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SUPPORTING INFORMATION FOR

Catalytic hydrosilylation of oxalic acid: chemoselective formation of functionalized C_2 – products

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Experimental details

General considerations

All reactions and manipulations were performed in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 60 ºC before use. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to solvent residual peaks. Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. d_2-CH_2Cl_2 was dried over CaH_2 and C_6D_6 was dried over sodium and distilled before use. All reactions were carried in a medium walled J. Young NMR tube, and all the reactions were monitored by RMN ^{1}H and DEPT 135 after the addition of diphenylmethane as an internal standard.

Elemental analyses were performed at Medac Ltd at Chobham (United Kingdom). Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLB™-ms fused silica capillary column (30 m x 0.25 mm x 0.25 μm). Gas chromatography analysis were executed on a Shimadzu GC-2010 Plus gas chromatograph equipped with a Carboxen™ 1006 PLOT silica capillary column (30 m x 0.53 mm).

Preparation of anhydrous oxalic acid

Solid oxalic acid dihydrate (10g, 79.0 mmol) was heated at 60°C for 2 hours under reduced pressure (2.10^{-2} mbar) to afford anhydrous oxalic acid (7.1g; 79.0 mmol) as a white solid, in a quantitative yield.

^{1}H NMR (*d*^{6}–DMSO, 298 K) δ (ppm) = 8.20 (broad s, 2 H).

^{13}C NMR (*d*^{6}–DMSO, 298 K): δ (ppm) = 161.

Anal. Calcd. for $C_2H_2O_4$ (mol. wt. 90.03): C, 26.68; H, 2.24, O, 71.08. **Found:** C, 26.64; H, 2.18; O, 71.18.

Formation of 1:

A medium walled J. Young NMR tube was charged with anhydrous oxalic acid (9.0 mg, 0.10 mmol, 1.0 equiv.) and C_6D_6 (150 µL). $B(C_6F_5)_3$ (1.0 mg, 2.0 10^{-3} mmol, 2.0 mol %) was dissolved in a mixture of Et_3SiH (40.7 mg, 0.40 mmol, 3.5 equiv.) and C_6D_6 (150 µL) and the resulting solution was added dropwise, using a syringe, in the NMR tube, at RT. After the end of hydrogen evolution, the tube was closed and stirred for 5 h, at RT. 1 was obtained in 99 % conversion yield. **1** is highly sensitive to moisture and unstable under reduced pressure.

^{1}H NMR (200 MHz, C_6D_6, Me_4Si) δ (ppm) = 5.54 (1 H, s, **C-H**), 1.13 – 0.91 (27 H, m, **CH_3**), 0.87-0.44 (12 H, m, **CH_2**).

^{13}C NMR (50 MHz, C_6D_6, Me_4Si): δ (ppm) = 137.6, 90.2, 7.0, 6.6, 5.6, 4.7.

MS: IE (m/z): 405 (25); 377 (31); 275 (97) ; 217 (23) ; 189 (31) ; 161 (16) ; 115 (57) ; 87 (100) ; 59 (69).

Formation of 2:

A medium walled J. Young NMR tube was charged with anhydrous oxalic acid (9.0 mg, 0.10 mmol, 1.0 equiv.) and CD_2Cl_2 (150 µL). $B(C_6F_5)_3$ (0.50 mg, 1.0 10^{-3} mmol, 1.0 mol%) was dissolved in a mixture of Et_3SiH (34.9 mg, 0.30 mmol, 3.0 equiv.) and CD_2Cl_2 (150 µL)

and the resulting solution was added dropwise, using a syringe, in the NMR tube, at RT. After the end of hydrogen evolution, the tube was closed and stirred for 2.5 h, at RT. **2** was obtained in 31 % conversion yield. **2** is highly sensitive to moisture and unstable under reduced pressure.

^{1}H NMR (200 MHz, CD_2Cl_2, Me_4Si) δ (ppm) = 9.37 (1 H, s, **C-H**), 1.08 – 0.87 (9 H, m, **CH_3**), 0.64-0.44 (6 H, m, **CH_2**).

^{13}C NMR (50 MHz, CD_2Cl_2, Me_4Si): δ (ppm) = 185.6, 159.7, 6.4, 4.6.

