

#### Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1998 American Chemical Society

## Supporting Information

**Representative Preparations of Allylic Alcohols: (1E)-2-Methyldec-1-en-4-yn-3-ol.** To a stirred solution of heptyne (1.51g, 15.7 mmol) in THF (40 mL) at 20 °C was added *n*-butyllithium (6.8 mL as a 2.5 M solution in hexanes, 17.0 mmol). After 0.5 h, 2-methylpropenal (1.00g, 14.3 mmol) in THF (20 mL) was added. The mixture was stirred for a further 3 h, poured onto saturated ammonium chloride solution (20 mL) and the aqueous layer extracted with ether (3x15 mL). The combined organic extracts were dried over magnesium sulfate, filtered and evaporated. The residue was purified by column chromatography on silica using 1:9 ethyl acetate:petroleum ether as eluent to give **(1E)-2-methyldec-1-en-4-yn-3-ol** (2.04g, 86%) as a pale yellow oil; IR (liquid film) 3350, 2210, 1650  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 5.11 (1H, d, *J* 1.5 Hz), 4.80 (1H d, *J* 1.5 Hz), 4.68 (1H, bs), 2.15 (2H, dt, *J* 6, 1.5 Hz), 1.82 (3H, s), 1.60-1.45 (2H, m) 1.28 (4H, m), 0.83 (3H, t, *J* 6 Hz);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 144.7 (s), 111.8 (t), 86.6 (s), 79.3 (s), 66.3 (d), 31.0 (t), 28.2 (t), 18.7 (t), 18.0 (q), 13.9 (q); MS *m/z* (%) 166 (31,  $\text{M}^+$ ), 151 (79,  $\text{C}_{10}\text{H}_{15}\text{O}$ ), 123 (49,  $\text{C}_9\text{H}_{11}\text{O}$ ), 109 (82,  $\text{C}_7\text{H}_9\text{O}$ ), 95 (100,  $\text{C}_6\text{H}_7\text{O}$ ), 81 (80,  $\text{C}_5\text{H}_5\text{O}$ ), 55 (72,  $\text{C}_3\text{H}_3\text{O}$ ); HR-MS calcd for  $\text{C}_{11}\text{H}_{18}\text{O}$  166.1358, found 166.1349.

**7-Ethoxy-4-methyl-hept-3-en-6-yn-5-ol (3).** To a stirred solution of ethoxy acetylene (0.50g of a 50% w/w solution in hexanes, 3.6 mmol) in THF (10 mL) at 0 °C was added dropwise *n*-butyllithium (1.5 mL, 2.5M in hexanes; 3.8 mmol). After 0.5 h, a solution of 2-methyl-2-pentenal (0.27g, 2.7 mmol) in THF (20 mL) was added. After a further 18 h at 20 °C, work-up and column chromatography as for **1a** afforded **3** as a pale orange oil (0.37g, 61%); IR (liquid film) 3428, 2263, 1625  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.50 (1H, t, *J* 5Hz), 4.75 (1H, s), 4.20-3.95 (2H, m), 2.15-1.95 (2H, m), 1.90 (1H, s), 1.70 (3H, s), 1.35 (3H, t, *J* 6 Hz), 1.0 (3H, t, *J* 6 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  134.7 (s), 128.9 (d), 94.6 (s), 74.6 (s), 68.0 (t), 60.4 (t), 20.9 (t), 14.3 (q), 13.8 (q), 11.9 (q); MS *m/z* (%) 168 (30,  $\text{M}^+$ ), 139 (36,  $\text{C}_8\text{H}_{11}\text{O}_2$ ), 111 (60,  $\text{C}_6\text{H}_7\text{O}_2$ ), 97 (45,  $\text{C}_5\text{H}_5\text{O}_2$ ), 69 (100,  $\text{C}_3\text{HO}_2$ ); HR-MS calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_2$  168.1150, found 168.1146.

**Preparation of Epoxy Alcohols.** Although the current work did not in our hands afford any dangerous processes, the inherent explosion hazard of peroxides requires caution to be exercised whenever *tert*-butylhydroperoxide is used, particularly in solutions heated at reflux. For correct handling procedures see K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, **1979**, *12*, 63. Epoxidation frequently afforded two diastereoisomers that were not readily separable. NMR data for the major and minor diastereoisomers are denoted by the superscripts *ma* and *mi*, respectively.

