First Exclusive Regioselective Fragmentation of Primary Ozonides Controlled by Remote Carbonyl Groups and a New Method for Determining the Regiochemistry of Carbonyl Oxide Formation

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The first exclusive regioselective fragmentation of primary ozonides controlled by remote carbonyl groups on ozonolysis of norbornene derivatives and reaction of final ozonides with triethylamine as a new probe for determining the regiochemistry of carbonyl oxide formation from primary ozonide fragmentation are reported. Ozonolysis of the *endo* adducts **3a**−**d** and the deuterated compounds **8a** and **8b** in $CDCl_3$ at −78 °C gave the final ozonides **4a**−**d**, **9a**, and **9b** as the sole products (>95%), respectively. No detectable amount of the isomeric final ozonides **5**, **10**, **11**, and **12** was obtained. A mechanism is proposed to account for the exclusive regioselective fragmentation of the primary ozonides. Ozonolysis of **3a**−**d**, **8a**, and **8b** in CH_2Cl_2 at −78 °C followed by treatment with triethylamine exclusively gave the convex tetraquinane oxa cage compounds **16a**−**d**, **19a**, and **19b** in 85−90% yields, respectively. No detectable amount of the other regioisomers **17a**−**d**, **20a**, and **20b** was obtained. Ozonolysis of **3a**−**d**, **8a**, and **8b** in CH_2Cl_2 at −78 °C followed by reduction with dimethyl sulfide gave the tetraacetal tetraoxa cage compounds **21a**−**d**, **23a**, and **23b** in 85% yields, respectively. The difference in function between triethylamine and dimethyl sulfide in reaction with final ozonide is demonstrated. Ozonolysis of the *endo* adducts **24a** and **24b** in $CDCl_3$ at −78 °C exclusively gave the final ozonides **27a** and **27b**, respectively. The order of the preference of various remote carbonyl groups to control the fragmentation of the primary ozonides formed by ozonolysis of norbornene derivatives is investigated. Ozonolysis of the *endo* esters **32a**−**c** in CH_2Cl_2 at −78 °C followed by reduction with dimethyl sulfide gave the new tetraacetal oxa cages **35a**−**c**, with an alkoxyl group directly on the skeleton, and the novel triacetal oxa cages **36b** and **36c**, respectively. The structures of triacetal oxa cages are proven for the first time by X-ray analysis of the crystalline compound **36c**.

Introduction

Extensive investigation of the mechanism of alkene ozonolysis has confirmed the essential features of the pathway originally proposed by Criegee.[1] Apart from the long-established utility of ozonolysis in synthesis and structure determination, much of the current interest in this process centers on the factors affecting the direction of cleavage of the primary ozonide (PO) and the nature of the transient carbonyl oxide intermediate formed along with a carbonyl group by fragmentation of the PO.[2] Substituent effects on the regioselectivity of the PO fragmentation have been reported in cases in which the substituents are directly placed on the ozonation alkene bond.[3] The cleavage of the PO tends to occur along the path which results in the placement of electron-donating substituents on the carbonyl oxide fragment, while electron-withdrawing substituents are incorporated in the carbonyl product. To our knowledge, the regioselective fragmentation of the PO controlled by remote carbonyl groups has not yet been demonstrated.[2] We report here the first observation of exclusive regioselective fragmentation of primary ozonides controlled by remote different carbonyl groups and stereoselective formation of final ozonides on ozonolysis of norbornene derivatives. Also, we wish to demonstrate that reaction of final ozonides with triethylamine can act as a new method for determining the regiochemistry of carbonyl oxide formation from PO fragmentation. Usually, ozonolysis in a protic solvent, such as in methanol, is used to determine the regiochemistry of carbonyl oxide formation from PO fragmentation.[2,4]

Results and Discussion

Oxidation of 2-methylfuran (**1a**) (commercially available) with *m*-chloroperoxybenzoic acid (*m*-CPBA)[5] in dichloromethane at 0 °C gave the *cis*-enedione **2a**. Diels−Alder reaction of **2a** with cyclopentadiene at room temperature gave the *endo* product **3a** as major product in 80% yield. Metalation[6] of furan with *n*-BuLi in dry tetrahydrofuran (THF) followed by addition of 1 equiv

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(1) (a) Criegee, R.; Wenner, G. *Ann.* **1949**, *564*, 9. (b) Criegee, R. *Ann.* **1953**, *583*, 1. (c) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *11*, 745.

