

Supporting Information

for

Re₂O₇-catalyzed reaction of hemiacetals and aldehydes with *O*-, *S*-, and *C*-nucleophiles

Wantanee Sittiwong, Michael W. Richardson, Charles E. Schiaffo, Thomas J. Fisher and Patrick H. Dussault*

Address: Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588-0304, USA

Email: Patrick H. Dussault* - pdussault1@unl.edu

* Corresponding author

Experimental details

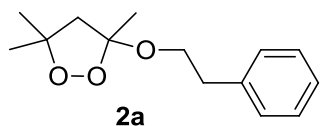
All reagents were used as received from commercial vendors, with the exception of CH₂Cl₂, which was distilled from CaH₂, and THF, which was distilled from sodium/benzophenone. Re₂O₇ (Strem, 99.9%) and Me₃SiOReO₃ (Gelest, 95%) were used as received. Reactions were conducted under an atmosphere of N₂ except where noted; flame-dried round bottom flasks (RBF) and 8 dram glass vials were used as reaction vessels. Thin layer chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates; developed plates were visualized by staining: 1% ceric sulfate and 10% ammonium molybdate in 10% H₂SO₄ (general stain, after charring); 1% *N,N'*-dimethyl-*p*-phenylenediamine solution in 1:20:100 acetic acid/ water/ methanol (specific for peroxides) [1]; 1% aqueous KMnO₄ (for unsaturated compounds). "Standard drying and purification procedures" refers to drying of organic extracts over Na₂SO₄,

removal of solvent under vacuum, and purification by flash chromatography using the indicated eluent. $^1\text{H}/^{13}\text{C}$ NMR spectra were recorded at 300 or 400 MHz (^1H frequency) in CDCl_3 ; peaks are reported as: chemical shift (multiplicity, J couplings in Hz, number of protons).

General procedure A: To a vial containing a 0.2 M CH_2Cl_2 solution of the hemiacetal (1–1.2 equiv, **3** or **4a**) or the *O*-silyl ether (**4b**) was added nucleophile (1–10 equiv) followed by catalyst (Re_2O_7 or $\text{TsOH}\cdot\text{H}_2\text{O}$). After stirring for the indicated time (typically 1 h) the reaction was concentrated in vacuo and the residue purified via flash column chromatography (EA/hex or Et_2O /pentane). Reactions employing toluenesulfonic acid monohydrate as a catalyst were run in the same manner except that the crude reaction mixture was diluted with sat. aq. NaHCO_3 (≈ 4 mL/mmol substrate) and H_2O (≈ 4 mL/mmol substrate), and the mixture was extracted with ether (20 mL/mmol substrate, 2 \times). The combined organic layers were washed with brine (25 mL) and dried over Na_2SO_4 . The residue was purified as described above.

General procedure B: A flame-dried round-bottom flask (RBF) was charged with catalyst followed by a 0.2 M solution of the acetal/hemiacetal (1 equiv) and nucleophile (2–10 equiv) in dry CH_2Cl_2 . The reaction was stirred for the indicated time (typically 1 h) and then concentrated in vacuo. The residue was purified by flash column chromatography (EA/hex or Et_2O /pentane) as described above.

General procedure for Table 4: A flame-dried RBF was charged with catalyst (1 mol %) and 2-phenylethanol (1 equiv), after which a 0.2 M solution of hemiacetal **4a** (1.2 equiv) in CH_2Cl_2 was added at the indicated rate using a syringe pump. The reaction was stirred for the indicated time and then concentrated in vacuo. The residue was purified by flash column chromatography using 5% EA/hex.

