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SUPPORTING INFORMATION

Allenation of Carbonyl Compounds with Alkenyl Titanocene Derivatives

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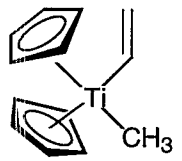
EXPERIMENTAL PROCEDURES AND SPECTROSCOPIC DATA OF SELECTED COMPOUNDS

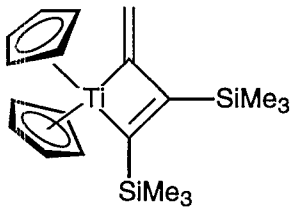
Methyl vinyl bis(cyclopentadienyl) titanium (15a): To a red solution of chloromethyltitanocene (250 mg, 1.14 mmol) in 5 mL of THF under nitrogen atmosphere was added dropwise vinylmagnesium bromide (1.15 mL, 1.0 M solution in THF) at -40°C. The mixture was slowly warmed to 0°C over 3 hrs. The brownish solution can be used directly for further reaction.



15a

^{1}H NMR (360 MHz, C_6D_6) δ 5.98 (m, 3 H, -CH=CH_2), 5.78 (s, 10 H, Cp), 0.55 (s, 3 H, -CH_3).

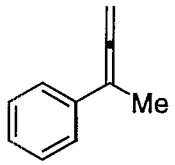
Titanacyclobutene 17: To a red solution of chloromethyltitanocene (250 mg, 1.14 mmol) in 5 mL of THF under nitrogen atmosphere was added dropwise vinylmagnesium bromide (1.15 mL, 1.0 M solution in THF) at -40°C. The brownish mixture was slowly warmed to 0°C over 3 hrs. Then bis(trimethylsilyl)acetylene (195 mg, 1.14 mmol) was added at once and the solution was allowed to stirr at room temperature for 6 hrs giving a purple solution. Evaporation of the volatiles gave the labile titanacyclobutene product with good purity.



17

^{1}H NMR (360 MHz, C_6D_6) δ 6.43 (s, 1 H, =CH_2), 5.77 (s, 5 H, Cp), 5.62 (s, 1 H, =CH_2), 5.31 (s, 5 H, Cp), 0.33 (s, 9 H, -$Si(CH_3)_3$), 0.31 (s, 9 H, -$Si(CH_3)_3$).

Typical carbonyl allenation procedure with 15a: To a solution of chloromethyltitanocene (250 mg, 1.14 mmol) in 5 mL of THF under nitrogen atmosphere was added dropwise vinylmagnesium bromide (1.15 mL, 1.0 M solution in THF) at -40°C. The mixture was slowly warmed to 0°C over 3 hrs. 3,4,5-trimethoxybenzaldehyde (190 mg, 0.95 mmol) was added at -10°C and the mixture was allowed to stir at room temperature for 3 hrs. The solution was concentrated to a volume of 1 mL and 25 mL of hexane was added to precipitate the titanium oxide which was removed by filtration. Evaporation of the solvent and purification by flash column chromatography (silica, 7% EtOAc in hexane) gave the corresponding allene product (172 mg, 88%).

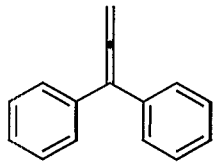


^{1}H NMR (360 MHz, C_6D_6) δ 7.40-7.01 (m, 5 H, Ph-H), 4.82 (q, 2 H, J = 3.0 Hz, =CH_2), 1.91 (t, 3 H, J = 3.0 Hz, -CH_3).

^{13}C NMR (90 MHz, C_6D_6) δ 209.49, 136.74, 128.57, 126.85, 126.09, 100.22, 76.66, 16.88.

MS m/z 130 (M^+), 115, (base), 102, 89, 77, 63, 51.

IR (KBr) cm^{-1} 1940, 840.

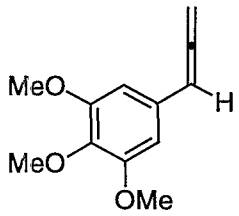


^{1}H NMR (250 MHz, C_6D_6) δ 7.42-7.02 (m, 10 H, Ph-H), 4.93 (s, 2 H, =CH_2).

^{13}C NMR (63 MHz, C_6D_6) δ 210.32, 136.75, 132.07, 130.26, 128.84, 128.71, 127.44, 109.77, 77.90.