MS: IE (m/z): 159 (9) ; 131 (100) ; 115 (33) ; 103 (36) ; 87 (38) ; 75 (32); 59 (32) ; 45 (27) ; 47 (26).

Formation of 2':

A medium walled J. Young NMR tube was charged with **3** (23.4 mg, 0.1 mmol, 1.0 equiv.) and CD_2Cl_2 (150 µL). $B(C_6F_5)_3$ (1.0 mg, 2.0 10^{-3} mmol, 2.0 mol %) was dissolved in a mixture of Et_3SiH (11.6 mg, 0.10 mmol, 1.0 equiv.) and CD_2Cl_2 (150 µL) and the resulting solution was added dropwise, using a syringe, in the NMR tube, at RT. The tube was closed and stirred for 2 h, at RT. **2** was obtained in 33 % conversion yield. **2** is highly sensitive to moisture and unstable under reduced pressure.

^{1}H NMR (200 MHz, C_6D_6, Me_4Si) δ (ppm) = 8.76 (1 H, s, **C-H**), 0.12 (9 H, s, **CH_3**).

^{13}C NMR (50 MHz, C_6D_6, Me_4Si): δ (ppm) = 184.2, 159.9, 2.1.

Formation of 3:

3 was synthesized using a modified procedure of Long *et al.*[1] In a 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser, chrlorotrimethylsilane (20.9 g, 0.19 mol, 2.9 equiv) was added under argon to anhydrous oxalic acid (6.00 g, 0.07 moles, 1 equiv). The mixture was then refluxed at 60 ^{0}C under an argon flux for 6 days (HCl was trapped using a solution of NaOH containing phenolphthalein). CH_2Cl_2 (10 mL) was then

added to the reaction mixture, at RT, and the solution was filtered through a fine porosity frit. The volatiles were removed under reduced pressure to yield colorless crystals of 3 (11.03g, 47.1 mmol) in 71 % yield. The ^{1}H NMR and ^{13}C NMR data were identical to the one reported in the literature.[2] X-ray suitable crystals of **3** were obtained from a saturated solution of 3 in CH_2Cl_2.

^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si) δ (ppm) = 0.36 (18 H, s, $\mathbf{CH_3}$)

^{13}C NMR (200 MHz, $CDCl_3$, Me_4Si): δ (ppm) = 158.4, -0.4.

Anal. Calcd. for $C_8H_{18}O_4Si_2$ (mol. wt. 234.40): C, 40.99; H, 7.74 % **Found:** C, 40.56; H, 7.76 %.

Formation of 4:

A medium walled J. Young NMR tube was charged with anhydrous oxalic acid (9.0 mg, 0.10 mmol, 1.0 equiv.) and CD_2Cl_2 (150 µL). $B(C_6F_5)_3$ (2.6 mg, 5.0 10^{-3} mmol, 5.0 mol %) was dissolved in a mixture of Et_3SiH (60.5 mg, 0.50 mmol, 5.2 equiv.) and CD_2Cl_2 (150 µL) and the resulting solution was added dropwise, using a syringe, in the NMR tube, at RT. After the end of hydrogen evolution, the tube was closed and stirred for 16 h, at RT. **4** was obtained in 95 % conversion yield. **4** is highly sensitive to moisture and unstable under reduced pressure.

^{1}H NMR (200 MHz, CD_2Cl_2, Me_4Si) δ (ppm) = 5.05 (1 H, t, ^{3}J = 4.4 Hz, **CH**), 3.39 (2 H, d, ^{3}J = 4.4 Hz, **O-$\mathbf{CH_2}$**), 1.00 – 0.83 (27 H, m, **$\mathbf{CH_3}$**), 0.73-0.44 (18 H, m, **$\mathbf{CH_2}$**).

^{13}C NMR (50 MHz, CD_2Cl_2, Me_4Si): δ (ppm) = 93.8, 69.2, 7.2, 7.1, 5.8, 4.9.

MS: IE (m/z): 391 (6); 319 (2); 276 (25); 275 (100); 189 (26); 161 (14); 133 (15); 115 (59); 87 (83); 75 (11); 59 (52).

