Supporting Information

AN INTERMOLECULAR [4+3] CYCLOADDITION REACTION USING 3-HYDROXY-2-PYRONE DERIVATIVES WITH AN OXYALLYL CATION

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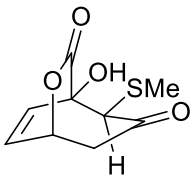
EXPELIMENTAL

General Information

Infrared spectra were recorded on a JASCO FT-IR 4100 spectrometer with an ATR unit. Absorbance frequencies are recorded in reciprocal centimeters (cm^{-1}). High-resolution mass spectra (HRMS) were obtained from a Thermo Scientific Exactive for electrospray ionization (ESI). HRMS data are reported as m/e (relative intensity), with accurate mass reported for the molecular ion $[M+Na]^+$, $[M+H]^+$. ^1H and ^{13}C NMR spectra were recorded on a JEOL ECA-500 spectrometer operating at either 500 MHz (^1H NMR) or 125 MHz (^{13}C NMR) in $CDCl_3$ as a solvent. Chemical shifts for NMR were reported in ppm relative to the chemical sift of the residual solvent (^1H NMR, 7.26 ppm for $CDCl_3$; ^{13}C NMR, 77.0 ppm for $CDCl_3$). Multiplicities are indicated as; br (broad), s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz).

All reactions sensitive to oxygen or moisture were performed under an atmosphere of dry argon in flame-dried glassware. Dry THF (41001-85), CH_2Cl_2 (1138-85), CH_3CN (01837-05), and methanol (25506-05) was purchased from KANTO Chemical Industries Ltd, in anhydrous Grade. Chemical reagents were commercial grades and were used without any purification unless otherwise noted. Flash chromatography was performed with Silica Gel 60N (spherical, neutral), purchased from KANTO Chemical Industries Ltd, unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using commercial silica gel plates (E. Merck, Silica Gel 60 F_{254}).

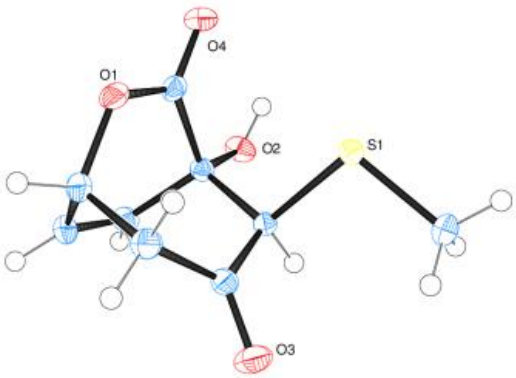
(1*R,2*R**,5*R**)-1-hydroxy-2-(methylthio)-6-oxabicyclo[3.2.2]non-8-ene-3,7-dione (3a)**



To a solution of Tf_2NH (2.17 mmol) in CH_2Cl_2 (6.6 mL) was added a solution of 3-hydroxy-2-pyrone **1a** (148 mg, 1.32 mmol) and acetate **2** (548 mg, 1.72 mmol) in CH_2Cl_2 (6.6 mL) at −78°C. The mixture was stirred for 2 h at −30°C. After completion of the reaction (by monitoring TLC), the reaction was quenched with sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (Hexane/AcOEt = 2/1 as eluent) to give cycloadduct **3a** (245 mg, 86%) as a white solid.

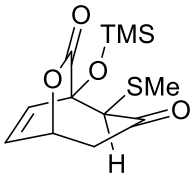
3a: m.p. 139-141 °C; R_f 0.14 (Hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$); δ 6.42 (dd, 1H, *J* = 9.2, 1.2 Hz), 6.33 (dd, 1H, *J* = 9.2, 5.8 Hz), 5.21 (m, 1H), 3.47 (dd, 1H, *J* = 17.2, 2.3 Hz), 3.45(d, 1H, *J* = 1.5 Hz), 2.70 (ddd, 1H, *J* = 17.2, 2.9, 1.5 Hz), 2.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 171.9, 135.2, 128.9, 73.1, 72.4, 63.4, 42.3, 16.4; IR (ATR) ν_{max} 3471, 2945, 2923, 1741, 1698, 1344, 1186, 1135, 1058, 1000, 796 cm^{-1}; HRMS (ESI): calcd. for $C_9H_{10}O_4NaS$ $[M+Na]^+$, 237.0192: found, 237.0193.

