Rate Acceleration of Anionic Oxy-Cope Rearrangements Induced by an Additional Unsaturation

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Supporting Information

Characterization data for compounds 8-10, 15-18 and 29-34.

Ketone 8

White solid mp 131-133°C (from Et₂O/petroleum ether 1:1). R_f 0.20 (15% EtOAc in petroleum ether). IR (CCl₄) ν_{max} 1685 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 4.34 (dd, J = 5.9, 2.0 Hz, 1H, H-4), 3.91 (dd, J = 11.5, 4.8 Hz, 1H, H-16), 3.61 (dd, J = 11.5, 6.6 Hz, 1H, H-16), 2.96-2.83 (m, 1H), 2.80 (qd, J = 7.0, 2.2 Hz, 1H, H-9), 2.56-2.36 (m, 1H, H-3), 2.35-1.75 (m, 10H), 1.63-1.50 (m, 1H), 1.55 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.23-1.17 (m, 1H), 0.96 (d, J = 6.7 Hz, 3H, H-18).

¹³C NMR (100 MHz, CDCl₃) δ 214.7 (C, C-10), 133.3 (C, C-8 or C-8a), 132.3 (C, C-8a or C-8), 99.2 (C, acetonide), 69.5 (CH, C-4), 63.7 (CH₂, C-16), 50.2 (CH), 44.6 (CH), 43.0 (CH₂), 42.7 (CH), 32.7 (CH), 31.9 (CH), 30.7 (CH₂), 28.4 (2 CH₂), 28.3 (CH₃), 22.2 (CH₃), 18.7 (CH₂), 18.7 (CH₃), 16.6 (CH₃). MS (PCI/NH₃) m/z 319 (MH⁺), 301 (M-H₂O+H)⁺, 278 (M-(CH₃)₂CO+NH₄)⁺, 261 (M-(CH₃)₂CO+H)⁺, 243 (M-(CH₃)₂CO-H₂O+H)⁺, 225 (M-(CH₃)₂CO-2H₂O+H)⁺.

The structure of this compound was confirmed by X-ray crystallographic analysis.

Ketone 9.

White solid. R_f 0.35 (15% EtOAc in petroleum ether) mp 141-145°C. IR (CCl₄) ν_{max} 1681 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 4.31 (dd, J = 7.8, 5.1 Hz, 1H, H-4), 3.67 (dd, J = 10.8, 5.6 Hz, 1H, H-16), 3.58 (t, J = 10.8 Hz, 1H, H-16), 2.75 (dq, J = 6.8, 2.0 Hz, 1H, H-9), 2.61-2.59 (m, 1H, H-1), 2.50-2.39 (m, 1H, H-3), 2.17-2.09 (m, 2H, H-4a, H-5), 1.99-1.84 (m, 6H, H-11, H-11, H-12, H-13, H-6, H-7), 1.77-1.70 (m, 2H, H-2, H-6), 1.64-1.50 (m, 1H, H-7), 1.50 (s, 3H, H-17), 1.45 (s, 3H, acetonide), 1.36 (s, 3H, acetonide), 1.36-1.27 (m, 1H, H-2), 0.98 (d, J = 6.8 Hz, 3H, iPr), 0.97 (d, J = 6.8 Hz, 3H, iPr), 0.82 (d,

$J = 6.8$ Hz, 3H, H-18). ^{13}C NMR (100 MHz, CDCl_3) δ 212.1 (C, C-10), 134.4 (C), 131.3 (C), 99.5 (C, acetonide), 68.4 (CH, C-4), 62.8 (CH_2 , C-16), 49.4 (CH, C-4a), 44.0 (CH, C-5), 42.1 (CH_2 , C-11), 41.9 (CH, C-12), 40.7 (CH, C-9), 34.2 (CH, C-1), 32.5 (CH, C-3), 27.4 (CH_2 , C-7), 27.2 (CH_3 , acetonide), 26.8 (CH, C-13), 25.1 (CH_2 , C-2), 23.2 (CH_3 , acetonide), 22.6 (CH_3 , iPr), 18.4 (CH_2 , C-6), 18.3 (CH_3 , C-17), 16.3 (CH_3 , C-18), 15.6 (CH_3 , iPr). MS (PCI/ NH_3) m/z 378 ($\text{M}+\text{NH}_4^+$), 361 (MH^+), 343 ($\text{M}-\text{H}_2\text{O}+\text{H}^+$), 320 ($\text{M}-(\text{CH}_3)_2\text{CO}+\text{NH}_4^+$), 303 ($\text{M}-(\text{CH}_3)_2\text{CO}+\text{H}^+$), 285 ($\text{M}-(\text{CH}_3)_2\text{CO}-\text{H}_2\text{O}+\text{H}^+$), 267 ($\text{M}-(\text{CH}_3)_2\text{CO}-2\text{H}_2\text{O}+\text{H}^+$). Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{O}_3$: C, 76.62; H, 10.06. Found C, 76.77; H, 10.18.