Formation of 5:

A medium walled J. Young NMR tube was charged with anhydrous oxalic acid (9.0 mg, 0.10 mmol, 1.0 equiv.) and C_6D_6 (150 µL). $B(C_6F_5)_3$ (3.8 mg, 7.5 10^{-3} mmol, 5.0 mol %) was dissolved in a mixture of Et_3SiH (48.8 mg, 0.40 mmol, 4.2 equiv.) and C_6D_6 (150 µL) and the resulting solution was added dropwise, using a syringe, in the NMR tube, at RT. After the end of hydrogen evolution, the tube was closed and stirred for 50 h, at RT. **5** was obtained in 90 % conversion yield. **5** is highly sensitive to moisture and unstable under reduced pressure.

^{1}H NMR (200 MHz, C_6D_6, Me_4Si) δ (ppm) = 5.05 (2 H, s, **CH**), 1.18 – 1.01 (36 H, m, **CH_3**), 0.88-0.71 (24 H, m, **CH_2**).

^{13}C NMR (50 MHz, C_6D_6, Me_4Si): δ (ppm) = 94.6, 7.2, 5.7.

MS: IE (m/z): 521 (13); 276 (26); 275 (100); 189 (11) ; 161 (11); 115 (32); 87 (67); 59 (30).

Formation of 6:

A medium walled J. Young NMR tube was charged with anhydrous oxalic acid (9.0 mg, 0.10 mmol, 1.0 equiv.) and C_6D_6 (150 µL). $B(C_6F_5)_3$ (3.8 mg, 7.5 10^{-3} mmol, 5.0 mol %) was dissolved in a mixture of Et_3SiH (48.8 mg, 0.40 mmol, 4.2 equiv.) and C_6D_6 (150 µL) and the resulting solution was added dropwise, using a syringe, in the NMR tube, at RT. After the end of hydrogen evolution, the tube was closed and stirred for 50 h at RT and 16 h at 100 °C. **6** was obtained in 60 % conversion yield. **6** is highly sensitive to moisture and unstable under reduced pressure.

^{1}H NMR (200 MHz, C_6D_6, Me_4Si) δ (ppm) = 4.16 (2 H, s, **O-CH_2**), 1.13 – 0.89 (18 H, m, **CH_3**), 0.87 – 0.48 (12 H, m, **CH_2**)

^{13}C NMR (50 MHz, C_6D_6, Me_4Si): δ (ppm) = 171.7, 62.2, 7.2, 6.6, 4.9, 4.8.

MS: IE (m/z): 275 (36); 219 (42); 217 (67); 115 (54); 95 (33); 87 (100); 81 (34); 59 (78);

