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Application of the Oxa-Di-π-Methane Photoisomerization in the Rearrangement of Carbocycles Possessing Bridgehead Unsaturation

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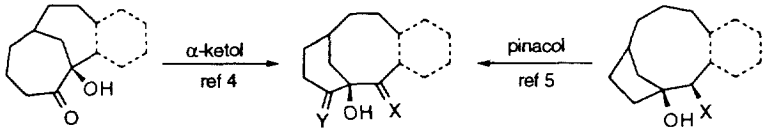
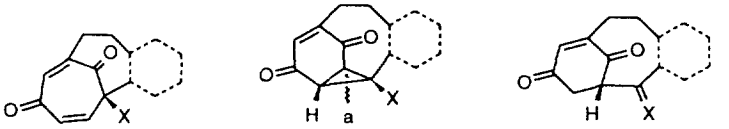
Abstract: Studies directed toward an application of the oxa-di-pi-methane (ODPM) photoisomerization to convert a bicyclo[4.4.1]undecene (**1**) to a bicyclo[5.3.1]undecene (**3**) are described. This transformation, which is equivalent to a 1,2-acyl shift, could find utility in the synthesis of bioactive natural products possessing bridgehead unsaturation. © 1997 Elsevier Science Ltd.

A structural feature shared by a select group of bicyclic natural products is bridgehead unsaturation.[1] Notable members of this group include the taxane diterpenes, eremantholides, and cerorubenic acid.[2] The unique architecture, and in some instances biological activity, associated with these natural products have attracted the interest of practitioners of organic synthesis. Among the successful strategies examined to assemble these bicyclic ring systems are the application of various sigmatropic rearrangements and cycloaddition processes.[1,3] In the taxane area, one strategy has been to access the saturated core ring system with the intention of introducing the unsaturation at a late stage in the synthesis. In order to achieve the former goal, Rigby has examined the rearrangement of a bicyclo[4.4.1]undecane to a bicyclo[5.3.1]undecane related to the taxane AB substructure.[4] Conceptually similar bond reorganizations have been examined by Paquette in his approach to the taxane ring system.[5] Both approaches made use of pinacol or α-ketol type rearrangements which required the use of a Lewis acid or strong base. Two limitations to this approach are that the reaction conditions are sometimes incompatible with existing functionality and that the product distribution is subject to thermodynamic control. An alternative approach which could circumvent these limitations, would be to effect a 1,2-acyl shift in the form of an oxa-di-pi-methane (ODPM) photoisomerization.[6]



Y = H, H; X = O (via α-ketol)
Y = O; X = H, H (via pinacol)



1a X = H
1b X = OCH_3

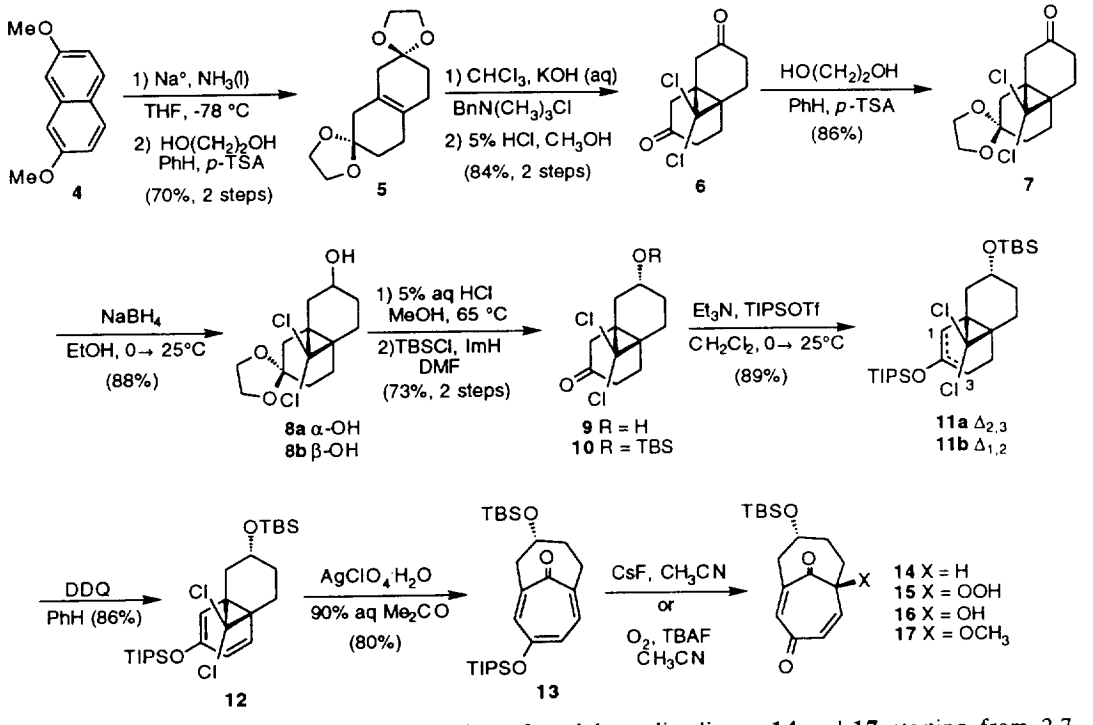
2a X = H
2b X = OCH_3

3a X = H, H
3b X = O

Dedicated with respect to Professor Samuel J. Danishefsky.

