Highly Stereoselective Synthesis of Trisubstituted vinylcyclopropane Derivatives via Arsonium Ylides

Hong Jiang, Xianming Deng, Xiuli Sun and Yong Tang^{*}, Li-Xin Dai

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic
Chemistry, 354 Fenglin Lu, Shanghai 200032, China.

tangy@mail.sioc.ac.cn

Supporting Information

Contents

General Information.....	S2
Spectral Data of All New Compounds.....	S2
Copies of NMR Spectra of All New Compounds.....	S7

General Information: All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with stirring. Tetrahydrofuran was dried by distillation over sodium/benzophenone ketyl.

1. Spectral Data of All New Compounds:

Diethyl *trans*-2-methyl-3-styrylcyclopropane-1,1-dicarboxylate(3b). ^1H NMR(300 MHz, CDCl_3) δ 7.35-7.15 (m, 5H), 6.63 (d, $J = 15.9\text{Hz}$, 1H), 5.87 (dd, $J = 15.9, 9.3\text{Hz}$, 1H), 4.35-4.05 (m, 4H), 2.55 (dd, $J = 9.0, 7.5\text{Hz}$, 1H), 2.25-2.14 (m, 1H), 1.35-1.15 (m, 9H); ^{13}C NMR(300 MHz, CDCl_3) δ 168.1, 167.7, 136.8, 133.0, 128.5, 127.3, 125.9, 124.9, 61.4, 42.3, 36.5, 27.3, 14.2, 14.1, 12.3; MS (EI) m/z (rel intensity) 302 (M^+ 7), 155 (100), 228 (61), 211 (42), 183 (37), 256 (35), 156 (35), 115 (34), 141 (26); IR (thin film)/ cm^{-1} : 2981 (m), 1724 (s), 1368 (m), 1290 (m), 1203 (m), 1140 (m), 964 (m), 693 (m); Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_4$: C, 71.50; H, 7.33. Found: C, 71.83; H, 7.57.

Diethyl *trans*-2-isopropyl-3-styrylcyclopropane-1,1-dicarboxylate(3c). ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.14 (m, 5H), 6.63 (d, $J = 15.9\text{Hz}$, 1H) 5.86 (dd, $J = 15.9, 9\text{Hz}$, 1H), 4.34-4.06 (m, 4H), 2.62 (t, $J = 7.8\text{Hz}$, 1H), 1.95 (dd, $J = 10.5, 7.8\text{Hz}$, 1H), 1.40-1.18 (m, 7H), 1.05 (d, $J = 6.6\text{Hz}$, 3H), 0.98 (d, $J = 6.9\text{Hz}$, 3H); ^{13}C NMR(300 MHz, CDCl_3) δ 168.1, 168.0, 136.8, 132.7, 128.5, 127.3, 126.0, 125.1, 61.4, 42.5, 40.7, 35.3, 27.8, 22.1, 21.5, 14.2, 14.1; MS (EI) m/z (rel intensity) 330 (M^+ , 9), 195 (100), 141 (78), 241 (73), 169 (60), 115 (58), 91 (51), 128 (47), 183 (47); IR (thin film)/ cm^{-1} : 2961 (m), 2935 (m), 1723 (s), 1367 (m), 1287 (m), 1200 (m), 1181 (m), 963 (m), 693 (m); Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_4$: C, 72.70; H, 7.93. Found: C, 73.07; H, 8.13.

Dimethyl *trans*-2-isobutyl-3-styrylcyclopropane-1,1-dicarboxylate(3d). ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.08 (m, 5H), 6.63 (d, $J = 15.9\text{Hz}$, 1H), 5.86 (dd, $J = 15.9, 9.0\text{Hz}$, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 2.60 (t, $J = 8.1\text{Hz}$, 1H), 2.22-2.12 (m, 1H), 1.78-1.62 (m, 1H), 1.58-1.40 (m, 1H),

1.20-1.06 (m, 1H), 0.94 (t, $J = 6.9\text{Hz}$, 6H); ^{13}C NMR(300 MHz, CDCl_3) δ 168.5, 168.3, 136.8, 133.1, 128.5, 127.4, 126.0, 124.8, 52.6, 41.4, 36.5, 36.3, 32.0, 28.0, 22.6, 22.1; MS (EI) m/z (rel intensity) 316 (M^+ , 13), 115 (100), 141 (87), 41 (73), 128 (64), 213 (64), 153 (62), 91 (58), 59 (56); IR (thin film)/ cm^{-1} : 2955 (m), 1728 (s), 1436 (m), 1298 (m), 1213 (m), 1144 (m), 964 (m), 693 (m); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{24}\text{O}_4$ [M^+]: 316.1675, found: 316.1665.