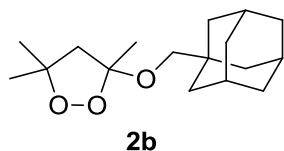


5-(2-Phenylethoxy)-3,3,5-trimethyl-1,2-dioxolane (2a) was prepared from 3,3,5-trimethyl-1,2-dioxolan-3-ol (**1a**, 190.9 mg, 1.44 mmol), 1-phenylethanol (22 mL, 183 mmol) and toluenesulfonic acid monohydrate ($\text{TsOH}\cdot\text{H}_2\text{O}$, 26.3 mg, 0.14 mmol) using general procedure A (Brønsted acid-catalysis), which is a variant of a procedure previously described for this

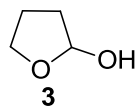
transformation [2]. The reaction was stirred for 5 h and subjected to standard workup and purification (5% EA/hex) to afford acetal **2a** as a yellow oil (234 mg, 73%). R_f (5% EA/hex) 0.46. The spectral properties matched those previously reported [3].

Re₂O₇-catalyzed (1% loading): **2a** was prepared from **1a** (175.6 mg, 1.3 mmol), 1-phenylethanol (0.8 mL, 6.7 mmol), and Re₂O₇ (6.4 mg, 0.013 mmol) in CH₂Cl₂ (13 mL) using general procedure A. The reaction was allowed to run for 1 h and then subjected to standard workup and purification (10% EA/hex) to afford **2a** as a yellow oil (262.1 mg, 83%); the product was identical to the material described above.

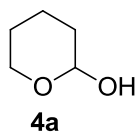
2a could also be prepared from 3,5,5-trimethyl-1,2-dioxolan-3-ol-*O*-trimethylsilyl ether (**1b**), which was prepared by a reported procedure.³



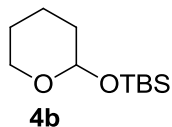
3-(Adamant-1-ylmethoxy)-3,5,5-trimethyl-1,2-dioxolane (2b) was prepared from 1-adamantane methanol and **1a** or **1b** by similar procedures as described for **2a** to afford **2b** (164 mg, 0.79 mmol, 33% yield, 10% PTSA), (0.33 g, 1.2 mmol, 78% yield, 1% Re₂O₇); (0.32 g, 1.1 mmol, 74% yield, 10% Re₂O₇). Spectral properties matched those in a previous report [3].



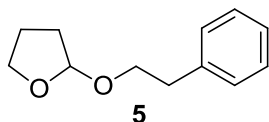
Tetrahydrofuran-2-ol (3) was prepared using a literature procedure; spectral properties matched those previously reported [4].



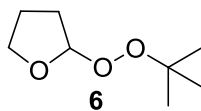
Tetrahydro-2H-pyran-2-ol (4a) was prepared using a literature procedure; spectral properties matched those previously reported [5].



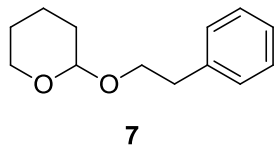
tert-Butyldimethyl((tetrahydro-2H-pyran-2-yl)oxy)silane (4b): Into a solution of imidazole (408 mg, 6.00 mmol) in THF (45 mL) in a flame-dried RBF was added **4a** (510 mg, 5.00 mmol), followed by a solution of TBSCl (900 mg, 6.00 mmol) in THF (5 mL). The reaction was stirred overnight and then quenched with H₂O (30 mL). The diethyl ether extract (3 × 10 mL) was subjected to standard drying and purification (10% EA/hex) to afford **4b** (287 mg, 13.3%). *R_f* (10% EA/hex): 0.48. ¹H NMR (400 MHz): 4.91 (m, 1H), 3.99 (m, 1H), 3.51 (m, 1H), 1.89-1.68 (6H), 0.91 (s, 9H), 0.12 (s, 3H), 0.90 (s, 3H). ¹³C NMR (100 MHz): 90.1, 62.8, 33.4, 25.7, 25.5, 19.7, 18.1, -4.4, -5.4. HRMS (ESI): calc for C₁₁H₂₄O₂Na 239.1443, found 239.1441 [6].



2-Phenethoxytetrahydrofuran (5) was prepared according to general procedure B using **3** (44 mg, 0.50 mmol), 2-phenylethanol (244 mg, 2.00 mmol), and Re₂O₇ (2.5 mg, 0.005 mmol) in CH₂Cl₂ (5 mL). The reaction was stirred for 1 h and the product was isolated and purified using standard procedures (5% EA/hex) to afford **48** (73.1 mg, 83.1%). *R_f* (25% EA/hex) 0.7. Spectral properties matched those in a previous report [7].

