Supporting Information for

Unusual Diastereoselectivity in Intramolecular Diels-Alder Reactions of Substituted 3,5-Hexadienyl Acrylates. Preference for a Boat-like Structure of the Six-Atom Tether due to Ester Overlap

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(*E*)-4-Methyl-3,5-hexadienyl) (*E*)-4-methyl-2-pentenoate (7). To a stirring solu-tion of alcohol **5** (200 mg, 1.783 mmol) in THF (10 mL) at 25 °C was added the carboxylic acid **6** (305 mg, 2.675 mmol), triphenylphosphine (935 mg, 3.566 mmol) followed by dropwise addition of diethyl azodicarboxylate (700 μL, 3.566 mmol) and the reaction was stirred for 20 min. Saturated sodium bicarbonate solution was added and the mixture was extracted with ether (3 x 10 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield a pale yellow oil. Flash column chromatography (silica gel, 2:1 hexanes:benzene) of the residue yielded the triene **7** (75% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.93 (1H, dd, J = 15.7, 6.6 Hz), 6.36 (1H, dd, J = 17.4, 10.7 Hz), 5.75 (1H, dd, J = 15.7, 1.4 Hz), 5.47 (1H, dd, J = 7.3, 1.4 Hz), 5.11 (1H, d, J = 17.4 Hz), 4.96 (1H, d, J = 10.7 Hz), 4.14 (1H, t, J = 7.0 Hz), 2.35-2.60 (3H, m), 1.75 (3H, s), 1.05 (6H, d, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.02, 155.70, 141.07, 136.45, 127.42, 118.45, 111.50, 63.41, 30.95, 27.85, 21.21, 11.78. IR (thin film): 3090, 2965, 2934, 2899, 2872, 1721, 1717, 1655, 1609, 1264 cm^{-1}.

(*E*)-5-Methyl-4,6-heptadien-2-yl) (*E*)-4-methyl-2-pentenoate (9). To a stirring solution of the alcohol **5** (441 mg, 3.929 mmol) in dichloromethane (35 mL) at 25 °C was added Dess-Martin periodinane (2.00 g, 4.715 mmol) and the reaction was stirred for 1 h. Sodium thiosulfate (1 g) was added and the reaction mixture stirred for an additional 1 h. A pH 7 buffer (15 mL) was added and the mixture was extracted with ether (2 x 15 mL). The combined ether layers were washed with pH 7 buffer (2 x 10 mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure to provide a clear oil that was carried on

to the next step without further purification. A solution of the resulting aldehyde in ether (5 mL) was added dropwise to a stirring solution of methylmagnesium bromide (3.0 M, 2.663 mL, 8.00 mmol) in ether (5 mL) at 25 °C. The reaction was stirred for 10 min and then quenched with water and extracted with ether (3 x 10 mL). The combined organic extracts were dried over magnes-ium sulfate, filtered, and concentrated under reduced pressure. Flash column chromatography (silica gel, 4:1 hexanes:ethyl acetate) provided the alcohol 5-methyl-4,6-heptadienol (220 mg, 44%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.43 (1H, dd, J = 17.4, 10.7 Hz), 5.51 (1H, dd, J = 7.4 Hz), 5.11 (1H, d, J = 17.4 Hz), 4.96 (1H, d, J = 10.7 Hz), 3.85 (1H, sextet, J = 6.2 Hz), 2.30 (2H, m), 1.89 (1H, s), 1.75 (3H, d, J = 0.5 Hz), 1.19 (3H, d, J = 6.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 141.27, 136.57, 128.39, 111.40, 67.81, 38.10, 22.93, 11.94. IR (thin film): 3359, 3090, 3038, 2971, 2928, 1642, 1607, 1121, 1076, 990 cm^{-1}. To a stirring solution of this alcohol (220 mg, 1.743 mmol) in THF (10 mL) at 25 °C was added the carboxylic acid **6** (398 mg, 3.487 mmol) and triphenyl-phosphine (915 mg, 3.487 mmol) followed by the dropwise addition of diethyl azodicarbox-ylate (687 μL, 3.487 mmol) and the reaction was stirred for 20 min. Saturated sodium bicarbonate solution was added and the mixture was extracted with ether (3 x 10 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield a pale yellow oil. Flash column chromatography (silica gel, 2:1 hexanes:benzene) of the residue yielded the triene **9** (300 mg, 77%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 6.81 (1H, dd, J = 15.7, 6.6 Hz), 6.33 (1H, dd, J = 17.4, 10.8 Hz), 5.71 (1H, dd, J = 14.5, 1.4 Hz), 5.46 (1H, dd, J = 7.4, 7.4 Hz), 5.08 (1H, d, J = 17.4 Hz), 4.92 (1H, d, J = 10.7 Hz), 4.85 (1H, sextet, J = 6.3 Hz), 2.20-2.45 (3H, m), 1.66 (3H, d, J = 0.5 Hz), 1.15 (3H, d, J = 6.3 Hz), 0.97 (6H, d, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.55, 155.33, 141.23, 136.38, 127.31, 118.90, 111.31, 70.27, 34.63, 30.90, 21.22, 19.60, 11.86. IR (thin film): 3090, 2965, 2934, 2872, 1717, 1653, 1265, 986 cm^{-1}.