**1-(2-Methyl-oxiranyl)-1-oct-2-yn-1-ol (1a).** To a stirred solution of 2-methyldec-1-en-4-yn-3-ol (0.50g, 3.0 mmol) in benzene (50 mL) at 20 °C was added vanadyl acetoacetate (0.01g). After 5 minutes aqueous *tert*-butylhydroperoxide (0.50g, 3.9 mmol, 70%; CAUTION!) was added. The mixture was heated at reflux for 1 h, allowed to cool to 20 °C and washed with saturated sodium sulfite solution (50 mL). The organic layer was separated, dried over magnesium sulfate, filtered and evaporated. The residue was purified by column chromatography on silica (1:9 ethyl acetate:petroleum ether) to give **1a** (0.37g, 67%) as a colourless oil, (71:29 mixture of diastereoisomers); IR (liquid film) 3430, 2215  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.32 (1H, m), 2.98 (1H, d, *J* 5Hz), 2.60 (1H, d, *J* 5Hz), 2.13 (2H, dt, *J* 6.5, 1.5), 1.46 (4H, m), 1.39 (3H, s), 1.12-1.35 (5H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  87.1 (s), 87.0 (s), 77.4 (s), 65.3<sup>ma</sup> (d), 64.3<sup>mi</sup> (d), 59.9<sup>ma</sup> (s), 58.9<sup>mi</sup> (d), 51.5<sup>ma</sup> (t), 51.1<sup>mi</sup> (t), 30.9 (t), 28.0 (t), 22.0 (t), 17.5<sup>ma</sup> (q), 16.5<sup>mi</sup> (q), 13.8 (q); MS *m/z* (%)

181 (19,  $M^+$ ), 167 (20,  $C_{10}H_{16}O$ ), 125 (50), 111 (83), 81 (84), 55 (100); HR-MS calcd for  $C_{11}H_{18}O_2$  181.1231, found 181.1229.

**1-(2-Methyl-oxiranyl)-3-phenyl-2-propyn-1-ol (1b).** To a stirred solution of 2-methyl-5-phenylpent-1-en-4-yn-3-ol (0.50g, 5.8 mmol) in benzene (50 mL) at 20 °C was added vanadyl acetoacetate (0.01g). After 5 minutes aqueous *tert*-butylhydroperoxide (0.50g, 3.9 mmol, 70%; CAUTION!) was added. The mixture was heated at reflux for 4 h, allowed to cool to 20 °C and worked up as for **1a**. Column chromatography on silica (1:9 ethyl acetate:petroleum ether) afforded **1b** (0.63g, 57%) as a pale yellow oil (3:1 mixture of diastereoisomers); IR (liquid film) 3420, 2205, 1600, 1490,  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.55-7.40 (2H, m), 7.35-7.20 (3H, m), 4.63 (1H<sub>ma</sub>, d, *J* 4Hz), 4.48 (1H<sub>mi</sub>, d, *J* 9Hz), 3.10 (1H<sub>ma</sub>, d, *J* 6Hz), 3.0 (1H<sub>mi</sub>, d, *J* 6Hz), 2.75 (1H, d, *J* 6Hz), 2.47 (1H, d, *J* 3Hz), 1.50 (3H, s);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  131.8 (d), 128.7 (d), 128.3 (d), 122.2 (s), 86.4<sub>mi</sub> (s), 86.2<sub>ma</sub> (s), 86.1<sub>ma</sub> (s), 65.6<sub>mi</sub> (d), 64.8<sub>ma</sub> (d), 59.2<sub>mi</sub> (s), 58.9<sub>ma</sub> (s), 51.7<sub>mi</sub> (t), 51.4<sub>ma</sub> (t), 17.7<sub>ma</sub> (q), 16.8<sub>mi</sub> (q); MS *m/z* (%) 188 (9,  $M^+$ ), 173 (9,  $C_{11}H_9O_2$ ), 145 (5,  $C_9H_5O_2$ ), 131 (99,  $C_8H_3O_2$ ), 118 (31), 115 (34,  $C_8H_3O$ ), 103 (38), 77 (37), 71 (41); HR-MS calcd for  $C_{12}H_{12}O_2$  188.0831, found 188.0837.