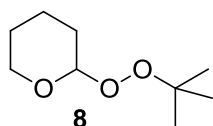
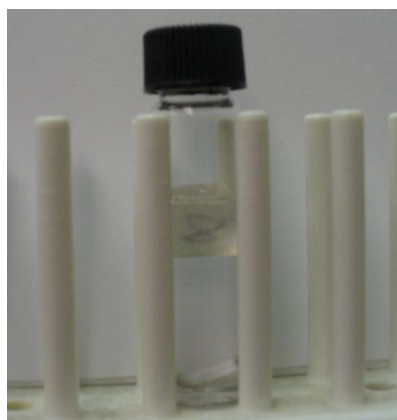


2-(tert-Butylperoxy)tetrahydrofuran (6): Into a vial containing a solution of Re₂O₇ (2.5 mg, 0.0050 mmol) in CH₂Cl₂ (3 mL) was added a decane solution of *t*-butylhydroperoxide (0.18 mL, 1.0 mmol, nominally 5.5 M), followed immediately by **4a** (44 mg, 0.50 mmol) neat. The reaction was stirred for 1 hour, then washed with 5 mL H₂O and extracted with CH₂Cl₂ (3 × 5 mL). Standard procedures for drying and purification (2.5% EA/hex) afforded **51** (54.4 mg, 68.0%). *R_f* (5% EA/hex) 0.29. Spectral properties matched those in a previous report [8].

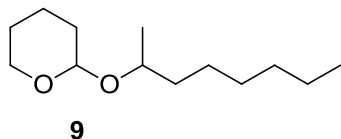


2-(2-Phenylethoxy)-tetrahydro-2H-pyran (7) could be prepared using general procedure A, B or C. Following a standard workup, the product was purified by column chromatography with 10% EA/hex. R_f (10% EA/hex) 0.41. The NMR spectra matched those previously reported [9].

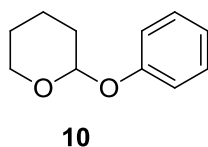
Figure S1: Reaction solution for Re(VII)-catalyzed etherification of **4a** with phenylethanol.



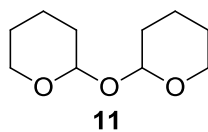
2-(tert-Butylperoxy)tetrahydro-2H-pyran (8) was prepared as described for **6** using **4a** (44 mg, 0.50 mmol), 5.5M (in deacane) *t*-butylhydroperoxide (0.18 mL, 1.0 mmol), and Re_2O_7 (2.5 mg, 0.0050 mmol) in CH_2Cl_2 (3 mL). The reaction was stirred for 1 h and was subjected to standard drying and purification procedures with 30% EA/hex to afford **51** (54.4 mg, 68%). R_f (30% EA/hex) 0.62. ^1H NMR (400 MHz) 5.07 (m, 1H), 4.05 (m, 1H), 3.63 (m, 1H), 1.83–1.71 (2H), 1.66–1.53 (4H), 1.30 (s, 9H). ^{13}C NMR (100 MHz): 101.2, 80.5, 62.7, 27.7, 26.4, 25.1, 20.0. HRMS (ESI): calc for $\text{C}_9\text{H}_{18}\text{O}_3\text{Na}$ 197.1154, found 197.1161 [10].



2-(Octan-2-yloxy)tetrahydro-2H-pyran (9) was prepared according to general procedures A or B using a solution of **4a** (102 mg, 1.00 mmol), 2-octanol (0.63 mL, 4.0 mmol), and Re_2O_7 (5.0 mg, 0.010 mmol) in CH_2Cl_2 (5 mL). The reaction was stirred for 1 h and the product was purified by flash column chromatography with 20% EA/hex to afford **9** (150 mg, 70.0%). R_f (20% EA/hex) 0.52. Spectral properties matched those previously reported [11].