The application of an ODPM photoisomerization to bicyclo[4.4.1]undecadiene **1a** should give rise to cyclopropyl ketone **2a**, which on selective reductive cleavage (bond a) would yield bicyclo[5.3.1]undecene **3a**.[7] The overall conversion of **1a** to **3a** would then constitute a reductive 1,2-acyl shift. Note, that in this approach the bridgehead unsaturation would be in place prior to the skeletal rearrangement. A second tactic would be to install a methoxy group at the bridging carbon (cf. **1b**). Photoisomerization of bicyclo[4.4.1]undecadiene **1b** could then yield triketone **3b** via intermediate **2b**.[6c] In this case, the overall conversion (**1b**→**3b**) would constitute an α-ketol rearrangement. Herein we describe preliminary results of our investigations into these photochemical rearrangements and the reductive cleavage of cyclopropylketone **2a**.

Scheme 1



Our studies began with the preparation of cycloheptadiendiones **14** and **17** starting from 2,7-dimethoxynaphthalene (**4**) (Scheme 1). Birch reduction of **4** followed by exchange of the methyl enol ethers for ethylene ketal groups provided **5**.[8] Addition of dichlorocarbene to the central olefin of **5** generated a dichlorocyclopropane which on hydrolysis gave rise to diketone **6** in 84% overall yield.[9] Notably, of the first four steps only one chromatography was required and the remaining intermediates were purified by either recrystallization or distillation. At this point we required differentiation of the two carbonyl groups within **6**. This was accomplished via monoketalization of **6** to provide ketone **7** (86%).[10] Sodium borohydride reduction of the latter generated an approximate 4:1 mixture of carbinols **8a** and **8b**. Hydrolytic removal of the ketal protecting group led to the isolation of **9** in 73% yield. Following silylation of **9**, the TBS ether derivative **10** was subjected to further silylation (TIPSOTf, Et_3N, CH_2Cl_2) to provide a mixture of TIPS enol ethers (**11a** and **11b**; 3.1:1).[11] The enol ethers were not separated but directly subjected to a DDQ oxidation

to provide divinyl dichlorocyclopropane **12** plus recovered **11b**.[12] Silver(I) assisted solvolytic opening of dichlorocyclopropane **12** occurred at room temperature to afford tropone **13** in 86% yield.[13] Desilylation of **13** with CsF in acetonitrile under oxygen-free conditions provided diene dione **14** (55-67%), while desilylation with TBAF in oxygenated THF provided peroxide **15** (48-53%) plus **14** (31%). The structures **14** and **15** were determined based on single-crystal X-ray analysis as well as spectroscopic data (Figures 1 and 2). Peroxide **15** was reduced (Ph_3P, PhH, reflux, 83%) and methylated (Ag_2O, CH_3I, DMF, 30%) to provide methyl ether **17**.

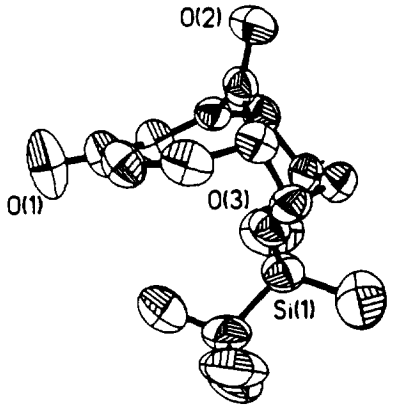


Figure 1. ORTEP drawing of dione **14**.

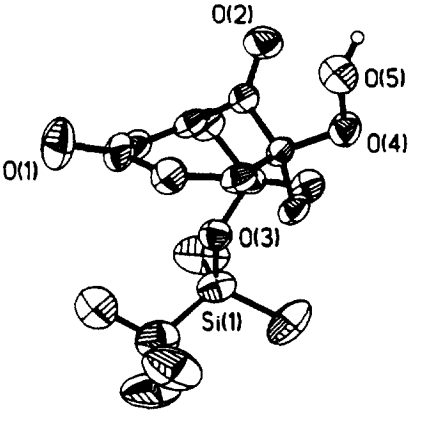
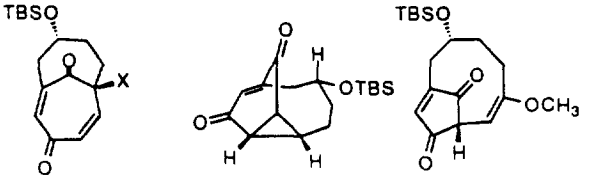


Figure 2. ORTEP drawing of peroxide **15**.

We first examined the photoisomerization of cycloheptadiendione **14**. Irradiation of a benzene solution of **14** (ca. 0.01 M) using a tungsten lamp at room temperature for 2.2 h resulted in the production of cyclopropylketone **18** (50%) plus recovered **14** (34%). Alternative reaction conditions (solvent and light wavelength) did not provide superior results. Photoisomerization of methyl ether **17** was also effected upon irradiation with a tungsten lamp and employing benzene as a solvent. However, in this case the isomerization proceeded by way of a 1,3-acyl shift to afford **19** (52%) rather than the expected ODPM photoisomerization product. Reaction conditions which favor triplet state excitation (irradiation using a 450W Hanovia lamp through a pyrex glass filter and acetone as a solvent) did not alter the reaction pathway, but provided **19** in 48% yield.[6c]