(2) (a) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978, Vol. 1; 1982, Vol. 2. (b) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335. (c) McCullough, K. J.; Nojima, M. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992. (d) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.

(3) (a) Fliszar, S.; Renard, J.; Simon, D. Z. *J. Am. Chem. Soc.* **1971**, *93*, 6953. (b) Griesbaum, K.; Greunig, H. J.; Volpp, W.; Jung, I. C. *Chem. Ber.* **1991**, *124*, 947. (c) Griesbaum, K.; Zwick, G. *Chem. Ber.* **1986**, *119*, 229. (d) Griesbaum, K.; Zwick, G.; Agarwal, S.; Keul, H.; Pfeffer, B.; Murray, R. W. *J. Org. Chem.* **1985**, *50*, 4194. (e) Wojciechowski, B. J.; Chiang, C. Y.; Kuczkowski, R. L. *J. Org. Chem.* **1990**, *55*, 1120.

(4) (a) Griesbaum, K.; Kiesel, G. *Chem. Ber.* **1989**, *122*, 145. (b) Paryzek, Z.; Martynow, J.; Swoboda, W. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1222. (c) Bunnelle, W. H.; Isbell, T. A. *J. Org. Chem.* **1992**, *57*, 729. (c) Teshima, K.; Kawamura, S. I.; Ushigoe, Y.; Nojima, M.; McCullough, K. J. *J. Org. Chem.* **1995**, *60*, 4755.

(5) (a) Williams, P. D.; LeGoff, E. *J. Org. Chem.* **1981**, *46*, 4143. (b) Williams, P. D.; LeGoff, E. *Tetrahedron Lett.* **1985**, *26*, 1367.

(6) (a) Ramanathan, V.; Levine, R. *J. Org. Chem.* **1962**, *27*, 1216. (b) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 31.

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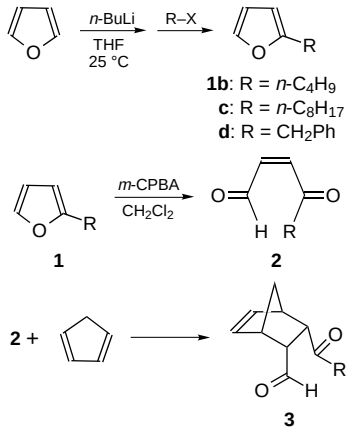
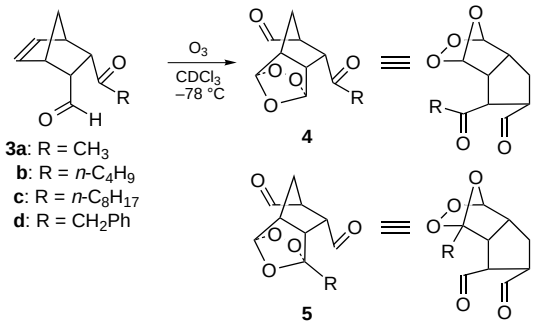
Scheme 1



Scheme 2



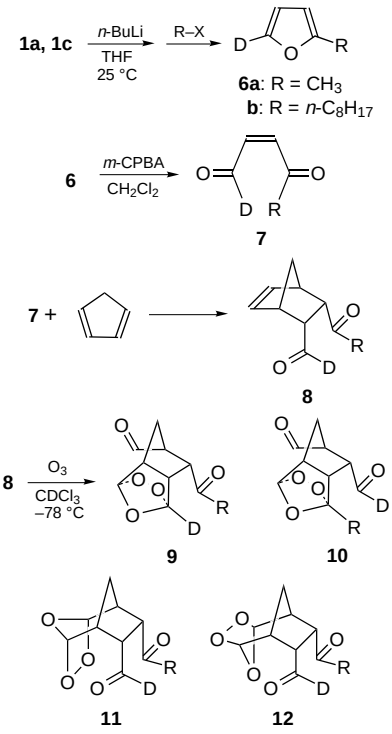
of *n*-butyl bromide, *n*-octyl bromide, and benzyl bromide at 25 °C for 4 h gave 2-*n*-butylfuran (**1b**), 2-*n*-octylfuran (**1c**), and 2-benzylfuran (**1d**) in 70−80% yields, respectively. Compounds **3b**, **3c**, and **3d** were prepared from **1b**, **1c**, and **1d** in a similar sequence, Scheme 1.

