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Ozonolysis of 2-*endo*-7-*anti*-Diacylnorbornenes. A New Entry for the Synthesis of 2,4,6,13-Tetraoxapentacyclo[5.5.1.$0^{3,11}$.$0^{5,9}$.$0^{8,12}$]tridecanes

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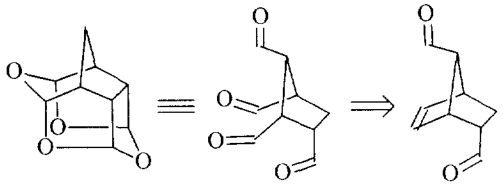
Abstract: A new route for the synthesis of the title compounds **4a**, **4b**, **10a**, and **10b** has been developed via ozonolysis of 2-*endo*-7-*anti*-diacylnorbornenes **3a**, **3b**, **9a**, and **9b**. The synthesis of the unsubstituted (parent) compound **4a** of tetraacetal tetraoxa-cages has been accomplished for the first time by this new entry. Ozonolysis reactions of **3a**, **3b**, and **9a** were also performed in $CDCl_3$ for understanding the final ozonide structures and the ozonation chemistry. Ozonolysis of **3a**, **3b**, and **9a** in CH_2Cl_2 at -78 °C followed by treatment with triethylamine provided an indirect support for the structures of the final ozonides **11a**, **11b**, and **14**.

Introduction

The synthesis and chemistry of polycyclic cage compounds have attracted considerable attention in recent years.[1] The vast majority of the work reported in this area has dealt with carbocyclic cage compounds. On the other hand, the synthesis and chemistry of heterocyclic cage compounds have received less attention. However, there are some reports regarding the chemistry[2] and synthesis[3-8] of oxa-cage compounds in the literature. This class of heterocyclic cages is synthesized by intramolecular alkene-oxirane (2σ-2π) photocycloaddition,[3] transannular cyclization of suitable compounds,[4] tandem cyclization,[5] dehydration of diols having the proper stereochemistry,[6] base-promoted rearrangement,[7] and intramolecular etherification of an alkene bond with organoselenium reagents.[8]

Recently, we visualized that the "creation" of tetraacetal tetraoxa-cages from homopentaprismane might be achieved by replacing the skeletal carbon atoms with oxygen atoms at the proper positions and by extending the skeletal backbone.[9] From the standpoint of retro-synthetic analysis, 2,3-*bis*-*endo*-diacylnorbornenes were chosen as the starting material for the synthesis of tetraoxa-cages by ozonolysis reaction. Therefore, we accomplished the synthesis of a series of oxa-cages along with this sequence.[10] Afterward, we realized that 2-*endo*-7-*anti*-diacylnorbornenes might be chosen as an alternative starting material for the synthesis of tetraoxa-cages (Scheme 1). As part of a program that involves the synthesis and chemistry of new heterocyclic cage compounds, we report here the first synthesis of the unsubstituted (parent) compound of tetraacetal tetraoxa-cages and its methyl derivatives by this new entry. We also wish to demonstrate the ozonation chemistry of 2-*endo*-7-*anti*-diacylnorbornenes.

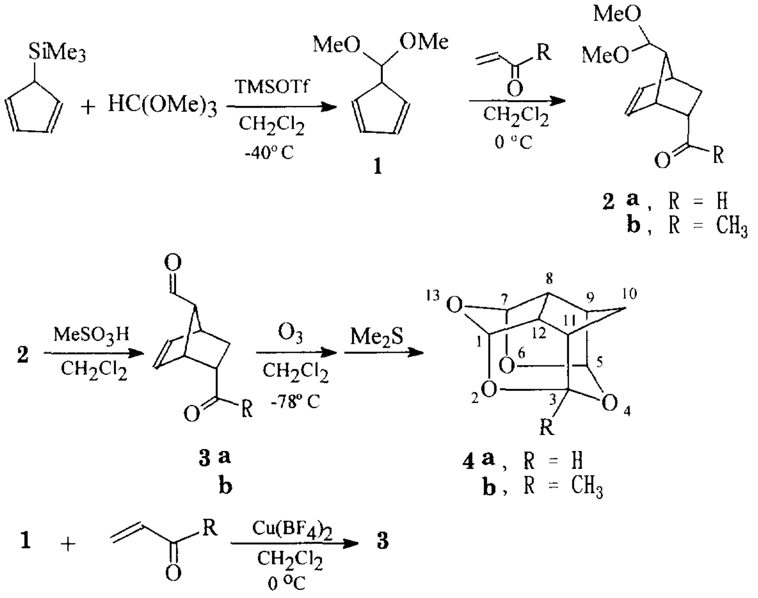
Scheme 1



Results and Discussion

Reaction of 5-trimethylsilylcyclopentadiene with trimethylorthoformate in dichloromethane at -40 °C in the presence of catalytic amount of TMSOTf gave compound **1**,[11] which was run for the next reaction without purification. Diels-Alder reaction of the crude **1** with acrolein and methyl vinyl ketone at 0 °C for 48 h gave the cycloadducts **2a** and **2b** in 70% yields, respectively. Reaction of **2a** and **2b** with one equivalent of methanesulfonic acid in dichloromethane for 1 h gave the *endo-anti* isomers **3a** and **3b** in 90% yields, respectively. Compounds **3a** and **3b** can be directly obtained by reaction of the crude **1** with acrolein and methyl vinyl ketone in the presence of $Cu(BF_4)_2$ in dichloromethane at 0 °C for 24 h in 80% yields. Ozonolysis of the *endo-anti* isomers **3a** and **3b** in dichloromethane at -78 °C followed by reduction with dimethyl sulfide gave the tetraoxa-cage **4a** and its 3-methyl derivative **4b** in 80% yields, respectively (Scheme 2). Thus, we have accomplished for the first time the synthesis of the unsubstituted (parent) tetraoxa-cage **4a** via ozonolysis of the *endo-anti* isomer **3a**, a new entry for the synthesis of tetraacetal tetraoxa-cages.

Scheme 2



The ^{1}H NMR spectrum of the parent compound **4a** showed a doublet at δ 5.84 for the acetal protons on C_1 and C_7, a doublet at δ 5. 51 for the acetal protons on C_3 and C_5, a multiplet at δ 3.42 for the protons on C_8 and C_{12}, a multiplet at δ 2.82 for the protons on C_9 and C_{11}, and a multiplet at δ 2.06-1.93 for the protons on C_{10}. The ^{13}NMR spectrum of **4a** revealed a peak at δ 109.6 for C_1 and C_7, a peak at δ 103.1 for C_3 and C_5, a peak at δ 53.1 for C_8 and C_{12}, a peak at δ 45.3 for C_9 and C_{11}, and a peak at δ 29.5 for C_{10}. The structure of these tetraacetal oxa-cage compounds was proven by X-ray analysis of the crystalline compound **4a**,[12] Figure 1. The conformation of the oxygen atom O-4 with respect to the apical carbon atom C-10 was proven to be boat conformation which is consistent with previous reports.[9] The bond angles of C(3)-O(4)-C(5) and C(9)-C(10)-C(11) are 117.5° and 99.5°, respectively, remarkably different from the ordinary bond angles with sp^3-hybridized atoms.

