Ozonolysis In The Presence Of Lewis Acids: Directed Addition To Carbonyl Oxides

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SUPPLEMENTARY MATERIAL

General Procedure for Ozonolysis

Nonene (200 mg, 1.58 mmole) was dissolved in freshly distilled dichloromethane (20 mL). The resulting solution was cooled to -78 ^{0}C under a stream of O_2. After an appropriate alcohol or Lewis acid (2 eq.) was then added, the power was turned on and a solution of O_2/O_3 was bubbled through the solution (1 mmol/min) for 2 min. The power was turned off and O_2 was bubbled through the solution to remove excess ozone. The reaction was added into 20 ml of sat. $NaHCO_3$, separated and washed twice with 20 ml of sat. $NaHCO_3$, dried (Na_2SO_4) and concentrated. The resulting oil was purified via flash chromatography with 8% Ethyl Acetate/Hexane. (Reactions involving Ti were filtered through celite prior to $NaHCO_3$ washes)

1-Methoxy-octyl hydroperoxide (3a): R_f = 0.44 (15% EtOAc/Hex); ^{1}H NMR (300 MHz) δ 8.17 (s, 1H), 4.74 (t, 1H, J = 5.8), 3.5 (s, 3H), 1.67 (m, 3H), 1.44-1.24 (10H), 0.87 (t, 3H, J = 6.8): ^{13}C NMR (75 MHz) δ 108.8, 55.8, 31.7, 31.2, 29.3, 29.1, 24.6, 22.6, 14.1; FTIR 3359 cm^{-1}

8-Hydroperoxy-11-methoxy-9,10-dioxaoctadecane (4a): R_f = 0.75 (15% EtOAc/Hex); ^{1}H NMR (300 MHz) δ 10.54 (s, 0.3H), 9.89 (s, 0.3H), 5.20 (t, 0.3H, J = 6.2), 5.14 (t, 0.4H, J = 6.3), 4.80 (t, 0.3H, J = 6.0), 4.77 (t, 0.4H, J = 6.0), 3.58 (s, 1.4H), 3.52 (s, 1.1H), 1.67 (m, 4.1H), 1.41 (m, 4.2H), 1.5-1.2 (17.1H), 0.88 (t, 6H, J = 6.0): ^{13}C NMR (75 MHz) δ 109.6, 108.7, 108.6, 108.1, 56.7, 54.9, 31.7, 31.1, 29.2, 29.1, 29.0, 28.9, 28.4, 24.9, 24.8 (d), 24.7, 22.6, 14.1, 14.0; FTIR 3355 cm^{-1}

1-Isopropoxy-octyl hydroperoxide (3b): R_f = 0.56 (15% EtOAc/Hex); ^{1}H NMR (300 MHz) δ 7.97 (s, 1H), 4.86 (t, 1H, J = 5.8), 4.00 (hept, 1H, J = 6.2), 1.67 (m, 3H), 1.46-1.28 (11H), 1.28 (d, 3H, J = 6.2), 1.18 (d, 3H, J = 6.2), 0.88 (t, 6H, J = 6.6): ^{13}C NMR (75 MHz) δ 106.3, 71.1, 32.4, 31.7, 29.3, 29.1, 24.7, 23.3, 22.6, 22.3, 14.0; FTIR 3373 cm^{-1}

8-Hydroperoxy-11-isopropoxy-9,10-dioxaoctadecane (4b): R_f = 0.68 (15% EtOAc/Hex), ^{1}H NMR (300 MHz) δ 10.88 (s, 0.2H), 9.71 (s, 0.1H), 5.30 (t, 0.6H, J = 6.0), 5.16 (t, 0.2H, J = 6.6), 4.98 (t, 0.5H, J = 5.7), 4.91 (t, 0.2H, J = 5.9), 4.08 (hept,