Ozonolysis of the *endo* adducts **3a**−**d** in $CDCl_3$ at −78 °C gave the final ozonides **4a**−**d** as the sole product (>95%) on the basis of their ^1H and ^{13}C NMR spectra, respectively, Scheme 2. The ^1H and ^{13}C NMR spectra of **4a**−**d** were taken at −30 °C right after the ozonation process without purification. No detectable amount of the isomeric final ozonides **5a**−**d** was observed from the ^1H and ^{13}C NMR spectra of the crude products of the ozonation reaction of compounds **3a**−**d**. The ^1H NMR spectrum of **4a** revealed two singlets at δ 6.45 and 5.70 for the 1,2,4-trioxolane ring protons and a singlet at δ 2.21 for the methyl ketone protons, consistent with structure **4a** rather than **5a**. The ^{13}C NMR spectrum of **4a** showed two peaks (CH) at δ 103.7 and 101.6 for the two tertiary bridgehead carbons of the 1,2,4-trioxolane ring indicating that there is no quaternary carbon present at the ozonide ring bridgehead.

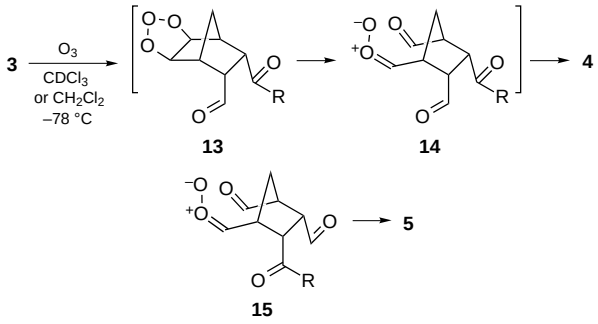
In order to confirm the structure of the final ozonides **4** to be intramolecular cross ozonides, the deuterated compounds **8a** and **8b** were prepared for ozonolysis study. Metalation of methylfuran (**1a**) and 2-*n*-octylfuran (**1c**) with *n*-BuLi in THF followed by addition of D_2O at 0 °C gave the deuterated furans **6a** and **6b** in 80−85% yields, respectively. Oxidation of **6a** and **6b** with *m*-CPBA in dichloromethane at 0 °C gave the *cis*-endiones **7a** and **7b** in 75% yields, respectively. Diels−Alder reaction of **7a** and **7b** with cyclopentadiene at 25 °C gave the *endo* adducts **8a** and **8b** as the major products in 85% yields, respectively.

Ozonolysis of the deuterated *endo* adducts **8a** and **8b** in $CDCl_3$ at −78 °C gave the final ozonides **9a** and **9b** as

Scheme 3



Scheme 4

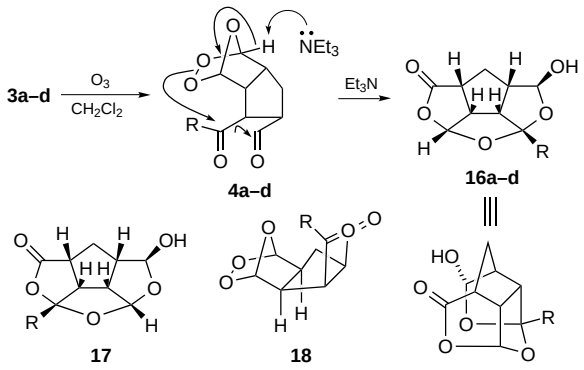


the sole product (>95%) respectively, Scheme 3. No detectable amount of the isomeric final ozonides **10a** and **10b** was observed. The crude ^1H NMR spectra of **9a** and **9b** revealed that the deuterium atom locates on the bridgehead of the trioxolane ring rather than on the aldehyde group. Thus, these experiments rule out the possibility of the final ozonides being **11** or **12**.