**1-(2-*n*-Butyl-oxiranyl)-oct-2-yn-1-ol (1c).** To a stirred solution of 2-butyldec-1-en-4-yn-3-ol (1.00g, 4.8 mmol) in benzene (50 mL) at 20 °C was added vanadyl acetoacetate (0.01g). After 5 minutes aqueous *tert*-butylhydroperoxide (0.87g, 6.7 mmol, 70%; CAUTION!) was added. The mixture was stirred at 20 °C for 18 h, allowed to cool to 20 °C and worked up as for **1a**. Column chromatography on silica (1:9 ethyl acetate: petroleum ether) afforded **1c** (1.03g, 96%) as a yellow oil (6:1 mixture of diastereoisomers); IR (liquid film) 3425, 2215  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  4.55-4.45 (1H<sub>ma</sub>, m), 4.35 (1H<sub>mi</sub>, dt, *J* 9, 1Hz), 2.95 (1H<sub>ma</sub>, d, *J* 6Hz), 2.90 (1H<sub>mi</sub>, d, *J* 6Hz), 2.70-2.60 (1H, m), 2.40 (1H, d, *J* 6Hz), 2.15 (2H, dt, *J* 9, 1.5Hz), 2.0-0.70 (18H, m);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  87.1 (s), 63.9<sub>mi</sub> (d), 62.8<sub>ma</sub> (d), 61.4<sub>ma</sub> (s), 61.2<sub>mi</sub> (s), 49.4 (t), 31.0 (t), 30.7<sub>ma</sub> (t), 30.3<sub>mi</sub> (t), 28.1 (t), 26.4<sub>mi</sub> (t), 26.3<sub>ma</sub> (t), 22.8 (t), 22.1 (t), 18.7 (t), 14.1 (q), 13.9 (q); MS *m/z* (%) 224 (24,  $M^+$ ), 223 (24,  $C_{14}H_{23}O_2$ ), 207 (27), 193 (23), 167 (11,  $C_{10}H_{15}O_2$ ), 153 (31,  $C_9H_{13}O_2$ ), 125 (38,  $C_7H_9O_2$ ), 111 (19,  $C_6H_7O_2$ ), 107 (21), 95 (30), 83 (57,  $C_4H_3O_2$ ), 81 (15); HR-MS calcd for  $C_{14}H_{24}O_2$  224.1776, found 224.1779.

**1-(*rel*-2*S*,3*S*-2-Methyl-3-ethyl-oxiranyl)-oct-2-yn-1-ol (1d).** To a stirred solution of (3*E*)-4-methyldodec-3-en-6-yn-5-ol (0.50g, 2.57 mmol) in benzene (50 mL) at 20 °C was added vanadyl acetoacetate (0.01g). After 5 minutes aqueous *tert*-butylhydroperoxide (0.47g, 3.6 mmol, 70%; CAUTION!) was added. The mixture was stirred at 20 °C for 20 h and worked up as for **1a**. Column chromatography on silica (1:9 ethyl acetate:petroleum ether) afforded **1d** (0.35g, 65%) as a pale yellow oil (2:1 mixture of diastereoisomers); IR (liquid film) 3420, 2210  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  4.30 (1H<sub>ma</sub>, s), 4.10 (1H<sub>mi</sub>, s), 3.05 (1H<sub>ma</sub>, t, *J* 6.5Hz), 2.92 (1H<sub>mi</sub>, t, *J* 6.5Hz), 2.43-2.36 (1H, bs), 2.15 (2H, dt, *J* 7, 2Hz), 1.70-1.15 (8H, m), 1.33 (3H, d, *J* 1Hz), 0.98 (3H<sub>ma</sub>, t, *J* 7.5Hz), 0.96 (3H<sub>mi</sub>, t, *J* 7.5Hz), 0.84 (3H, t, *J* 7Hz);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  86.8<sub>ma</sub> (s), 86.6<sub>mi</sub> (s), 77.1<sub>mi</sub> (s), 76.6<sub>ma</sub> (s), 66.9<sub>mi</sub> (d), 65.2<sub>ma</sub> (d), 63.5<sub>mi</sub> (s), 62.6<sub>ma</sub> (s), 61.5<sub>mi</sub> (d), 60.4<sub>ma</sub> (d), 30.9 (t), 28.1 (t), 22.1 (t), 21.4<sub>ma</sub> (t), 21.3<sub>mi</sub> (t), 18.6 (t), 13.9<sub>ma</sub> (q), 13.5<sub>mi</sub> (q), 12.0 (q), 10.3 (q); MS *m/z* (%) 195 (5,  $M^+$ ), 181 (33,  $C_{11}H_{17}O_2$ ), 139 (7), 125 (32), 95 (27), 86 (100), 83 (35), 71 (99); HR-MS calcd for  $C_{12}H_{19}O_2$  195.1385, found 195.1381.

