***N*-Heterocyclic Carbene-Initiated α -Acylvinyl Anion Reactivity: Additions of α -Hydroxypropargylsilanes to Aldehydes**

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Supporting Information

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General Information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. THF was purified by passage through a bed of activated alumina.¹ Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.² Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain or potassium permanganate stain followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ¹H-NMR spectra were recorded on a Varian Inova 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ¹³C-NMR spectra were recorded on a Varian Inova 500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.0 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer.

Acylsilanes and α -hydroxypropargylsilanes were prepared using the procedure developed in our laboratory.^{3,4} The *N*-heterocyclic carbene **2** was prepared according to the procedure by Arduengo.⁵

Procedure for 8-(tert-butyldimethylsilyloxy)-3-(dimethyl(phenyl)silyl)oct-4-yn-3-ol

To a flame-dried round bottom flask containing a magnetic stirring bar was added EtMgBr (3M solution in ether, 1.7 mL, 5.05 mmol) and THF. The TBS-protected 4-pentyn-1-ol (1 g, 5.05 mmol) was added slowly via syringe to the Grignard solution. After stirring at room temperature for 1 h, the resulting solution was cooled to -78 °C and acylsilane (500 mg, 2.52 mmol) in THF was added slowly over 5 minutes. Upon consumption of the acylsilane as determined by thin layer chromatography (20% ethyl acetate/hexanes), the mixture was quenched with saturated aqueous NH₄Cl. The mixture was diluted with ethyl acetate and the resulting layers were separated. The aqueous layer was extracted with EtOAc (3 X 30 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated to provide the unpurified propargylsilane. Purification by flash chromatography on silica gel (5% EtOAc/Hex)

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provided **750 mg (76%)** as a yellow oil. Analytical data: IR (film) 3435, 3050, 2945, 2931, 2858, 2213, 1716, 1460, 1420, 1253, 1103, 953, 835, 778, 701, 656 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 6.2$ Hz, 2H), 7.39 (m, 3H), 3.69 (t, $J = 6.2$ Hz, 2H), 2.35 (t, $J = 7.0$ Hz, 2H), 1.73 (t, $J = 6.6$ Hz, 2H), 1.70-1.55 (m, 4H), 1.44 (s, 1H), 1.03 (t, $J = 7.3$ Hz, 3H), 0.92 (s, 9H), 0.46 (s, 3H), 0.45 (s, 3H), 0.07 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.0, 134.9, 129.7, 127.9, 88.2, 82.6, 65.3, 61.9, 32.4, 30.8, 26.3, 15.7, 8.1, 7.9, -5.0, -5.4, -5.5;

For complete analytical data for α -hydroxypropargylsilanes, see reference 4.

General Procedure for Addition of α -Hydroxypropargylsilanes to Aldehydes

To a flame-dried 10 mL round bottom flask containing a magnetic stirring bar and fitted with septum was added α -hydroxypropargylsilane (1 equiv) and THF (2 mL) under a nitrogen atmosphere. The flask was cooled to 0 $^\circ\text{C}$ in an ice bath and *n*-BuLi (5 mol%) was added. After conversion to the silyloxyallene as determined by thin layer chromatography, the flask was cooled to -78 $^\circ\text{C}$. Aldehyde (2 equiv) was added followed by *N*-heterocyclic carbene **2** (0.2 equiv). The resulting solution was stirred at -78 $^\circ\text{C}$ until the aldehyde was completely consumed (15 min to 18 h) as determined by thin layer chromatography (20% ethyl acetate/hexanes). After consumption of the aldehyde, the reaction mixture was then filtered through a plug of silica gel with ether (40 mL). The ether solution was concentrated giving the unpurified silyl protected product, which was dissolved in THF (5 mL) and treated with 1N HCl (1mL). After stirring at room temperature for 1-5 h, this solution was diluted with ether (20 mL) and H_2O (10 mL) and poured into a separatory funnel. The aqueous layer was discarded and the ether layer was washed with saturated NaHCO_3 (10 mL) and brine (10 mL). The resulting ether layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo to provide the unpurified carbinols. The products were purified by flash chromatography (10% EtOAc/hexanes).

For complete analytical data for compounds **3–7**, **9–11**, **13**, see reference 4.