A mechanism is proposed for the exclusive formation of the final ozonides **4** from ozonation of **3**, Scheme 4. 1,3-Dipolar cycloaddition of an ozone molecule with the alkene bond of **3** via the *exo* face gave the 1,2,3-trioxolane **13**. A least-motion fragmentation[7] of the 1,2,3-trioxolane ring of the primary ozonides **13** affected by the carbonyl groups led exclusively to the *syn*-oriented carbonyl oxides **14**. Rapid intramolecular 1,3-dipolar cycloaddition of the *syn* carbonyl oxide group of **14** with the *endo* formyl group gave the final ozonides **4** with *endo* stereochemistry. Since no detectable amount of the isomeric final ozonides **5** was obtained, formation of the isomeric carbonyl oxides **15** from **13** would be excluded. The exclusively regioselective fragmentation of the primary ozonides **13** to form

(7) (a) Bailey, P. S.; Ferrell, T. M. *J. Am. Chem. Soc.* **1978**, *100*, 899. (b) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. L. *J. Am. Chem. Soc.* **1974**, *96*, 348. (c) Kuczkowski, R. L. *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; pp 197−276. (d) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3619.

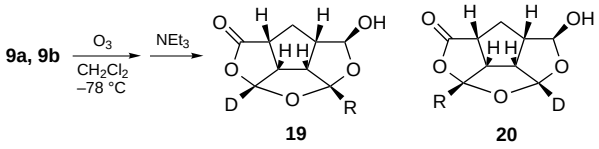
Scheme 5



the carbonyl oxides **14** is controlled by the two different carbonyl groups. According to the above results, it is the formyl group rather than the acyl group that induces the space-closed trioxolane carbon to form the carbonyl oxide group. If the fragmentation of the primary ozonides **13** was not preferentially controlled by the *endo* formyl group, both the carbonyl oxides **14** and **15** should be formed. Consequently, both the final ozonides **4** and **5** should be obtained. Since both the formyl group and the acyl group are three σ bonds remote to the primary ozonide ring, we propose here that the fragmentation of the trioxolane ring of **13** is induced by the *endo* formyl group through space rather than through bond. We also propose that it is the oxygen atom of the formyl group rather than the oxygen atom of the acyl group that adopts a conformation in proximity to the 1,2,3-trioxolane ring of **13**.

Ozonolysis of **3a**−**d** in dichloromethane at −78 °C followed by reaction with triethylamine regioselectivity gave the convex tetraquinane oxa cage compounds **16a**−**d** in 85−90% yields, respectively, Scheme 5. No detectable amount of the other regioisomers **17a**−**d** was obtained in each case. These results indicate that ozonolysis of **3a**−**d** in CH_2Cl_2 or $CDCl_3$ at −78 °C exclusively gives the corresponding final ozonides **4a**−**d**, which, in reaction with triethylamine, give **16a**−**d** as the sole products, respectively. The regiochemistry of the angular alkyl groups of **16a**−**d** was assigned by H−H COSY 2D spectral analysis. A mechanism is proposed for formation of **16** from **4**, Scheme 5. Proton abstraction of the trioxolane ring proton of **4** by triethylamine followed by heterolytic cleavage of the peroxide bond and sequential nucleophilic addition of the newly-formed alkoxide ions to the adjacent carbonyl groups gave the sole product **16**. If both the isomeric final ozonides **4** and **5** were formed from ozonolysis of **3**, both isomeric compounds **16** and **17** should be obtained via reaction of triethylamine with **4** and **5**. These experimental results support the regioselective fragmentation of primary ozonides, shown as Scheme 2. Thus, we have demonstrated for the first time that ozonolysis of alkenes in CH_2Cl_2 at −78 °C followed by treatment with triethylamine can act as a new probe to determine the regiochemistry of carbonyl oxide formation from fragmentation of primary ozonide. Usually, ozonolysis of alkenes in a protic solvent, such as in methanol, is used to determine the regiochemistry of carbonyl oxide formation because the structures of the solvent-derived products provide direct information on the mode of interaction of a carbonyl oxide with the solvent, and the product composition reflects the regioselectivity in the primary ozonides cleavage.[2,4]

Scheme 6



The structure of the stereochemistry of the final ozonides formed by ozonolysis of **3a**−**d** in CH_2Cl_2 or $CDCl_3$ at −78 °C is deduced to be the *endo* isomer **4** instead of the exo isomer **18** (Scheme 5). If the final ozonides were the isomers **18a**−**d**, with an *exo* stereochemistry, proton abstraction of the trioxolane ring proton of **18** by triethylamine followed by heterolytic cleavage of the peroxide bond could not give the observed products **16a**−**d** since the sequential nucleophilic addition of the newly-formed alkoxide ions to the carbonyl groups is stereochemically impossible.