MS m/z 192 (M^+, base), 189, 165, 152, 139, 126, 115, 98, 89.

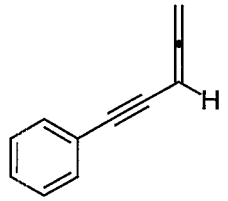
IR (KBr) cm^{-1} 1929, 847.



^{1}H NMR (250 MHz, C_6D_6) δ 6.52 (s, 2 H, Ph-H), 6.08 (t, 1 H, J = 6.8 Hz, =CH-), 4.95 (d, 2 H, J = 6.8 Hz, =CH_2), 3.83 (s, 3 H, -OCH_3), 3.37 (s, 6 H, -OCH_3).

^{13}C NMR (63 MHz, C_6D_6) δ 209.96, 154.40, 138.86, 129.33, 104.81, 94.95, 78.97, 60.53, 55.69.

MS m/z 206 (M^+), 191, 176, 163, 148 (base), 133, 120, 105, 103, 89, 77, 63, 51.

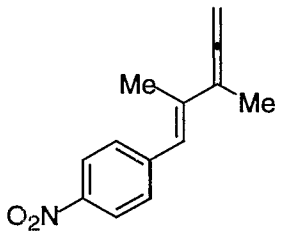


^{1}H NMR (360 MHz, C_6D_6) δ 7.40 -6.91 (m, 5 H, Ph-H), 5.48 (t, 1 H, J = 6.8 Hz, =CH-), 4.62 (d, 2 H, J = 6.8 Hz, =CH_2).

^{13}C NMR (90 MHz, C_6D_6) δ 216.97, 131.67, 128.52, 123.96, 121.46, 91.73, 82.22, 77.07, 76.09.

MS m/z 140 (M^+, base), 114, 87, 63.

IR (KBr) cm^{-1} 1932, 847.

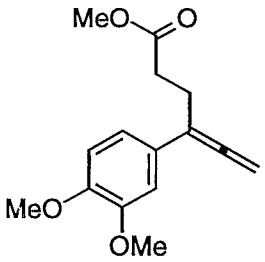


^{1}H NMR (360 MHz, C_6D_6) δ 7.85 (d, 2 H, J = 8.3 Hz, Ph -H), 6.78 (d, 2 H, J = 8.3 Hz, Ph-H), 6.12 (s, 1 H, =CH-), 4.75 (s, 2 H, =CH_2), 1.83, (s, 3 H, -CH_3), 1.80 (s, 3 H, -CH_3).

^{13}C NMR (90 MHz, C_6D_6) δ 211.50, 144.69, 137.38, 129.63, 123.43, 123.32, 104.48, 103.85, 76.73, 16.90, 16.52.

MS m/z 215 (M^+), 200 (base), 169, 153, 141, 128, 115, 89, 77, 63, 51.

IR (KBr) cm^{-1} 1929, 852.

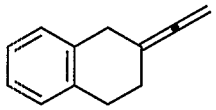


^{1}H NMR (250 MHz, C_6D_6) δ 7.02 (d, 1 H, J = 2.0 Hz, Ph-H), 6.92 (dd, 1 H, J_1 = 8.3 Hz, J_2 = 2.0 Hz, Ph-H), 6.59 (d, 1 H, J = 8.3 Hz, Ph-H), 4.91 (t, J = 3.9 Hz, =CH_2), 3.44 (s, 3 H, -CH_3), 3.40 (s, 3 H, -CH_3), 3.36 (s, 3 H, -CH_3), 2.70 (m, 2 H, -CH_2-), 2.47 (t, 2 H, J = 7.5 Hz, -CH_2-).

^{13}C NMR (63 MHz, C_6D_6) δ 208.07, 172.88, 150.18, 149.55, 128.63, 118.34, 112.15, 110.83, 104.77, 79.45, 55.53, 55.49, 51.10, 32.53, 24.85.

MS m/z 262 (M^+), 247, 231, 219, 203, 189, 175, 159, 145, 131, 115 (base), 102, 89, 77, 63, 59, 51.

IR (KBr) cm^{-1} 1938, 856.

