Supporting Information

Percarboxylic Acid Oxidation of \(\alpha\)-Hydroxy-Substituted Alkoxyallenes: The Unexpected Formation of Acyloxy-Substituted 1,2-Diketones and Synthesis of Functionalized Quinoxalines


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General Information: Reactions were generally performed under argon in flame-dried flasks. Solvents and reagents were added by syringes. Solvents were dried using standard procedures. Reagents were purchased and were used as received without further purification unless stated. Reactions were monitored by thin-layer chromatography (TLC). Products were purified by column chromatography on silica gel (32-63 \(\mu\)m). Unless otherwise stated, yields refer to chromatographically homogeneous and spectroscopically pure materials (\(^1\)H-NMR spectroscopy). NMR spectra were recorded with JEOL (ECX 400, Eclipse 500) instruments. Chemical shifts are reported relative to TMS (\(^1\)H: \(\delta = 0.00\) ppm) and CDCl\(_3\) (\(^13\)C: \(\delta = 77.0\) ppm). Integrals are in accordance with assignments; coupling constants are given in Hz. \(^13\)C-NMR spectra are \(^1\)H-decoupled. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet),
m (multiplet), m<sub>c</sub> (centered multiplet), dd (doublet of doublet), br s (broad singlet). MS and HRMS analyses were performed with a Varian Ionspec QFT-7 instrument (ESI-FT ICRMS). Elemental analyses were carried out with a Vario EL Elemental Analyzer. Melting points were measured with a Reichert apparatus (Thermovar) and are uncorrected. Optical rotations ([α]<sub>D</sub>) were determined with Perkin–Elmer 141 or Perkin–Elmer 241 polarimeters at the temperatures given.

Pre-treatment of mCPBA according to ref. [1]:

**General procedure 3 (GP3):** Preparation of α-hydroxy-substituted methoxyallene derivatives 4

A solution of methoxyallene (1; 1.1 equiv) in dry diethyl ether (2 mL/ mmol of 1) was treated at -40 °C with n-BuLi (2.5 M in hexane; 1 equiv) under an Ar atmosphere (deprotonation time ca 10 min). Then, the corresponding aldehyde (0.3-1.1 equiv) was added within 5-10 min. The solution was stirred for 0.5-1 h at -40 °C and then quenched with water (2 mL/ mmol of 1). Warm up to r.t. was followed by extraction with diethyl ether (3 × 2 mL/ mmol of 1). The combined organic extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude methoxyallene derivative 3 was used without further purification.

1-Cyclohexy-2-methoxybuta-2,3-dien-1-ol (4a):

![Chemical structure of 4a](image)

According to GP3, methoxyallene (1; 3.10 mL, 37.2 mmol), n-BuLi (14.0 mL, 35.0 mmol) and freshly distilled cyclohexylcarbaldehyde (1.22 g, 10.9 mmol) afforded 4a (2.02 g, quant.) as pale yellow oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz): δ = 0.90-1.80 (m, 10 H, 5 CH₂), 2.06 (d, J = 7.4 Hz, 1 H, OH), 3.44 (s, 3 H, OMe), 3.33 (d, J = 7.4 Hz, 1 H, CH), 5.51 (s, 2 H, =CH₂).

3-Methoxypentadeca-1,2-dien-4-ol (4b):

![Chemical structure of 4b](image)
According to GP3, methoxyallene (1; 3.10 mL, 37.2 mmol), n-BuLi (14.0 mL, 35.0 mmol) and freshly distilled laurinaldehyde (2.01 g, 10.9 mmol) afforded 4b (2.78 g, quant.) as pale yellow oil.

$^1$H NMR (CDCl$_3$, 250 MHz): $\delta = 0.88$ (t, $J = 6.6$ Hz, 3 H, Me), 1.20-1.40, 1.50-1.90 (2 m, 18 H, 2 H, 10 CH$_2$), 1.94 (d, $J = 5.2$ Hz, 1 H, OH), 3.45 (s, 3 H, OMe), 4.12-4.19 (m, 1 H, CH), 5.54 (d, $J = 2.2$ Hz, 2 H, =CH$_2$).

1-Benzyl-3-methoxypenta-3,4-dien-2-ol (4d):

Three steps starting from allyl benzyl ether (I).

Step 1:[3]

Allyl benzyl ether (3.70 g, 25.4 mmol) was dissolved in acetonitrile (305 mL). Then, a mixture of RuCl$_3$·H$_2$O (0.458 g, 1.78 mmol) and NaIO$_4$ (8.15 g, 38.1 mmol) in water (50 mL) was added and the reaction mixture was vigorously stirred for 3 min at r.t. After filtration of the reaction mixture (SiO$_2$, eluted with EtOAc), the eluent was concentrated under reduced pressure and the residue was purified by column chromatography (hexanes/EtOAc, 1:1) affording II (1.20 g, 26%) as colorless oil.