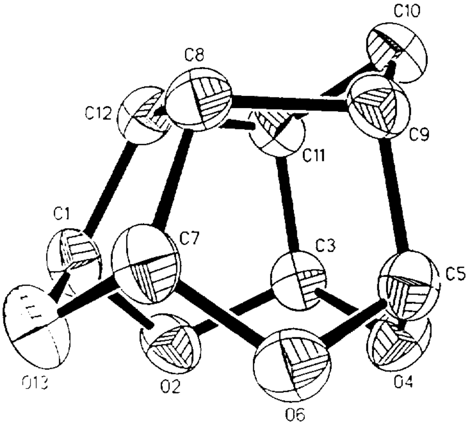
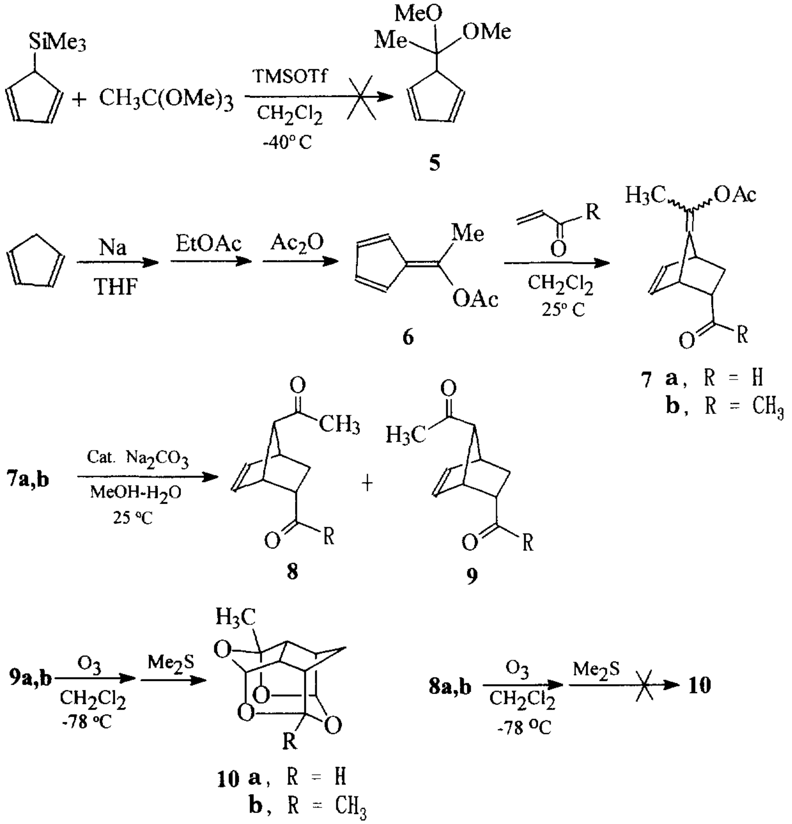


Figure 1. ORTEP diagram of the parent compound **4a**.

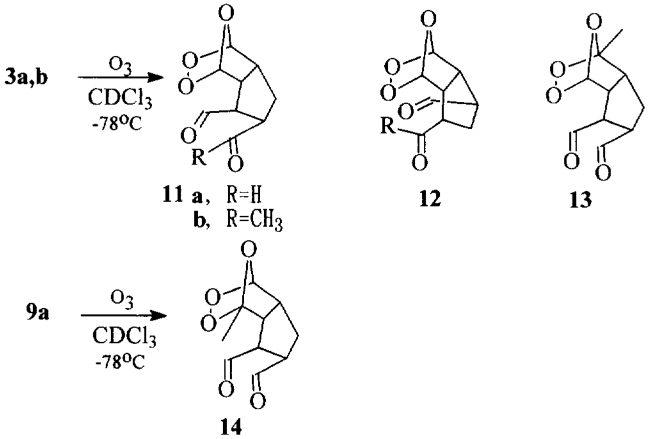
In order to extend the synthesis of tetraoxa-cages via this new entry, 7-*anti*-acetylnorbornenes were prepared for ozonolysis. Reaction of 5-trimethylsilyl cyclopentadiene with trimethyl orthoacetate in dichloromethane at -40 °C in the presence of catalytic amount of TMSOTf did not give compound **5**.[11] Therefore, we adopted another method to prepared compounds **9a,b** (Scheme 3). Reaction of cyclopentadiene with sodium in dry tetrahydrofuran (THF) at 0 °C followed by addition of ethyl acetate at 25 °C, then acetylation of the reaction mixture *in situ* with acetic anhydride gave compound **6** in 85% yield.[13] Diels-Alder reaction of **6** with acrolein and methyl vinyl ketone at room temperature for 48 h gave the *endo* adducts **7a** and **7b** as major products in 50-55% yields along with unreacted starting material. Reaction of **6** with acrolein and methyl vinyl ketone at 25 °C in the presence of Lewis acids ($TiCl_4$, BF_3-OEt_2) for 6 h gave **7a** and **7b** in lower yields (20-25%), with unidentified polymeric products. Both compounds **7a** and **7b** contained two regioisomers from their ^{1}H and ^{13}C NMR spectra and were subjected to the following hydrolysis without seperation of the regioisomers. Hydrolysis of the mixture of the two regioisomers **7a** with a catalytic amount of sodium carbonate in aqueous methanol (1 : 1) at 25 °C gave the *endo-syn* isomer **8a** and the *endo-anti* isomer **9a** in a ratio of 5 : 1 in 80% yield. Hydrolysis of the mixture of the two regioisomers **7b** under the same reaction conditions gave **8b** and **9b** in a ratio of 5 : 1 in 80% yield. The stereochemistry of the formyl group on the apical carbon of compounds **8a,b** and **9a,b** was confirmed by the next step ozonolysis reaction. Ozonolysis of the *endo-anti* isomers **9a,b** in dichloromethane at -78 °C followed by reduction with dimethyl sulfide gave the tetraacetal tetraoxa-cages **10a,b** in 80% yields. Ozonolysis of the *endo-syn* isomers **8a,b** under the same reaction conditions did not give any detectable amount of **10a,b**.

