Electronic Supporting Information

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General information:

¹H and ¹³C NMR spectra were recorded on a Bruker dpx300, Bruker AV400 or Bruker AV(III)400 spectrometer. The chemical shifts and the coupling constants were obtained through analysis of the relevant spectra using ACD/SpecManager software version 12 and all spectra were referenced to CDCl₃ (7.28 ppm for ¹H-NMR, 77.00 ppm for ¹³C-NMR). All GC data was obtained using a Shimadzu GC-2010 online GLC. All chemicals were purchased from Sigma Aldrich unless otherwise stated. FTIR spectra were recorded using a Nicolet 380 FT-IR spectrometer. BET surface area measurements were conducted using a Micrometrics ASAP 2020 Volumetric Sorptometer and analysed using ASAP 2020 V1.05 software. Powder X-ray diffraction patterns were obtained using a PANalytical multi-purpose diffractometer with a Cu source. Thermogravimetric analysis was conducted using a TA Instruments SDT Q600 Analyser and using TA Instruments Universal Analysis 2000 software. Photochemical experiments were irradiated using 4 x 5 x Citizen Electronics Co. Ltd 1000 lumen white light LEDs unless otherwise stated.

Synthesis of 4-methylpent-3-en-2-ol (2)

\[
\begin{align*}
\text{method a: LiAlH}_4 \\
\text{method b: H-transfer}
\end{align*}
\]

Method a: Reduction of mesityl oxide using LiAlH₄

Under an N₂ atmosphere, LiAlH₄ (4.9 g) was added to dry diethyl ether (75 mL) with stirring. The mixture was cooled (0 - 10 °C) and a solution of mesityl oxide (58.3 mL, 0.5 mol) in dry diethyl ether (75 mL) was added dropwise. After stirring (1 h), the reaction mixture was treated slowly with ice water (15 mL), NaOH solution (15 %, 15 mL) and finally water (50 mL). After extraction of the
organic phase, the aqueous layer was washed with diethyl ether (2 x 20 mL) and the combined ether extracts were dried over anhydrous Na₂SO₄. Evaporation of the volatiles under reduced pressure afforded pure allylic alcohol (37.5 g, 0.37 mol, 75 %).¹

Method b: Continuous reduction of mesityl oxide via hydrogen transfer from IPA, over MgO

 IPA and 1 were pumped separately through a mixer (M1) at 250 °C and two ¼” o.d. stainless steel reactors filled with a total of 1 g high surface area MgO catalyst (see section “Synthesis of High Surface Area MgO”). The temperature of the reactors was controlled between 250 and 350 °C and the internal and external reactor temperatures were monitored using PicoLog software. The mixture was monitored by online gas-liquid chromatography (GLC) using a high pressure sample loop to study the effect of varying the reaction parameters and the activity of the catalyst. Typical experiments were conducted using an IPA:1 molar ratio of 10:1.

Synthesis of High Surface Area MgO

Magnesium nitrate hexahydrate (80g) was dissolved in water (500mL) at 80 °C. K₂CO₃ (4 M) was then added dropwise until pH 10. The resulting mixture was then filtered and washed with water before the solid was dried overnight at 150 °C. The dry white solid was finally calcined in air at 400°C for 4h and was confirmed as MgO by powder X-ray diffraction.

Surface area (BET): 83.97 m²/g
Fig. ESI-2: Powder X-ray diffraction pattern for our high surface area MgO compared with the literature. 

Fig. ESI-3: Thermogram of synthesised MgO.
Structure of 4-methylpent-3-en-2-ol\textsuperscript{13}:

\textsuperscript{1}H-NMR: (300 MHz, CDCl\textsubscript{3})
δ (ppm) = 1.19 (d, 3H, J = 6.1 Hz, CH\textsubscript{3}CH), 1.65 (d, 3H, J = 1.3 Hz, CH\textsubscript{3}C=C), 1.67 (d, 3H, J = 1.3 Hz, CH\textsubscript{3}C=C), 4.47 (dq, 1H, J = 8.5, 6.3 Hz, CH\textsubscript{3}OH), 5.14 (dsep, 1H, J = 8.5, 1.4 Hz, CH=C)

\textsuperscript{13}C-NMR: (75.5 MHz, CDCl\textsubscript{3})
δ (ppm) = 17.86 (CH\textsubscript{3}CH), 23.48 (CH\textsubscript{3}C=C), 25.53 (CH\textsubscript{3}C=C), 64.53 (CH\textsubscript{3}OH), 129.45 (CH=C), 133.42 (C=CH)

Fig. ESI-4: Representative GLC trace for the continuous flow hydrogen transfer reduction of 1 with IPA.