Similarly, ozonolysis of **8a** and **8b** in dichloromethane at −78 °C followed by reaction with triethylamine exclusively gave the convex tetraquinane oxa cages **19a** and **19b** in 85−90% yields, respectively, Scheme 6. No detectable amount of the other regioisomers **20a** and **20b** was obtained in both cases.

Ozonolysis of **3a**−**d** in dichloromethane at −78 °C followed by reduction with dimethyl sulfide gave the tetraacetal oxa cage compounds **21a**−**d** in 85−90% yields, respectively. Electron donation from dimethyl sulfide to the sterically less hindered oxygen atom of the *endo* peroxide bond of the final ozonides followed by heterolytic cleavage of the peroxide bond via **22A** and sequential nucleophilic addition of the newly-formed alkoxide ions to the adjacent carbonyl groups gave the intermediates **22B** or **22C**. Loss of a neutral dimethyl sulfoxide molecule from **22B** or **22C** followed by intramolecular nucleophilic addition of the alkoxide ion to the oxonium ion gave the tetraoxa cage compounds **21**, Scheme 7. Nevertheless, we cannot rule out the possibility that reaction of **4** with dimethyl sulfide proceeded via **22E**. Similarly, oznolysis of **8a** and **8b** under the same reaction conditions gave the deuterated tetraacetal oxa cages **23a** and **23b** in 85% yields, respectively.

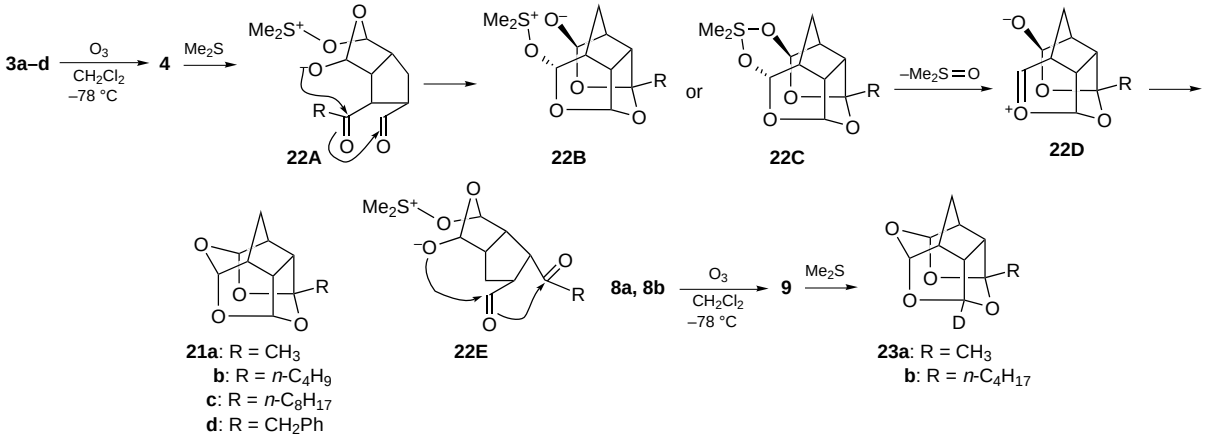
In the reaction of final ozonides with triethylamine, Razumovskii *et al.*[8] reported that an oxidation−reduction electron transfer process occurred between the amine and the ozonides. In our experimental results, reaction of the final ozonides **4** and **9** with triethylamine gave the convex tetraquinane oxa cages **16** and **19** whereas reaction of the final ozonides **4** and **9** with dimethyl sulfide gave the tetraacetal oxa cages **21** and **23**. Thus, our result indicated that the reaction between the final ozonides and triethylamine proceeded via an acid−base proton transfer process.[9] In other words, triethylamine acts as a base rather than as a reducing agent in the reaction with final ozonides if there is at least one proton present at the final ozonide ring.