Scheme 3



Next, we turn our attention on the ozonolysis chemistry to clarify the problem that which carbonyl group, the *endo* carbonyl group or the carbonyl group on the apical carbon, reacts intramolecularly with the carbonyl oxide to form the final ozonide. Ozonolysis of **3a,b** in dichloromethane at -78 °C followed by removal of the solvent at room temperature without reduction gave oligomeric or polymeric products which were not soluble in $CDCl_3$, acetone-d_6, or methanol-d_4 for NMR spectral analysis.[9] Ozonolysis of **3a,b** in $CDCl_3$ at -78 °C gave the final ozonides **11a,b** (> 90%). No detectable amount of the other isomers **12a,b** was obtained. In the case of **3b**, no detectable amount of of **13** was obtained. Ozonolysis of **9a** in $CDCl_3$ at -78 °C gave the final ozonide **14** as major product in about 80% yield. The ^1H and ^{13}C NMR spectra of **11a,b** and **14** were taken at -30 °C right after the ozonation reaction without purification. Thus, our experimental results may indicate that it is the *anti* carbonyl group on the apical carbon rather than the *endo* carbonyl group to react preferentially with the carbonyl oxide group to form the final ozonide.

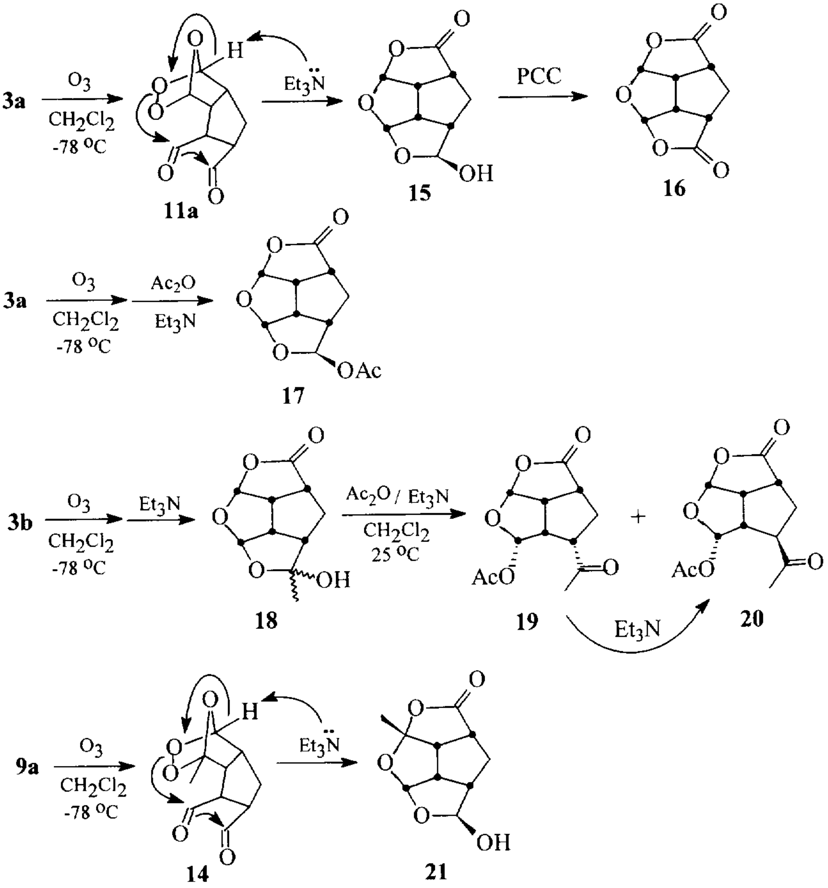
Scheme 4



The ^1H NMR spectrum of **11a** showed two singlets at δ 9.84 and 9.50 for the two aldehyde protons and two singlets at δ 6.25 and 5.77 for the 1,2,4-trioxolane ring protons. The final ozonide obtained from ozonolysis of **3a** is not the structure **12a**, since **12a** possesses a symmetry plane. The ^1H NMR spectrum of **11b** showed a singlet at δ 9.69 for the aldehyde proton, two singlets at δ 6.16 and 5.72 for the 1,2,4-trioxolane ring protons and a singlet at δ 2.17 for the methyl ketone protons. The ^1H NMR spectrum of **14** displayed two singlets at δ 9.97 and 9.71 for the two aldehyde protons, a singlet at δ 5.76 for the 1,2,4-trioxolane ring proton and a singlet at δ 1.68 for the angular methyl protons. The ^{13}C NMR spectrum of **14** revealed a singlet at δ 110.2 and a peak at δ 104.6 (d) for the quaternary carbon and the tertiary carbon of the trioxolane ring, respectively.

Recently, we demonstrated a new method for determining the regiochemistry of carbonyl oxide formation and hence the structure of the final ozonide.[10a,b] Now, we apply this method to support the structures of the final ozonides **11a,b** and **14**. Ozonolysis of **3a** in dichloromethane at -78 °C followed by treatment with triethylamine gave the hydroxy lactone **15** in 85% yield (Scheme 5). Oxidation of **15** with PCC in dichloromethane gave the symmetrical bislactone **16**. Ozonolysis of **3a** in dichloromethane at -78 °C followed by addition of triethylamine and acetic anhydride gave the acetate **17**. Ozonolysis of **3b** in dichloromethane at -78 °C followed by treatment with triethylamine gave the hydroxy lactone **18** in 85% yield, which contained two stereoisomers. Acetylation of **18** with acetic anhydride and triethylamine in dichloromethane at 25 °C for 2 h gave **19** as major product and **20** as minor product. Reaction of **19** with triethylamine in dichloromethane at 25 °C for 24 h gave the thermodynamically more stable isomer **20** in 95% yield. Ozonolysis of **9a** in dichloromethane at -78 °C followed by treatment with triethylamine gave the hydroxy lactone **21** in 70% yield. These results support indirectly for the structures of the final ozonides **11a,b** and **14**.

Scheme 5



Conclusion

A new entry for the synthesis of the tetraacetal tetraoxa-cage compounds has been developed. The synthesis of the unsubstituted (parent) compound **4a** of the tetraacetal tetraoxa-cages has been accomplished for the first time by this new route. The structure of the parent compound **4a** is proven by X-ray analysis. Ozonolysis reactions of **3a,b** and **9a** are also performed in $CDCl_3$ for understanding the final ozonide structures and the ozonation chemistry. In the ozonolysis of 2-*endo*-7-*anti*-diacylnorbornenes, we found that it was the carbonyl group on the apical carbon instead of the *endo* carbonyl group to react intramolecularly with the carbonyl oxide group to form the final ozonides. Ozonolysis of **3a**, **3b**, and **9a** in dichloromethane at -78 °C followed by treatment with triethylamine gave the hydroxy lactones **15**, **18**, and **21**. This reaction gives an indirect support for the structures of the final ozonides **11a**, **11b**, and **14**.

