32), 135 (100); IR (neat) 1626, 1576, 1492, 1442 cm^{-1}; HRMS calcd for $C_{15}H_{24}O$ 220.1827. Found 220.1824.

2-Heptyl-5-methylfuran (9):[6] liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.83 (s, 2 H), 2.55 (t, *J* = 7.6 Hz, 2 H), 2.24 (s, 3 H), 1.54-1.71 (m, 2 H), 1.19-1.44 (m, 8 H), 0.87 (t, *J* = 6.5 Hz, 3 H); MS (m/e) 180 (M^+, 45), 95 (100); IR (neat) 1626, 1576, 1492, 1442 cm^{-1}; HRMS calcd for $C_{15}H_{24}O$ 220.1827. Found 220.1824.

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