Two electron reduction of tricyclic ketone **18** could proceed by way of several reaction pathways. First, reduction of the carbon-carbon double bond would result in loss of the bridgehead unsaturation and produce the corresponding saturated ketone. A second reaction manifold would result in reductive cleavage of one of three cyclopropane bonds. Depending on which cyclopropane bond is cleaved, one of three isomeric bicyclic ketones could be produced. As discussed in the introduction, cleavage of bond a would serve to generate the bicyclo[5.3.1]undecene ring system related to the taxane ring system. We first examined the reduction of **18** using samarium diiodide. Under these conditions bicyclic ketone **20** was exclusively produced in 53% yield; the result of bridgehead olefin saturation as well as cyclopropane bond cleavage. On the other hand, reduction of **18** with an excess of lithium dimethylcuprate led to cleavage of the cyclopropane ring without loss of the bridgehead unsaturation in the form of **21** (18%) in addition to the previously observed ketone **20** (18%), presumably the result of a secondary two electron reduction of **21**. The mode of cyclopropane cleavage was elucidated following monoketalization of **21** to afford monoketal **22** as a crystalline derivative, which was subjected to single crystal X-ray analysis. The final ORTEP diagram of **22** is depicted in Figure 3 and reveals that reduction of **18**, using either SmI_2 or $LiCuMe_2$, resulted in selective cleavage of bond b.

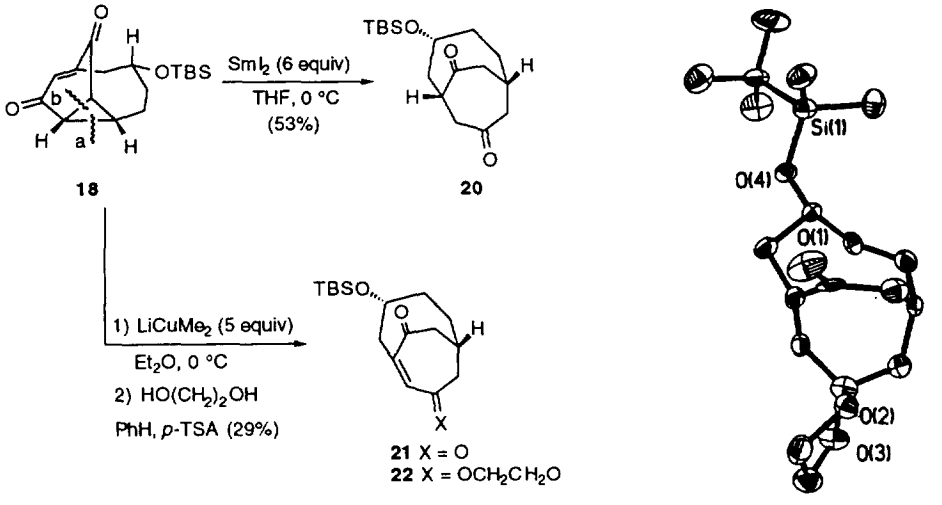


Figure 3. ORTEP drawing of monoketal **22**.

The reduction of cyclopropyl ketones using samarium diiodide has been demonstrated to proceed by way of cyclopropyl carbinyl ketyls.[14] Furthermore, the mode of ring fragmentation of these strained intermediates is subject to stereoelectronic as well as radical stabilizing affects.[7,14] In the case of **18**, molecular models suggest bond cleavage of either bond a or b to be equally probable based on stereoelectronic considerations. The determining factor appears to be the ability of the apical carbonyl to exert a stabilizing effect on the intermediate radical resulting in the observed selectivity (bond b cleavage).[7] Currently we are investigating the reductive cleavage of derivatives of **18** which may disfavor cleavage of bond b to provide a pathway to the desired bicyclo[5.3.1]undecene ring system.

Experimental

General Procedures. 2,7-Dimethoxynaphthalene was purchased from the Aldrich chemical company, and reagents were obtained from commercial suppliers, and where appropriate were purified prior to use. All reactions were carried out under a nitrogen or argon atmosphere using dry glassware which had been flame-dried under a stream of nitrogen, unless otherwise noted. All necessary solvents were purified prior to use. Tetrahydrofuran and ethyl ether were distilled from sodium/benzophenone; dichloromethane and benzene were distilled from calcium hydride. Triisopropylsilyltriflate was distilled prior to use. Triethylamine was distilled from calcium hydride and stored over sodium hydroxide. Reactions were monitored by thin-layer chromatography (TLC) using 0.25-mm E. Merck precoated silica gel plates. Visualization was accomplished with UV light and aqueous ceric ammonium molybdate solution or anisaldehyde stain followed by charring on a hot-plate. Flash chromatography was perfomed with the indicated solvents using silica gel 60 (particle size 230-400 mesh) with the indicated solvent. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. Melting points are uncorrected unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on Varian 300, 400 and 500 MHz spectrometers at ambient temperature. ^{1}H and ^{13}C NMR data are reported as δ values relative to tetramethylsilane. High-resolution mass spectra were obtained at Texas A&M University Mass Spectrometry Service Center by Dr. Lloyd Sumner on a VG Analytical 70S high resolution, double focusing, sectored (EB) mass spectrometer. The single-crystal X-ray diffraction anaylsis was performed by Dr. Joseph Reibenspies of Texas A&M University using a R3m/V single-crystal X-ray diffractometer.

Bisketal 5. To a solution of 2,7-Dimethoxy-1,4,5,8-tetrahydronaphthalene (25.3 g, 132 mmol) in benzene (200 mL) were added ethylene glycol (17.4 mL, 395 mmol), and a catalytic amount of *p*-toluenesulfonic acid (ca. 25 mg). The mixture was refluxed for one hour, allowed to cool to room temperature, and washed with water (200 mL). The aqueous layer was extracted with diethyl ether (3 x 150 mL). The combined organic extracts were washed once with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by vacuum distillation (158-160 °C at 1.2 mm Hg) to afford 28.5 g (86%) of bisketal **5** as a colorless oil that crystallized on standing: mp 48-50 °C; IR ($CHCl_3$) 2956, 2893, 1215 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (m, 8H), 2.14 (m, 8H), 1.77 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.8, 123.4, 108.1, 64.3, 40.0, 31.0, 28.6. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 8.00. Found: C, 66.34, H, 7.95.