Experimental Section

General. Melting points were determined in capillary tubes with a Laboratory Devices melting point apparatus and uncorrected. Infrared spectra were recorded in $CHCl_3$ solutions or on neat thin films between NaCl disks. ^1H NMR spectra were determined at 300 MHz, and ^{13}C NMR were determined at 75 MHz Fourier transform spectrometers. Chemical shifts are reported in ppm relative to TMS in the solvents specified. The multiplicities of ^{13}C signals were determined by DEPT techniques. High resolution mass values were obtained with a high resolution mass spectrometer at the Department of Chemistry, National Tsing Hua University. Elemental analyses were performed at the microanalysis laboratory of National Taiwan University. X-ray analysis were carried out on a diffractometer at the Department of Chemistry, National Chung Hsing University. For thin-layer chromatography (TLC) analysis, precoated TLC plates (Kieselgel 60 F_{254}) were used, and column chromatography was done by using Kieselgel 60 (70-230 mesh) as the stationary phase. THF was distilled immediately prior to use from sodium benzophenone ketyl under nitrogen. CH_2Cl_2 was distilled from CaH_2 under nitrogen.

Preparation of Compound 1 and the Diels-Alder Reaction of 1 with Acrolein and Methyl Vinyl Ketone. To a solution of 5-trimethylsilyl cyclopentadiene (1.0 g, 7.3 mmol) in dichloromethane (20 mL) was added trimethyl orthoformate (0.85 g, 8.0 mmol) at 25 °C. The mixture was cooled to -40 °C, and a catalytic amount of TMSOTf (0.16 g, 0.73 mmol) was added at -40 °C. The reaction mixture was stirred at -40 °C for 1 h. The mixture was quenched by addition of ice. Extractive workup with dichloromethane (3 x 10 mL) followed by an ice-water wash (1 x 10 mL), drying over K_2CO_3, and evaporating the solvent at 0 °C afforded the crude product **1**, which was kept at 0 °C without purification for the Diels-Alder reaction. To this crude product **1** in dichloromethane (20 mL) was added acrolein (0.45 g, 7.9 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 12 h and at room temperature for 36 h. The solvent was evaporated, and the crude product was purified by column chromatography to give the *endo* adduct **2a** in 70% overall yield. The same reaction conditions and procedure were applied to the preparation of **2b** in 70% yield.

2-*endo*-Formyl-7-*anti*-dimethoxymethylbicyclo[2.2.1]-5-heptene 2a : pale yellow oil; IR (neat) 2970, 1720, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.47 (d, J = 2.4 Hz, 1H), 6.14 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 5.93 (dd, J = 5.4 Hz, J = 2.7 Hz, 1H), 4.21 (d, J = 8.4 Hz, 1H), 3.30 (s, 6H), 3.25 (d, J = 1.2 Hz, 1H), 2.99-2.94 (m, 2H), 2.03-1.94 (m, 2H), 1.49 (dd, J = 12 Hz, J = 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 203.60 (CHO), 135.45 (CH), 129.42 (CH), 102.79 (CH) 63.19 (CH), 53.25 (CH_3), 53.20 (CH_3), 52.35 (CH), 45.85 (CH),44.05 (CH), 27.93 (CH_2); LRMS *m/z* (rel inten) 196 (M^+, 3), 165 (16), 75 (100); HRMS (EI) calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1101. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.22; H, 8.20.

2-*endo*-Acetyl-7-*anti*-dimethoxymethylbycyclo[2.2.1]-5-heptene 2b: pale yellow oil; IR (neat) 2970, 1710, 1600, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.08 (dd, J = 5.7 Hz, J = 3.0 Hz, 1H), 5.79 (dd, J = 5.7 Hz, J = 2.7 Hz, 1H), 4.19 (d, J = 8.4 Hz, 1H), 3.30 (s, 3H), 3.28 (s, 3H), 3.22 (brs, 1H), 3.07-3.02 (m, 1H), 2.85 (brs, 1H), 2.12 (s, 3H), 2.02 (d, J = 9 Hz, 1H), 1.86-1.78 (m, 1H), 1.53 (dd, J = 11.7 Hz, J = 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 207.62 (C=O), 134.98 (CH), 128.48 (CH), 102.96 (CH), 63.34 (CH), 53.17 (CH_3), 52.88 (CH_3), 52.06 (CH), 46.76 (CH), 43.70 (CH), 28.66 (CH_3), 27.53 (CH_2); LRMS *m/z* (rel inten) 210 (M^+, 3), 135 (22), 75 (100); HRMS (EI) calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1258. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.42; H, 8.51.

Hydrolysis of 2a and 2b. To a solution of **2a** (1.01 g, 5.10 mmol) in dichloromethane (20 mL) was added methanesulfonic acid (CH_3SO_3H) (0.49 g, 5.10 mmol) at 25 °C. The reaction mixture was stirred at room temperature for 1 h. After addition of saturated $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (2 x 30 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give **3a** (0.7 g) in 90% yield. The same reaction conditions and procedure were applied to the preparation of **3b** in 90% yield.

2-*endo*-7-*anti*-Diformylnorbornene 3a: pale yellow oil; IR (neat) 2970, 1718, 1600, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.62 (d, J = 2.1 Hz, 1H), 9.52 (d, J = 1.5 Hz, 1H), 6.24 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H), 6.05 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H), 3.63 (brs, 1H), 3.33 (brs, 1H), 3.07-3.03 (m, 1H), 2.42 (d, J = 1.2 Hz, 1H), 2.10-2.02 (m, 1H), 1.65-1.59 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 203.69 (CHO), 202.43 (CHO), 135.80 (CH), 130.41 (CH), 70.85 (CH), 51.88 (CH), 45.82 (CH), 44.51 (CH), 27.76 (CH_2); LRMS *m/z* (rel inten) 150 (M^+, 7), 121 (16), 94 (100); HRMS (EI) calcd for $C_9H_{10}O_2$ 150.0681, found 150.0683. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.85; H, 6.79.

2-*endo*-Acetyl-7-*anti*-formylnorbornene 3b : pale yellow oil; IR (neat) 2970, 1720,1708, 1600, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.60 (d, J = 2.7 Hz, 1H), 6.19 (dd, J = 5.7 Hz, J = 3.3 Hz, 1H), 5.94 (dd, J = 5.7 Hz, J = 2.7 Hz, 1H), 3.58 (brs, 1H), 3.26 (brs, 1H), 3.13-3.10 (m, 1H), 2.41 (brs, 1H), 2.15 (s, 3H), 1.94-1.90 (m, 1H), 1.66-1.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 207.15 (C=O), 204.27 (CHO), 135.48 (CH), 129.88 (CH), 71.20 (CH), 51.97 (CH), 46.96 (CH), 44.48 (CH), 29.07 (CH_3) 27.88 (CH_2); LRMS *m / z* (rel inten) 164 (M^+, 12), 136 (18), 121 (100); HRMS (EI) calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0841. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.02; H, 7.28.