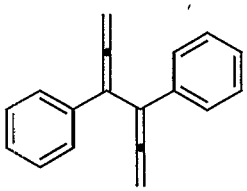


^{1}H NMR (250 MHz, C_6D_6) δ 7.02-6.85 (m, 4 H, Ph-H), 4.65 (m, 2 H, =CH_2), 3.39 (t, 2 H, J = 3.0 Hz, -CH_2-), 2.60 (t, 2 H, J = 6.9 Hz, -CH_2-), 2.28 (m, 2 H, -CH_2-).

^{13}C NMR (63 MHz, C_6D_6) δ 204.53, 136.95, 130.21, 128.86, 128.66, 126.32, 126.00, 97.85, 74.54, 33.04, 30.25, 27.98.

MS m/z 156 (M^+), 141, 128 (base), 115, 103, 91, 77, 63, 51.

IR (KBr) cm^{-1} 1960, 860.

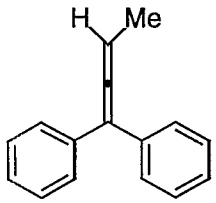


^{1}H NMR (360 MHz, C_6D_6) δ 7.57-7.00 (m, 10 H, Ph-H), 5.05 (s, 2 H, =CH_2), 5.03 (s, 2 H, =CH_2).

^{13}C NMR (63 MHz, C_6D_6) δ 207.41, 148.97, 133.01, 128.91, 128.84, 125.82, 93.66.

MS m/z 230 (M^+, base), 215, 202, 189, 176, 163, 152, 139, 126, 115, 98, 89, 77, 63, 51.

IR (KBr) cm^{-1} 855.

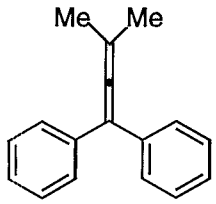


^{1}H NMR (250 MHz, C_6D_6) δ 7.46-7.03 (m, 10 H, Ph-H), 5.41 (q, 1 H, J = 6.8 Hz, =CHMe), 1.55 (d, 3 H, J = 6.8 Hz, -CH_3).

^{13}C NMR (63 MHz, C_6D_6) δ 206.80, 137.78, 132.37, 128.90, 128.64, 127.30, 124.73, 110.00, 88.93, 14.19.

MS m/z 206 (M^+), 205, 191 (base), 178, 165, 152, 139, 128, 115, 102, 91, 77.

IR (KBr) cm^{-1} 1941, 840.

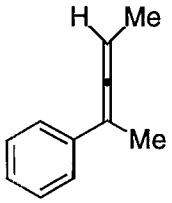


^{1}H NMR (360 MHz, C_6D_6) δ 7.49-7.07 (m, 10 H, Ph-H), 1.64 (s, 6 H, $-CH_3$).

^{13}C NMR (90 MHz, C_6D_6) δ 204.25, 138.60, 132.37, 128.98, 128.73, 127.13, 124.74, 108.65, 98.43, 20.28.

MS m/z 220 (M^+), 205 (base), 203, 190, 178, 165, 152, 141, 128, 115, 101, 91, 77.

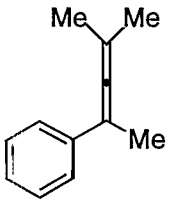
IR (KBr) cm^{-1} 1945.



^{1}H NMR (360 MHz, C_6D_6) δ 7.44-7.03 (m, 5 H, Ph-H), 5.25 (m, 1H, =CHMe), 1.98 (d, J = 3 Hz, $-CH_3$), 1.56 (d, J = 7.3 Hz, $-CH_3$).

^{13}C NMR (90 MHz, C_6D_6) δ 205.36, 138.07, 128.54, 126.70, 126.14, 100.35, 87.75, 17.19, 14.30.

MS m/z 144 (M^+), 129 (base), 115, 102, 89, 77, 63, 51



^{1}H NMR (360 MHz, C_6D_6) δ 7.46-7.05 (m, 5 H, Ph-H), 2.01 (s, 3 H, $-CH_3$), 1.66 (s, 6 H, $-CH_3$).

^{13}C NMR (90 MHz, C_6D_6) δ 202.11, 138.67, 128.20, 126.17, 125.88, 98.54, 96.67, 20.05, 17.14.

MS m/z 158 (M^+), 143, 128 (base), 115, 103, 91, 77, 65, 51.