Dichlorocyclopropane 5a. To a solution of bisketal **5** (2.0 g, 7.9 mmol) in chloroform (5 mL) was added 50% aqueous NaOH (12 mL), followed by benzyltriethylammonium bromide (ca. 10 mg) and absolute ethanol (2 drops). The thickening solution was stirred at room temperature for 18 h. The suspension was diluted with water (15 mL) and extracted with chloroform (3 x 15 mL). The organic layer was filtered through a bed of Celite over silica gel, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography (2:1 hexane/EtOAc) to afford 2.5 g (92%) of dichlorocyclopropane **5a**, as a crystalline solid: mp 73-74 °C; IR ($CHCl_3$) 2949, 1176, 1087 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (m, 6H), 3.86 (m, 3H), 2.12 (d, J =15.2 Hz, 2H), 2.04 (dt, J = 14.7, 6.1 Hz, 2H), 1.95-1.84 (m, overlapping signals, 4H), 1.66 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 108.3, 77.4, 64.1 (2C), 39.8, 30.5, 29.2, 28.4 (2C). Anal. Calcd. for $C_{15}H_{20}Cl_2O_4$: C, 53.74; H, 6.01. Found: C, 53.36, H, 5.92.

Diketone 6. A solution of dichlorocyclopropane **5a** (9.32 g, 37.7 mmol) in methanol (50 mL) and 10% aqueous HCl (50 mL) was refluxed for 1 h. The methanol was removed *in vacuo* and the remaining aqueous solution was extracted with methylene chloride (3 x 100 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ solution (75 mL) and then brine solution (100 mL), were dried over $MgSO_4$, filtered, concentrated *in vacuo*, and recrystallized from diethyl ether to afford 6.1 g (90%) of diketone **6** as a white crystalline solid: mp 127-128 °C; IR ($CHCl_3$) 2953, 1716, 1228 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.80 (A of AB, J_{AB} = 17.4 Hz, 2H), 2.40 (B of AB, J_{AB} = 17.4 Hz, 2H), 2.54-2.23 (m, overlapping signals, 8H); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 207.8, 77.2, 43.3, 36.9, 33.7, 30.2, 28.3. Anal. Calcd. for $C_{11}H_{12}O_2Cl_2$: C, 53.46; H, 5.83. Found: C, 53.17, H, 6.15.

Monoketal 7. To a solution of diketone **6** (7.38 g, 40.5 mmol) in benzene (200 mL) were added ethylene glycol (2.37 mL, 44.5 mmol), and a catalytic amount of *p*-toluenesulfonic acid (ca. 30 mg). The mixture was refluxed for 1 h with water removal using a Dean-Stark apparatus. The reaction mixture was cooled to room temperature, washed with saturated aqueous $NaHCO_3$ solution, and then with brine (50 mL). The solution was dried over $MgSO_4$, filtered, and was concentrated *in vacuo*. The residue was purified by flash chromatography (2:1 hexane/EtOAc) to afford 7.51 g (86%) of monoketal **7** as a crystalline solid: mp 83-85 °C; IR ($CHCl_3$) 2974, 1716, 1222 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.98-3.77 (m, 4H); 2.67 (A of AB, J_{AB} = 17.1 Hz, 1H); 2.43 (B of AB, J_{AB} = 17.1 Hz, 1H), 2.56 (m, 1H), 2.34-2.00 (m, overlapping signals, 6H), 1.79 (dd, J = 15.0, 2.4 Hz, 1H), 1.75-1.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 107.4, 77.2, 64.7, 64.0, 47.0, 36.7, 34.8, 30.5, 30.4, 29.3, 28.1, 27.0. Anal. Calcd. for $C_{13}H_{16}O_3Cl_2$: C, 53.63; H, 5.54. Found: C, 53.35, H, 5.59.

Alcohols 8a and 8b. To a solution of monoketal **7** (3.40g, 11.6 mmol) in absolute ethanol (50 mL) at 0° C was added $NaBH_4$ (0.46 g, 12.2 mmol). The reaction mixture was allowed to warm to room temperature, and stirring was continued for one hour. The mixture was concentrated *in vacuo*, and the residue was diluted with water (40 mL), and extracted with diethyl ether (3 x 40 mL). The combined organics were dried over $MgSO_4$, filtered, concentrated *in vacuo*, and the residue was purified by flash chromatography (2:1 hexanes/EtOAc) to provide 3.00 g of a 4:1 mixture of inseparable alcohols **8a** and **8b** (88%) as a white solid: mp 62-64 °C; IR ($CHCl_3$) 3465, 3018, 2943, 1215 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.04-3.82 (m, overlapping signals, 5H), 2.29-1.38 (m, overlapping signals, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.1, 108.4, 77.2, 66.0, 64.5, 64.3, 64.1, 64.0, 40.3, 39.3, 39.3, 38.7, 30.9, 30.4, 29.9, 29.5, 28.6, 28.4, 28.2, 27.2, 26.6, 26.5, 24.7; Anal. Calcd. for $C_{13}H_{18}O_3Cl_2$: C, 53.26; H, 6.19. Found: C, 53.37, H, 6.19.