One Pot Procedure for the Preparation of 3a and 3b from 5-Trimethylsilyl Cyclopentadiene. To a solution of 5-trimethylsilyl cyclopentadiene[11] (1.0 g, 7.3 mmol) in dichloromethane (20 mL) was added trimethyl orthoformate (0.85 g, 8.0 mmol) at 25 °C. The mixture was cooled to -40 °C, and a catalytic amount of TMSOTf (0.144 g, 0.67 mmol) was added at -40 °C. The reaction mixture was stirred at -40 °C for 1 h. The mixture was quenched by addition of ice. Extractive workup with dichloromethane (3 x 10 mL) followed by an ice-water wash (1 x 10 mL), drying over K_2CO_3, and evaporating the solvent at 0 °C afforded the crude product **1**, which was kept at 0 °C without purification for the Diels-Alder reaction. To this product **1** in dichloromethane (20 mL) was added acrolein (0.45 g, 7.9 mmol) at 0 °C. After ten minutes, to this solution was added $Cu(BF_4)_2$ (0.17 g, 0.73 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 12 h. The solvent was evaporated, and the crude product was purified by column chromatography to give **3a** (0.76 g) in 70% overall yield. The same reaction conditions and procedure were applied for the preparation of **3b** from 5-trimethylsilyl cyclopentadiene in 70% overall yield.

Ozonolysis of 3a. Synthesis of the Unsubstituted (Parent) Compound 4a. A solution of **3a** (0.10 g, 0.67 mmol) in dichloromethane (20 mL) was cooled to -78 °C, and ozone was bubbled through it at -78 °C until the solution turned light blue. To this solution was added dimethyl sulfide (0.20 g, 3.3 mmol) at -78 °C. Then, the reaction mixture was stirred at room temperature for 5 h. The solvent was evaporated, and the crude product was purified by column chromatography to give the parent compound **4a** (0.098 g, 80%). The same reaction conditions and procedure were applied to the preparation of **4b** in 80% yield.

2,4,6,13-tetraoxapentacyclo[5.5.1.$0^{3,11}$.$0^{5,9}$.$0^{8,12}$]tridecane 4a : white waxy solid; IR ($CHCl_3$) 2980, 2880,1060 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (d, J = 5.1 Hz, 2H), 5.51 (d, J = 5.7 Hz, 2H), 3.43-3.39 (m, 2H), 2.82 (brs, 2H), 2.06-1.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 109.60 (2CH), 103.05 (2CH), 53.14 (2CH), 45.27 (2CH), 29.48 (CH_2); LRMS *m/z* (rel inten) 182 (M^+, 56), 108 (100); HRMS (EI) calcd for $C_9H_{10}O_4$ 182.0579, found 182.0579. Anal. Calcd for $C_9H_{10}O_4$: C, 59.34; H, 5.53. Found: C, 59.30; H, 5.51.

3-Methyl-2,4,6,13-tetraoxapentacyclo[5.5.1.$0^{3,11}$.$0^{5,9}$.$0^{8,12}$]tridecane 4b : white waxy solid; IR ($CHCl_3$) 2980, 2880, 1060 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (d, J = 5.1 Hz, 1H), 5.77 (d, J = 5.1 Hz, 1H), 5.49 (d, J = 6.6 Hz, 1H), 3.51-3.38 (m, 2H), 2.87-2.78 (m, 1H), 2.70-2.62 (m, 1H), 1.95-1.93 (m, 2H), 1.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 109.34 (C), 109.17 (CH), 108.44 (CH), 102.73 (CH), 54.30 (CH), 53.17 (CH), 49.44 (CH), 44.78 (CH), 29.89 (CH_2), 25.81 (CH_3); LRMS *m/z* (rel inten) 196 (M^+, 12), 99 (76), 79 (100); HRMS (EI) calcd for $C_{10}H_{12}O_4$ 196.0736, found 196.0731. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 61.20; H, 6.14.

Diels-Alder Reaction of Compound 6 with Acrolein and Methyl Vinyl Ketone. To a solution of **6**[13] (2.0 g, 13 mmol) in dichloromethane (10 mL) was added acrolein (0.83 g, 14.3 mmol) at 25 °C. The reaction mixture was stirred at 25 °C for 48 h. The solvent was evaporated, and the crude product was purified by column chromatography to give the *endo* adduct **7a** (50%), which was a mixture of two regioisomers without further separation. The same reaction conditions and procedure were applied to the preparation of **7b** in 50% yield.

2-*endo*-Formyl-7-(α-acetoxyethylidene)bicyclo[2.2.1]-5-heptene 7a : pale yellow oil; IR (neat) 2960, 1750, 1720, 1190 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 and 9.49 (s, 1H), 6.34-6.28 (m, 1H), 6.15-6.05 (m, 1H), 3.67-3.60 (m, 1H), 3.35-3.29 (m, 1H), 3.08-2.98 (m, 1H), 2.17 and 2.14 (s, 3H), 2.08-1.98 (m, 1H), 1.81 and 1.77 (s, 3H), 1.65-1.53 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 203.54 (CHO), 202.75 (CHO), 168.90 (2CO), 139.82 (C), 139.70 (C), 137.46 (CH), 136.88 (CH), 131.86 (CH), 131.25 (CH), 125.11 (C), 124.99 (C), 51.36 (CH), 50.54 (CH), 44.08 (CH), 43.23 (CH), 42.27 (CH), 41.48 CH), 27.85 (CH_2), 27.18 (CH_2), 27.03 (CH_3), 20.45 (CH_3), 15.90 (CH_3), 15.76 (CH_3); LRMS *m/z* (rel inten) 206 (M^+, 11), 93 (17), 108 (100); HRMS (EI) calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0930.

2-endo-Acetyl-7-(α-acetoxyethylidene)bicyclo[2.2.1]-5-heptene 7b : pale yellow oil; IR (neat) 2960, 1751, 1710, 1190 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30-6.21 (m, 1H), 6.06-5.97 (m, 1H), 3.59-3.52 (m, 1H), 3.27-3.22 (m, 1H), 3.15-3.03 (m, 1H), 2.15 and 2.13 (s, 3H), 2.07 and 2.05 (s, 3H), 2.02-1.87 (m, 1H), 1.81 and 1.76 (s, 3H), 1.64-1.53 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 207.88 (CO), 207.68 (CO), 169.28 (CO), 169.22 (CO), 140.78 (C), 140.69 (C), 137.34 (CH), 136.79 (CH), 131.75 (CH), 131.25 (CH), 124.99 (C), 124.90 (C), 51.74 (CH), 50.89 (CH), 45.27 (CH), 44.45 (CH), 42.56 (CH), 41.80 (CH), 29.10 (CH_2), 29.04 (CH_3), 28.58 (CH_3), 27.82 (CH_3), 20.80 (CH_2), 15.93 (CH_3); LRMS *m/z* (rel inten) 220 (M^+, 8), 85 (75), 71 (100); HRMS (EI) calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1102.