2-Phenoxytetrahydro-2H-pyran (10): (CAS 4203-50-3) was prepared according to general procedure A using a solution of **4a** (51 mg, 0.5 mmol), phenol (92 mg, 1.0 mmol) and Re_2O_7 (2.5 mg, 0.05 mmol) in CH_2Cl_2 (3 mL). The reaction was stirred for 1 h and the product was purified by flash column chromatography with 10% EA/hex to afford **10** (6 mg, 7%); or using a solution of **4b** (51 mg, 0.24 mmol), phenol (44 mg, 0.5 mmol) and Re_2O_7 (2.5 mg, 0.05 mmol) in CH_2Cl_2 (1.5 mL), with standard work up and purification to afford **10** with inseparable impurity (19 mg, 44%). R_f (10% EA/hex) 0.55. ^1H NMR (400 MHz): 7.35–7.25 (m, 2H), 7.07 (m, 2H), 7.00 (m, 1H), 5.44 (t, $J = 3.3$, 1H), 3.95 (ddd, $J = 11$, 9.4 and 1.2, 1H), 3.63 (ddt, $J = 11$, 4.3 and 1.5, 1H), 2.10–1.97 (m, 1H), 1.95–1.85 (m, 1H), 1.80–1.58 (m, 3H). ^{13}C NMR (100 MHz): 157.1, 129.4, 121.6, 116.5, 96.3, 62.1, 30.4, 25.2, 18.8.

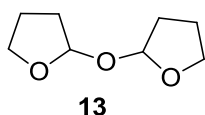


2,2'-Oxybis(tetrahydro-2H-pyran) (11): To a solution of **4a** (51 mg, 0.5 mmol) in CH_2Cl_2 (1 mL) was added Re_2O_7 (1 mg, ≈ 0.01 mmol). The reaction was stirred for 5 min and then concentrated in vacuo. The residue was purified by gradient flash column chromatography (2.5–15% Et_2O /pentane) to afford two diastomers of bisacetal **11** (major, 25.5 mg, 54%; minor 1.2 mg, 3%) accompanied by aldehyde **12** (2.5 mg, 5%).

11-Major: R_f (10% EA/hex) 0.45. ^1H NMR (400 MHz): 4.95 (dd, $J = 4.9$ and 2.5 , 2H), 3.89 (ddd, $J = 11$, 7.5 and 3.3 , 2H), 3.52 (m, 2H), 1.92–1.80 (m, 2H), 1.80–1.70 (m, 2H), 1.65–1.48 (m, 8H). ^{13}C (100 MHz): 94.6, 62.9, 30.6, 25.4, 19.7.

11-Minor: R_f (10% EA/hex) 0.33. ^1H NMR (400 MHz): 4.84 (dd, $J = 4.5$ and 2.9 , 2H), 4.05 (m, 2H), 3.58 (m, 2H), 1.92–1.50 (m, 12H). ^{13}C NMR (100 MHz): 98.5, 63.4, 31.0, 25.4, 19.8.

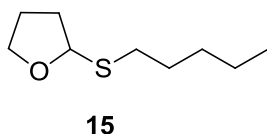
Aldehyde **12:** R_f (10% EA/hex) 0.20. Spectral properties matched those previously reported [12].



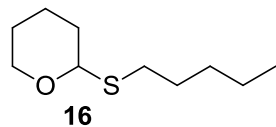
2,2'-Oxybis(tetrahydrofuran) (13) was prepared as described for **11**. The products were purified by gradient flash column chromatography (5–20% Et₂O/pentane) to afford major isomer **13** (45.7 mg, 30% yield) and 54.5 mg of a 4:1 mixture of aldehyde **14** and minor isomer **13** (7% and 28% yield based on ^1H NMR).

13-Major: R_f (10% EA/hex) 0.5; ^1H NMR (400 MHz): 5.44 (dd, $J = 4.4$ and 1.2 , 2H), 3.95–3.82 (m, 4H), 2.05–1.78 (m, 8H). ^{13}C NMR (100 MHz): 100.0, 67.0, 32.3, 23.4. 0.50, IR (ZnSe): 2953, 2875, 1108, 986, 921 cm^{-1} .