Ketoalcohols 9a and 9b. To a solution of alcohols **8** (4.38g, 14.9 mmol) in methanol (50 mL) was added 5% aqueous HCl (5 mL), and the mixture was warmed at 65°C for one hour. The solution was concentrated *in vacuo* and diluted with methylene chloride (30 mL) and water (15 mL). The aqueous layer was extracted with methylene chloride (3 x 30 mL). The combined organics were dried over $MgSO_4$, filtered, concentrated *in vacuo*, and the residue was purified by flash chromatography (2:1 hexanes/EtOAc, residue loaded as silica gel absorbate) to give ketoalcohols **9a** and **9b** as white solids.

The first to elute was ketoalcohol **9a** (2.66 g, 75%): TLC, R_f 0.58 (1:1 hexane/EtOAc); mp 113-115 °C; IR ($CHCl_3$) 3464, 2937, 1711, 1227, 1207, 1053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.00 (m, 1H), 2.74 (A of AB, J_{AB} =16.8 Hz, 1H), 2.57 (ddd, J =19.4, 11.7, 2.1 Hz, 1H), 2.46 (B of AB, J_{AB} =16.8 Hz, 1H), 2.22 (ddd, J =18.0, 3.3, 2.7 Hz, 1H), 2.19-1.93 (m, overlapping signals, 5H), 1.84 (ddd, J =15.3, 3.6, 1.5 Hz, 1H), 1.60 (m, 1H), 1.48 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5, 77.0, 62.9, 47.5, 36.0, 35.4, 29.9, 27.9, 27.7, 26.7, 21.8; Anal. Calcd. for $C_{11}H_{14}O_2Cl_2$: C, 53.03; H, 5.66. Found: C, 53.19, H, 5.72.

The second to elute was ketoalcohol **9b** (0.59 g, 16%): TLC, R_f 0.42 (1:1 hexane/EtOAc); mp 92-94 °C; IR ($CHCl_3$) 3440, 3018, 2951, 1716, 1448, 1223 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.48 (m, 1H), 2.76 (A of AB, J_{AB} =17.3 Hz, 1H), 2.46 (B of AB, J_{AB} =17.3 Hz, 1H), 2.39 (ddd, J =15.2, 6.8, 1.8 Hz, 1H), 2.31(m, 1H), 2.22 (ddd, J =12.9, 6.3, 0.7 Hz, 1H), 2.16 (m, 1H), 2.09 (dd, J =12.9, 4.5 Hz, 1H), 2.06-1.87, (m, overlapping signals, 3H), 1.72 (m, 1H), 1.42 (ddd, J =12.9, 11.8, 6.9 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 76.8, 66.9, 46.4, 37.3, 35.7, 30.4, 30.1, 29.4, 28.0, 27.9; LRMS (FAB) *m/e* 249 [(M+H) calcd. for $C_{11}H_{15}O_2Cl_2$: 249].

Silylether 10 To a solution of alcohol **9a** (2.7 g, 10.7 mmol) in DMF (20 mL) was added imidazole (1.8 g, 26.7 mmol) and TBSCl (1.78 g, 11.8 mmol). The reaction mixture was stirred at room temperature for 24 h, and then was and diluted with water (20 mL). The mixture was extracted with diethyl ether (3 x 20 mL), and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography (4:1 hexane/EtOAc) to give 3.8 g (98%) of

TBS ether **10** as a white solid: mp 53-55 °C; IR ($CHCl_3$) 2956, 2931, 1711, 1221 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.96 (m, 1H), 2.77 (A of AB, J_{AB} = 17.7 Hz, 1H), 2.52 (ddd, J = 18.3, 10.2, 10.2 Hz, 1H), 2.47 (B of AB, J_{AB} = 17.7 Hz, 1H), 2.26 (ddd, J = 16.8, 3.0, 3.0 Hz, 1H), 2.15-1.92 (m, overlapping signals, 6H), 1.85 (ddd, J = 15.0, 1.8, 1.8 Hz, 1H), 1.48 (m, 1H), 0.78 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 77.8, 64.2, 47.3, 36.7, 35.7, 30.1, 28.4, 27.8, 26.7, 25.9, 22.2, 18.3, -5.0, -5.0; HRMS (FAB) *m/e* 363.1324 [$(M+H)^+$, calcd for $C_{17}H_{29}O_2Cl_2Si$: 363.1314].

Silylenol ethers 11a and 11b. A solution of ketone **10** (1.05 g, 2.89 mmol) in dichloromethane (45 mL) was cooled to 0 °C and triethylamine (0.84 mL, 6.08 mmol) was added dropwise. The solution was stirred at 0 °C for 5 min and freshly distilled TIPSOTf (.85 mL, 3.19 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirring was continued for 10 h. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (30:1→9:1 hexane/EtOAc) to provide 1.33 g (89%) of a 3.1:1 mixture of silyl enol ethers **11a** and **11b** as a colorless oil: IR (CH_2Cl_2) 2949, 1267, 1225, 1203 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.85 (br s, minor diastereomer, 1H), 4.62 (br s, major diastereomer, 1H), 3.65 (m, 2H), 2.85-1.62 (m, overlapping signals, 20H), 1.40-1.10 (m, overlapping signals, 42H), 0.95 (s, 18H), 0.02 (s, 6H), 0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 147.7, 105.5, 99.3, 79.8, 76.6, 65.4, 38.2, 36.4, 35.7, 32.8, 32.2, 29.8, 29.6, 29.5, 28.6, 27.8, 27.6, 27.0, 26.7, 26.1, 26.0, 25.8, 25.6, 18.2, 18.2, 13.0, 12.9, -4.7, -4.8, -4.9; HRMS (FAB) *m/e* 518.2552 [$(M)^+$ calcd for $C_{17}H_{48}O_2Cl_2Si_2$: 518.2570].

