Synthesis of Highly Substituted Cyclopentenones via the [4+1] Cycloaddition of Nucleophilic Carbenes and Vinyl Ketenes

James H. Rigby* and Zhengqiang Wang

Department of Chemistry, Wayne state University, Detroit, MI 48202

jhr@chem.wayne.edu

Supporting Information

General procedure: a solution of vinylketene (1 equiv., ca. 0.05M) and carbene precursor (2 equiv. for N-heterocyclic carbene and bis(propylthio)carbene, 4 equiv. for dimethoxycarbene) in xylene (N-heterocyclic carbene and dimethoxycarbene) or benzene (bis(propylthio)carbene) was heated at reflux till the completion of the reaction (typically 1-2 h). The resulting solution was cooled down to room temperature and directly chromatographed on silica gel (hexane, then EtOAc / hexane).

Yield 55%, yellow crystal: mp (benzene / pentane) 144-146 °C; IR (neat) ν 2952, 2859, 1706 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.38 (m, 3H), 7.21 (t, J = 7.6 Hz, 4H), 7.03-7.06 (m, 2H), 6.88 (t, J = 7.6 Hz, 2H), 6.77 (d, J = 8.8 Hz, 4H), 3.86 (dt, J = 14.4, 8.4 Hz, 2H), 3.63 (dt, J = 14.4, 8.4 Hz, 2H), 3.27 (s, 2H), -0.04 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 212.8, 181.1, 144.4, 143.4, 138.9, 129.6, 129.2, 128.5, 126.7, 120.6, 117.2, 83.7, 47.2, 42.9, -0.6; MS (EI) m/e (rel. intensity) 438 (M^+ , 16), 410 (2), 365 (3), 337 (5), 236 (100); HRMS calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{OSi}$ (M^+) 438.2127, found 438.2129; Anal. calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{OSi}$: C, 76.68; H, 6.90; N, 6.39. Found: C, 76.70; H, 6.82; N, 6.41.

Yield 88%, colorless oil: IR (neat) ν 2960, 2871, 1692 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.39-7.40 (m, 3H), 7.25-7.27 (m, 2H), 3.23 (s, 2H), 2.70-2.82 (m, 4H), 1.63 (sextet, J = 7.5 Hz, 4H), 1.00 (t, J = 7.5 Hz, 6H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.0, 178.3, 138.3, 138.2,

129.7, 128.5, 127.2, 61.3, 53.3, 32.2, 22.8, 14.0, -0.5; MS (EI) m/e (rel. intensity) 378 (M^+ , 0.3), 363 (3), 335 (3), 304 (100), 287 (42), 261 (7), 245 (23); HRMS calcd for $C_{19}H_{27}OS_2Si$ ($M^+ - CH_3$) 363.1273, found 363.1271.

Yield 63%, colorless oil: IR (neat) ν 2951, 2833, 1707 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.41 (m, 3H), 7.26-7.28 (m, 2H), 3.42 (s, 6H), 3.00 (s, 2H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 179.7, 139.0, 138.7, 129.8, 128.5, 127.2, 100.7, 50.9, 46.1, 25.1, -0.4; MS (EI) m/e (rel. intensity) 290 (M^+ , 11), 275 (11), 260 (5), 243 (2), 201 (2), 159 (19), 129 (18), 88 (100); HRMS calcd for $C_{16}H_{22}O_3Si$ (M^+) 290.1338, found 290.1338; Anal. calcd for $C_{16}H_{22}O_3Si$: C, 66.18; H, 7.64. Found: C, 66.42; H, 7.68.

Yield 80%, colorless oil: IR (neat) ν 2941, 2864, 1706 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 3.38 (s, 3H), 3.30 (s, 3H), 2.75 (q, $J = 7.2$ Hz, 1H), 2.15 (s, 3H), 1.50 (septet, $J = 7.6$ Hz, 3H), 1.15 (d, $J = 7.2$ Hz, 3H), 1.04 (dd, $J = 7.6, 3.0$ Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 187.7, 132.1, 101.0, 51.0, 50.6, 49.8, 19.8, 18.9, 14.5, 11.9; MS (EI) m/e (rel. intensity) 326 (M^+ , 0.5), 311 (1), 295 (7), 283 (82), 255 (4), 237 (3), 209 (4), 59 (100); HRMS calcd for $C_{18}H_{34}O_3Si$ (M^+) 326.2277, found 326.2273; Anal. calcd for $C_{18}H_{34}O_3Si$: C, 66.21; H, 10.50. Found: C, 65.99; H, 10.52.

