Supporting Information

Ni-Catalyzed Alkylative Dimerization of Vinyl Grignard Reagents Using Alkyl Fluorides

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Typical Experimental Procedures and Analytical Data of Products.

3-Methyl-1-undecene (2) CAS Registry Number 18435-37-5

To a mixture of 1-fluorooctane (129 mg, 0.98 mmol) and a catalytic amount of NiCl_2 (4 mg, 0.03 mmol) was added a THF solution of vinylmagnesium chloride (1.20 M, 2.5 mL, 3.0 mmol) at 25 °C under nitrogen. After stirring for 2 h at 25 °C, 1 N HCl(aq) was added to the solution. A saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over MgSO_4 , and evaporated to give a pale yellow crude product (94 % GC yield). Purification by column chromatography with hexane afforded 149 mg (91 %) of 2.

IR (neat) 2958, 2924, 2855, 1465, 993, 910 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.69 (ddd, $J = 17.2$ Hz, 10.0 Hz, 7.2 Hz, 1H), 4.94 (d, $J = 17.2$ Hz, 1H), 4.90 (d, $J = 10.0$ Hz, 1H), 2.15-2.05 (m, 1H), 1.33-1.19 (m, 14H), 0.97 (d, $J = 6.8$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 112.0, 37.9, 36.8, 32.0, 29.9, 29.8, 29.5, 27.4, 22.9, 20.3, 14.3; MS (EI) m/z (relative intensity, %) 168 (M^+ , 1), 139 (5), 111 (3), 97 (11), 83 (25), 70 (100), 55 (63), 43 (33), 41 (31); HRMS calcd for $\text{C}_{12}\text{H}_{24}$ 168.1878, found 168.1869. Anal. Calcd for $\text{C}_{12}\text{H}_{24}$: C, 85.63; H, 14.37. Found: C, 85.47; H, 14.08.

3-Cyclohexyl-1-butene (3) CAS Registry Number 3645-01-0

To a mixture of fluorocyclohexane (99 mg, 0.97 mmol) and a catalytic amount of $\text{NiCl}_2(\text{PPh}_3)_2$ (20 mg, 0.03 mmol) was added a THF solution of vinylmagnesium chloride (1.25 M, 2.4 mL, 3.0 mmol) at 25 °C under nitrogen. After stirring for 20 h at 25 °C, 1 N HCl(aq) was added to the solution. A saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over MgSO_4 , and evaporated to give a pale yellow crude product (75 % NMR yield). Purification by column chromatography with hexane afforded 83 mg (62 %) of 3.

IR (neat) 2923, 2852, 1448, 994, 909 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.76-5.67 (m, 1H), 4.94-4.90 (m, 2H), 1.99-1.91 (m, 1H), 1.74-1.08 (m, 11H), 0.96 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.3, 112.7, 43.4, 42.7, 30.3, 30.2, 26.6, 17.1; MS (EI) m/z (relative intensity, %) 138 (M^+ , 5), 110 (43), 96 (15), 83 (91), 67 (49), 55 (100), 41 (21); HRMS calcd for $\text{C}_{10}\text{H}_{18}$ 138.1408, found 138.1412. Anal. Calcd for $\text{C}_{10}\text{H}_{18}$: C, 86.88; H, 13.12. Found: C, 86.62; H, 12.83.

9,12-Diphenyl-10-eicosene (4)

To a mixture of 1-fluorooctane (252 mg, 1.91 mmol) and a catalytic amount of $\text{NiCl}_2(\text{PPh}_3)_2$ (39 mg, 0.06 mmol) was added a THF solution of vinylmagnesium bromide (0.31 M, 9.7 mL, 3.0 mmol) at 25 °C under nitrogen. After stirring for 14 h at 25 °C, 1 N HCl_{aq} was added to the solution. A saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over MgSO_4 , and evaporated to give a pale yellow crude product (69 % NMR yield). Purification by HPLC with CHCl_3 as an eluent afforded 260 mg (63 %) of 4. IR (neat) 3026, 2955, 2925, 2854, 1601, 1493, 1452, 969, 758, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.14 (m, 10H), 5.58-5.52 (m, 2H), 3.60-3.19 (m, 2H), 1.64-1.50 (m, 4H), 1.40-1.05 (m, 24H), 0.87 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) (*trans* isomer) δ 145.3, 133.6, 128.1, 127.4, 125.7, 48.7, 36.2, 32.0, 29.7, 29.6, 29.4, 27.7, 22.8, 14.3; (*cis* isomer) δ 145.6, 133.4, 128.2, 127.2, 125.7, 43.9, 37.3, 32.0, 29.7, 29.6, 29.4, 27.8, 22.8, 14.3; MS (EI) m/z (relative intensity, %) 432 (M^+ , 3), 354 (9), 319 (43), 241 (14), 229 (26), 216 (16), 193 (14), 129 (16), 117 (66), 105 (10), 91 (100), 57 (8), 43 (8); HRMS calcd for $\text{C}_{32}\text{H}_{48}$ 432.3756, found 432.3758. Anal. Calcd for $\text{C}_{32}\text{H}_{48}$: C, 88.82; H, 11.18. Found: C, 88.56; H, 10.90.