Diethyl *trans*-2-phenyl-3-styrylcyclopropane-1,1-dicarboxylate (3e)⁸. ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.19 (m, 10H), 6.78 (d, $J = 15.9\text{Hz}$, 1H), 6.04 (dd, $J = 15.9, 8.7\text{Hz}$, 1H), 4.30-4.16 (m, 2H), 4.00-3.82 (m, 2H), 3.49 (d, $J = 7.8\text{Hz}$, 1H), 3.32 (t, $J = 9.0\text{Hz}$, 1H), 1.24 (t, $J = 7.2\text{Hz}$, 3H), 0.92 (t, $J = 7.2\text{Hz}$, 3H).

Dimethyl *trans*-2-styryl-3-*p*-tolylcyclopropane-1,1-dicarboxylate(3f). Mp 84-85 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.19 (m, 5H), 7.16-7.06 (m, 4H), 6.78 (d, $J = 15.9\text{Hz}$, 1H), 6.02 (dd, $J = 15.9, 9.0\text{Hz}$, 1H), 3.77 (s, 3H), 3.49-3.42 (m, 4H), 3.33 (t, $J = 8.1\text{Hz}$, 1H), 2.31 (s, 3H); ^{13}C NMR(300 MHz, CDCl_3) δ 168.0, 166.9, 137.1, 136.7, 133.9, 131.1, 128.9, 128.5, 128.3, 127.6, 126.1, 124.0, 52.8, 52.4, 44.4, 36.7, 34.0; MS (EI) m/z (rel intensity) 350 (M^+ , 3), 231 (100), 290 (100), 318 (85), 215 (68), 286 (51), 216 (49), 115 (48), 258 (47); IR (thin film)/ cm^{-1} : 2952 (m), 1729 (s), 1519 (m), 1435 (m), 1292 (m), 1211 (m), 1100 (m), 964 (m), 755 (m), 693 (m); HRMS (MALDI/DHB) calcd for $\text{C}_{22}\text{H}_{22}\text{O}_4\text{Na}^+$ [$\text{M}^+ + \text{Na}$]: 373.1423, Found: 373.1410.

Diethyl *trans*-2-(4-bromophenyl)-3-styrylcyclopropane-1,1-dicarboxylate(3g). Mp 71-72 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.45-7.13 (m, 9H), 6.79 (d, $J = 15.9\text{Hz}$, 1H), 6.01 (dd, $J = 15.9, 8.7\text{Hz}$, 1H), 4.36-4.10 (m, 2H), 4.04-3.84 (m, 2H), 3.42 (d, $J = 8.1\text{Hz}$, 1H), 3.28 (t, $J = 8.1\text{Hz}$, 1H), 1.25 (t, $J = 7.2\text{Hz}$, 3H), 1.00 (t, $J = 6.9\text{Hz}$, 3H); ^{13}C NMR(300 MHz, CDCl_3) δ 167.2, 166.1, 136.5, 134.1, 133.5, 131.3, 130.3, 128.5, 127.6, 126.1, 123.6, 121.3, 61.8, 61.5, 44.5, 35.9, 33.5, 14.2,

13.8; MS (EI) m/z (rel intensity) 443 (M^+ , 3), 215 (100), 370 (88), 368 (84), 216 (83), 297 (79), 295 (75), 49 (70), 115 (60); IR (thin film)/ cm^{-1} : 2981 (m), 1724 (s), 1492 (m), 1369 (m), 1289 (m), 1095 (m), 1012 (m), 963 (m), 759 (m), 693 (m); HRMS (MALDI/DHB) calcd for $\text{C}_{23}\text{H}_{23}\text{O}_4\text{BrNa}^+$ [$M^+ + \text{Na}$]: 465.0685, Found: 465.0672.