**1-(*rel*-2*S*,3*S*-2-Methyl-3-ethyl-oxiranyl)-but-2-yn-1,4-diol (1e).** To a stirred solution of *m*-CPBA (0.76g, 4.54 mmol, 70%) in chloroform (50 mL) at 0 °C, was added (5*E*)-5-methyloct-6-en-2-yn-1,4-diol (0.50g, 3.24 mmol) in chloroform (30 mL). The mixture was allowed to warm to 20

°C and stirred for 18 h. The mixture was then washed with saturated aqueous sodium hydrogen carbonate (50 mL), dried over magnesium sulfate, filtered and evaporated. The residue was taken up in dichloromethane (10 mL), and potassium fluoride (0.50g) was added. After stirring at 20 °C for 2 h, the solution was filtered, the filtrate evaporated. The residue was purified by column chromatography on silica (7:3 ethyl acetate:petroleum ether) to give **1e** (0.25g, 53%) as a colourless oil (2:1 mixture of diastereoisomers); IR 3385, 2220 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.25 (1H<sub>ma</sub>, s), 4.20 (1H, d, *J* 7Hz), 4.15 (1H<sub>mi</sub>, d, *J* 7Hz), 3.85-3.65 (1H, bs), 3.10-2.95 (1H, m *J* 6Hz), 1.65-1.45 (2H, m), 1.35 (3H, s), 1.0 (3H, dt, *J* 7, 1Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 84.8<sub>ma</sub> (s), 84.5<sub>mi</sub> (s) 82.7<sub>mi</sub> (s) 82.6<sub>ma</sub> (s), 66.3<sub>mi</sub> (d), 65.5<sub>ma</sub> (d), 63.0<sub>mi</sub> (s), 62.4<sub>ma</sub> (s), 62.3<sub>ma</sub> (d), 62.1<sub>mi</sub> (d), 50.7 (t), 21.5<sub>ma</sub> (t), 21.3<sub>mi</sub> (t), 13.4<sub>ma</sub> (q), 12.6<sub>mi</sub> (q), 10.4. (q).

**1-(rel-2S,3S-2-Phenyl-3-ethyl-oxiranyl)-oct-2-yn-1-ol (1f).** To a stirred solution of (3E)-4-phenyldodec-3-en-6-yn-5-ol (1.00g, 3.90 mmol) in benzene (50 mL) at 20 °C was added vanadyl acetoacetate (0.01g). After 5 minutes aqueous *tert*-butylhydroperoxide (0.70g, 5.5 mmol, 70%; CAUTION!) was added. The mixture was stirred at 20 °C for 72 h and worked up as for **1a**. Column chromatography on silica (1:9 ethyl acetate: petroleum ether) afforded **1f** (0.78g, 73%) as a colourless oil; IR (thin film) 3445, 2235, 1605, 1500 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.50-7.35 (2H, m), 7.35-7.15 (3H, m), 4.50 (1H, m), 3.33 (1H, t, *J* 6Hz), 2.40 (1H, d, *J* 6Hz), 2.15 (2H, dt, *J* 6, 3Hz), 1.55-0.75 (14H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 131.5 (s), 128.8 (d), 128.5 (d), 128.0 (d), 127.9 (d), 127.7 (d), 88.1 (s), 76.6 (s), 67.1 (s), 65.5<sub>ma</sub> (d), 65.3<sub>mi</sub> (d), 63.1<sub>ma</sub> (d), 62.5<sub>mi</sub> (d), 31.0<sub>ma</sub> (t), 30.8<sub>mi</sub> (t), 28.1 (t), 22.2 (t), 22.1 (t), 18.7<sub>ma</sub> (t), 18.6<sub>mi</sub> (t), 14.2<sub>ma</sub> (q), 14.0<sub>mi</sub> (q), 10.0 (q); MS *m/z* (%) 272 (13, M<sup>+</sup>), 243 (16, C<sub>16</sub>H<sub>19</sub>O<sub>2</sub>), 157 (10, C<sub>11</sub>H<sub>9</sub>O), 148 (70), 133 (33), 105 (99), 91 (13), 71 (35); 55 (19); HR-MS calcd for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub> 272.1780, found 272.1776.