Retention times:

2: 3.077 min
1: 3.395 min
4-methylpent-4-en-2-ol: 2.718 min
Iso-mesityl oxide: 2.863 min
Prior to further experimentation, the effect of pressure on the flow H-transfer reduction of 1 using IPA was examined. As can be seen in Fig. ESI-5, above 2 MPa the conversion to 2 only changed by ca. 2 %, between atmospheric pressure and 10 MPa, and so 2 MPa was the pressure used for all experiments, unless otherwise stated.

**Fig. ESI-5:** Effect of pressure on the conversion of 1 to 2 over 1 g MgO. The temperature remained constant at 350 °C with a total flow rate of 0.3 mL min⁻¹ IPA + 1 in a 10:1 molar ratio. The pressure was gradually increased from atmospheric pressure to 10 MPa at a rate of 0.01 MPa/min over 600 min. The reacting stream was monitored by online GLC taken every 10 min. The traces are labelled as follows; ●: 2; ○: 1; ▲: 4-methylpent-4-en-2-ol; X: iso-mesityl oxide
Photo-oxidation of 2 with \(^1\)O\(_2\) to give hydroperoxides (3)

\[
\begin{align*}
\text{OH} & \quad \text{hv, O}_2 \quad \text{TPFPP, scCO}_2 \\
2 & \quad \text{OH} \quad \text{OOH} \quad \text{syn-3} \quad + \quad \text{OOH} \quad \text{anti-3}
\end{align*}
\]

**Method a: Batch**

The batch photo-oxidation of 2 in scCO\(_2\) was performed in a high pressure batch cell (0.78 mL, 2 mm pathlength). 20 \(\mu\)L of a solution of \(2 + \text{TPFPP (2 mg mL}^{-1}\)) and cyclopentanone or cyclohexanone (such that the molar ratio of ketone:2 \(= 2:1\)) were injected into the cell, which was then filled with a CO\(_2/O_2\) (O\(_2\): 2 molar ratio = 4:1) mixture to 18 MPa. The batch cell was irradiated with a single white 1000 lumen LED, and FTIR spectra were taken every 30 s to monitor the reaction.\(^4\) The hydroperoxides were isolated in ca. 80 % yield as a mixture of two isomers (\(\text{syn:anti} 85:15\)).

**Method b: Flow**

The continuous flow photo-oxidation of 2 in scCO\(_2\) was performed in a custom built high pressure rig, consisting of two individual sapphire tube reactors for increased residence time.\(^5\) A solution of \(2\), cyclopentanone or cyclohexanone (1:1 ketone:2, mol:mol) and TPFPP (2 mgmL\(^{-1}\)) of 2) was pumped into the rig at 0.03 mLmin\(^{-1}\), together with CO\(_2\) (0.3 mLmin\(^{-1}\)) and O\(_2\) (6 % in CO\(_2\), molar ratio O\(_2\):2 \(= 2:1\)) at a pressure of 18 MPa. The system was irradiated and the product stream was analysed by NMR. The maximum conversion to the hydroperoxides was 86 %, as a mixture of two isomers (\(\text{syn:anti} 85:15\)).

**Syn-3-Hydroperoxy-4-methylpent-4-en-2-ol\(^6\):**

\(^1\)H-NMR: (300 MHz, CDCl\(_3\))
\[\delta (ppm) = 1.08 (d, 3H, J = 6.4 Hz, \text{CH}_3\text{CH}), 1.72 (t, 3H, J = 1.1 Hz, \text{CH}_2\text{C}=), 3.83 (dq, 1H, J = 8.4, 6.4 Hz, \text{CH-OH}), 4.09 (d, 1H, J = 8.4 Hz, \text{CH}-\text{OOH}), 5.02 (m, 2H, \text{CH}_2=\text{C})\]

\(^13\)C-NMR: (75.5 MHz, CDCl\(_3\))
\[\delta (ppm) = 17.94 (\text{CH}_3\text{CH}), 18.75 (\text{CH}_2\text{C}=), 67.23 (\text{CH}-\text{OH}), 94.82 (\text{CH}-\text{OOH}), 116.47 (\text{CH}_2=\text{C}), 141.43 (\text{C}=\text{CH}_2)\]