3-Octyl-4-pentenoic acid (6)

To a mixture of 1-fluorooctane (127 mg, 0.96 mmol) and a catalytic amount of $\text{NiCl}_2(\text{PPh}_3)_2$ (20 mg, 0.03 mmol) was added a THF solution of vinylmagnesium chloride (1.25 M, 2.4 mL, 3.0 mmol) at 25 °C under nitrogen. After stirring for 2 h at 25 °C, CO_2 was added to the solution. A saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over MgSO_4 , and evaporated to give a crude product (85 % NMR yield). Purification by column chromatography with 2:1 hexane/ Et_2O afforded 171 mg (84 %) of 6. IR (neat) 3080, 2956, 2926, 2855, 1712, 1641, 1466, 1421, 1293, 1239, 993, 917 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 11.6 (br s, 1H), 5.64 (ddd, J = 17.2, 10.0, 8.0 Hz, 1H), 5.05 (d, J = 17.2 Hz, 1H), 5.01 (d, J = 10.0 Hz, 1H), 2.56-2.47 (m, 1H), 2.44-2.28 (m, 2H), 1.45-1.21 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.9, 140.6, 115.1, 40.2, 40.0, 34.6, 32.0, 29.7, 29.7, 29.4, 27.1, 22.8, 14.2; MS (EI) m/z (relative intensity, %) 212 (M^+ , 1), 152 (100), 123 (12), 114 (12), 99 (27), 82 (30), 69 (36), 55 (44), 43 (38), 41 (33); HRMS calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ 212.1776, found 212.1759.

9-Vinyloctacosane (8)

To a mixture of 1-fluorooctane (131 mg, 0.99 mmol) and a catalytic amount of NiCl_2 (4 mg, 0.03 mmol) was added a THF solution of vinylmagnesium chloride (1.24 M, 2.4 mL, 3.0 mmol) at 25 °C under nitrogen. After stirring for 7 h at 25 °C, 1,3-butadiene (24 mL, 1.0 mmol) and 1-bromooctadecane (983 mg, 2.9 mmol) was added to the solution. After stirring for 14 h, 1 N HCl_{aq} was added to the solution. A saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over MgSO_4 , and evaporated to give a pale yellow crude product (80 % GC yield). Purification by HPLC with CHCl_3 as an eluent afforded 280 mg (67 %) of 8. IR (neat) 2958, 2916, 2843, 1463, 994, 912, 746, 720 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.52 (ddd, J = 17.0, 10.6, 8.8 Hz, 1H), 4.93 (d, J = 10.6 Hz, 1H), 4.92 (d, J = 17.0 Hz, 1H), 1.95-1.85 (m, 1H), 1.35-1.16 (m, 50H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 113.4, 44.0, 35.0, 31.9, 29.6, 29.3, 27.1, 22.6, 14.1; MS (EI) m/z (relative intensity, %) 420 (M^+ , 3), 322 (3), 308 (10), 168 (12), 154 (42), 139 (30), 125 (20), 111 (40), 97 (73), 83 (73), 70 (100), 57 (73), 55 (51), 43 (47); HRMS calcd for $\text{C}_{30}\text{H}_{60}$ 420.4695, found 420.4699. Anal. Calcd for $\text{C}_{30}\text{H}_{60}$: C, 85.63; H, 14.37. Found: C, 85.42; H, 14.08.

1,1-diphenyl-7-methyl-1,8-nonadiene (9)

To a mixture of 6,6-diphenyl-1-floro-5-hexene (131 mg, 0.52 mmol) and a catalytic amount of $\text{NiCl}_2(\text{PPh}_3)_2$ (10 mg, 0.015 mmol) was added a THF solution of vinylmagnesium chloride (1.25 M, 1.2 mL, 1.5 mmol) at 25 °C under nitrogen. After stirring for 6 h at 25 °C, 1 N HCl(aq) was added to the solution. A saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over MgSO_4 , and evaporated to give a pale yellow crude product (71 % NMR yield). Purification by HPLC with CHCl_3 as an eluent afforded 80 mg (54 %) of 9. IR (neat) 3079, 3057, 3022, 2959, 2925, 2854, 1495, 1444, 910, 761, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.16 (m, 10H), 6.07 (t, $J = 7.6$ Hz, 1H), 5.66 (ddd, $J = 17.2$ Hz, 10.2 Hz, 7.6 Hz, 1H), 4.92 (d, $J = 17.2$ Hz, 1H), 4.88 (d, $J = 10.2$ Hz, 1H), 2.13-2.07 (m, 3H), 1.44-1.40 (m, 2H), 1.30-1.22 (m, 4H), 0.95 (d, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 142.7, 141.2, 140.1, 130.1, 129.8, 127.93, 127.88, 127.0, 126.63, 126.57, 112.2, 37.8, 36.5, 30.2, 29.9, 27.0, 20.3; MS (EI) m/z (relative intensity, %) 290 (M^+ , 16), 233 (17), 219 (11), 205 (65), 193 (89), 180 (100), 167 (50), 165 (32), 129 (11), 115 (91), 91 (56); HRMS calcd for $\text{C}_{22}\text{H}_{26}$ 290.2035, found 290.2043. Anal. Calcd for $\text{C}_{22}\text{H}_{26}$: C, 90.98; H, 9.02. Found: C, 90.72; H, 8.86.