Crystal data for 3a



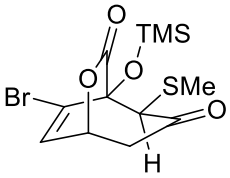
CCDC 1864564, $C_9H_{10}O_4S$, size 0.40 x 0.30 x 0.20 mm^3, monoclinic, $P2_1/n$, a = 8.6212(8) Å, b = 9.7269(6) Å, c = 11.0767(7) Å, α= 90°, β= 91.961(4)°, γ= 90°, Z = 4, μ = 0.332 mm^{-1}, Independent reflections 1810, R(int) = 0.0093, Goodness-of-fit on F2 = 1.057, Final R indices [I>2σ(I)] R_1 = 0.0254, wR_2 = 0.0674.

(1*R,2*R**,5*R**)-2-(methylthio)-1-(trimethylsilyloxy)-6-oxabicyclo[3.2.2]non-8-ene-3,7-dione (4a)**



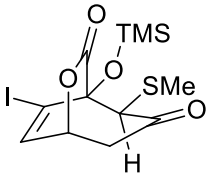
4a: a white solid; m.p. 148−149 °C; R_f 0.41 (Hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31 (s, 2H), 5.13 (m, 1H), 3.48 (d, 1H, *J* = 2.9 Hz), 3.45 (dd, 1H, *J* = 17.2, 2.3 Hz), 2.64 (ddd, 1H, *J* = 17.2, 2.9, 2.3 Hz), 2.12 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 170.5, 137.7, 128.7, 76.2, 72.3, 64.6, 42.6, 16.5, 1.9; IR (ATR) ν_{max} 2979, 1753, 1699, 1370, 1251, 1218, 1167, 1145, 1088, 1013, 898, 838 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{18}O_4NaSSi$ $[M+Na]^+$, 309.0587: found, 309.0594.

(1*R,2*R**,5*R**)-8-bromo-2-(methylthio)-1-(trimethylsilyloxy)-6-oxabicyclo[3.2.2]non-8-ene-3,7-dione (4b)**



4b: a white solid; m.p. 85−86 °C; R_f 0.52 (Hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.60 (d, 1H, *J* = 5.7 Hz), 5.11 (m, 1H), 3.49 (d, 1H, *J* = 1.7 Hz), 3.40 (dd, 1H, *J* = 17.2, 2.3 Hz), 2.63 (ddd, 1H, *J* = 17.2, 4.6, 1.7 Hz), 2.12 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, 168.5, 130.3, 128.8, 78.3, 71.7, 63.9, 41.5, 16.5, 1.9; IR (ATR) ν_{max} 2980, 1765, 1701, 1621, 1380, 1248, 1222, 1169, 1151, 844 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{17}BrO_4NaSSi$ $[M+Na]^+$, 386.9692: found, 386.9701.

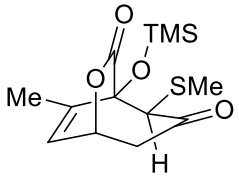
(1*R,2*R**,5*R**)-8-iodo-2-(methylthio)-1-(trimethylsilyloxy)-6-oxabicyclo[3.2.2]non-8-ene-3,7-dione (4c)**



4c: a brown solid; m.p. 73−74 °C; R_f 0.48 (Hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, 1H, *J* = 6.3 Hz), 5.04 (m, 1H), 3.41 (s, 1H), 3.37 (d, 1H, *J* = 17.2 Hz), 2.62 (dd, 1H, *J* = 17.2, 4.6 Hz), 2.11 (s, 3H), 0.32 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, 167.6, 137.1, 108.3, 78.4,

