Reverse of Regioselectivity in Intramolecular Nucleophilic Substitution of π–Allyl Palladium Species. Highly Selective Formation of Vinylic Cyclopropanes via the Pd(0)–Catalyzed Coupling-Cyclization Reaction of Organic Iodides with 2-(2',3'-Dienyl)malonates

Shengming Ma* and Shimin Zhao

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, P. R. China

To a mixture of methyl 2,3-butadienylmalonate (117 mg, 0.64 mmol), phenyl iodide(156 mg, 0.76 mmol), potassium carbonate(352 mg, 2.55 mmol) and TBAB(20 mg, 0.064 mmol, 10 mol%) in CH_3CN(3 mL) was added $Pd(PPh_3)_4$ (37 mg, 0.032 mmol, 5mol%) under Ar, and the resulting mixture was refluxed for 23 h as monitored by TLC. The mixture was filtered, washed with ether. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford 132 mg of **3a** (80 %).

1,1-(Bismethoxycarbonyl)-2-(1'-phenylethenyl)cyclopropane (3a): ^{1}H NMR δ 1.60 (dd, *J* = 8.05 and 5.15 Hz, 1 H), 2.04 (dd, *J* = 8.05 and 5.15 Hz, 1 H), 2.99 (t, *J* = 8.05 Hz, 1 H), 3.44 (s, 3 H), 3.78 (s, 3 H), 5.05 (s, 1 H), 5.51 (s, 1 H), 7.20-7.40 (m, 3 H), 7.47 (d , *J* = 8.17 Hz, 2 H); IR (neat) 1624, 1728 cm^{-1}; MS(m/e) 260 (M^+, 2.91), 200 (100); HRMS calcd for $C_{15}H_{16}O_4$(M^+) 260.1049, found 260.1053.

***E*-1,1-(Bismethoxycarbonyl)-2-(1'-methylene-2'-heptenyl)cyclopropane (3b):** ^{1}H NMR δ 0.87 (t, *J* = 7.02 Hz, 3 H), 1.10-1.35 (m, 4 H), 1.41 (dd, *J* = 8.18 and 4.88 Hz, 1 H), 1.88 (dd, *J* = 8.18 and 4.88 Hz, 1 H), 2.01 (q, *J* = 6.74 Hz, 2 H), 2.69 (t, *J* = 8.18 Hz,1 H), 3.53 (s, 3 H), 3.71 (s, 3 H), 4.79 (s, 1 H), 4.95 (s, 1 H), 5.80 (dt, *J* = 16.36 and 6.82 Hz, 1 H), 6.00 (d, *J* = 16.36 Hz, 1 H); IR (neat) 1607, 1647, 1730 cm^{-1}; MS(m/e) 91 (100), 265 (M^+-1, 0.52); HRMS calcd for $C_{15}H_{22}O_4$(M^+) 266.1518, found 266.1516.

1,1-(Bismethoxycarbonyl)-2-(1'-(4"-methoxyphenyl)ethenyl)cyclopropane (3c): ^{1}H NMR δ 1.59 (dd, *J* = 8.00 and 5.04 Hz, 1 H), 2.06 (dd, *J* = 8.00 and 5.04 Hz, 1 H), 2.97 (t, *J* = 8.00 Hz, 1 H), 3.47 (s, 3 H), 3.80 (s, 3 H) , 3.82 (s, 3 H), 4.97 (s, 1 H),

5.43 (s, 1 H), 6.86 (d, *J* = 7.06 Hz, 2 H), 7.46 (d, *J* = 7.06 Hz, 2 H); IR (neat) 1606, 1724 cm^{-1}; MS(m/e) 290 (M^+, 9.31), 230 (100); HRMS calcd for $C_{16}H_{18}O_5$ (M^+) 290.1154, found 290.1145.

1,1-(Bismethoxycarbonyl)-2-(1'-(4"-methylphenyl)ethenyl)cyclopropane (3d): ^1H NMR δ 1.63 (dd, *J* = 8.52 and 5.02 Hz, 1 H), 2.05 (dd, *J* = 8.52 and 5.02 Hz, 1 H), 2.32 (s, 3 H), 2.98 (t, *J* = 8.52 Hz, 1 H), 3.46 (s, 3 H), 3.78 (s, 3 H), 5.00 (s, 1 H), 5.47 (s, 1 H), 7.12 (d, *J* = 7.95 Hz, 2 H), 7.36 (d, *J* = 7.95 Hz, 2 H); IR (neat) 1606, 1732 cm^{-1}; MS(m/e) 274 (M^+, 6.36), 155 (100); HRMS calcd for $C_{16}H_{18}O_4$(M^+) 274.1205, found 274.1205.

1,1-(Bismethoxycarbonyl)-2-(1'-(4"-methoxycarbonylphenyl)ethenyl)cyclo-propane (3e): ^1H NMR δ 1.63 (dd, *J* = 8.52 and 5.15 Hz, 1 H), 2.03 (dd, *J* = 8.52 and 5.15 Hz, 1 H), 2.98 (t, *J* = 8.52 Hz, 1 H), 3.43 (s, 3 H), 3.79 (s, 3 H), 3.90 (s, 3 H), 5.17 (s, 1 H), 5.62 (s, 1 H), 7.52 (d, *J* = 8.44 Hz, 2 H), 7.98 (d, *J* = 8.44 Hz, 2 H); IR (neat) 1608, 1727 cm^{-1}; MS(m/e) 318 (M^+, 1.08), 258 (100); HRMS calcd for $C_{17}H_{18}O_6$ (M^+) 318.1103, found 318.1098 ;

***E*-1,1-(Bismethoxycarbonyl)-2-(1'-methylene-3'-phenyl-2-propenyl)cyclopropa-ne (3f):** ^1H NMR δ 1.48 (dd, *J* = 8.40 and 4.97 Hz, 1 H), 1.95 (dd, *J* = 8.40 and 4.97 Hz, 1 H), 2.81 (t, *J* = 8.40 Hz, 1 H), 3.49 (s, 3 H), 3.75 (s, 3 H), 5.02 (s, 1 H), 5.21 (s, 1 H), 6.71 (s, 2 H), 7.10-7.38 (m, 5 H); IR (neat) 1603, 1730 cm^{-1}; MS(m/e) 286 (M^+, 9.77), 167 (100); HRMS calcd for $C_{17}H_{18}O_4$(M^+) 286.1205, found 286.1198.