Yield 96%, colorless oil: IR (neat) ν 2968, 2864, 1690 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 2.99 (q, $J = 7.2$ Hz, 1H), 2.55-2.74 (m, 4H), 2.14 (s, 3H), 1.46-1.65 (m, 7H), 1.31 (d, $J = 8.0$ Hz, 3H), 1.05 (dd, $J = 7.2, 2.8$ Hz, 18H), 0.95-1.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 184.9, 131.7, 66.7, 55.2, 32.1, 31.9, 22.7, 22.4, 19.1, 19.0, 15.7, 14.1, 12.0; MS (EI) m/e (rel. intensity) 371 ($M^+ - C_3H_7$, 5), 340 (6), 296 (11), 253 (12), 211 (4), 43 (100); HRMS calcd for $C_{19}H_{35}OS_2Si$ ($M^+ - C_3H_7$) 371.1899, found 371.1892.

Yield 78%, red oil: IR (neat) ν 3342, 2943, 2864, 1675 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, $J = 7.6$ Hz, 2H), 7.14 (t, $J = 8.0$ Hz, 2H), 6.79-6.86 (m, 3H), 6.65 (t, $J = 7.2$ Hz, 1H), 6.59 (t, $J = 8.4$ Hz, 2H), 5.25 (s, 1H), 5.05 (s, 1H), 4.77 (bs, 1H), 3.90-4.03 (m, 2H), 3.39-3.46 (m, 1H), 3.30-3.35 (m, 1H), 3.29 (s, 1H), 1.71 (s, 3H), 1.38 (heptet, $J = 7.6$ Hz, 3H), 1.15 (dd, $J = 7.2, 3.2$ Hz, 18H);

^{13}C NMR (100 MHz, CDCl_3) δ 203.9, 152.5, 148.6, 146.2, 146.0, 145.9, 129.3, 129.3, 120.1, 117.4, 117.0, 112.8, 106.3, 48.4, 42.0, 40.6, 19.1, 12.7, 12.1; MS (EI) m/e (rel. intensity) 474 (M^+ , 43), 429 (4), 368 (90), 312 (23), 275 (9), 248 (19), 59 (100); HRMS calcd for $\text{C}_{30}\text{H}_{42}\text{N}_2\text{OSi}$ (M^+) 474.3066, found 474.3067.

Yield 82%, colorless oil: IR (neat) ν 2940, 2863, 1703 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.38 (s, 3H), 3.33 (s, 3H), 2.97 (d, $J = 14.0$ Hz, 1H), 2.69 (dd, $J = 11.0, 5.0$ Hz, 1H), 2.20 (dt, $J = 14.0, 5.0$ Hz, 1H), 1.95-2.03 (m, 2H), 1.85-1.88 (m, 1H), 1.39-1.55 (m, 6H), 1.03 (t, $J = 7.0$ Hz, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 204.2, 188.8, 129.7, 99.2, 52.2, 50.8, 50.5, 33.2, 29.4, 27.5, 25.1, 19.0, 18.9, 11.8; MS (EI) m/e (rel. intensity) 321 ($\text{M}^+ - \text{CH}_3\text{O}$, 4), 309 (100), 263 (2), 235 (2), 179 (4); HRMS calcd for $\text{C}_{20}\text{H}_{36}\text{O}_3\text{Si}$ (M^+) 352.2434, found 352.2428; Anal. calcd for $\text{C}_{20}\text{H}_{36}\text{O}_3\text{Si}$: C, 68.13; H, 10.30. Found: C, 68.42; H, 10.48.

Yield 85%, colorless oil: IR (neat) ν 2924, 2862, 1692 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.01 (d, $J = 14.0$ Hz, 1H), 2.85 (dd, $J = 12.0, 5.0$ Hz, 1H), 2.62-2.74 (m, 4H), 2.20 (dt, $J = 8.5, 5.0$ Hz, 2H), 1.89-1.99 (m, 2H), 1.47-1.62 (m, 10H), 1.05 (dd, $J = 7.5, 3.5$ Hz, 18H), 0.98 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 204.5, 186.5, 129.1, 65.1, 58.2, 32.7, 32.0, 31.8, 31.7, 27.6, 25.7, 22.8, 22.4, 19.0, 18.9, 14.1, 14.1, 11.9; MS (EI) m/e (rel. intensity) 394 ($\text{M}^+ - \text{C}_3\text{H}_7$, 64), 366 (76), 354 (13), 322 (100), 279 (51), 251 (8), 235 (8); HRMS calcd for $\text{C}_{21}\text{H}_{37}\text{OS}_2\text{Si}$ ($\text{M}^+ - \text{C}_3\text{H}_7$) 397.2055, found 397.2051.