**1-[rel-2S,3R-2-Methyl-3(2-propyl)-oxiranyl]-oct-2-yn-1-ol (1g).** To a stirred solution of heptyne (0.09g, 0.93 mmol) in THF (5 mL) at 20 °C was added dropwise *n*-butyllithium (0.4 mL, 2.5M solution in hexanes, 1.01 mmol). After 0.5 h, a solution of 3-(2-propyl)-2-methyloxiranemethanal (0.09g, 0.72 mmol) in THF (5 mL) was added. The mixture was stirred for 18 h and then poured onto saturated ammonium chloride solution (15 mL). The aqueous layer was extracted with ether (2x10 mL), the organic layers combined, dried over magnesium sulfate, filtered and evaporated. The residue was purified by column chromatography on silica (1:9 ethyl acetate: petroleum ether) to give **1g** (0.10g, 65%) as a pale yellow oil; IR 3425, 2230 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.25 (1H, s), 3.35-3.15 (1H, bs), 2.50 (1H, d, *J* 7Hz), 2.15 (2H, dt, *J* 6, 1Hz), 1.85-1.60 (1H, dq, *J* 12, 7Hz), 1.55-0.75 (18H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 87.3 (s), 71.1 (d), 69.0 (s), 63.8<sub>mi</sub> (d), 62.8<sub>ma</sub> (s), 31.0 (t), 26.9 (t), 22.1 (t), 20.1 (q), 19.1 (q), 18.3 (q), 15.3<sub>mi</sub> (q), 13.9<sub>ma</sub> (q); MS *m/z* (%) 207 (M-H<sub>2</sub>O, 7), 195 (12, C<sub>12</sub>H<sub>19</sub>O<sub>2</sub>), 177 (11), 139 (12, C<sub>8</sub>H<sub>11</sub>O<sub>2</sub>), 125 (13, C<sub>7</sub>H<sub>9</sub>O<sub>2</sub>), 121 (22), 111 (14, C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>), 107 (18), 95 (45), 71 (100), 55 (85).

**3-Methyl-6-pentyl-2,3-dihydro-4H-pyran-4-one (2a).** To a stirred solution of 1-(2-methyl-oxiranyl)-oct-2-yn-1-ol (0.30g, 1.65 mmol) in acetone (30 mL, HPLC grade) at 20 °C was added a solution of yellow mercury(II) oxide dissolved in 2.5% sulfuric acid (0.3 mL, 0.1M Hg(II)). The mixture was stirred for 10 min. then neutralized by addition of powdered sodium hydrogen carbonate. The mixture was stirred at 20 °C for a further 1.5 h, filtered and the filtrate evaporated. The residue was taken up into ether (15 mL) and the solution was washed with water (25 mL). The aqueous layer was extracted with ether (2 x15 mL), and the combined extracts washed with saturated aqueous sodium hydrogen carbonate (30 mL), then brine (30 mL), dried over magnesium sulfate, filtered and evaporated. The residue was purified by column chromatography on silica (1:9 ethyl acetate: petroleum ether) to give **2a** (0.223g, 74%) as a pale yellow oil; IR (liquid film) 1685, 1610  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ( $\text{CDCl}_3$ ) 5.25 (1H, s), 4.40 (1H, dd,  $J$  11Hz, 5.5Hz), 3.98 (1H, t,  $J$  11Hz), 2.48 (1H, m), 2.18 (2H, t,  $J$  7Hz), 1.55-1.45 (2H, m), 1.35-1.15 (4H, m), 1.08 (3H, d,  $J$  6.5Hz), 0.85 (3H, t,  $J$  7Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  195.5 (s), 177.4 (s), 103.3 (d), 73.1 (d), 38.5 (d), 34.5 (t), 31.1 (t), 25.9 (t), 22.2 (t), 13.8 (q), 11.1 (q); MS  $m/z$  (%) 183 (88,  $M+1$ ), 139 (22,  $\text{C}_8\text{H}_{11}\text{O}_2$ ), 123 (40), 99 (100), 71 (67); HR-MS calcd for  $\text{C}_{11}\text{H}_{18}\text{O}_2$  182.1307, found 182.1301.