dl 4aα,8β,10aα-3,4,4a,7,8,10a-Hexahydro-5-methyl-8-(1-methylethyl)-2-[1H]-benzopyran-1-one (8a) and dl 4aα,8α,10aβ-3,4,4a,7,8,10a-Hexhydro-5-methyl-8-(1-methylethyl)-2-[1H]-benzopyran-1-one (8b). Triene **7** (33 mg, 0.158 mmol) was

dissolved in degassed 1,2-dichlorobenzene (3 mL) and heated in a sealed tube under argon at 150-160 °C for 10 days. Flash column chromatography (silica gel, 6:1 hexanes:ethyl acetate) of the crude solid gave the *cis*-fused lactone **8a** (22 mg, 67%) and the *trans*-fused lactone **8b** (4 mg, 12%).

(8a). ^{1}H NMR (benzene-d_6, 400 MHz) δ: 5.25 (1H, bs), 3.69 (1H, m), 3.59 (1H, m), 2.51 (1H, dd, J = 5.7, 5.4 Hz), 2.20 (1H, m), 2.10 (1H, m), 1.96 (1H, m), 1.81 (1H, m), 1.48 (1H, m), 1.31 (3H, s), 1.22 (2H, m), 0.85 (3H, d, J = 6.6 Hz), 0.75 (3H, d, J = 6.7 Hz). ^{13}C NMR (benzene-d_6, 100 MHz) δ: 171.94, 132.30, 123.69, 65.25, 42.77, 39.21, 32.86, 26.87, 25.96, 24.36, 20.77, 20.23, 20.15. IR (thin film): 2961, 2917, 2870, 1728, 1262, 1152, 1090 cm^{-1}.

(8b). ^{1}H NMR (benzene-d_6, 400 MHz) δ: 5.21 (1H, bd, J = 3.9 Hz), 3.68 (1H, m), 3.52 (1H, m), 3.23 (1H, dh, J = 7.0, 3.5 Hz), 2.04 (1H, dd, J = 11.5, 11.3 Hz), 1.92 (2H, m), 1.79 (1H, m), 1.40-1.70 (2H, m), 1.33 (3H, s), 0.91 (3H, d, J = 7.1 Hz), 0.77 (1H, m), 0.69 (3H, d, J = 7.0 Hz). ^{13}C NMR (benzene-d_6, 100 MHz) δ: 173.31, 132.82, 122.20, 63.63, 42.38, 37.83, 37.70, 26.35, 26.12, 22.68, 20.98, 19.91, 14.81. IR (thin film): 2963, 2926, 2872, 1746, 1156, 1103 cm^{-1}.

dl 3α,4aα,8β,10aα-3,4,4a,7,8,10a-Hexahydro-3,5-dimethyl-8-(1-methylethyl)-2-[1H]-benzopyran-1-one (10a) and dl 3α,4aβ,8β,10aα-3,4,4a,7,8,10a-Hexahydro-3,5-dimethyl-8-(1-methylethyl)-2-[1H]-benzopyran-1-one (10b). Triene **9** (32 mg, 0.144 mmol) was dissolved in degassed 1,2-dichlorobenzene (3 mL) and heated in a sealed tube under argon at 150-160 °C for 10 d. Flash column chromatography (silica gel, 10:1 hexanes:ethyl acetate) of the crude solid gave the *cis*-fused lactone **10a** (20 mg, 63%) and the *trans*-fused lactone **10b** (4 mg, 13%).

(10a). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.40 (1H, m), 4.40 (1H, qdd, J = 16.2, 2.4 Hz), 2.74 (1H, dd, J = 7.1, 6.8 Hz), 2.56 (1H, m), 2.22 (1H, m), 2.15 (1H, ddd, J = 14.1, 6.9, 2.4 Hz), 1.93 (1H, m), 1.86 (1H, m), 1.68 (1H, m), 1.64 (3H, m), 1.65 (1H, s), 1.37 (3H, d, J = 6.6 Hz), 0.92 (6H, d, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 174.34, 133.52, 121.36,

74.34, 40.89, 37.45, 34.73, 34.48, 27.31, 23.70, 21.35, 21.20, 20.98, 19.00. IR (thin film): 2961, 2917, 2932, 2870, 1732, 1229, 1184 cm^{-1}.