Diethyl *trans*-2-phenyl-3-vinylcyclopropane-1,1-dicarboxylate (3h)⁸. ^1H NMR (300 MHz, CDCl_3) δ 7.22-7.13 (m, 5H), 5.65-5.10 (m, 1H), 5.36 (dd, $J = 17.1, 1.5\text{Hz}$, 1H), 5.14 (dd, $J = 10.2, 1.8\text{Hz}$, 1H), 4.28-4.09 (m, 2H), 3.90-3.75 (m, 2H), 3.30 (d, $J = 8.1\text{Hz}$, 1H), 3.10 (t, $J = 7.8\text{Hz}$, 1H), 1.21 (t, $J = 7.2\text{Hz}$, 3H), 0.84 (t, $J = 7.2\text{Hz}$, 3H).

Diethyl *trans*-2-phenyl-3-(2-(trimethylsilyl)vinyl)cyclopropane-1,1-dicarboxylate (3j)⁸. ^1H NMR (300 MHz, CDCl_3) δ 7.26-7.20 (m, 5H), 6.23 (d, $J = 18.3\text{Hz}$, 1H), 5.76 (dd, $J = 18.6, 8.1\text{Hz}$, 1H), 4.24 (q, $J = 6.9\text{Hz}$, 2H), 3.95-3.85 (m, 2H), 3.41 (d, $J = 7.8\text{Hz}$, 1H), 3.19 (t, $J = 8.1\text{Hz}$, 1H), 1.28 (t, $J = 6.9\text{Hz}$, 3H), 0.91 (t, $J = 7.2\text{Hz}$, 3H), 0.06 (s, 9H).

Diethyl *trans*-2-ethyl-3-(2-(trimethylsilyl)vinyl)cyclopropane-1,1-dicarboxylate (3k). ^1H NMR (300 MHz, CDCl_3) δ 5.93 (d, $J = 18.6\text{Hz}$, 1H), 5.57 (dd, $J = 18.6, 8.1\text{Hz}$, 1H), 4.30-4.08 (m, 4H), 2.43 (t, $J = 7.8\text{Hz}$, 1H), 2.04 (q, $J = 7.8\text{Hz}$, 1H), 1.54-1.30 (m, 2H), 1.23 (q, $J = 6.9\text{Hz}$, 6H), 0.96 (t, $J = 7.2\text{Hz}$, 3H), 0.00 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ 167.9, 140.8, 134.2, 61.4, 61.3, 42.2, 37.9, 34.1, 20.7, 14.2, 14.1, 13.0, -1.4; MS (EI) m/z (rel intensity) 312 (M^+ , 4), 75 (100), 73 (91), 223 (52), 283 (49), 59 (37), 121 (31), 91 (27), 205 (24); IR (thin film)/ cm^{-1} : 2960 (m), 1726 (s), 1368 (m), 1291 (m), 1249 (m), 1202 (m), 1147 (m), 864 (m), 839 (m); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{28}\text{O}_4\text{Si}$ [M^+]: 312.1757, found: 312.1774.

Diethyl 2-isopropyl-3-phenylcyclopropane-1,1-dicarboxylate(3m). (trans/cis = 1/1) ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.14 (m, 5H), 4.35-4.15 (m, 2H), 4.15-3.95 (m, 1H), 3.94-3.76 (m, 1H),

3.10 (d, $J = 8.1\text{Hz}$, 0.5H), 3.06 (d, $J = 9.9\text{Hz}$, 0.5H), 2.34-2.14 (m, 1H), 1.67 (t, 0.5H), 1.34-1.24 (m, 3.5H), 1.16 (dd, $J = 9.0$, 6.6Hz, 3H), 1.09 (t, $J = 7.2\text{Hz}$, 1.5H), 1.03 (d, $J = 6.9\text{Hz}$, 1.5H), 0.95 (d, $J = 6.3\text{Hz}$, 1.5H), 0.89 (t, $J = 7.2\text{Hz}$, 1.5H); MS (EI) m/z (rel intensity) 305 ($M^+ + 1$, 5), 187 (100), 261 (98), 115 (62), 43 (42), 91 (32), 41 (32), 170 (26), 105 (22); IR (thin film)/ cm^{-1} : 2978 (m), 2962 (m), 1726 (s), 1368 (m), 698 (m); Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$: C, 71.03; H, 7.95. Found: C, 71.31; H, 8.17.