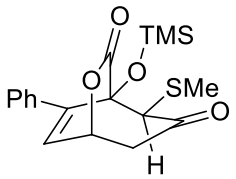
73.8, 63.6, 41.4, 16.5, 2.5; IR (ATR) ν_{max} 2955, 2926, 1762, 1698, 1607, 1381, 1250, 1165, 1148, 835, 575; HRMS (ESI): calcd for $C_{12}H_{17}IO_4NaSSi$ $[M+Na]^+$, 434.9554: found, 434.9565.

(1*R,2*R**,5*R**)-8-methyl-2-(methylthio)-1-(trimethylsilyloxy)-6-oxabicyclo[3.2.2]non-8-ene-3,7-dione (4d)**



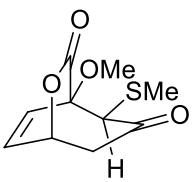
4d: a pale yellow solid; m.p. 182−184 °C; R_f 0.43 (Hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.96 (d, 1H, *J* = 4.0 Hz), 5.03 (s, 1H), 3.41 (d, 1H, *J* = 16.6 Hz), 3.37 (s, 1H), 2.55 (1H, dd, *J* = 16.6, 4.6 Hz), 2.07 (s, 3H), 2.03 (s, 3H), 0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.9, 170.6, 145.0, 122.2, 78.0, 71.2, 64.1, 41.9, 16.9, 16.4, 2.1; IR (ATR) ν_{max} 2925, 2853, 1759, 1699, 1387, 1249, 1152, 883, 841, 758, 588; HRMS (ESI): calcd. for $C_{13}H_{20}O_4NaSSi$ $[M+Na]^+$, 323.0744: found, 323.0750.

(1*R,2*R**,5*R**)-2-(methylthio)-8-phenyl-1-(trimethylsilyloxy)-6-oxabicyclo[3.2.2]non-8-ene-3,7-dione (4e)**



4e: a pale yellow solid; m.p. 86−87 °C; R_f 0.43 (Hexanae/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 3H) , 7.30 (m, 2H), 6.25 (d, 1H, *J* = 5.8 Hz), 5.21 (m, 1H), 3.78 (s, 1H), 3.56 (d, 1H, *J* = 17.2 Hz), 2.69 (dd, 1H, *J* = 17.2, 4.6 Hz), 2.16 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 170.3, 148.4, 134.4, 128.8, 128.4, 128.2, 125.1, 78.6, 71.4, 65.9, 42.2, 16.5, 1.7; IR (ATR) ν_{max} 2952, 2925, 1753, 1695, 1385, 1151, 845; HRMS (ESI): calcd. for $C_{18}H_{22}O_4NaSSi$ $[M+Na]^+$, 385.0900: found, 385.0908.

(1*R,2*R**,5*R**)-1-methoxy-2-(methylthio)-6-oxabicyclo[3.2.2]non-8-ene-3,7-dione (4f)**



4f: a pale yellow solid; m.p. 102−104 °C; R_f 0.22 (Hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, CDCl3) δ 6.54 (dd, 1H, *J* = 9.2, 5.8 Hz), 6.45 (d, 1H, *J* = 9.2 Hz), 5.21 (dd, 1H, *J* = 6.9, 5.2 Hz), 3.54 (s, 3H), 3.45 (s, 1H), 3.11 (d, 1H, *J* = 16.6 Hz), 3.02 (dd, 1H, *J* = 16.6, 6.9 Hz), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 169.1, 133.0, 131.3, 78.0, 72.0, 64.1, 54.0, 40.5, 15.9; IR (ATR) ν_{max} 2979, 2943, 1751, 1695, 1376, 1232, 1139, 984, 796, 726 cm^{-1}; HRMS (ESI): calcd. for $C_{10}H_{12}O_4NaS[M+Na]^+$, 251.0359: found, 251.0354.