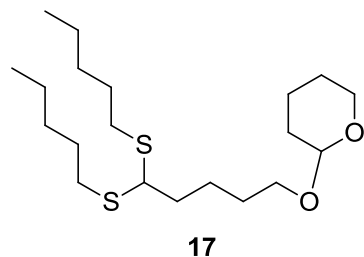
Aldehyde **14** and **13-Minor:** R_f (10% EA/hex) 0.11; Spectral properties of aldehyde **14** matched those previously reported [13].



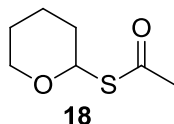
2-(Pentylthio)tetrahydrofuran (15) was prepared according to general procedure A or B. Standard workup and purification (3% and 5% EA/hex) afforded **15** (61.6 mg, 0.35 mmol, 71% yield) [14]. R_f (10% EA/hex) 0.61. ^1H NMR (400 MHz): 4.62 (m, 1H), 3.76 (m, 2H), 2.54 (m, 2H), 1.83–1.63 (6H), 1.39–1.26 (4H), 0.91 (t, $J = 6.92$, 3H). ^{13}C NMR (100 MHz): 84.4, 66.7, 32.6, 31.2, 29.7, 24.8, 22.3, 14.0. HRMS (ESI): calc for C₉H₁₈OSNa 197.0976, found 197.0984.



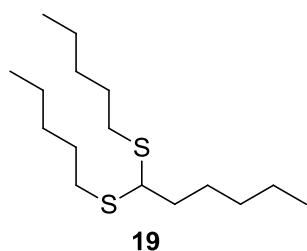
2-(Pentylthio)tetrahydro-2H-pyran (16) was prepared according to general procedure A or B. Standard workup and purification (2.5% EA/hex) afforded thioacetal **16** (73 mg, 0.39 mmol, 78% yield, 1% Re₂O₇); (43.4 mg, 0.23 mmol, 62% yield, 10% PTSA); and a trace amount of aceta/dithioacetal **17** (1.7 mg, 0.0045 mmol, 2% yield, 1% Re₂O₇) and (7.4 mg, 0.02 mmol, 8% yield, 10% PTSA). *R_f* (10% EA/hex) 0.66. ¹H NMR (400 MHz) 4.86 (m, 1H), 4.11 (m, 1H), 3.52 (m, 1H), 2.63 (m, 2H), 1.94 (m, 1H), 1.84 (m, 1H), 1.73–1.53 (6H), 1.43–1.29 (4H), 0.91 (t, *J* = 6.92, 3H). ¹³C NMR (100 MHz): 82.1, 64.5, 31.4, 31.1, 30.3, 29.6, 25.6, 22.2, 21.8, 13.9. HRMS (ESI): calc for C₁₀H₂₀OSNa 211.1133, found 211.1130 [14,15].



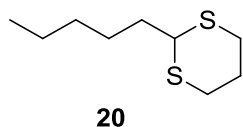
2-((5,5-bis(pentylthio)pentyl)oxy)tetrahydro-2H-pyran (17): *R_f* (10% EA/hex) 0.58. IR (ZnSe): 2924, 2858, 1120, 1034 cm⁻¹. ¹H NMR (400 MHz) 4.60 (m, 1H), 3.89 (m, 1H), 3.76 (t, *J* = 6.8, 1H), 3.75 (m, 1H), 3.52 (m, 1H), 3.41 (m, 1H), 2.67 (dt, *J* = 12.4, 7.4, 2H), 2.57 (dt, *J* = 12.4, 7.4, 2H), 1.90–1.81 (m, 2H), 1.78–1.69 (m, 1H), 1.67–1.50 (m, 12H), 1.43–1.29 (m, 8H), 0.91 (t, *J* = 7.2, 6H). ¹³C NMR (100 MHz): 98.9, 67.3, 62.3, 51.6, 36.0, 31.2, 30.8, 30.1, 29.3, 29.1, 25.5, 24.3, 22.3, 19.7, 14.0. HRMS (ESI): calc for C₂₀H₄₀O₂S₂Na 399.2367, found 399.2355.