**3-Methyl-6-phenyl-2,3-dihydro-4H-pyran-4-one (2b).** To a stirred solution of 1-(2-methyl-oxiranyl)-3-phenyl-2-propyn-1-ol (0.30g, 1.56 mmol) in acetone (30 mL, HPLC grade) at 20 °C was added a solution of yellow mercury(II) oxide dissolved in 2.5% sulfuric acid (0.25 mL, 0.1M Hg(II)). The mixture was stirred for 1 h then neutralized by addition of powdered sodium hydrogen carbonate. After work-up as for **1a**, the residue was purified by column chromatography on silica (1:19 ethyl acetate: petroleum ether) to give **2b** (0.24g, 80%) as a white solid which crystallized from petroleum ether as plates, mp 94°C; IR (nujol mull) 1660, 1600, 1570  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.80-7.70 (2H, m), 7.55-7.35 (3H, m), 6.00 (1H, s), 4.58 (1H, dd,  $J$  5Hz), 4.15 (1H, t,  $J$  11Hz), 2.60 (1H, ddq,  $J$  12, 5, 6 Hz), 1.10 (3H, d,  $J$  6Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  195.9 (s), 170 (s), 132.7 (s), 131.6 (t), 128.7 (d), 126.5 (d), 101.4 (d), 73.4 (t), 38.9 (d), 11.1 (q); MS  $m/z$  (%) 188 (42,  $M^+$ ), 147 (22), 105 (99,  $\text{C}_6\text{HO}_2$ ), 77 (26); anal. calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$  C, 76.57%; H, 6.43%; found C, 76.15%; H, 6.48%; HR-MS calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$  188.0837; found 188.0835.

**3-Butyl-6-pentyl-2,3-dihydro-4H-pyran-4-one (2c).** To a stirred solution of 1-(2-*n*-butyl-oxiranyl)-oct-2-yn-1-ol (0.20g, 0.89 mmol) in acetone (30 mL, HPLC grade) at 20 °C was added a solution of yellow mercury(II) oxide dissolved in 2.5% sulfuric acid (0.4 mL, 0.1M Hg(II)). The mixture was stirred for 18 h then neutralized by addition of powdered sodium hydrogen carbonate. After work-up as for **1a**, the residue was purified by column chromatography on silica (1:9 ethyl acetate: petroleum ether) to give **2c** as a colourless oil (0.134g, 67%); IR (liquid film) 1670, 1610  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.23 (1H, s), 4.35 (1H, dd,  $J$  6, 12 Hz), 4.15 (1H, dd,  $J$  6, 12Hz), 2.35-2.20 (1H, m), 2.20 (2H, t,  $J$  5Hz), 0.95-0.70 (6H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  195.4 (s), 177.1 (s), 103.5 (t), 71.4 (t), 43.9 (d), 34.5 (t), 31.2 (t), 29.1 (t), 26.6 (t), 26.0 (t), 22.7, (t) 22.3 (t), 13.9 (q); MS  $m/z$  (%) 224 (32,  $M^+$ ), 194 (12), 181 (9,  $\text{C}_{11}\text{H}_{17}\text{O}_2$ ), 168 (99), 141 (75), 112 (50), 97 (21); HR-MS calcd for  $\text{C}_{14}\text{H}_{24}\text{O}_2$  224.1176, found 224.1177.