Divinyldichlorocyclopropane 12. To a solution of silyl enol ethers **11a** and **11b** (0.29 g, 0.56 mmol, 3.10:1 mixture) in benzene (6 mL) was added DDQ (0.19 g, 0.84 mmol). The orange mixture was stirred at room temperature for 24 hours, and was quenched with a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with diethyl ether (3 x 15 mL) and the combined organics were dried over $MgSO_4$, filtered, concentrated *in vacuo*, and the residue was purified by flash chromatography (19:1 hexanes/EtOAc) to give 0.25 g (86%, combined yield) of divinyldichlorocyclopropane **12** and silyl enol ether **11b** (3.10:1 mixture) as a colorless oil: IR ($CHCl_3$) 3047, 3022, 1655, 1583 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.96 (dd, J = 9.6, 1.7 Hz, 1H), 5.67 (d, J = 9.6 Hz, 1H), 4.85 (s, 1H), 3.83 (m, 1H), 2.43 (dd, J = 14.0, 4.2 Hz, 1H), 2.25 (m, 1H), 1.94 (m, 1H), 1.63 (dd, J = 14.1, 5.8 Hz, 1H), 1.48 (m, 1H), 1.32 (m, 1H), 1.18-1.05 (m, overlappping signals, 21H), 0.80 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.5, 128.7, 126.1, 106.4, 77.2, 65.5, 43.3, 41.6, 38.9, 30.0, 26.8, 25.7, 17.9 (3C), 12.5, -4.4, -4.5.

Tropone 13. To a solution of divinyldichlorocyclopropane **12** (2.94 g, 5.69 mmol, 2.64:1 mixture) in 10% aqueous acetone (50 mL) was added $AgClO_4 \cdot H_2O$ (1.86 g, 8.25 mmol). The resulting suspension was stirred at room temperature for 20 min, and filtered through Celite. The filtrate was concentrated *in vacuo* and the residue was diluted with water (20 mL) and diethyl ether (30 mL). The aqueous layer was extracted with diethyl ether (3 x 30 mL), and the combined organics were washed once with brine, dried over $MgSO_4$, filtered, concentared *in vacuo*, and the residue was purified by flash chromatography (hexanes→50:1 hexanes/EtOAc) to provide 1.52 g (80%) of tropone **13** as a colorless oil: IR ($CHCl_3$) 3018, 2949, 2868, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 2H), 5.94 (s, 1H), 4.13 (m, 1H), 2.69 (ddd, J =9.4, 3.6, 2.0 Hz, 1H), 2.62 (dt, J =13.6, 5.1 Hz, 1H), 2.24 (m, 1H), 2.19 (dd, J = 13.3, 5.6 Hz, 1H), 1.80-1.62 (m, 2H), 1.15-1.02 (m, overlapping signals, 21H), 0.74 (s, 9H), -0.04 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.0, 154.9, 127.9, 127.8, 119.5, 118.6, 113.9, 67.1, 39.0, 33.1, 25.5, 24.5, 17.8 (3C), 12.5, -4.4, -4.5; HRMS (FAB) *m/z* 463.3039 [$(M+H)^+$, calcd for $C_{26}H_{47}O_3Si_2$: 463.3064].

Cycloheptadiendione 14. A solution of tropone **13** (103 mg, 0.22 mmol) in acetonitrile (3 mL) was deoxygenated by bubbling argon gas through the solution for 30 min at room temperature. CsF (102 mg, 0.67 mmol) was added, all at once. The suspension was stirred vigorously for eight hours, after which additional CsF (100 mg, 0.67 mmol) was introduced, and stirring was continued for an additional 30 h. The reaction was diluted with diethyl ether (5 mL), and was quenched by the addition of a solution of saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL), and the combined organics

were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography (10:1 hexanes/EtOAc) to afford 46 mg (67%) of diketone **14** as a tan solid: mp 69-70 °C; UV ($CHCl_3$) λ_{max} (log ε): 240 (4.22), 276 sh (3.58) 284 (3.33) 315 (2.53) nm; IR ($CHCl_3$) 3018, 2956, 2857, 1728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.67 (dd, *J* = 12.0, 8.0 Hz, 1H), 6.10 (dd, *J* = 12.7, 1.7 Hz, 1H), 6.03 (s, 1H), 4.45 (br s, 1H), 3.23 (dd, *J* = 10.2, 7.8 Hz, 1H), 2.61 (ddd, *J* = 12.5, 4.2, 1.3 Hz, 1H), 2.41 (dt, *J* = 12.5, 1.9 Hz, 1H), 2.11-1.95 (m, 3H), 1.25 (m, 1H), 0.88 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.9, 191.1, 149.6, 141.4, 131.7, 126.0, 65.6, 52.2, 43.3, 32.5, 25.7, 23.1, 18.0, -4.8, -4.9; HRMS (FAB) *m/z* 307.1728 [$(M+H)^+$, calcd for $C_{17}H_{27}O_3Si$ 307.1729].

Cycloheptadiendione 15. A stream of oxygen was passed through a solution of tropone **13** (95 mg, 0.207 mmol) in THF (2 mL) 0°C for 30 minutes. Tetrabutylammonium fluoride (220 μL, 1.0 M soln. in THF) was added all at once. The resulting yellow solution was quenched with a solution of saturated aqueous NH_4Cl (5 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL), dried over $MgSO_4$, filtered, concentrated *in vacuo*, and the residue was purified by flash chromatography (10:1 hexanes/EtOAc). The first to elute was **14**: TLC, R_f 0.40 (4:1 hexanes/EtOAc).