Tetrahydro-2H-pyran-2-thiol, acetate ester (18) was prepared according to general procedure A or B using **4a** (65 mg, 0.64 mmol), thioacetic acid (76 mg, 1.0 mmol), and Re_2O_7 (2.5 mg, 0.0052 mmol) in CH_2Cl_2 (3 mL). After reaction for 1h, standard workup and purification (10% EA/hex) furnished **18** (10 mg, 10% yield). R_f (20% EA/hex) 0.51. Spectral properties matched those from literature reports [16].



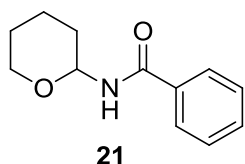
1,1-Bisthiopentylhexane (19): To a solution of hexanal (50 mg, 0.5 mmol) and pentanethiol (0.13 mL, 1.0 mmol) in CH_2Cl_2 (3 mL) was added Re_2O_7 (2.5 mg, 0.05 mmol). The reaction was stirred for 30 min and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane) to afford **19** (0.1286 g, 89%). R_f (hex) 0.22. IR (ZnSe): 2955, 2924, 2857, 1465, 732 cm^{-1} . ^1H NMR (400 MHz): 3.76 (t, $J = 9.2$, 1H), 2.68 (dt, $J = 16.4$ and 10, 2H), 2.57 (dt, $J = 16.4$ and 10, 2H), 1.80 (m, 2H), 1.70–1.22 (m, 19H), 0.92 (m, 9H). ^{13}C NMR (100 MHz): 52.1, 36.1, 31.4, 31.2, 30.1, 29.1, 27.2, 22.5, 22.3, 14.01, 13.96. HRMS (ESI): calc for $\text{C}_{16}\text{H}_{34}\text{S}_2\text{Na}$ 313.2000, found 313.1998.



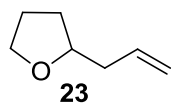
2-Pentyl-1,3-dithiane (20) was prepared as described for **19** using hexanal (50 mg, 0.5 mmol) and 1,3-propanedithiol (0.06 mL, 0.6 mmol) in CH_2Cl_2 (3 mL) and Re_2O_7 (2.5 mg, 0.05 mmol) to afford **20** (40 mg, 42% yield) R_f (hex) 0.23. Spectral properties matched those previously reported [17].



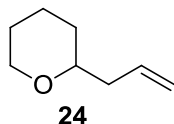
Figure S2: Reaction solutions for Re(VII)-catalyzed etherification of **4a** with phenylethanol (left) vs pentanethiol (right).



N-(Tetrahydro-2H-pyran-2-yl)benzamide (21) was prepared according to general procedure A using **4a** (51 mg, 0.5 mmol), benzamide (0.30 mg, 2.5 mmol), and Re_2O_7 (2.5 mg, 0.005 mmol) in CH_2Cl_2 (5 mL). The reaction was stirred for 2 h. The product was purified by column chromatography with 40% EA/hex and after evaporation of the solvent the resulting solid was washed with 20% EA/hex (1 mL \times 2) to afford **21** (10 mg, 10% yield). R_f (20%EA/hex) 0.51. Spectral properties matched those previously reported [18].



2-Allyltetrahydrofuran (23) was prepared according to general procedure A or B using **4a** (44 mg, 0.50 mmol), allyltrimethylsilane (0.79 mL, 2.50 mmol), and Re_2O_7 (2.5 mg, 0.0050 mmol) in CH_2Cl_2 (3mL). The reaction was stirred for 4 h and the product was purified with 10% Et_2O /pentane to afford **23** (19 mg, 33% yield). R_f (20%EA/hex) 0.52. Spectra matched literature reports [4].



2-Allyltetrahydro-2H-pyran (24) was prepared general procedure A or B using **4a** (102 mg, 1.00 mmol), allyltrimethyl silane (1.58 mL, 5.00 mmol), and Re_2O_7 (5.0 mg, 0.0010 mmol) in CH_2Cl_2 (5mL). The reaction was stirred for 4 h and the product was purified by column chromatography with 10% Et_2O /pentane to afford **24** (26 mg, 41% yield). R_f (20%EA/hex) 0.54. Spectra matched literature reports [19].