**2-Ethyl-3-methyl-5-pentyl-2,3-dihydro-4H-pyran-4-one (2d).** To a stirred solution of 1-(*rel*-2*S*,3*S*-2-methyl-3-ethyl-oxiranyl)-oct-2-yn-1-ol (0.30g, 1.47 mmol) in acetone (30 mL, HPLC grade) at 20 °C was added a solution of yellow mercury(II) oxide dissolved in 2.5% sulfuric acid (0.3 mL, 0.1M Hg(II)). The mixture was stirred for 30 min then neutralized by addition of powdered sodium hydrogen carbonate. After work-up as for **1a**, the residue was purified by column chromatography on silica (1:19 ethyl acetate: petroleum ether) to give **2d** (0.16g, 56%) as a pale yellow oil; IR (liquid film) 1685, 1610  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.17 (1H, s), 4.10 (1H, m), 2.35-2.10 (3H, m), 1.95-1.70 (1H, m), 1.70-1.40 (3H, m), 1.40-1.10 (4H, m), 1.05-0.70 (9H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  198.1 (s), 177.3 (s), 102.5 (d), 83.2 (d), 42.5 (d), 34.5 (t), 31.4 (t), 26.1 (t), 23.4 (t), 22.3 (t), 13.9, (q) 9.8 (q), 9.6 (q); MS  $m/z$  (%) 210 (42,  $\text{M}^+$ ), 181 (61,  $\text{C}_{11}\text{H}_{17}\text{O}_2$ ), 167 (8,  $\text{C}_{10}\text{H}_{15}\text{O}_2$ ), 152 (16), 141 (100), 111 (8,  $\text{C}_6\text{H}_7\text{O}_2$ ), 99 (14), 84 (14), 70 (46), 55 (51); HR-MS calcd for  $\text{C}_{13}\text{H}_{22}\text{O}_2$  210.1620, found 210.1614.

**2-Ethyl-3-methyl-6-methanol-2,3-dihydro-4H-pyran-4-one (2e).** To a stirred solution of 1-(*rel*-2*S*,3*S*-2-methyl-3-ethyl-oxiranyl)-but-2-yn-1,4-diol (0.30g, 1.76 mmol) in acetone (30 mL, HPLC grade) at 20 °C was added a solution of yellow mercury(II) oxide dissolved in 2.5% sulfuric acid (0.3 mL, 0.1M Hg(II)). The mixture was stirred for 1 h then neutralized by addition of powdered sodium hydrogen carbonate. After work-up as for **1a**, the residue was purified by column chromatography on silica (1:1 ethyl acetate: petroleum ether) to give **2e** (0.17g, 57%) as a pale yellow oil; IR (liquid film) 3400, 1650, 1615  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.50 (1H, s), 4.30-4.20 (1H, m), 4.20 (2H, s), 2.95-2.70 (1H, bs), 2.40 (1H, ddq,  $J$  10, 3.5, 1Hz), 1.95-1.45 (2H, m,  $J$  3.5 Hz), 1.10-0.85 (6H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  198.1 (s), 175.2, (s) 100.7 (d), 83.8 (d), 61.5 (t), 42.9 (d), 23.2 (t), 9.7 (q), 9.5 (q); MS  $m/z$  (%) 170 (22,  $\text{M}^+$ ), 130 (61), 122 (35), 101 (99), 99 (28,  $\text{C}_4\text{H}_3\text{O}_3$ ), 83 (27) 71 (66); HR-MS calcd for  $\text{C}_9\text{H}_{14}\text{O}_3$  170.0943, found 170.0947.

**2-Ethyl-3-phenyl-6-pentyl-2,3-dihydro-4H-pyran-4-one (2f).** To a stirred solution of 1-(*rel*-2*S*,3*S*-2-phenyl-3-ethyl-oxiranyl)-oct-2-yn-1-ol (0.30g, 1.10 mmol) in acetone (30 mL, HPLC grade) at 20 °C was added a solution of yellow mercury(II) oxide dissolved in 2.5% sulfuric acid (0.3 mL, 0.1M Hg(II)). The mixture was stirred for 25 min then neutralized by addition of powdered sodium hydrogen carbonate. After work-up as for **1a**, the residue was purified by column chromatography on silica (1:19 ethyl acetate: petroleum ether) to give **2f** (0.16g, 53%) as a pale yellow oil; IR (liquid film) 1665, 1605, 1500  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.35-7.02 (5H, m), 5.45 (1H, s), 4.45 (1H, m), 3.40 (1H, d,  $J$  3.5Hz), 1.85 (2H, dt,  $J$  7, 1.5Hz), 1.80-1.20 (8H, m), 1.05-0.80 (6H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  193.4 (s), 178.0, (s) 134.3 (s), 129.0 (d), 128.7 (d), 127.5 (d), 104.1 (d), 83.7 (d), 54.6 (d), 34.9 (t), 31.3 (t), 26.0 (t), 24.5 (t), 22.4 (t), 14.0 (q), 9.8 (q); MS  $m/z$  (%) 272 (7,  $\text{M}^+$ ), 243 (61,  $\text{C}_{16}\text{H}_{19}\text{O}_2$ ), 214 (77), 157 (99), 128 (20,  $\text{C}_9\text{H}_4\text{O}$ ), 115 (70,  $\text{C}_8\text{H}_3\text{O}$ ), 105 (8), 77 (9); HR-MS calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_2$  272.1776, found 272.1771.