The structure of this compound was confirmed by X-ray crystallographic analysis.

Hydroxyketone 10

White solid. R_f 0.10 (20% EtOAc in petroleum ether). IR (CCl_4) ν_{max} 3530, 1695, 1455, 1378, 1224, 1115 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 5.03 (br s, 1H, H-14), 4.97 (br s, 1H, H-14), 4.37 (dd, $J = 7.8, 5.2$ Hz, 1H, H-4), 3.87 (d, $J = 11.1$ Hz, 1H, H-11), 3.67 (dd, $J = 10.9, 5.6$ Hz, 1H, H-16), 3.57 (dd, $J = 10.9, 9.5$ Hz, 1H, H-16), 2.93 (qd, $J = 6.7, 1.9$ Hz, 1H, H-9), 2.87 (t, $J = 11.4$ Hz, 1H), 2.80 (dt, $J = 11.4, 2.8$ Hz, 1H), 2.61-2.49 (m, 1H), 2.22 (br d, $J = 8.2$ Hz, 1H), 2.13 (br s, 1H), 2.00-1.86 (m, 2H), 1.82-1.77 (m, 1H), 1.80 (s, 3H, H-15), 1.72-1.60 (m, 3H), 1.54 (br s, 3H, H-17), 1.47 (s, 3H, acetonide), 1.36 (s, 3H, acetonide), 1.33-1.23 (m, 1H), 1.08 (d, $J = 6.7$ Hz, 3H, H-18). ^{13}C NMR (100 MHz, CDCl_3) δ 206.2 (C, C-10), 142.8 (C, C-13), 133.4 (C, C-8 or C-8a), 133.1 (C, C-8a or C-8), 115.3 (CH_2 , C-14), 99.6 (C, acetonide), 88.9 (CH, C-11), 68.3 (CH, C-4), 62.8 (CH_2 , C-16), 49.6 (CH), 48.0 (CH), 44.0 (CH), 40.4 (CH), 31.8 (CH), 31.7 (CH), 27.5 (CH_2), 27.4 (CH_3), 25.4 (CH_2), 23.5 (CH_3), 18.6 (CH_3), 18.2 (CH_2), 18.1 (CH_3), 16.2 (CH_3). MS (PCI/ NH_3) m/z 375 (MH^+), 357 ($\text{M}-\text{H}_2\text{O}+\text{H}^+$), 334 ($\text{M}-(\text{CH}_3)_2\text{CO}+\text{NH}_4^+$), 318 ($\text{M}-(\text{CH}_3)_2\text{CO}+\text{H}^+$), 299 ($\text{M}-(\text{CH}_3)_2\text{CO}-\text{H}_2\text{O}+\text{H}^+$), 281 ($\text{M}-(\text{CH}_3)_2\text{CO}-2\text{H}_2\text{O}+\text{H}^+$).

Hydroxy ketone 15a:

White solid mp 99.5-100 °C (from petroleum ether). IR (CCl₄) ν_{max}

3627, 1677 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 3.83 (m, 1H, H₄), 3.63 (qd, J = 6.9 and 1.6 Hz, 1H, H₉), 2.75 (dddd, J = 13, 11, 3.6 and 2.2 Hz, 1H, H₁₂), 2.58 (ddd, J = 11, 8.4 and 3.1 Hz, 1H, H₁), 2.31 (dt, J = 13 and 8.0 Hz, 1H, H₇), 2.16 (br d, J = 8.4 Hz, 1H, H₅), 2.10 (dd, J = 17 and 13 Hz, 1H, H₁₁), 1.95-1.80 (m, 4H, H₆, H₇, H₁₁ and H₁₅), 1.78 (br d, J = 6.4 Hz, 1H, H_{4a}), 1.66 (ddd, J = 8.2, 6.0 and 2.9 Hz, 1H, H₂), 1.62 (m, 1H, H₂), 1.61 (br s, 3H, H₁₃), 1.48 (m, 1H, H₃), 1.44 (dddd, J = 14, 11, 8.5 and 2.3 Hz, 1H, H₆), 1.21 (dddd, J = 14, 11, 8 and 2.1 Hz, 1H, H₃), 1.10 (d, J = 6.8 Hz, 1H, H₁₄), 0.96 (br s, 1H, OH), 0.89 (d, J = 7.0 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 214.5 (C₁₀), 135.1 and 133.7 (C₈ and C_{8a}), 69.0 (C₄), 47.2 (CH), 46.6 (CH), 44.7 (CH), 42.5 (C₁₁), 40.9 (CH), 32.6 (CH), 29.7 (CH₂), 28.1 (CH), 27.6 (CH₂), 22.9 (Me), 21.8 (CH₂), 20.2 (CH₂), 18.7 (Me), 16.3 (Me) and 15.7 (Me). Anal. Calcd for C₁₉H₃₀O₂: C, 78.57; H, 10.41. Found C, 78.83; H, 10.45.

The structure of this compound was confirmed by X-ray crystallographic analysis.

Hydroxyketone 16.

White solid mp 133-135 °C (EtAOc/petroleum ether). R_f 0.35 (10% EtOAc in petroleum ether) IR (CCl₄) ν_{max} 3624, 3490, 3071, 1679, 1639 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 4.89 (br s, 1H, H-14), 4.84 (br s, 1H, H-14), 4.39-4.36 (m, 1H), 3.72 (td, J = 11.2, 3.1 Hz, 1H), 3.57 (qd, J = 6.8, 1.8 Hz, 1H), 2.75 (t, J = 9.6 Hz, 1H), 2.35 (d, J = 8.2 Hz, 1H), 2.19 (dd, J = 17.3, 13.3 Hz, 1H), 2.10-1.70 (m, 10H), 1.70 (s, 3H, H-15), 1.56 (s, 3H, H-17), 1.56-1.47 (m, 1H), 0.92(d, J = 6.8 Hz, 3H, H-18). ¹³C NMR (100 MHz, CDCl₃) δ 213.0 (C, C-10), 147.3 (C, C-13), 134.3 (C), 134.1 (C), 112.5 (CH₂, C-14), 69.1 (CH, C-4), 49.1 (CH), 48.6 (CH₂), 47.2

(CH), 44.5 (CH), 40.9 (CH), 32.2 (CH), 29.4 (CH₂), 27.5 (CH₂), 20.5 (CH₂), 20.1 (CH₂), 19.0 (CH₃), 18.6 (CH₃), 16.2 (CH₃). MS (PCI/NH₃) *m/z* 289 (MH⁺), 271 (M-H₂O+H)⁺.

Hydroxy ketone 18.

White solid. *R_f* 0.30 (10% EtOAc in petroleum ether). IR (CCl₄) ν_{max} 3619, 3082, 1692, 1643 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 4.81 (s, 1H, H-14), 4.55 (s, 1H, H-14), 4.42-4.37 (m, 1H, H-4), 3.68 (qd, *J* = 6.8, 4.3 Hz, 1H, H-9), 3.33 (t, *J* = 11.9 Hz, 1H), 3.12-3.05 (m, 1H), 2.98-2.92 (m, 1H), 2.57-2.51 (m, 1H), 2.39-2.34 (m, 1H), 1.97 (dd, *J* = 11.9, 2.3 Hz, 1H), 1.92-1.73 (m, 5H), 1.80 (s, 3H, H-15), 1.65-1.57 (m, 1H), 1.63 (s, 3H, H-17), 1.44-1.33 (m, 2H), 0.94 (d, *J* = 6.8 Hz, 3H, H-18). ¹³C NMR (100 MHz, CDCl₃) δ 219.2 (C, C-10), 147.6 (C, C-13), 135.0 and 131.0 (C-8 and C-8a), 110.1 (CH₂, C-14), 69.0 (CH, C-4), 50.1 (CH), 47.4 (CH), 44.9 (CH), 44.2 (CH₂), 43.1 (CH), 32.6 (CH), 31.1 (CH₂), 29.5 (CH₂), 22.3 (CH₃), 19.5 (CH₂), 19.1 (CH₃), 17.0 (CH₂), 15.3 (CH₃). MS (PCI/NH₃) *m/z* 289 (MH⁺), 271 (M-H₂O+H)⁺.