0.9H, J = 6.2), 3.96 (hept, 0.1H, J = 6.2), 1.84-1.56 (3.4H), 1.48-1.12 (28.2H), 0.87 (t, 6.0H, J = 6.6); ^{13}C NMR (75 MHz) δ 109.9, 105.1, 101.0, 72.3, 33.1, 32.8, 31.7, 29.3, 29.2, 29.1, 29.0, 24.9, 24.8, 24.5, 23.1, 22.6, 22.5, 22.3, 22.2, 21.8, 14.1; FTIR 3344 cm^{-1}

1-Phenoxy-octyl hydroperoxide (3c): R_f = 0.61 (15% EtOAc/Hex); ^{1}H NMR (300 MHz) δ 8.22 (s, 1H), 7.30 (m, 2H), 7.06 (m, 3H), 5.55 (t, 1H, J = 5.8), 1.90 (m, 2H), 1.48 (p, 2H, J = 7.2), 1.48-1.22 (8H), 0.88 (t, 3H, J = 6.7): ^{13}C NMR (75 MHz) δ 157.2, 129.6, 122.6, 117.3, 106.6, 31.8, 31.7, 29.2, 29.1, 24.4, 22.6, 14.0; FTIR 3413, 1598 cm^{-1}

8-Hydroperoxy-11-phenoxy-9,10-dioxaoctadecane (4c): R_f = 0.72 (15% EtOAc/Hex); ^{1}H NMR (300 MHz) δ 9.76 (s, 0.5H), 8.99 (s, 0.2H), 7.32 (m, 2H), 7.10 (m, 3H), 5.62 (t, 0.4H, J = 5.9), 5.56 (t, 0.6H, J = 6.0), 5.31 (t, 0.8H, J = 6.0), 5.25 (t, 0.5H, J = 5.9), 1.95 (m, 1.8H), 1.63 (m, 2.3H), 1.52-1.20 (21.9H), 0.89 (t, 6H, J = 6.2): ^{13}C NMR (500 MHz) δ 129.6, 123, 118.3, 117.6, 110.0, 109.6, 106.7, 106.2, 32.3, 32.0, 31.5, 29.2, 29.1, 29.0, 28.9, 26.9, 26.8, 24.3, 22.5, 13.9; FTIR 3427, 1599 cm^{-1}

1-(2-hydroxyphenoxy)-octyl hydroperoxide (3d): R_f = 0.49 (15% EtOAc/Hex); ^{1}H NMR (300 MHz) δ 7.92 (s, 0.1H), 7.01-6.80 (m, 4H), 5.36 (t, 1H, J = 5.8), 1.91 (dt, 2H, J_d = 9.2, J_t = 6.3), 1.49 (p, 2H, J = 7.1), 1.40-1.27 (8H), 0.88 (t, 3H, J = 6.7): ^{13}C NMR (90 MHz) δ 148.0, 144.1, 124.4, 120.5, 118.9, 116.0, 109.0, 32.0, 31.7, 29.2, 29.1, 24.5, 22.6, 14.0; FTIR 3380, 1653 cm^{-1}

3,6-dioctyl-1,2,4,5-tetroxane (5): R_f = 0.89 (15% EtOAc/Hex); ^{1}H NMR (300 MHz) δ 5.87 (t, 0.1H, J = 5.2), 5.19 (t, 1.9H, J = 5.2), 1.68 (dt, 4.2H, J_d = 9.0, J_t = 5.1), 1.46-1.20 (25.1H), 0.88 (t, 6.7H, J = 7.1); ^{13}C NMR (75 MHz) δ 108.7, 104.3, 32.3, 31.7, 31.6, 29.6, 29.3, 29.2, 29.1, 28.9, 23.9, 22.6, 14.1.

2-octyl-1,2,4-trioxolane (6): R_f = 0.83 (15% EtOAc/Hex); ^{1}H NMR (300 MHz) δ 5.19 (s, 1H), 5.13 (t, 1H, J = 4.9), 5.03 (s, 1H), 1.72 (m, 2H), 1.50-1.20 (10H), 0.88 (t, 3H, J = 6.8); ^{13}C NMR (75 MHz) δ 103.8, 94.0, 31.7, 31.1, 29.3, 29.0, 23.8, 22.6, 14.0.