4-Oxatricyclo[4.3.1.1^{3,8}]undecan-5-ol (22): To a flame-dried RBF containing a solution of 2-adamantanone (3.0 g, 20 mmol) in CH_2Cl_2 (100 mL) was added sequentially *m*-chloroperoxybenzoic acid (7.15 g, 25 mmol), 20 mL of water and 20 mL of sat. NaHCO_3 . After stirring for 24 h, the reaction was quenched with Na_2SO_3 (1 g) and then washed sequentially with sat. aq. NaHCO_3 (20 mL) and brine (20 mL). The combined organic layers were dried with MgSO_4 , and the residue obtained upon concentration was purified by column chromatography with 60% EA/hex to afford 4-oxatricyclo[4.3.1.1^{3,8}]-undecan-5-one (2.8522 g, 86%) as a white solid. R_f (60% EA/hex):0.48. Spectral properties matched those reported [20].

To a flame dried flask containing a $-78\text{ }^\circ\text{C}$ solution of 4-oxatricyclo[4.3.1.1^{3,8}]undecan-5-one (2.0 g, 11 mmol) in CH_2Cl_2 (60 mL) was dropwise added a solution of DIBAL-H in toluene (8.3 mL, 12.5 mmol, nominally 1.5 M). The reaction was stirred at $-78\text{ }^\circ\text{C}$ for 1 h and then quenched with MeOH (0.5 mL). The reaction was allowed to warm to rt, and then stirred for 45 min. A solution of sat. aq. Rochelle's salt (30 mL) was added and the resulting suspension was extracted with CH_2Cl_2 (3×40 mL). The combined organic layers were washed with H_2O (40 mL) and dried with MgSO_4 . The residue obtained upon concentration was subjected to chromatography with 40 % EA/hex to afford hemiacetal **22** (1.9104 g, quant) as a white solid: mp $254\text{--}260\text{ }^\circ\text{C}$ (uncorrected; literature $243\text{--}252$) [17]; R_f (40 % EA/hex) 0.43. The NMR spectra matched those previously reported [21].

5-Allyl-4-oxatricyclo[4.3.1.1^{3,8}]undecane (25) was prepared according to general procedure A using oxadamantyl hemiacetal **22** (168.4 mg, 1 mmol), allyltrimethylsilane (0.8 mL, 5 mmol) and Re₂O₇ (4.8 mg, 0.01 mmol) in CH₂Cl₂ (10 mL). The reaction was stirred for 1 h and then treated with sat. aq. NaHCO₃ (5 mL) and H₂O (5 mL). The suspension was extracted with CH₂Cl₂ (3 × 20 mL) and the combined organic layers were dried with Na₂SO₄. The residue obtained upon concentration was subjected to chromatography (initially 10% EA/hex; repeat with 5% EA/hex) to afford **25** (166.5 mg, 90%). *R_f* (10% EA/hex) 0.6; ¹H NMR (400 MHz): 5.83 (m, 1H), 5.10–5.00 (2H), 4.18 (m, 1H), 3.81 (t, *J* = 6.8, 1H), 2.37 (m, 1H), 2.18 (m, 1H), 2.00–1.64 (10H), 1.61–1.49 (3H). ¹³C NMR (100 MHz): 136.6, 116.5, 81.9, 71.8, 41.5, 40.9, 40.0, 26.1, 36.0, 34.6, 30.0, 26.9, 26.4. HRMS (EI): calc for C₁₃H₂₀O 192.1514, found: 192.1519.

1-Methoxynonyl hydroperoxide (26), **1-ethoxynonyl hydroperoxide (27)**, and **1-isopropoxynonyl hydroperoxide (28)** were prepared as previously described [22].

Procedure for Re₂O₇ and Brønsted acid catalyzed exchange of hydroperoxyacetals:

A flame-dried 8 mL vial was charged with catalyst, followed by a 0.2 M solution of the starting material (1 equiv) and alcohol nucleophile (10 equiv) in dry acetonitrile. The reaction was stirred for the indicated time (typically 2–5 h) and then filtered through a short silica plug (ethyl acetate/hexane rinse). The resulting solution was concentrated in vacuo and the residue purified by flash chromatography (ethyl acetate/hexane). The spectra of products **26**, **27** and **28** matched literature reports [22].