Hydrolysis of 7a and 7b. To a solution of **7a** (1.6 g, 7.8 mmol) in methanol (10 mL) and H_2O (10 mL) was added a catalytic amount of Na_2CO_3 (80 mg, 0.78 mmol) at 25 °C. The reaction mixture was stirred at 25 °C for 1 h. After addition of saturated NH_4Cl (20 mL) and extraction with ether (5 x 30 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give compounds **8a** (64%) and **9a** (16%). The same reaction conditions and procedure were applied to the preparation of **8b** (65%) and **9b** (15%).

2-*endo*-Formyl-7-*syn*-acetylnorbornene 8a: pale yellow oil; IR (neat) 2970, 1720, 1708, 1600, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.53 (d, J = 1.5 Hz, 1H), 6.23 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H), 6.06 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H), 3.48 (brs, 1H), 3.18 (brs, 1H), 3.06-3.03 (m, 1H), 2.54 (s, 1H), 2.11 (s, 3H), 1.91-1.83 (m, 1H), 1.58-1.52 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 206.89 (C=O), 203.31 (CHO), 137.95 (CH), 132.74 (CH), 70.68 (CH), 50.08 (CH), 44.75 (CH), 43.81 (CH), 27.50 (CH_3), 25.20 (CH_2); LRMS *m/z* (rel inten) 164 (M^+, 16), 136 (17), 108 (100); HRMS (EI) calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0838. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.10; H, 7.31.

2-*endo*-Formyl-7-*anti*-acetylnorbornene 9a : pale yellow oil; IR (neat) 2970, 1720, 1708, 1600, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.48 (d, J = 1.5 Hz, 1H), 6.18 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H), 6.00 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H), 3.64 (brs, 1H), 3.34 (brs, 1H), 3.07-3.03 (m, 1H), 2.55 (brs, 1H), 2.11 (s, 3H), 2.08-2.02 (m, 1H), 1.59-1.54 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 207.18 (C=O), 202.96 (CHO), 135.68 (CH), 130.35 (CH), 71.06 (CH), 51.71 (CH), 46.06 (CH), 44.72 (CH), 29.80 (CH_3), 27.82 (CH_2); LRMS *m/z* (rel inten) 164 (M^+, 21), 149 (18), 108 (100); HRMS (EI) calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0832. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.04; H, 7.27.

2-*endo*-7-*syn*-diacetylnorbornene 8b : pale yellow oil; IR (neat) 2980, 1708, 1600, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.19 (dd, J = 5.7 Hz, J = 3.0 Hz, 1H), 5.95 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H), 3.44-3.42 (m, 1H), 3.15-3.10 (m, 2H), 2.53 (brs, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 1.76-1.68 (m, 1H), 1.60-1.54 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 208.12 (C=O), 207.24 (C=O), 137.60 (CH), 132.33 (CH), 70.94 (CH), 49.87 (CH), 45.65 (CH), 43.81 (CH), 29.07 (CH_3), 27.47 (CH_3), 25.22 (CH_2); LRMS *m/z* (rel inten) 178 (M^+, 24), 149 (51), 85 (100); HRMS (EI) calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.1003. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.01; H, 7.90.

2-*endo*-7-*anti*-diacetylnorbornene 9b : pale yellow oil; IR (neat) 2980, 1708, 1600, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.12 (dd, J = 5.7 Hz, J = 3.0 Hz, 1H), 5.88 (dd, J = 5.7 Hz, J = 2.7 Hz, 1H), 3.61 (brs, 1H), 3.27 (brs, 1H), 3.13-3.07 (m, 1H), 2.53 (brs, 1H), 2.16 (s, 3H), 2.08 (s, 3H), 1.97-1.89 (m, 1H), 1.63-1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 207.68 (C=O), 207.53 (C=O), 135.30 (CH), 130.03 (CH), 71.44 (CH), 51.80 (CH), 47.19 (CH), 44.78 (CH), 29.77 (CH_3), 28.95 (CH_3), 27.96 (CH_2); LRMS *m/z* (rel inten) 178 (M^+, 27), 149 (56), 85 (100); HRMS (EI) calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0998. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.02; H, 7.88.

Ozonolysis of the *endo-anti*-Norbornenes 9a and 9b. The same reaction conditions and procedure for the ozonolysis of **3a** and **3b** were applied for the ozonolysis of **9a** and **9b** in 80% yields.

1-Methyl-2,4,6,13-tetraoxapentacyclo[5.5.1.$0^{3,11}$.$0^{5,9}$.$0^{8,12}$]tridecane 10a : white waxy solid; mp 92-93 °C; IR ($CHCl_3$) 2980, 2880, 1060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.83 (d, J = 6.0 Hz, 1H), 5.51 (d, J = 5.7 Hz, 2H), 3.52-3.45 (m, 1H), 3.12-3.06 (m, 1H), 2.95-2.89 (m, 1H), 2.85-2.78

(m, 1H), 2.08-1.82 (m, 2H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 117.65 (C), 109.52 (CH), 103.28 (CH), 102.84 (CH), 56.58 (CH), 54.24 (CH), 45.85 (CH), 45.33 (CH), 29.42 (CH_2), 24.73 (CH_3); LRMS *m/z* (rel inten) 196 (M^+, 12), 79 (100); HRMS (EI) calcd for $C_{10}H_{12}O_4$ 196.0736, found 196.0734. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 61.30; H, 6.08.

1,5-Dimethyl-2,4,6,13-tetraoxapentacyclo[5.5.1.0^{3,11}.0^{5,9}.0^{8,12}]tridecane 10b : white waxy solid; mp 104-105 °C; IR ($CHCl_3$) 2980, 2880, 1060 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (d, *J* = 6.0 Hz, 1H), 5.50 (d, *J* = 6.6 Hz, 1H), 3.55-3.47 (m, 1H), 3.08-3.03 (m, 1H), 2.92-2.86 (m, 1H), 2.63-2.57 (m, 1H), 1.94-1.84 (m, 2H), 1.56 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 117.30 (C), 109.23 (C), 108.44 (CH), 103.08 (CH), 56.78 (CH), 55.61 (CH), 49.64 (CH), 45.45 (CH), 29.94 (CH_2), 25.95 (CH_3), 24.67 (CH_3); LRMS *m/z* (rel inten) 210 (M^+, 14), 139 (65), 79 (100); HRMS (EI) calcd for $C_{11}H_{14}O_4$ 210.0892, found 210.0889. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.63; H, 6.60.