Yield 56%, yellow oil: IR (neat) ν 3334, 2941, 2864, 1668 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.20 (t, $J = 8.0$ Hz, 2H), 7.13 (t, $J = 7.5$ Hz, 2H), 6.79-6.83 (m, 3H), 6.64 (t, $J = 7.5$ Hz, 1H), 6.58 (d, $J = 8.0$ Hz, 2H), 5.84 (t, $J = 9.0$ Hz, 1H), 4.87 (bs, 1H), 3.96 (t, $J = 6.0$ Hz, 2H), 3.30-3.40 (m, 2H), 3.20 (s, 1H), 2.22-2.26 (m, 2H), 2.11 (t, $J = 7.0$ Hz, 2H), 1.62-1.67 (m, 2H), 1.38 (heptet, $J = 7.5$ Hz, 3H), 1.15 (t, $J = 7.5$ Hz, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 203.9, 154.0, 148.7, 145.9, 141.5, 136.7, 129.3, 129.2, 123.2, 119.8, 117.2, 116.9, 112.8, 48.3, 42.1, 39.2, 25.9, 25.6, 22.0, 19.1, 12.1; MS (EI) m/e (rel. intensity) 500 (M^+ , 0.7), 394 (3), 364 (2), 332 (2), 302 (7), 290 (19), 229 (20); HRMS calcd for $\text{C}_{32}\text{H}_{44}\text{N}_2\text{OSi}$ (M^+) 500.3223, found 500.3221.

Yield 71%, yellow oil: IR (neat) ν 2919, 2864, 1713 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, J = 2.5 Hz, 1H), 7.09-7.17 (m, 4H), 6.85 (t, J = 7.5 Hz, 1H), 6.67-6.73 (m, 5H), 3.92-3.97 (m, 1H), 3.71-3.77 (m, 2H), 3.60-3.65 (m, 1H), 3.41 (dq, J = 7.5, 2.5 Hz, 1H), 1.42 (heptet, J = 7.5 Hz, 3H), 1.22 (d, J = 7.5 Hz, 3H), 1.11 (dd, J = 22.5, 15.0 Hz, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 213.0, 177.3, 145.6, 144.4, 143.2, 129.3, 129.0, 120.3, 118.2, 116.2, 115.9, 84.9, 48.0, 46.8, 44.1, 18.8, 13.8, 11.2; MS (EI) m/e (rel. intensity) 460 (M^+ , 8), 417 (5), 303 (4), 287 (4), 250(100); HRMS calcd for $\text{C}_{29}\text{H}_{40}\text{N}_2\text{OSi}$ (M^+) 460.2910, found 460.2910.

Yield 76%, yellow crystal: mp (benzene / pentane) 133-135 $^{\circ}\text{C}$; IR (neat) ν 2917, 2849, 1706 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.16 (t, J = 7.6 Hz, 4H), 6.82 (t, J = 7.6 Hz, 2H), 6.73 (d, J = 8.0 Hz, 4H), 3.87 (dt, J = 14.0, 8.0 Hz, 2H), 3.62 (dt, J = 13.6, 8.0 Hz, 2H), 3.13 (s, 2H), 2.25 (s, 3H), 1.53 (heptet, J = 7.6 Hz, 3H), 0.99 (d, J = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 214.0, 184.7, 144.7, 139.0, 129.6, 129.3, 129.2, 120.0, 119.8, 116.4, 116.2, 82.9, 47.0, 44.2, 44.0, 18.9, 12.1; MS (EI) m/e (rel. intensity) 460 (M^+ , 10), 417 (2), 354 (1), 287 (3), 236(100); HRMS calcd for $\text{C}_{29}\text{H}_{40}\text{N}_2\text{OSi}$ (M^+) 460.2910, found 460.2905; Anal. calcd for $\text{C}_{29}\text{H}_{40}\text{N}_2\text{OSi}$: C, 75.60; H, 8.76; N, 6.08. Found: C, 75.60; H, 8.80; N, 6.16.