Silane Promoted Cycloisomerization of Functionalized 1,6-Dienes Catalyzed by a Cationic π-Allyl Palladium Complex

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Supporting Information

Experimental procedures and analytical and spectroscopic data for new compounds (5 pages).

Experimental

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR were obtained on a General Electric QE 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. ^{13}C Peak multiplicities where indicated were determined via a combination of DEPT and APT techniques. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m polydimethylsiloxane capillary column. Flash chromatography was performed employing 200-400 mesh silica gel (EM) eluting with mixtures of hexane and ethyl acetate. Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ). CH_2Cl_2 and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. Dimethyl diallylmalonate (Lancaster) and triethylsilane (Aldrich) were used as received. The syntheses of the remaining dienes have been reported.[1] The precatalysts $(\eta^3\text{-}C_3H_5)Pd(Cl)PCy_3$,[2] $(\eta^3\text{-}C_3H_5)Pd(Me)PCy_3$,[2] $NaBAr_4$ and $HBAr_4{\cdot}OEt_2$ [Ar = 3,5-$C_6H_3(CF_3)_2$]$_4$ were prepared by known procedures.[3]

Substrates

4-Trimethylacetoxymethyl-4-phenyl-1,6-heptadiene (Table 2, entry 7). Trimethylacetyl chloride (2.5 g, 21 mmol) was added slowly to a solution of 4-hydroxymethyl-4-phenyl-1,6-heptadiene (2.0 g, 10 mmol), NEt_3 (1.6 g, 18 mmol), and dimethylaminopryridine (100 mg, 1 mmol), in CH_2Cl_2 (25 mL) at 0 °C and the resulting solution was stirred overnight at room temperature. Water (25 mL) and CH_2Cl_2 (25 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL) and the combined organic fractions were washed with water and brine, dried ($MgSO_4$), concentrated and distilled under vacuum (0.1 torr, 120 °C) to give the diene (2.1 g, 70 %) as a pale yellow oil. ^1H NMR: δ 7.28 (m, 5 H), 5.51 (tdd, J = 7.35, 10.5, 17.2 Hz, 2 H), 5.00 (m, 4 H), 4.29 (s, 2 H), 2.51 (d, J = 7.5 Hz, 4 H), 1.12 (s, 9 H). $^{13}C\{^1H\}$NMR: δ 178.0, 143.1, 133.7, 128.3, 126.5, 126.3, 118.3, 67.2, 44.2, 40.9, 38.9, 27.2,

26.6. HRMS (EI) calcd (found) for $C_{19}H_{25}O_2$: ($M-H^+$): 285.1854 (285.1850). Anal. calcd (found) for $C_{19}H_{26}O_2$: H, 9.15 (9.41); C, 79.68 (79.84).

4,4-Dicarbomethoxy-3-phenyl-1,6-heptadiene (Table 2, entry 11). A suspension of dimethyl (1-phenyl)-2-propenylmalonate (374 mg, 1.5 mmol), NaH (60 % in oil, 100 mg, 2.5 mmol), and allyl bromide (0.5 g, 3.0 mmol) in THF (10 mL) was refluxed for 12 h. Water (10 mL) and ether (10 mL) were added and the layers were separated. The aqueous layer was extracted with ether (2 × 10 mL) and the combined ether fractions were washed with water and brine, dried ($MgSO_4$), concentrated, and chromatographed (12:1) to give the diene (305 mg, 71 %) as a colorless oil. ^{1}H NMR: δ 7.25 (m, 3 H), 7.12 (d, J = 6.62 Hz, 2 H), 6.37 (ddd, J = 8.6, 10.2, 17.2 Hz, 1 H), 5.74 (m, 1 H), 5.14 - 4.96 (m, 4 H), 3.99 (d, J = 8.5 Hz, 1 H), 3.72 (s, 3 H), 3.65 (s, 3 H), 2.57 (ddd, J = 1.1, 6.3, 14.1 Hz, 1 H), 2.39 (dd, J = 8.2, 14.1 Hz, 1 H). ^{13}C{^{1}H}NMR: δ 170.6, 170.4, 139.0, 137.8, 133.4, 129.3, 128.4, 127.3, 118.6, 117.3, 63.1, 54.6, 52.1, 52.0, 39.6. IR (neat, cm^{-1}): 3079, 3028, 2982, 2950, 1729, 1453, 1220, 1065. Anal. calcd (found) for $C_{17}H_{20}O_4$: H, 6.99 (6.92); C, 70.81 (70.69).

Cyclopentenes

4,4-Dicarbomethoxy-1,2-dimethylcyclopentene (Table 1, entry 1). ^{1}H NMR: δ 3.69 (s, 6 H), 2.92 (s, 4 H), 1.56 (s, 6 H). ^{13}C{^{1}H}NMR: δ 172.9, 127.9, 57.0, 45.8, 13.1. IR (neat, cm^{-1}): 2954, 1731, 1434, 1257, 1199, 1078. Anal. calcd (found) for $C_{11}H_{16}O_4$: H, 7.60 (7.33); C, 62.26 (61.99).