**Anti-3-Hydroperoxy-4-methylpent-4-en-2-ol\(^6\):**

\(^1\)H-NMR: (300 MHz, CDCl\(_3\))
\[\delta (ppm) = 1.18 (d, 3H, J = 6.4 Hz, \text{CH}_3\text{CH}), 1.78 (t, 3H, J = 1.2 Hz, \text{CH}_2\text{C}=), 3.93 (m, 1H, \text{CH}-\text{OH}), 4.25 (d, 1H, J = 4.9 Hz, \text{CH}-\text{OOH}), 5.08 (m, 2H, \text{CH}_2=\text{C})\]

\(^13\)C-NMR: (75.5 MHz, CDCl\(_3\))
\[\delta (ppm) = 18.06 (\text{CH}_3\text{CH}), 19.71 (\text{CH}_2\text{C}=), 66.89 (\text{CH}-\text{OH}), 92.26 (\text{CH}-\text{OOH}), 115.26 (\text{CH}_2=\text{C}), 141.34 (\text{C}=\text{CH}_2)\]
Condensation of hydroperoxides with cyclic ketone

Method a: using BF$_3$.Et$_2$O

The product stream from the flow photo-oxidation of 2, containing cyclohexanone, was collected in a flask containing BF$_3$.Et$_2$O hydrate (0.2 mL) in dichloromethane (100 mL) at 0 – 10 °C. Once the photo-oxidation process was terminated, the mixture was slowly warmed to room temperature before stirring for 12 h. The desired product 4b was isolated from the crude solution by thick layer silica gel chromatography (hexane:ethyl acetate 10:1) with an overall yield of ca. 25%.

Method b: using Silica/BF$_3$

The isomeric mixture of 2 was diluted in cyclopentanone and was pumped over 0.5 g silica/BF$_3$ at 50 °C, 10 atm pressure at a total flow rate of 0.05 mL/min$^{-1}$. The product stream was collected periodically over 10 minutes and the resulting solutions were analysed by NMR. Trioxane 4a was isolated in a pure form from the collected fractions after thick layer chromatography (hexane:ethyl acetate 10:1). The maximum conversion was found to be 60 %, and the overall yield of pure 4a of was ca. 30 %.

4a - 8-Isopropenyl-9-methyl-6,7,10-trioxaspiro[4.5]decane$^6$

$^1$H-NMR: (400 MHz, CDCl$_3$)

$\delta$ (ppm) = 1.07 (d, 3H, J = 6.2 Hz, CH$_3$CH), 1.60 - 1.87 (m, 7H, CH$_3$), 1.72 (m, 3H, CH$_3$C=), 2.47 (m, 1H, CH$_2$), 3.84 (dq, 1H, J = 9.5, 6.3 Hz, OCH), 4.24 (d, 1H, $J$ = 9.4 Hz, OOCH), 5.05 (m, 2H, CH$_2$C=C)

$^{13}$C-NMR: (100 MHz, CDCl$_3$)

$\delta$ (ppm) = 16.72 (CH$_3$CH), 19.50 (CH$_3$C=), 23.12 (CH$_2$), 24.73 (CH$_3$), 32.93(CH$_3$), 37.32 (CH$_2$), 68.36 (OCH), 88.63 (OOCH), 114.64 (OOCO), 117.63 (CH$_2$C=C), 139.10 (C=CH$_2$)

HMBC – 400 MHz and 100 MHz
Green shading = quaternary carbon, indicating cyclopentane ring connected to trioxane core structure.

4b - 3-Isopropenyl-4-methyl-1,2,5-trioxa-spiro[5.5]undecane

$^1$H-NMR: (400 MHz, CDCl$_3$)

$\delta$ (ppm) = 1.09 (d, 3H, $J = 6.4$ Hz, CH$_3$CH), 1.30 - 1.60 (m, 8H, 4 x CH$_2$), 1.77 (m, 3H, CH$_2$C=C), 1.93 (m, 1H, CH$_3$), 2.22 (m, 1H, CH$_2$), 4.08 (dq, 1H, $J = 9.5$, 6.1 Hz, OCH), 4.20 (d, 1H, $J = 9.7$ Hz, OOCH), 5.07 (m, 2H, CH$_2$C=C)

$^{13}$C-NMR: (100 MHz, CDCl$_3$)

$\delta$ (ppm) = 16.95 (CH$_3$CH), 19.69 (CH$_3$C=), 22.22 (CH$_3$), 22.41 (CH$_3$), 25.57 (CH$_3$), 29.49 (CH$_3$), 35.51 (CH$_3$), 65.61 (OCH), 88.76 (OOCO), 102.80 (OOCO), 117.61 (CH$_2$C=), 139.24 (C=CH$_2$)

HMBC – 400 MHz and 100 MHz
Green shading = quaternary carbon, indicating cyclohexane ring connected to trioxane core structure.