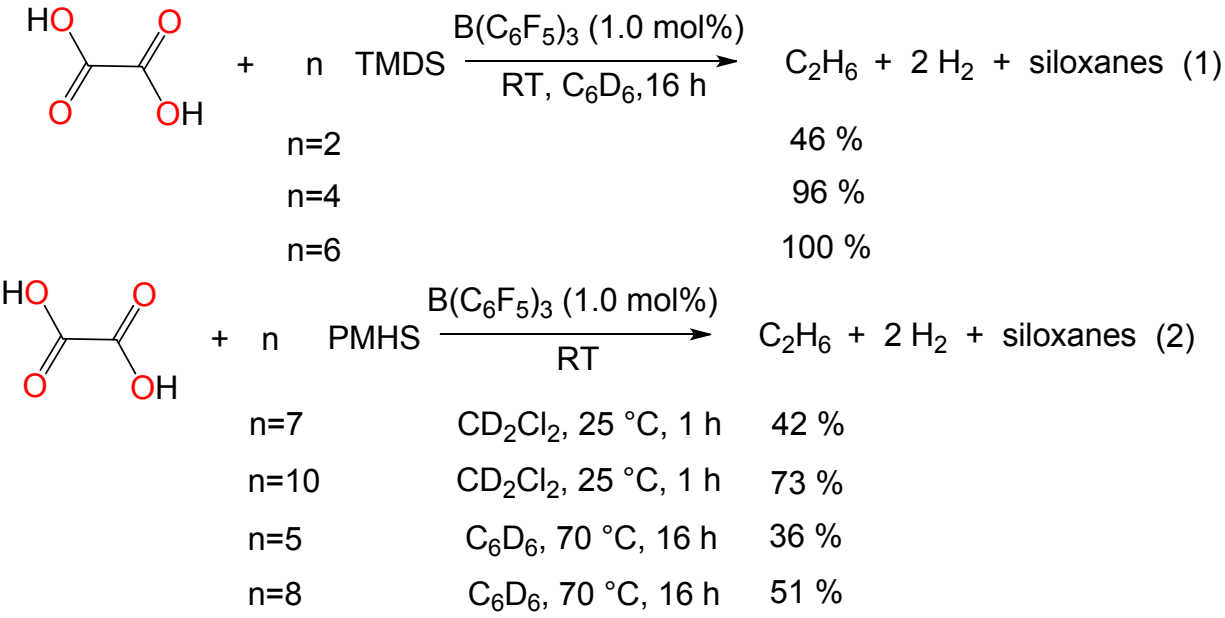
Reduction of oxalic acid to ethane

A medium walled J. Young NMR tube was charged with anhydrous oxalic acid (9.0 mg, 0.10 mmol, 1.0 equiv.) and C_6D_6 (150 µL). $B(C_6F_5)_3$ (0.5 mg, 1.0 10^{-3} mmol, 1.0 mol %) was dissolved in a mixture of TMDS (57.3 mg, 0.43 mmol, 4.3 equiv.) and C_6D_6 (150 µL) and the resulting solution was added dropwise, using a syringe, in the NMR tube, at RT. The tube was closed and stirred at RT. Oxalic acid was fully consumed within 16 h at RT and ethane was identified as the only organic product, by ^1H and ^{13}C NMR and GC analyses. Ethane yield was thus deduced from the conversion of oxalic acid. Ethane was characterized by analyzing the gas phase of the NMR tube using gas chromatography (GC), by comparison with an authentic sample obtained after hydrolysis of $AlEt_3$.

^{1}H NMR (200 MHz, CD_2Cl_2, Me_4Si) δ (ppm) = 0.87 (s, 6 H). **^{13}C NMR** (200 MHz, CD_2Cl_2, Me_4Si) δ (ppm) = 7.3.

^{1}H NMR (200 MHz, C_6D_6, Me_4Si) δ (ppm) = 0.81 (s, 6 H). **^{13}C NMR** (50 MHz, C_6D_6, Me_4Si) δ (ppm) = 7.0.

Conversions obtained with various reaction conditions:



Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[3] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal was introduced into a glass capillary with a protecting coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ- and ω-scans giving a complete data set up to θ = 28.7°, with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[4] Absorption effects were corrected empirically with the program SCALEPACK.[4] The structure was solved by direct methods with SHELXS-97, and refined by full-matrix least-squares on F^2 with SHELXL-97.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.5 times that of the parent atom. The molecular plot was drawn with ORTEP-3.[6]

Crystal data for **3**: $C_8H_{18}O_4Si_2$, M = 234.40, monoclinic, space group $P2_1/n$, a = 10.5425(7), b = 11.9183(8), c = 11.4221(8) Å, β = 108.364(4)°, V = 1362.08(16) Å^3, Z = 4. Refinement of 133 parameters on 3501 independent reflections out of 48592 measured reflections (R_{int} = 0.032) led to R_1 = 0.040, wR_2 = 0.106, S = 1.030, $\Delta\rho_{min}$ = –0.18, $\Delta\rho_{max}$ = 0.24 e Å^{-3}.

References:

1. M. D. Green, C. Schreiner, and T. E. Long, *J. Phys. Chem. A*, **2011**, *115*, 13829–13835.
2. Angell, Charles A., Xu, Wu, *US2004/34253 A1*, **2004**.
3. R. W. W. Hooft, *COLLECT*, Nonius BV: Delft, The Netherlands, 1998.
4. Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
5. G. M. Sheldrick, *Acta Crystallogr., Section A*, 2008, **64**, 112.

6. L. J. Farrugia, *J. Appl. Crystallogr.,* 1997, **30***,* 565.