To determine the relative ability between a thioester group and a ketone or aldehyde carbonyl group to control the fragmentation of the primary ozonides, we prepared

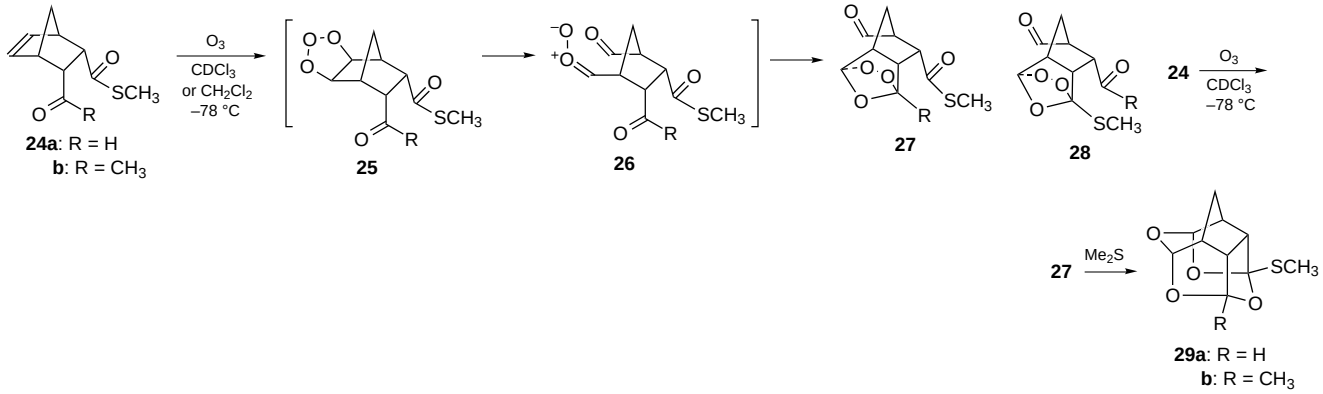
(8) (a) Razumovskii, S. D.; Zaikov, G. E. *Ozone and its Reaction with Organic Compounds*; Elsevier: The Netherlands, 1984; Chapter 9, p 370. (b) Pobedimskii, D. G.; Razumovskii, S. D. *Izv. Akad. Nauk SSSR, Ser. Khim* **1970**, *3*, 602; *Chem. Abstr.* **1970**, *73*, 13853n.

(9) Hon, Y. S.; Yan, J. L. *Tetrahedron Lett.* **1993**, *34*, 6591.