The second to elute was hydroperoxide **15**: TLC, R_f 0.33 (4:1 hexane/EtOAc); mp 72-74 °C; IR ($CHCl_3$) 3452, 3020, 2954, 2931, 1728, 1655 cm^{-1}; ^1H-NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H, OOH), 6.88 (d, *J* = 12.7 Hz, 1H), 6.16 (dd, *J* = 12.7, 1.7 Hz, 1H), 6.04 (s, 1H), 4.24 (br s, 1H), 2.72 (ddd, *J* = 12.5, 4.1, 1.4 Hz, 1H), 2.53 (m, 1H), 2.44 (dt, *J* = 12.5, 1.9 Hz, 1H), 1.95-1,78 (m, overlapping signals, 2H), 1.51 (m, 1H), 0.83 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 205.2, 189.4, 147.8, 144.3, 130.6, 126.8, 91.6, 65.6, 44.4, 30.9, 28.8, 25.6, 18.0, -4.8; HRMS (FAB) *m/z* 307.1753 [$(M-O_2+H)^+$, calcd for $C_{17}H_{27}O_3Si$ 307.1730].

Alcohol 16. To a solution of hydroperoxide **15** (36 mg, 0.105 mmol) in benzene (2 mL) was added triphenyl phosphine (29 mg, 0.110 mmol). The reaction mixture was allowed to stir for 15 min at room temperature, was concentrated *in vacuo*, and the residue purified by flash chromatography (10:1 hexanes/EtOAc) to provide 28 mg (83%) of alcohol **16** as a white solid: mp 48-50 °C; IR ($CHCl_3$) 3510, 3020, 2954, 2931, 2858, 2885, 1728, 1655, 1630, 1215, 1070 cm^{-1}; ^1H-NMR (400 MHz, $CDCl_3$) δ 6.60 (d, *J* =12.6 Hz, 1H), 6.06 (s, 1H), 5.96 (dd, *J* =12.6, 1.5 Hz, 1H), 4.25 (m, 1H), 3.98 (br s, 1H), 2.63 (ddd, *J* =12.6, 4.2, 1.5 Hz, 1H), 2.52-2.44 (m, overlapping signals, 2H), 1.89-1.81 (m, overlapping signals, 2H), 1.36 (app dd, *J* =15.0, 11.4 Hz, 1H), 0.85 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 204.8, 189.5, 148.4, 147.1, 128.9, 126.8, 80.8, 65.8, 44.2, 31.2, 30.1, 25.7, 18.0, -4.8, -4.9; HRMS (FAB) *m/z* 323.1664 [$(M+H)^+$, calcd for $C_{17}H_{27}O_3Si$ 323.1678].

Methyl ether 17. To a solution of alcohol **16** in acetonitrile (0.75 mL) was added methyl iodide (0.75 mL, 12.0 mmol), and Ag_2O (30 mg, 0.13 mmol). The mixture was warmed to 70°C, and this temperature was maintained for 4.5 h. The suspension was filtered through Celite, concentrated *in vacuo*, and the residue was purified by flash chromatography (11:1 hexanes/EtOAc) to furnish 12 mg (30%) of methyl ether **17** as a white solid: mp 46-49°C; UV ($CHCl_3$) λ_{max} (log ε): 238 (3.94), 277 sh (3.39), 285 (3.30), 325 sh (2.73) nm; IR ($CHCl_3$) 3020, 2956, 1736, 1666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.66 (d, *J* =12.6 Hz, 1H), 6.11 (dd, *J* =12.6, 1.8, 1H), 5.98 (s, 1H), 4.22 (br s, 1H), 3.60 (s, 3H), 2.69 (ddd, *J* =12.3, 3.9, 1.2 Hz, 1H), 2.51-2.37 (m, overlapping signals, 2H), 1.95-1.86 (m, overlapping signals, 2H), 1.50 (dd, *J* =14.4, 12.3, 1H), 0.83 (s, 9H), 0.05 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9, 190.0, 150.4, 144.8, 131.1, 125.8, 86.5, 66.1, 55.0, 44.6, 31.2, 30.8, 25.7, 18.0, -4.8, -4.9; HRMS (FAB) *m/e* 337.1836 [$(M+H)^+$, calcd for $C_{18}H_{29}O_4Si$: 337.1835].

Photoisomerization of Diketone 14. A solution of diketone **14** (55 mg, 0.18 mmol) in benzene (18 mL) was deoxygenated by bubbling argon gas for thirty minutes. The solution was then irradiated with a 200 W Tungsten lamp for 2.2 h. The mixture was concentrated *in vacuo*, and was purified by flash chromatography (10:1→5:1 hexanes/EtOAc). The first to elute was starting diketone **14** (19 mg, 34%). The second to elute was cyclopropylketone **18** (28 mg, 50%) as a colorless oil: IR ($CHCl_3$) 3020, 2931, 1693, 1668 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 6.17 (s, 1H), 4.18 (app t, *J* = 5.1 Hz, 1H), 2.98 (dd, *J* = 12.0, 5.1 Hz,

1H), 2.45 (m, 2H), 2.27 (m, 2H), 2.23 (d, J = 12.6 Hz, 1H), 1.93 (m, 2H), 1.21 (m, 1H), 0.92 (s, 9H), 0.04 (s, 3H), -.01 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 200.4 , 195.6, 148.6, 128.8, 66.5 (CHOTBS), 39.4 (CH_2), 36.0 (CH), 33.2 (CH), 32.1 (CH_2), 27.9 (CH), 25.7 , 18.0, 15.7 (CH_2), -4.9 (2C); HRMS(FAB) *m/z* 307.1737 [(M+H)$^+$, calcd for $C_{17}H_{27}O_3Si$ 307.1729].