4,4-Dicarbobenzyloxy-1,2-dimethylcyclopentene (Table 2, entry 2). ^{1}H NMR: δ 7.25 (m, 10 H), 5.10 (s, 4 H), 2.94 (s, 4 H), 1.56 (s, 6 H). ^{13}C{^{1}H}NMR: δ 172.3, 135.8, 128.7, 128.4, 128.3, 128.1, 67.2, 57.5, 46.0, 13.5. IR (neat, cm^{-1}): 3033, 1731, 1454, 1241, 1162, 1064. Anal. calcd (found) for $C_{23}H_{24}O_4$: H, 6.64 (6.52); C, 75.80 (75.86).

4,4-Dicarbo-*t*-butoxy-1,2-dimethylcyclopentene (Table 2, entry 3). ^{1}H NMR: δ 2.80 (s, 4 H), 1.56 (s, 6 H), 1.43 (s, 18 H). ^{13}C{^{1}H}NMR: δ 172.0, 128.2, 81.0, 58.3, 45.9, 28.1, 13.6. Anal. calcd (found) for $C_{17}H_{28}O_4$: H, 9.53 (9.63); C, 68.87 (68.79).

4-Carbomethoxy-1,2-dimethyl-4-phenylcyclopentene (Table 2, entry 4). ^{1}H NMR: δ 7.27 (m, 5 H), 3.62 (s, 3 H), 3.28 (dd, *J* = 0.7, 14.3 Hz, 2 H), 2.70 (dd, *J* = 0.8, 15.3 Hz, 2 H), 1.63 (s, 6 H). ^{13}C{^{1}H}NMR: δ 177.1, 155.6, 129.4, 128.5, 126.8, 126.6, 56.7, 52.6, 48.4, 13.9. IR (neat, cm^{-1}): 3059, 2950, 2853, 1730, 1495, 1263, 1218, 1166, 1036. Anal. calcd (found) for $C_{15}H_{18}O_2$: H, 7.88 (8.09); C, 78.22 (78.07).

4-Acetyl-4-carbomethoxy-1,2-dimethylcyclopentene (Table 2, entry 5). ^{1}H NMR: δ 3.62 (s, 3 H), 2.83 (m, 4 H), 2.13 (s, 3 H), 1.56 (s, 6 H). ^{13}C{^{1}H}NMR: δ 202.4, 173.1, 127.3, 62.9, 51.9, 43.6, 25.1, 12.6. IR (neat, cm^{-1}): 2951, 2922, 2854, 1738, 1703, 1428, 1377, 1360, 1234, 1159, 1125, 1079, 1005, 971, 931, 845. Anal. calcd (found) for $C_{11}H_{16}O_3$: H, 8.22 (8.00); C, 67.32 (67.34).

4-Acetoxymethyl-1,2-dimethyl-4-phenylcyclopentene (Table 2, entry 6). ^{1}H NMR: δ 7.26 (m, 5 H), 4.10 (m, 2 H), 2.72 (d, *J* = 14.9 Hz, 2 H), 7.25 (d, *J* = 14.6 Hz, 2 H), 1.94 (s, 3 H), 1.62 (s, 6 H). ^{13}C{^{1}H}NMR: δ 170.5, 146.4, 128.4, 127.4, 126.2, 125.3, 71.0, 47.2, 47.1, 20.2, 13.1. IR (neat, cm^{-1}): 3058, 3026, 2966, 2910, 2851, 1748, 1495, 1444, 1376, 1238, 1034. Anal. calcd (found) for $C_{16}H_{20}O_2$: H, 8.25 (8.12); C, 78.65 (78.43).

4-Trimethylacetoxymethyl-1,2-dimethyl-4-phenylcyclopentene (Table 2, entry 7). ^{1}H NMR: δ 7.25 (m, 5 H), 4.04 (s, 2 H), 2.74 (d, *J* = 14.8 Hz, 2 H), 2.55 (d, *J* = 14.6 Hz, 2 H), 1.62 (s, 6 H), 1.07 (s, 9 H). ^{13}C{^{1}H}NMR: δ 178.7, 147.4, 129.3, 128.2, 127.2, 126.1, 72.3, 48.2, 48.1, 39.1, 27.3, 14.0. IR (neat, cm^{-1}): 2969, 2909, 1729, 1479, 1445, 1283, 1158. Anal. calcd (found) for $C_{19}H_{26}O_2$: H, 9.15 (8.91); C, 79.68 (79.42).

4,4-Bis(acetoxymethyl)-1,2-dimethylcyclopentene (Table 2, entry 8). ^{1}H NMR: δ 3.99 (s, 2 H), 2.15 (s, 2 H), 2.04 (s, 3 H), 1.55 (s, 3 H). ^{13}C{^{1}H}NMR: δ 170.5, 127.9, 66.7, 43.7, 42.0, 20.2, 12.9. IR (neat, cm^{-1}): 2966, 2914, 2894, 2844, 1741, 1444, 1378, 1363, 1319, 1234, 1034, 977, 912, 848. Anal. calcd (found) for $C_{13}H_{20}O_4$: H, 8.39 (8.67); C, 64.98 (64.96).