**2-Isopropyl-3-methyl-6-pentyl-2,3-dihydro-4H-pyran-4-one (2g).** To a stirred solution of 1-[*rel*-2*S*,3*R*-2-methyl-3(2-propyl)-oxiranyl]-oct-2-yn-1-ol (0.1g, 0.45 mmol) in acetone (30 mL, HPLC grade) at 20 °C was added a solution of yellow mercury(II) oxide dissolved in 2.5% sulfuric acid (0.15 mL, 0.1M Hg(II)). The mixture was stirred for 1 h then neutralized by addition of powdered sodium hydrogen carbonate. After work-up as for **1a**, the residue was purified by column chromatography on silica (1:9 ethyl acetate: petroleum ether) to give **2g** (0.05g, 50%) as a pale yellow oil; IR (liquid film) 1665, 1660  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.25 (1H, s), 3.78 (1H, dd,  $J$  12, 5Hz), 2.35 (1H, dq,  $J$  6, 5Hz), 2.20-2.05 (2H, dt,  $J$  6, 1Hz), 2.05-1.85 (1H, m), 1.60-1.10 (6H, m), 1.0 (6H, dd,  $J$  7, 1Hz), 0.95-0.70 (6H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  196.0 (s), 176.9 (s), 102.9 (d), 87.7 (d), 68.2 (d), 40.8 (d), 34.6 (t), 31.1 (t), 28.5 (t), 25.9 (t), 20.2, (q), 18.1 (q), 17.4 (q), 14.9 (q),

13.9 (q); MS  $m/z$  (%) 224 (8,  $M^+$ ), 141 (100), 125 (7,  $C_7H_9O_2$ ), 84 (19), 69 (47); HR-MS calcd for  $C_{14}H_{24}O_2$  224.1776, found 224.1778.

**6-Ethoxy-2-ethyl-3-methyl-2,3-dihydro-4H-pyran-4-one (4).** To a stirred solution of 1-ethoxy-4-methylhept-4-en-1-yn-3-ol (0.25g, 1.49 mmol) in benzene (30 mL) at 20 °C was added vanadyl acetoacetate (0.01g). After 5 minutes aqueous *tert*-butylhydroperoxide (0.27g, 2.1 mmol, 70%; CAUTION!) was added. The mixture was stirred at 20 °C for 72 h and worked up as for 1a. Column chromatography on silica (3:7 ethyl acetate: petroleum ether) afforded **4** (0.137g, 55%) as a pale orange oil; IR (liquid film)  $1655\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.75 (1H, s), 4.37-4.27 (1H, m), 4.04 (2H, q,  $J$  7Hz), 2.30 (1H, dq,  $J$  7.5, 2.5Hz), 1.95-1.73 (1H, ddq,  $J$  7.5, 2, 1Hz), 1.70-1.45 (1H, ddq,  $J$  7.5, 2, 1Hz), 1.33 (3H, t,  $J$  7Hz), 1.07-0.85 (6H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  197.8 9 (s), 172.9, (s), 154.8 (d), 84.2 (d), 81.2 (d), 64.9 (t), 23.6 (t), 14.2 (q), 9.8 (q), 9.7 (q); MS  $m/z$  (%) 184 (77,  $M^+$ ), 144 (10), 115 (100), 87 (64), 69 (64); HR-MS calcd for  $C_{10}H_{16}O_3$  184.1100, found 184.1101.