Photoisomerization of Methyl ether 17. Methyl ether **17** was dissolved in $(CD_3)_2CO$ (0.8 mL), and the solution was transferred to an nmr tube (5 mm). After recording the initial 300 MHz ^{1}H nmr spectrum (time=0), the sample was irradiated (Hanovia 450 W bulb, pyrex filter) for 10 min and judged complete by NMR analysis. The sample was concentrated *in vacuo* and purified by flash chromatography (10:1 hexanes/EtOAc) to provide 2.6 mg (52%) of cyclopentadienone **19** as a yellow oil: IR (CH_2Cl_2) 2965, 1762, 1712, 1643, 1473, 1372, 1265 cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6) δ 6.53 (s, 1H), 4.39 (A of AX, J_{AX} = 9.0 Hz, 1H), 3.73 (br m, 1H), 3.10 (X of AX, J_{AX} = 9.0 Hz, 1H), 2.91 (dd, J =12.5, 6.0, 1H), 2.88 (s, 3H), 2.40 (dt, J = 16.0, 7.0 Hz, 1H), 2.01 (dd, J = 13.0, 4.0 Hz, 1H), 1.86 (m, 1H), 1.62 (m, 1H), 1.54 (m, 1H), 0.79 (s, 9H), -0.16 (s, 3H), -0.21 (s, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ 205.4, 197.8, 162.7, 161.9, 144.5, 92.4, 68.9, 54.1, 52.8, 34.3, 27.1, 25.9, 25.8, 18.1, -5.0, -5.1; HRMS(FAB) *m/z* 337.1846 [(M+H)$^+$, calcd for $C_{18}H_{29}O_4Si$ 337.1835].

Diketones 20 and 21. To a suspension of copper(I) iodide (104 mg, 0.54 mmol) in diethyl ether (1.0 mL) at 0°C, a solution of methyllithium (780 mL, 1.09 mmol, 1.4 M in diethyl ether) was added dropwise. The temperature was maintained at 0°C for 10 minutes, and then a solution of ketone **18** (33 mg, 0.11 mmol) in diethyl ether (1.0 mL) was added by rapid cannulation. The resulting pale green solution was qu ıed with saturated aqueous ammonium chloride, and the mixture was filtered through a pad of Celite. The filtrate was extracted with diethyl ether (3 x 3 mL), was dried over $MgSO_4$, was filtered, and was concentrated *in vacuo*. The products were separated by flash chromatography (4:1→2:1 hexanes/EtOAc). The first product to elute was **21** (5 mg, 18%) as a colorless oil: TLC, R_f 0.8 (2:1 hexane-EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.09 (s, 1H), 3.94 (app dd, J =7.8, 4.8 Hz, 1H), 3.01 (ddd, J =12.3 5.7, 0.9 Hz, 1H), 2.85-2.45 (m, overlapping signals, 5H), 2.24-2.14 (m, overlapping signals, 2H), 2.00-1.82 (m, overlapping signals, 2H), 1.50 (m, 1H), 0.88 (s, 9H), 0.20 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3, 204.5, 147.8, 127.7, 69.1, 50.4, 43.7, 43.7, 33.1, 27.9, 26.4, 25.8, 18.1, -4.8, -4.9; HRMS (FAB) *m/z* 309.1909 [(M+H)$^+$, cald for $C_{17}H_{29}O_3Si$ 309.1886].

The second product to elute was diketone **20** (4 mg, 18%) as a white solid: TLC, R_f 0.4 (2:1 hexane-EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.40 (m, 1H), 3.03 (ddd, J =16.2, 3.0, 1.5 Hz, 1H), 2.98-2.88 (m, overlappling signals, 2H), 2.74-2.62 (m, overlapping signals, 3H), 2.56-2.46 (m, overlapping signals, 2H), 2.36 (m, 1H), 1.96 (m, 1H), 1.67-1.49 (m, overlapping signals, 4H), 0.81 (s, 9H), -0.02 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 210.9, 71.0, 50.3, 48.8, 45.9, 42.5, 39.2, 34.2, 31.6, 30.8, 25.7, 18.0, -4.9, -4.9.

Acetal 22. To a solution of diketone **21** (4.6 mg, 0.015 mmol) in benzene (1 mL) were added ethylene glycol (2 mL, 0.036 mmol) and one crystal of *p*-toluenesulfonic acid. The mixture was refluxed for one hour with removal of water, and cooled to room temperature. Concentration *in vacuo* gave a residue which was purified by flash chromatography (6:1 hexanes/EtOAc) to afford 1.5 mg (29%) of monoketal **22** as a white solid. Recrystallization from chloroform gave thin needles suitable for single crystal x-ray analysis: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (s, 1H), 3.92-3.74 (overlapping signals, 4H), 3.56 (dt, J =6.0, 8.4 Hz, 1H), 3.09 (dd, J =19.5, 2.7 Hz, 1H), 2.85 (dd, J =11.4, 5.7 Hz, 1H), 2.40-2.24 (m, overlapping signals, 2H), 2.17-1.82 (m, overlapping signals, 5H), 1.69-1.46 (m, overlapping signals, 2H), 0.85 (s, 9H), 0.01 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 133.8, 107.2, 71.2, 64.5, 63.7, 43.5, 43.2, 39.6, 53.3, 34.9, 27.9, 25.8, 18.1, -4.75, -4.94.

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Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, and structure factors data for **14**, **15** and **22** (21 pages). This information can be obtained on request from The Director, Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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