Supporting Information for

A Novel Pathway in the Photooxygenation of Cyclic Allenes

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Photooxygenation of Cyclic Allenes. General Procedure. In a 50 mL round-bottomed flask equipped with a magnetic spin-bar and a gas inlet was placed a solution of 100 mg of allene in 25 mL of dry CCl_4 containing 5 mg of *meso*-tetraphenylporphyrin (TPP). The stirred solution was irradiated at room temperature with a 250W sodium high-pressure lamp under a positive pressure of dry oxygen. The progress of the photooxygenation was monitored by TLC. During the singlet oxygenations some bleaching of the sensitizer occurred, therefore, additional amounts of TPP were added when necessary. Some of the hydrates formed precipitated from the CCl_4 solution during the reaction. The solvent was removed at reduced pressure and the residue purified on a silica gel column eluting with petroleum ether/ethyl acetate (4:6).

^{1}H NMR (300 MHz, $CDCl_3$, TMS) of **2a, δ:** 7.8 (br. s, 2H); 2.35 (t, ^{3}J= 7.5 Hz, 4H); 1.67 (m, 4H); 1.35 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, TMS), δ: 180.8, 120.0, 34.7, 29.4, 25.2 ppm; FT-IR: 3432, 2934, 2861, 1712, 1194, 1190, 1127, 1098, 1026 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$, TMS) of **2b**, δ: 10.5 (br. s, 2H); 2.3 (t, ^{3}J= 7.5 Hz, 4H); 1.63 (m, 4H); 1.3 (m, 12 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, TMS), δ: 180.8, 121.2, 30.0, 29.8, 29.7, 25.3 ppm; FT-IR: 3440, 3190 (shoulder), 2926, 2854, 1709, 1464, 1413, 1245, 1184, 1108, 914, 736 cm^{-1}.

Cycloaddition of 1a with MTAD. A solution of MTAD (46 mg, 0.4 mmol) in 1 mL of CH_2Cl_2 was added to a solution of **1a** (50 mg, 0.4 mmol) in 1 mL of tetrahydrofuran (THF) and two drops of H_2O at 0 ˚C. After the red color of MTAD disappeared the solvent was concentrated under reduced pressure and the residue purified by column chromatography on silica gel, eluting with ether.
^{1}H NMR (300 MHz, $CDCl_3$, TMS) of **11**, δ: 7.8 (br. s, 1H); 6.55 (m, 1H); 6.1 (d, 12.3 Hz, 1H); 5.61 (dd, 3J= 11.4, 10.50 Hz, 1H); 3.1 (s, 3H); 2.78 (m, 1H); 2.5 (m, 1H); 1.5-2.1 (m, 8H) ppm; ^{13}C (75 MHz, $CDCl_3$, TMS), δ: 200, 155.5, 154.2, 148.2, 130.7, 62.8, 41.7, 33.6, 29.3, 27.2, 23.7 ppm.

Cycloaddition of 12 with MTAD. The procedure was identical to the one described above for the preparation of **11**. The mixture was purified by column chromatography on silica gel, eluting with ether. The top fraction (8% yield) was a 6:1 mixture of **16** and **17**.

16:^{1}H NMR (300 MHz, $CDCl_3$, TMS), δ: 8.5 (br. s, 1H); 5.8 (t, 8.7 ^{3}J= Hz, 1H); 5.73 (m, 1H); 3.1 (s, 3H); 2.2 (m, 4H); 1.82 (s, 3H); 1.3-1.7 (m, 6 H); signals due to **17**: 5.83 (t, ^{3}J= 8.7 Hz, 1H), 5.29 (d, ^{2}J= 1.8 Hz); 5.175 (d, ^{2}J= 1.8 Hz, 1H); 3.18 (s, 3H); the other signals overlap with those of compound **16**. The second fraction was due to compound **15**; ^{1}H NMR (300 MHz, $CDCl_3$, TMS); δ: 8.2 (br. s, 1H); 5.8 (s, 1H); 5.67 (s, 1H); 5.45 (dd, ^{3}J= 8.1 Hz and 5.7 Hz, 1H); 3.1 (s, 3H); 2.7 (m, 1H); 2.25 (m, 1H); 2.0 (m, 1H); 1.85 (m, 1H); 1.2-1.8 (m, 8H) ppm.

Photooxygenation of 12. Compound **12** was photooxygenated under the same conditions as described for **1a** and **1b**. The product was purified on a silica gel column, eluting with hexane/ethyl acetate (2:1) to give a 2:3 mixture of **13** and **14**, respectively (86% isolated yield); **13**: ^{1}H NMR ($CDCl_3$, TMS); δ: 5.57 (s, 1H); 5.56 (s, 1H); 4.8 (m, 1H); 3.71 (d, ^{3}J= 4.5 Hz, OH); 2.0-2.5 (m, 4H); 1.2-1.9 (m, 8H); **14**: ^{1}H NMR ($CDCl_3$, TMS); δ: 6.2 (m, 1H); 4.8 (m, 1H); 4.05 (d, 3J= 4.8 Hz, OH); 2.76 (m, 1H); 2.45 (m, 1H) ppm; other signals overlap with those of **13**; ^{13}C NMR ($CDCl_3$, TMS) of **13** and **14**; δ: 206.5, 148.7 (**13**), 140.1 (**14**), 135.35 (**14**), 121.5 (**13**), 75.75, 74.97, 36.7, 33.7, 30.3, 28.7, 27.3, 27.2, 26.4, 22.5, 21.2, 21.14, 21.1, 17.5 ppm.