4,4-Bis(trimethylacetoxymethyl)-1,2-dimethylcyclopentene (Table 2, entry 9). ^{1}H NMR: δ 3.97 (s, 4 H), 2.17 (s, 4 H), 1.55 (s, 4 H), 1.17 (s, 18 H). ^{13}C{^{1}H}NMR: δ 178.5,

128.8, 67.7, 44.9, 43.3, 39.1, 27.4, 13.8. IR (neat, cm^{-1}): 2971, 1730, 1396, 1282, 1148, 1034, 994, 938. Anal. calcd (found) for $C_{19}H_{32}O_4$: H, 9.95 (9.84); C, 70.32 (70.35).

4,4-Dicarboethoxy-1,2,3-trimethylcyclopentene (Table 2, entry 10). ^1H NMR: δ 4.18 (m, 4 H), 3.32 (q, *J* = 3.9 Hz, 1 H), 3.19 (d, *J* = 16.6 Hz, 1 H), 2.51 (d, *J* = 16.8 Hz, 1 H), 1.56 (s, 6 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 1.21 (t, *J* = 7.1 Hz, 1 H), 0.91 (d, *J* = 7.1 Hz, 3 H). $^{13}C\{^1H\}$NMR: δ 172.8, 171.0, 133.4, 127.1, 62.6, 61.3, 61.2, 48.9, 44.1, 14.3, 14.2, 13.7, 12.0. IR (neat, cm^{-1}): 2975, 2934, 2873, 1720, 1445, 1300, 1105, 859. Anal. calcd (found) for $C_{14}H_{22}O_4$: H, 8.72 (8.93); C, 66.12 (66.31).

4,4-Dicarbomethoxy-1,2-dimethyl-3-phenylcyclopentene (Table 2, entry 11). ^1H NMR: δ 7.25 (m, 3 H), 7.10 (d, *J* = 6.8 Hz, 2 H), 4.56 (s, 1 H), 3.72 (s, 3 H), 3.28 (d, *J* = 16.8 Hz, 1 H), 3.09 (s, 3 H), 2.62 (d, *J* = 17.0 Hz, 1 H), 1.72 (s, 3 H), 1.44 (s, 3 H). $^{13}C\{^1H\}$NMR: δ 173.2, 170.3, 139.2, 132.0, 130.2, 129.4, 128.2, 127.3, 64.1, 61.8, 53.1, 44.9, 13.8, 12.8. IR (neat, cm^{-1}): 3027, 2950, 2859, 1737, 1453, 1433, 1252, 1137, 1078. HRMS (EI) calcd (found) for $C_{17}H_{19}O_4$ ($M-H^+$): 287.1283 (287.1288).

4,4-Dicarbomethoxy-1,2,3,3-tetramethylcyclopentene (Table 2, entry 12). ^1H NMR: δ 3.67 (s, 6 H), 2.72 (s, 2 H), 1.59 (s, 3 H), 1.49 (s, 3 H), 1.05 (s, 6 H). $^{13}C\{^1H\}$NMR: δ 171.9, 136.1, 126.3, 66.4, 52.2, 52.0, 43.1, 22.4, 14.0, 9.8. IR (neat, cm^{-1}): 2952, 2861, 1733, 1456, 1248, 1087, 1042. Anal. calcd (found) for $C_{13}H_{20}O_4$: H, 8.39 (8.46); C, 64.98 (64.93).

4,4-Dicarbomethoxy-1-ethyl-2-methylcyclopentene (major isomer) and 1,1-dicarbomethoxy-3-ethylidene-4-methylcyclopentane (minor isomer) (Table 2, entry 13). ^1H NMR [major isomer]: δ 3.84 (s, 6 H), 30.6 (br s, 4 H), 2.15 (q, *J* = 7.8 Hz, 2 H), 1.67 (s, 3 H), 1.06 (t, *J* = 7.8 Hz, 3 H). ^1H NMR [minor isomer]: Most resonances of the minor isomer were obscured by the major isomer. However a doublet (*J* = 6.4 Hz) at δ 1.02 was assigned to a methyl group of the minor isomer. $^{13}C\{^1H\}$NMR [major isomer]: δ 173.2 (s), 134.1 (s), 127.5 (s), 57.4 (s), 52.9 (q), 46.1 (t), 43.4 (t), 21.2 (t), 13.3 (q), 12.6 (q). $^{13}C\{^1H\}$NMR [minor isomer]: δ 172.7 (s), 144.0 (s), 115.3 (d), 58.5 (s), 42.7 (t), 37.4 (t), 37.3 (d), 20.6 (q), 18.1 (q), 14.6 (q). IR

(neat, cm^{-1}): 2957, 2932, 2858, 1737, 1434, 1253, 1197, 1156, 1074, 957. Anal. calcd (found) for $C_{12}H_{18}O_4$: H, 8.02 (7.88); C, 63.70 (66.31).

References.

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