General Procedure for the Ozonolysis of 3a, 3b, and 9a in $CDCl_3$ for Taking the ^{1}H and ^{13}C NMR Spectral Data of the Final Ozonides 11a, 11b, and 14. A solution of **3a** (20 mg, 0.13 mmol) in $CDCl_3$ (1.5 mL) was cooled to -78 °C, and ozone was bubbled through it at -78 °C until the solution turned light blue. After bubbling with N_2 to get rid of excess ozone, the solution was transferred to an NMR tube, and the ^{1}H and ^{13}C NMR spectra were taken at -30 °C. The NMR spectral data of the crude ozonolysis product indicated that ozonolysis of **3a** in $CDCl_3$ at -78 °C gave the final ozonide **11a** (> 90%). The same reaction conditions and procedure were applied to the preparation of **11b** (> 90%) and **14** (80%).

3,4-*bis-endo*-Diformyl-8,9,10-trioxatricyclo[5.2.1.0^{2,6}]decane 11a : ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H), 9.50 (s, 1H), 6.25 (s, 1H), 5.77 (s, 1H), 3.17-3.11 (m, 1H), 3.00-2.86 (m, 2H), 2.79-2.71 (m, 1H), 2.21-2.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 201.27 (CHO), 198.09 (CHO), 103.51 (CH), 101.04 (CH), 55.35 (CH), 52.32 (CH), 46.84 (CH), 45.10 (CH), 27.53 (CH_2).

3-*endo*-Formyl-4-*endo*-acetyl-8,9,10-trioxatricyclo[5.2.1.0^{2,6}]decane 11b : ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (s, 1H), 6.16 (s, 1H), 5.72 (s, 1H), 3.18-3.14 (m, 1H), 2.96-2.70 (m, 3H), 2.17 (s, 3H), 2.26-2.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 207.24 (C=O), 198.15 (CHO), 103.19 (CH), 101.42 (CH), 54.62 (CH), 54.42 (CH), 47.14 (CH), 45.42 (CH), 29.86 (CH_2), 27.56 (CH_3).

1-Methyl-3,4-*bis-endo*-diformyl-8,9,10-trioxatricyclo[5.2.1.0^{2,6}]decane 14 : ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 9.71 (s, 1H), 5.76 (s, 1H), 3.23-2.79 (m, 4H), 2.31-2.01 (m, 2H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 200.89 (CHO), 198.76 (CHO), 110.22 (C), 104.62 (CH), 56.08 (CH), 52.53 (CH), 51.16 (CH), 46.90 (CH), 27.61 (CH_2), 14.33 (CH_3).

Formation of the Tetraquinane Oxa-Cage Compound 15. A solution of **3a** (0.42 g, 2.9 mmol) in dichloromethane (20 mL) was cooled to -78 °C, and ozone was bubbled through it at -78 °C until the solution turned light blue. To this solution was added triethylamine (0.29 g. 2.9 mmol) at -78 °C. Then, the reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated, and the crude product was purified by column chromatography to give **15** (0.48 g, 85%).

8β-Hydroxy-2-oxo-3,5,7-trioxatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecane 15 : white waxy solid; mp 162-163 °C; IR ($CHCl_3$) 3450, 2960, 1770, 1107 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 6.01 (d, *J* = 6.0 Hz, 1H), 5.86 (d, *J* = 5.4 Hz, 1H), 5.07 (d, *J* = 3.6 Hz, 1H), 3.64-3.58 (m, 3H), 3.41-3.37 (m, 1H), 3.19-3.12 (m, 1H), 2.56-2.50 (m, 1H), 2.43-2.34 (m, 1H); ^{13}C NMR (75 MHz, CD_3OD, DEPT) δ 181.06 (C=O), 111.70 (CH), 109.25 (CH), 105.67 (CH), 56.34 (CH), 53.17 (CH), 52.90 (CH), 48.16 (CH), 37.37 (CH_2); LRMS *m/z* (rel inten) 198 (M^+, 27), 117 (96), 97 (100); HRMS (EI) calcd for $C_9H_{10}O_5$ 198.0528, found 198.0532. Anal. Calcd for $C_9H_{10}O_5$: C, 54.55; H, 5.09. Found: C, 54.38; H, 5.19.

Oxidation of 15 with PCC. To a solution of **15** (0.20 g, 1.0 mmol) in dichloromethane (30 mL) was added PCC (0.44 g, 2.0 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 12 h. The solution was filtered through silica gel and Celite. The solvent was evaporated, and the crude product was purified by column chromatography to give the symmetrical bislactone **16** in 80% yield.

2,8-Dioxo-3,5,7-trioxatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecane 16 : white waxy solid; mp 255-256 °C; IR ($CHCl_3$) 2960, 1770, 1107 cm^{-1}; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 6.19 (d, *J* = 3.6 Hz, 2H), 4.04 (brs, 2H), 3.34 (brs, 2H), 2.67 (brs, 2H); ^{13}C NMR (75 MHz, CD_3COCD_3, DEPT) δ 177.26 (2CO), 108.03 (2CH), 52.70 (2CH), 46.70 (2CH), 37.93 (CH_2); LRMS *m/z* (rel inten) 196 (M^+, 5), 97 (78), 152 (100); HRMS (EI) calcd for $C_9H_8O_5$ 196.0372, found 196.0374. Anal. Calcd for $C_9H_8O_5$: C, 55.11; H, 4.11. Found: C, 55.20; H, 4.07.

Formation of the Acetate 17. A solution of **3a** (0.42 g, 2.9 mmol) in dichloromethane (20 mL) was cooled to -78 °C, and ozone was bubbled through it at -78 °C until the solution turned light blue. To this solution was added triethylamine (0.31 g, 3.1 mmol) and acetic anhydride (0.31 g, 3.1 mmol) at -78 °C. Then, the reaction mixture was stirred at 25 °C for 3 h. The solvent was evaporated, and the crude product was purified by column chromatography to give **17** (0.61 g, 85%).