Dimethyl *trans*-2-phenyl-3-styrylcyclopropane-1,1-dicarboxylate(3n). ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.18 (m, 10H), 6.79 (d, $J = 15.9\text{Hz}$, 1H), 6.03 (dd, $J = 15.6$, 8.4Hz, 1H), 3.78 (s, 3H), 3.50 (d, $J = 8.4\text{Hz}$, 1H), 3.44 (s, 3H), 3.34 (t, $J = 8.4\text{Hz}$, 1H); ^{13}C NMR(300 MHz, CDCl_3) δ 167.9, 166.8, 136.7, 134.3, 134.1, 128.6, 128.4, 128.2, 127.6, 127.4, 126.2, 123.9, 52.9, 52.4, 44.5, 36.9, 33.9; MS (EI) m/z (rel intensity) 336 (M^+ , 2), 276 (100), 217 (80), 304 (64), 115 (40), 244 (33), 202 (32), 215 (32), 59 (30); IR (thin film)/ cm^{-1} : 1728 (s), 1435 (m), 1292 (m), 1105 (m), 761 (m), 742 (m), 695 (s); Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4$: C, 74.98; H, 5.99. Found: C, 74.92; H, 6.09.

Diethyl *trans*-2,3-diphenylcyclopropane-1,1-dicarboxylate (3o)⁸. ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.20 (m, 10H), 3.95 (q, $J = 7.2\text{Hz}$, 4H), 3.83 (s, 2H), 0.95 (t, $J = 6.9\text{Hz}$, 6H).

Cinnamyltriphenylarsonium tetraphenylborate(Table 1, entry 4). The salt (5) was obtained by mixing Cinnamyltriphenylarsonium bromide (0.85 g, 1.69 mmol) with sodium tetraphenylborate (0.65 g, 1.9 mmol) in methanol (20 mL). Yield: 1.16 g (92%); Mp 160-161 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.54 (m, 3H), 7.47-7.36 (m, 14H), 7.30-7.20 (m, 3H), 7.14-7.04 (m, 8H), 6.93-6.83 (m, 8H), 6.79-6.70 (m, 4H), 6.14 (d, $J = 15.9\text{Hz}$, 1H), 5.64-5.48 (m, 1H), 2.79 (d, $J = 7.8\text{Hz}$, 2H); ^{13}C NMR(300 MHz, CDCl_3) δ 165.1, 164.4, 163.7, 163.1, 139.5, 136.2, 135.0, 134.3, 132.3, 128.7, 126.4, 125.6, 125.5, 121.7, 120.0, 113.9, 28.7; MS (ESI, positive mode, m/z) 423

(M⁺-BPh₄); IR (thin film)/cm⁻¹: 3054 (s), 2998 (m), 1579 (m), 1482 (m), 1439 (m), 1084 (m), 734 (s), 706 (s), 689 (s), 612 (m), 466 (m); Anal. Calcd for C₅₁H₄₄AsB: C, 82.48; H, 5.97. Found: C, 82.47; H, 6.00.

Cinnamyltriphenylarsonium tetrafluoroborate(Table 1, entry 5). A solution of

Cinnamyltriphenyl- arsonium bromide (1.52g, 3.02mmol) in CH₂Cl₂ (40 mL) is added a solution of silver tetrafluoroborate (680mg, 3.50mmol) in water (20mL), and the mixture is stirred vigorously for 10 min. The silver bromide formed is filtered off, the filtrate is allowed to settle and the organic phase is washed with saturated brine (5mL) and evaporated to dryness. Yield:

1.51g(97%); Mp 147-148 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.76-7.60 (m, 15H), 7.35-7.15 (m, 5H), 6.73 (d, *J* = 15.9Hz, 1H), 6.17-6.03 (m, 1H), 4.59 (d, *J* = 7.8Hz, 2H); ¹³C NMR(300 MHz, CDCl₃) δ 139.8, 135.4, 134.1, 132.8, 130.8, 128.6, 128.4, 126.5, 120.8, 114.5, 29.8; MS (ESI, positive mode, m/z) 423(M⁺-BF₄); IR (thin film)/cm⁻¹: 1485 (m), 1440 (s), 1059 (s), 997 (m), 741 (s), 690 (s), 467 (m); HRMS (ESI) calcd for C₂₇H₂₄As⁺(M⁺): 423.1087, Found: 423.1088.

2. Copies of NMR Spectra of All New Compounds

168.059
167.990

136.830
132.731
128.480
127.305
125.977
125.135

77.419
77.000
76.572

61.450
61.411

42.507
40.687

35.316

27.853

22.137
21.519

14.176
14.123

trans/cis = 1/1