References

- (1) Smith, L, Hill, F. L. *J. Chrom.* **1972**, *66*, 101.
- (2) Dussault, P. H.; Liu, X. *Org. Lett.* **1999**, *1*, 1391.
- (3) Schiaffo, C. E.; Rottman, M.; Wittlin, S.; Dussault, P. H. *ACS Med. Chem. Lett.* **2011**, *2*, 316-319
- (4) Saito, T.; Nishimoto, Y.; Yasuda, M.; Baba, A., *J. Org. Chem.*, **2006**, *71*, 8516.
- (5) Kimura, M.; Shimizu, M.; Tanaka, S.; Tamaru, Y. *Tetrahedron* **2005**, *61*, 3709.

- (6) Reported without details: McDonald, C. E.; Beebe, T. R.; Beard M.; McMillen, D.; Selski, D. *Tetrahedron Lett.* **1989**, *30*, 4791.
- (7) Baati, R.; Valleix, A.; Mioskowski, C.; Barma, D. K.; Falck, J. R. *Org. Lett.* **2000**, *2*, 485.
- (8) Nikalje, M. D.; Sudalai, A. *Tetrahedron* **1999**, *55*, 5903.
- (9) Hajipour, A. R.; Nasresfahani, Z. *Synth. Commun.* **2012**, *42*, 1995; Williams, D. B. G.; Simelane, S. B.; Lawton, M.; Kinfé, H. H. *Tetrahedron* **2010**, *66*, 4573.
- (10) Rigaudy, J.; Izoret, G. *Compt. Rend.* **1953**, *236*, 2086.
- (11) Matsumoto, Y.; Mita, K.; Hashimoto, K.; Iio, H.; Tokoroyama, T. *Tetrahedron* **1996**, *52*, 9387.
- (12) Clasby, M. C.; Craig, D.; Slawin, A. M. Z.; White, A. J. P.; Williams, D. J. *Tetrahedron*, **1995**, *51*, 1509.
- (13) Guy, F.; Balme, G.; Barieux, J. J.; Gore, J. *Tetrahedron*, **1988**, *44*, 5821.
- (14) Zorin, V. V.; Batyrvaev, N. A.; Zlotskii, S. S.; Rakhmankulov, D. L. *Zh. Org. Khim.* (Russ. J. Org. Chem.) **1984**, *20*, 387.
- (15) Cerny, M.; Trka, A. *Coll. of Czech. Chem. Comm.* **1983**, *48*, 1749; Eliel, E. L.; Nowak, B. E.; Daignault, R. A. *J. Org. Chem.* **1965**, *30*, 2448.
- (16) Kansikas, J.; Leskela, M.; Sipila, K.; Hase, T. *Acta Chem. Scand.* **1995**, *49*, 809; Martin, M.; Bassery, L.; Leroy, C. *Bull. Soc. Chim. Fr.* **1972**, 4763.
- (17) Huckins, J. R.; Rychnovsky, S. D. *J. Org. Chem.* **2003**, *68*, 10135.
- (18) Sugiura, M.; Hagio, H.; Hirabayashi, R.; Kobayashi, S. *J. Am. Chem. Soc.*, **2001**, *123*, 12510.
- (19) Ross, A. G.; Li, X.; Danishefsky, S. J.; *J. Am. Chem. Soc.*, **2012**, *134*, 16080.
- (20) Uyanik, M.; Nakashima, D.; Ishihara, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 9093; Gonzalez-Nunez, M. E.; Mello, R.; Olmos, A. G.; Asensio, G.; *J. Org. Chem.* **2006**, *71*, 6432.
- (21) Marchand, A. P.; Kumar, V. S.; Hariprakash, H. K. *J. Org. Chem.* **2001**, *66*, 2072.
- (22) Fisher, T. J.; Dussault, P. H. *Tetrahedron Letters*, **2010**, *51*, 5615.