1,1-(Bismethoxycarbonyl)-2-(1'-(4"-bromophenyl)ethenyl)cyclopropane (3g): ^1H NMR δ 1.59 (dd, *J* = 8.54 and 5.34 Hz, 1 H), 2.02 (dd, *J* = 8.54 and 5.34 Hz, 1 H), 2.92 (t, *J* = 8.54 Hz, 1 H), 3.47 (s, 3 H), 3.78 (s, 3 H), 5.07 (s, 1 H), 5.50 (s, 1 H), 7.33 (d, *J* = 8.62 Hz, 2 H), 7.44 (d, *J* = 8.62 Hz, 2 H); IR (neat) 1585, 1622, 1716 cm^{-1}; MS(m/e) 340 ($M(^{81}Br)^+$, 4.50), 338 ($M(^{79}Br)^+$, 4.65), 278(100); HRMS calcd for $C_{15}H_{15}BrO_4$(M^+) 338.0154, found 338.0148.

1,1-(Bismethoxycarbonyl)-2-(1'-naphthylethenyl)cyclopropane (3h): ^1H NMR δ 1.64 (dd, *J* = 8.53 and 5.06 Hz, 1 H), 1.95 (dd, *J* = 8.53 and 5.06 Hz, 1 H), 3.07 (t, *J* = 8.53 Hz, 1 H), 3.61 (s, 3 H), 3.69 (s, 3 H), 5.32 (s, 1 H), 5.44 (s, 1 H), 7.10–8.15 (m, 7 H). IR (neat) 1580, 1625, 1723 cm^{-1}; MS 310 (M^+, 5.39), 191 (100); HRMS calcd for $C_{19}H_{18}O_4$ (M^+) 310.1205, found 310.1244.

1,1-(Bismethoxycarbonyl)-2-(1'-phenyl-2'-butyl)ethenylcyclopropane (3i):

***Z*-isomer:** ^1H NMR δ 0.74 (t, *J* = 7.10 Hz, 3 H), 1.10-1.25 (m, 2 H), 1.25-1.38 (m, 2

H), 1.45 (dd, *J* = 8.70 and 5.10 Hz, 1 H), 1.00-2.00 (m, 3 H), 2.75 (t, *J* = 8.70 Hz, 1 H), 3.53 (s, 3 H), 3.64 (s, 3 H), 5.44 (t, *J* = 7.40 Hz, 1 H), 7.00-7.25 (m, 5 H).

***E*-isomer:** 0.85 (t, *J* = 7.10 Hz, 3 H), 1.10-1.25 (m, 2 H), 1.25-1.38 (m, 2 H), 1.63 (dd, *J* = 9.30 and 4.70 Hz, 1 H), 1.72 (dd, *J* = 9.30 and 4.70 Hz, 1 H), 2.22 (m, 2 H), 2.96(t, *J* = 9.30 Hz, 1 H), 3.30 (s, 3 H), 3.71 (s, 3 H), 5.79 (t, *J* = 7.40 Hz, 1 H), 7.00-7.25 (m, 5 H).

IR (neat) 1598, 1724 cm^{-1}; MS(m/e) 316 (M^+, 24.59), 141 (100); HRMS calcd for $C_{19}H_{24}O_4$(M^+) 316.1669, found 316.1669.

1-Phenyl-4,4-(bismethoxycarbonyl)cyclopentene (4a):[1] ^{1}H NMRδ3.22 (s, 2 H), 3.43 (s, 2 H), 3.77 (s, 6 H), 6.03 (s, 1 H), 7.15-7.55 (m, 5 H); IR (neat) 1600, 1734 cm^{-1}; MS(m/e) 260 (M^+, 19.96), 200 (100).

1-Phenyl-4,4-(bismethoxycarbonyl)-5-(*n*-butyl)cyclopentene (4i): ^{1}H NMRδ0.72 (t, *J* = 6.82 Hz, 3 H), 1.10-1.60 (m, 6 H), 2.91 (dd, *J* = 17.5 and 2.29 Hz, 1 H), 3.39 (d, *J* = 17.51 Hz, 1 H), 3.70 (s, 3 H), 3.74 (s, 3 H), 3.99 (t, *J* = 5.02 Hz, 1 H), 5.85 (d, *J* = 2.29 Hz, 1 H), 7.10-7.60 (m, 5 H); IR (neat) 1600, 1732cm^{-1}; MS(m/e) 316 (M^+, 3.63), 256 (100); HRMS calcd for $C_{19}H_{24}O_4$ (M^+) 316.1675, found 316.1670.

1-Phenyl-4,4-(biscyano)cyclopentene (4j): ^{1}H NMR δ 3.40 (s, 2 H), 3.57 (s, 2 H), 6.11 (s, 1 H), 7.30-7.45 (m, 5 H); IR (neat) 1628, 2250 cm^{-1}; MS(m/e) 194 (M^+, 48.81), 116 (100); HRMS calcd for $C_{13}H_{10}N_2$(M^+) 194.0844, found 194.0838 .

Reference:

1. Ahmar, M.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1985**, *26*, 3795;