Compound 29

Colorless oil. *R_f* 0.40 (5% EtOAc in petroleum ether). IR (CCl₄) ν_{max} 3081, 1697, 1644 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 5.51-5.46 (m, 1H), 4.73 (s, 1H), 4.71 (s, 1H), 2.82 (t, *J* = 12 Hz, 1H), 2.75 (dd, *J* = 11, 7 Hz, 1H), 2.74-2.69 (m, 1H), 2.62-2.52 (m, 1H), 2.41 (dd, *J* = 12.3, 5.2 Hz, 1H), 2.36 (br s, 2H), 2.22 (d, *J* = 10.9 Hz, 1H), 2.14 (d, *J* = 12.3 Hz, 1H), 2.10-2.02 (m, 1H), 2.01-1.90 (m, 1H), 1.89-1.78 (m, 2 H), 1.74 (s, 3H), 1.48-1.60 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 215.0 (C), 148.5 (C), 136.4 (C), 127.6 (CH), 108.9 (CH₂), 52.1 (CH), 51.1 (CH₂), 46.0 (CH₂), 40.9 (CH₂), 34.6 (CH₂), 32.8 (CH), 26.3 (CH₂), 22.5 (CH₂), 20.4 (CH₃).

Compound 30

Colorless oil. R_f 0.30 (5% EtOAc in petroleum ether). IR (CCl_4) ν_{max} 1697 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 5.50-5.38 (m, 1H), 2.74 (dd, $J = 11, 7$ Hz, 1H), 2.62 (t, $J = 12$ Hz, 1H), 2.60-2.46 (m, 1H), 2.39-2.15 (m, 4H), 2.10-1.90 (m, 4H), 1.80 (dd, $J = 14, 7$ Hz, 1H), 1.79-1.45 (m, 3 H), 0.91 (d, $J = 4.5$ Hz, 3H), 0.89 (d, $J = 4.5$ Hz, 3H). MS (EI) m/z 206 (M^+).

Compound 33

Colorless oil. R_f 0.40 (5% EtOAc in petroleum ether). IR (CCl_4) ν_{max} 3086, 3028, 1705, 1644 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 6.10-5.95 (m, 2H), 4.87 (s, 1H), 4.84 (s, 1H), 2.96 (t, $J = 10.6$ Hz, 1H), 2.72-2.62 (m, 2H), 2.62-2.52 (m, 2H), 2.40-2.25 (m, 2H), 2.25-2.10 (m, 1H), 2.10-2.00 (m, 1H), 1.90-1.80 (m, 1H), 1.77 (s, 3H), 1.75-1.55 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 214.0 (C), 147.1 (C), 133.4 (CH), 132.1 (CH), 110.7 (CH_2), 55.3 (CH_2), 45.5 (CH), 43.0 (CH_2), 34.0 (CH), 29.1 (CH), 27.3 (CH_2), 23.0 (CH_3), 19.4 (CH_2). MS (PCI/ NH_3) m/z 191 (MH^+), 208 ($\text{M}+\text{NH}_4$) $^+$.

Compound 34

Colorless oil. R_f 0.50 (5% EtOAc in petroleum ether). IR (CCl_4) ν_{max} 3088, 3024, 1718, 1646 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 5.78-5.88 (m, 1H), 5.50 (br d, $J = 10.6$ Hz, 1H), 4.97 (s, 1H), 4.62 (s, 1H), 2.73 (br s, 1H), 2.52-2.22 (m, 4H), 2.25 (br d, $J = 12$ Hz, 1H), 2.18-2.08 (m, 3H), 1.95-1.85 (m, 1H), 1.79 (s, 3H), 1.70-1.60 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 212.8 (C), 144.7 (C), 129.0 (CH), 124.0 (CH), 111.1 (CH_2), 46.5 (CH), 41.2 (CH_2), 40.9 (CH_2), 35.5 (2CH), 26.8 (CH_2), 22.6 (CH_3), 20.9 (CH_2). MS (PCI/ NH_3) m/z 191 (MH^+), 208 ($\text{M}+\text{NH}_4$) $^+$.