$^1$H NMR (CDCl$_3$, 250 MHz): $\delta = 2.28$, 2.70 (2 s, 1 H each, 2 OH), 3.53 (dd, $J = 3.9$, 6.0 Hz, 1 H, CH$_2$), 3.58 (dd, $J = 3.5$, 6.0 Hz, 1 H, CH$_2$), 3.63 (dd, $J = 3.4$, 7.2 Hz, 1 H, CH$_2$), 3.72 (dd, $J = 2.4$, 7.2 Hz, 1 H, CH$_2$), 3.86-3.92 (m, 1 H, CHOH), 4.55 (s, 2 H, OCH$_2$), 7.25-7.40 (m, 5 H, Ph).

Step 2:[4]

To a solution of NaH$_2$PO$_4$ (2.37 g, 17.2 mmol) dissolved in water (35 mL) [pH 7-7.5] and diol II (1.16 g, 6.37 mmol) dissolved in 1,4-dioxane (17 mL) NaIO$_4$ (1.64 g, 7.64 mmol) dissolved in water (11 mL) was slowly added at r.t. and the mixture was stirred for 1 h. After addition of EtOAc (35 mL) the aqueous phase was extracted with EtOAc (2 × 20 mL). The combined organic extracts were subsequently washed with sat aq. NaHCO$_3$ solution and brine (15 mL
each), dried (Na$_2$SO$_4$) and concentrated. Distillation using a Kugelrohroven (95 °C, 0.02 mbar) of the crude product gave aldehyde III (0.590 g, 62%) as colorless oil.

$^1$H NMR (CDCl$_3$, 250 MHz): $\delta =$ 4.10 (s, 2 H, CH$_2$), 4.65 (s, 2 H, OCH$_2$), 7.40 (m, 5 H, Ph), 9.73 (s, 1 H, CHO).

Step 3:

According to GP3, methoxyallene (1; 0.46 mL, 5.39 mmol), n-BuLi (1.95 mL, 4.87 mmol) and aldehyde III (0.590 g, 3.93 mmol) afforded 4d (0.724 g, 84%, purity ca 95%) as pale yellow oil.

$^1$H NMR (CDCl$_3$, 250 MHz): $\delta =$ 2.52 (d, $J =$ 5.2 Hz, 1 H, OH), 3.41 (s, 3 H, OMe), 3.45-3.64 (m, 3 H, OCH, OCH$_2$), 4.58 (s, 2 H, OCH$_2$), 5.56 (d, $J =$ 1.7 Hz, 2 H, =CH$_2$), 7.25-7.40 (m, 5 H, Ph).

1,1,1-Trifluoro-3-methoxy-2-methylpenta-3,4-dien-1-ol (7b):

![7b and IV](image)

According to GP3, methoxyallene (1; 3.50 g, 50.0 mmol), n-BuLi (18.4 mL, 46.0 mmol) and trifluoroacetone (5.60 g, 50.0 mmol) afforded mixture of 7b and alkyne IV (5.47 g, 65%, 7b:IV = 80:20) as colorless oil.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta =$ 1.40 (s, 3 H, Me), 3.30 (br s, 1 H, OH), 3.85 (s, 3 H, OMe), 5.67, 5.70 (AB system, $J_{AB} =$ 4.4 Hz, 1 H each, =CH$_2$).

$^{13}$C NMR (CDCl$_3$, 100.8 MHz): $\delta =$ 20.7 (q, Me), 65.6 (q, OMe), 72.4 (q, $^2J_{CF} =$ 27.6 Hz, COH), 94.8 (t, =CH$_2$), 126.0 (q, $^1J_{CF} =$ 285 Hz, CF$_3$), 132.4 (s, =C), 197.0 (s, =C=).

Spectroscopic data of the side-product IV:

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta =$ 1.43 (s, 3 H, Me), 2.46, 2.62 (AB system, $J_{AB} =$ 10 Hz, 1 H each, CH$_2$), 3.30 (br s, 1 H, OH), 3.47 (s, 3 H, OMe).

$^{13}$C NMR (CDCl$_3$, 100.8 MHz): $\delta =$ 19.7 (q, Me), 25.9 (t, CH$_2$), 56.9 (q, OMe), 72.8 (q, $^2J_{CF} =$ 32.1 Hz, COH), 80.1, 94.1 (2 s, =C), 125.3 (q, $^1J_{CF} =$ 287 Hz, CF$_3$).
To a solution of α-hydroxy-substituted methoxyallene 4c (2.38 g, 13.8 mmol) dissolved in DMF (13.5 mL) and CH₂Cl₂ (13.5 mL) were added imidazole (3.01 g, 34.1 mmol), followed by TBSCI (2.48 g, 16.4 mmol) under an Ar atmosphere. The mixture was stirred overnight at r.t. After addition of diethyl ether (40 mL) the mixture was washed with brine (3 × 30 mL). The combined organic layers were dried (Na₂SO₄) and concentrated under reduced pressure. A short filtration (neutral Al₂O₃; hexanes/EtOAc, 2:1) of the crude product gave the silylated methoxyallene derivative 8 (4.20 g, quant) as yellow oil.

1H NMR (CDCl₃, 250 MHz): δ = 0.08 (s, 6 H, OSiMe₂), 0.92 (s, 9 H, OSiBu), 3.37 (s, 3 H, OMe), 5.26 (s, 1 H, CH), 5.47 (s, 2 H, =CH₂), 7.00-7.50 (m, 5 H, Ph).

References:
Copies of NMR data of selected compounds
5e (dr = 90:10)

7a