(10b). ^1H NMR ($CDCl_3$, 400 MHz) δ: 5.43 (1H, bd, J = 4.0 Hz), 4.52 (1H, ddq, J = 16.5, 10.3, 6.2 Hz), 3.79 (1H, m), 2.85 (1H, d of septet, J = 7.1, 3.3 Hz), 2.41 (1H, dd, J = 12.1, 10.1 Hz), 2.34 (1H, bdd, J = 10.0 Hz), 1.70-2.10 (4H, m), 1.64 (3H, d, J = 1.2 Hz), 1.39 (3H, d, J = 6.2 Hz), 0.92 (3H, d, J = 7.0 Hz), 0.72 (3H, d, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 175.19, 133.10, 122.37, 71.86, 42.18, 38.07, 37.25, 35.06, 25.91, 22.59, 21.11, 20.99, 20.24, 14.83. IR (thin film): 2969, 2965, 2872, 1740, 1281, 1111, 1053 cm^{-1}.

3α,4aα,8β,10aα-3,4,4a,7,8,10a-Hexahydro-3-[(4*S*)-2,2,4-trimethyl-1,3-dioxolan-4-yl]-5-methyl-8-(1-methylethyl)-2-[1H]-benzopyran-1-one (13a) and 3α,4aβ,8β,10aα-3,4,4a,7,8,10a-Hexahydro-3-[(4*S*)-2,2,4-trimethyl-1,3-dioxolan-4-yl]-5-methyl-8-(1-methylethyl)-2-[1H]-benzopyran-1-one (13b). The triene **12** (7.60 mg, 0.0236 mmol) was dissolved in 0.5 mL toluene-d_8 along with trace of 2,6-di-*tert*-butyl-4-methylphenol in a sealed tube. Argon was bubbled through the reaction mixture for 30 min. Then the reaction mixture was heated at 150-155 °C for 10 d. Concentration gave a colorless oily residue. Flash column chromatography (silica gel, 30:1 haxanes:etheyl acetate) of the crude product gave **13a** (6.3 mg, 83%) and **13b** (1.3 mg, 17%).

(13a). ^1H NMR ($CDCl_3$, 500 MHz) δ: 5.46 (1H,bs), 4.22 (1H, d, J = 8.9 Hz), 4.21 (1H, dd, J = 6.7, 3.0 Hz), 3.78 (1H, d, J = 8.9 Hz), 2.79 (1H, dd, J = 7.2, 7.2 Hz), 2.58 (1H, ddd, J = 6.4, 6.0, 5.7 Hz), 2.24-2.30 (1H, m), 2.20-2.30 (1H, m), 1.96-2.01 (1H, m), 1.91-1.96 (1H, m), 1.74-1.79 (1H, m), 1.72 (3H, d, J = 1.4 Hz), 1.52-1.60 (1H, m), 1.47 (3H, s), 1.45 (3H, s), 1.44 (6H, s), 0.98 (3H, d, J = 6.6 Hz), 0.98 (3H, d, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 173.24, 133.40, 121.51, 110.01, 81.10, 81.05, 70.32, 41.43, 36.86, 34.44, 27.40, 27.20, 26.67, 26.25, 23.62, 23.60, 21.08, 21.02, 18.14.

(13b). ^1H NMR ($CDCl_3$, 500 MHz) δ: 5.50 (1H, bs), 4.30-4.33 (1H, m), 4.22 (1H, d, J = 9.1Hz), 3.82 (1H, J = 9.1 Hz), 2.90 (1H, dh, J = 6.9, 3.3 Hz), 2.44 (1H, dd, J = 11.4, 11.0 Hz), 2.31-2.38 (1H, m), 2.03-2.08 (1H, m), 1.89-1.95 (1H, m), 1.85-1.88 (1H, m), 1.73-1.75

(1H, m), 1.71 (3H, bs), 1.48 (3H, s), 1.47 (6H, s), 0.98 (3H, d, J = 7.0 Hz), 0.79 (3H, d, J = 7.0 Hz).

Triene 12. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.06 (1H, d, J = 15.7 Hz), 6.40 (1H, dd, J = 17.4, 10.7 Hz), 5.84 (1H, dd, J = 15.7, 1.5 Hz), 5.54 (1H, dd, J = 7.4, 7.4 Hz), 5.33 (1H, dd, J = 9.8, 3.6 Hz), 5.08 (1H, d, J = 17.4 Hz), 4.92 (1H, d, J = 10.7 Hz), 3.96 (1H, d, J = 8.8 Hz), 3.52 (1H, d, J = 8.8 Hz), 2.53-2.60 (1H, m), 2.36-2.40 (1H, m), 2.05-2.08 (1H, m), 1.70 (3H, bs), 1.48 (3H, s), 1.35 (3H, s), 1.23 (3H, s), 0.79 (6H, d, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 166.36, 155.91, 141.06, 136.13, 127.55, 118.14, 111.06, 109.84, 81.83, 75.67, 71.43, 30.84, 29.14, 26.72, 26.34, 21.08, 21.04, 11.72.