8β-Acetoxyl-2-oxo-3,5,7-trioxatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecane 17: white waxy solid; mp 185-186 °C; IR ($CHCl_3$) 2890, 1770, 1745, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17 (d, *J* = 5.1 Hz, 1H), 6.09 (s, 1H), 6.04 (d, *J* = 5.1 Hz, 1H), 3.74-3.66 (m, 2H), 3.20 (dd, *J* = 9.6 Hz, *J* = 9.6 Hz, 1H), 2.86 (dd, *J* = 9.3 Hz, *J* = 9.3 Hz, 1H), 2.71 (d, *J* = 14.7 Hz, 1H), 2.59-2.51 (m, 1H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 176.94 (C=O), 169.42 (C=O), 112.17 (CH), 107.74 (CH), 104.10 (CH), 55.03 (CH), 52.06 (CH), 49.87 (CH), 46.47 (CH), 37.46 (CH_2), 21.09 (CH_3); LRMS *m/z* (rel inten) 240 (M^+, 22), 152 (34), 117 (100); HRMS (EI) calcd for $C_{11}H_{12}O_6$ 240.0634, found 240.0637. Anal. Calcd for $C_{11}H_{12}O_6$: C, 55.00; H, 5.04. Found: C, 55.12; H, 5.06.

Formation of the Tetraquinane Oxa-Cage Compound 18. The same reaction conditions and procedure for the preparation of **15** from **3a** were applied to the preparation of **18** from ozonolysis of **3b** in 85% yield.

8-Hydroxy-8-methyl-2-oxo-3,5,7-trioxatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecane 18 which is a mixture of two stereoisomers: white waxy solid; mp 116-117 °C; IR ($CHCl_3$) 3450, 2960, 1768, 1100 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 6.08 (d, *J* = 6.0 Hz, 1H), 5.86 (d, *J* = 6.6 Hz, 1H), 5.73 (d, *J* = 4.2 Hz, 1H), 5.69 (d, *J* = 6.0 Hz, 1H), 3.68-3.59 (m, 4H), 3.23-3.07 (m, 2H), 2.63-2.56 (m, 2H), 2.45-2.08 (m, 6H), 1.33 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD, DEPT) δ 181.83 (CO), 180.49 (CO), 111.94 (CH), 110.77 (CH), 110.33 (CH), 109.31 (C), 108.50 (C), 108.09 (CH), 58.56 (CH), 57.65 (CH), 55.61 (CH), 54.07 (CH), 52.99 (CH), 52.41 (CH), 49.84 (CH), 48.97 (CH), 35.54 (CH_2), 34.05 (CH_2), 28.95 (CH_3), 24.53 (CH_3); LRMS *m/z* (rel inten) 212 (M^+, 11), 194 (87), 152 (100); HRMS (EI) calcd for $C_{10}H_{12}O_5$ 212.0685, found 212.0674. Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.47; H, 5.61.

Acetylation of 18. To a solution of **18** (0.21 g, 1.0 mmol) in dichloromethane (20 mL) was added acetic anhydride (0.11 g, 1.1 mmol) and triethylamine (0.11 g, 1.1 mmol) at room temperature. The reaction mixture was stirred at 25 °C for 4 h. After addition of saturated NH_4Cl (10 mL) and extracted with ether (3 x 20 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give compound **19** as major product (60%) and compound **20** as minor product (20%).

6α-Acetoxy-8α-acetyl-2-oxo-3,5-dioxatricyclo[5.2.1.0^{4,10}]decane 19 : white waxy solid; mp 112-113 °C; IR ($CHCl_3$) 2980, 1775, 1740, 1704, 1370 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.12 (s, 1H), 6.11 (d, J = 6.0 Hz, 1H), 3.75-3.70 (m, 1H), 3.35-3.12 (m, 3H), 2.48-2.36 (m, 1H), 2.25 (s, 3H), 2.22-2.12 (m, 1H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 205.70 (C=O), 176.36 (C=O), 169.28 (C=O), 106.05 (CH), 99.38 (CH), 57.28 (CH), 50.95 (CH), 49.29 (CH), 42.56 (CH), 30.94 (CH_2), 29.92 (CH_3), 20.91 (CH_3); LRMS *m/z* (rel inten) 254 (M^+, 11), 231 (14), 117 (100); HRMS (EI) calcd for $C_{12}H_{14}O_6$ 254.0790, found 254.0786. Anal. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.52; H, 5.46.

6α-Acetoxy-8β-acetyl-2-oxo-3,5-dioxatricyclo[5.2.1.0^{4,10}]decane 20: white waxy solid; mp 120-121 °C; IR ($CHCl_3$) 2980, 1775, 1740, 1704, 1370 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (s, 1H), 6.10 (d, J = 6.6 Hz, 1H), 3.75-3.67 (m, 1H), 3.26-3.15 (m, 2H), 2.84-2.75 (m, 1H), 2.62-2.55 (m, 1H), 2.26 (s, 3H), 2.23-2.09 (m, 1H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 205.90 (C=O), 177.06 (C=O), 169.39 (C=O), 106.20 (CH), 100.57 (CH), 54.07 (CH), 51.62 (CH), 47.57 (CH), 44.92 (CH), 36.09 (CH_2), 29.89 (CH_3), 21.03 (CH_3); LRMS *m/z* (rel inten) 254 (M^+, 9), 195 (31), 152 (100); HRMS (EI) calcd for $C_{12}H_{14}O_6$ 254.0790, found 254.0798. Anal. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.54; H, 5.42.

Conversion of 19 to 20 : To a solution of **19** (0.15 g, 0.60 mmol) in dichloromethane (20 mL) was added triethylamine (0.12 g, 1.2 mmol) at 25 °C. The reaction mixture was stirred at 25 °C for 24 h. After addition of saturated NH_4Cl (10 mL) and extracted with ether (3 x 20 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give **20** in 95% yield.

Formation of the Tetraquinane Oxa-Cage Compound 21. The same reaction conditions and procedure for the preparation of **15** from **3a** were applied to the preparation of **21** from ozonolysis of **9a** in 70% yield.

8β-Hydroxy-4-methyl-2-oxo-3,5,7-trioxatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecane 21 : white waxy solid; mp 158-159 °C; IR ($CHCl_3$) 2980, 1770, 1107 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.01 (d, J = 5.1 Hz, 1H), 5.39 (d, J = 2.1 Hz, 1H), 3.75-3.67 (m, 1H), 3.38-3.23 (m, 2H), 2.97 (d, J = 3.0 Hz, 1H), 2.75 (m, 1H), 2.62 (d, J = 14.7 Hz, 1H), 2.48-2.37 (m, 1H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 177.55 (CO), 116.71 (C), 110.57 (CH), 104.36 (CH), 56.17 (CH), 56.02 (CH), 50.72 (CH), 48.07 (CH), 36.91 (CH_2), 24.85 (CH_3); LRMS *m/z* (rel inten) 212 (M^+, 59), 119 (60), 197 (100); HRMS (EI) calcd for $C_{10}H_{12}O_5$ 212.0685, found 212.0682. Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.52; H, 5.66.

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