(Z)-4-(1-hydroxy-2-methylpropyl)non-4-en-3-one (8): Prepared according to general procedure using **1** (100 mg, 0.36 mmol), isobutyraldehyde (66 μL , 0.72 mmol) and *N*-heterocyclic carbene **2** (28 mg, 0.073 mmol) to afford **35 mg (45%) of 8** as a colorless oil. Analytical data for **8**: IR (film) 3448, 2959, 2929, 2870, 1681, 1460, 1378, 1251, 1179, 1118, 1018 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.75 (t, $J = 7.7$ Hz, 1H), 3.81 (t, $J = 6.9$ Hz, 1H), 2.62 (doublet of quartets, $J = 15.2, 7.3$ Hz, 2H), 2.36 (d, $J = 6.2$ Hz, 1H), 2.15 (quartet, $J = 7.3$ Hz, 2H), 1.70 (doublet of triplets, $J = 6.9$ Hz, 1H), 1.40-1.33 (m, 4H), 1.09 (t, $J = 7.3$ Hz, 3H), 0.96 (d, $J = 6.6$ Hz, 3H), 0.90 (t, $J = 7.3$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.1, 143.2, 136.0, 81.4, 37.8, 33.0, 31.9, 29.4, 22.6, 19.9, 18.4, 14.1, 8.0; LRMS (electrospray): Exact mass calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ [$2\text{M}+\text{Na}$] $^+$, 447.36. Found [$2\text{M}+\text{Na}$], 447.5.

(Z)-8-hydroxy-4-(hydroxy(phenyl)methyl)oct-4-en-3-one (12): Prepared according to general procedure using 8-(tert-butyldimethylsilyloxy)-3-(dimethyl(phenyl)silyl)oct-4-yn-3-ol (70 mg, 0.18 mmol), benzaldehyde (36 μ L, 0.36 mmol) and *N*-heterocyclic carbene **2** (14 mg, 0.036 mmol) to afford **32 mg (72%)** of **12** as a colorless oil. Analytical data for **12**: IR (film) 3374, 2927, 1679, 1447, 1387, 1053, 692 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34 (m, 5H), 5.77 (t, $J = 8.0$ Hz, 1H), 5.48 (d, $J = 4.8$ Hz, 1H), 3.65 (q, $J = 6.0$ Hz, 2H), 2.54 – 2.39 (m, 4H), 2.31 (quartet, $J = 7.0$ Hz, 2H), 1.70 (double of triplets, $J = 6.2$ Hz, 2H), 1.56 (s, 1H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.6, 144.7, 141.5, 135.8, 128.8, 128.1, 126.7, 75.6, 61.5, 36.8, 31.6, 25.7, 7.7; LRMS (electrospray): Exact mass calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3$ $[\text{2M}+\text{Na}]^+$, 519.28. Found $[\text{2M}+\text{Na}]$, 519.2.

Procedure for 14

To a flame-dried 25 mL round bottom flask with chlorodimethylphenylsilane (45 mL, 0.27 mmol) and benzaldehyde (27 mL, 0.27 mmol) in THF (4 mL) at -78°C was added **2** (105 mg, 0.270 mmol) dissolved in THF (1 mL) slowly via syringe. After stirring for 15 minutes, solvent was removed under reduced pressure. The resulting solid was recrystallized from CH_2Cl_2 and hexanes. Quality single crystals were formed and analyzed by x-ray diffraction.

X-ray diffraction was performed at -120°C and raw frame data were processed using SAINT. The structure was solved by direct methods and expanded using Fourier

techniques. The distances of the chlorine and carbon atoms on the disordered dichloromethane were restrained and atoms were refined with a group anisotropic displacement parameter. The site occupancies were fixed on the chlorine atoms. The disordered oxygen was refined with a group anisotropic displacement parameter. O1b was fixed from where it was found in the difference map. There was 94% of the time oxygen is found at the O1a position. The remaining non-hydrogen atoms were refined anisotropically. The hydrogen on O1A (H1O) was refined isotropically. The hydrogen for O1B was not found in the difference map (only 6% of a hydrogen). The remaining hydrogen atoms were included in idealized positions, but not refined. The GOF = 0.976 for 415 variables refined to $R1 = 0.0906$ for 9255 reflections with $I > 2\sigma(I)$. Further information is contained in the CIF file.

Selected NMR Spectra