Scheme 7



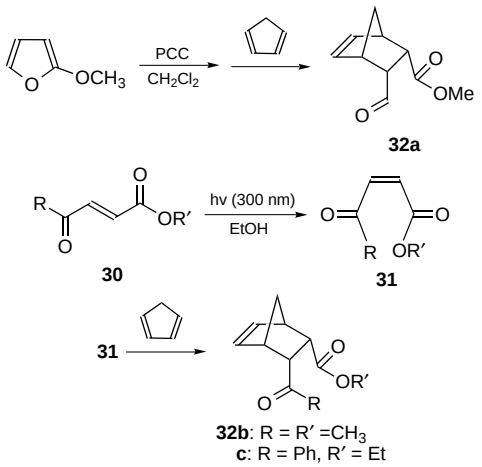
Scheme 8



compounds **24a** and **24b** from furan and 2-methylfuran,[10] respectively. Ozonolysis of **24a** and **24b** in $CDCl_3$ at −78 °C exclusively gave the final ozonides **27a** and **27b**, respectively. No detectable amount of the isomeric final ozonides **28a** and **28b** was observed from the ^1H and ^{13}C NMR spectra of the crude products of the ozonolysis of compounds **24a** and **25b**, Scheme 8. 1,3-Dipolar cycloaddition of an ozone molecule with the alkene bond of **24** gave the PO **25**. A least-motion fragmentation of the 1,2,3-trioxolane ring of **25** controlled by the carbonyl groups rather than by the thioester group led exclusively to the carbonyl oxide **26**. Intramolecular 1,3-dipolar cycloaddition of the carbonyl oxide group of **26** with the *endo* acyl group gave the final ozonide **27**. According to the above results, it is the formyl group and the acetyl group rather than the thioester group that induces the space-closed trioxolane carbon of **25** to form the carbonyl oxide group. Thus, the order of the preference of various carbonyl groups to control through space the fragmentation of the primary ozonides formed by ozonolysis of norbornene derivatives is as follow: aldehyde carbonyl > ketone carbonyl > thioester. Ozonolysis of **24a** and **24b** in CH_2Cl_2 at −78 °C followed by reduction with dimethyl sulfide gave the tetraacetal oxa cage compounds **29a** and **29b** in 65−70% yields, respectively.[10]

To determine the relative ability between an ester group and carbonyl group to control the fragmentation of the primary ozonides, we prepared compounds **32a**, **32b**, and **32c**. Oxidation of 2-methoxyfuran (commercially available) with pyridinium dichlorochromate (PCC) in dichloromethane at 25 °C followed by addition of cyclopentadiene gave the *endo* adduct **32a** as major product in 50% yield. Photoisomerization of compounds **30b** and **30c** (commercially available) with ultraviolet light (300 nm) in absolute ethanol at 25 °C gave the *cis* isomers **31b** and **31c** in 60% and 80% yields, respectively. Diels−Alder reaction of **31b** and **31c** with cyclopentadiene at room temperature gave the *endo* adducts **32b** and **32c** as major products, Scheme 9.

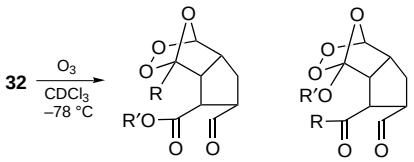
Scheme 9



Ozonolysis of the *endo* adduct **32a** in $CDCl_3$ at −78 °C gave the final ozonides **33a** and **34a** in a ratio of 85:15, Scheme 10. On the other hand, ozonolysis of **32b** in $CDCl_3$ at −78 °C gave the final ozonides **33b** and **34b** in a ratio of 30:70. Ozonolysis of **32c** in $CDCl_3$ at −78 °C

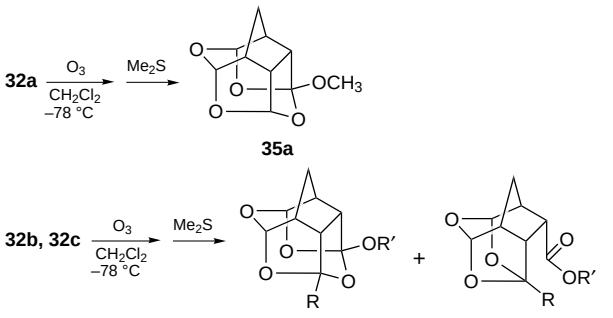
(10) (a) Wu, H. J.; Huang, F. J.; Lin, C. C. *J. Chem. Soc., Chem. Commun.* **1991**, 770. (b) Wu, H. J.; Lin, C. C.; Huang, F. J.; Lin, J. C. Submitted for publication.

Scheme 10



a: R = H, R′ = CH_3
b: R = R′ = CH_3
c: R = Ph, R′ = Et

Scheme 11



gave **33c** and **34c** in a ratio of 25:75. These results may indicate that the ability of an ester group to affect the primary ozonide fragmentation to form a carbonyl oxide group is in between that of an aldehyde carbonyl group and a ketone carbonyl group.

Ozonolysis of **32a** in CH_2Cl_2 at −78 °C followed by reduction with dimethyl sulfide gave the tetraacetal oxa cage compound **35a** in 70% yield, Scheme 11. Ozonolysis of **32b** in CH_2Cl_2 at −78 °C followed by reduction with dimethyl sulfide gave the tetraacetal oxa cage **35b** (66%) and the triacetal oxa cage **36b** (9%). Ozonolysis of **32c** under the same reaction conditions gave **35c** (67%) and **36c** (8%). Thus, we have achieved for the first time the synthesis of tetraacetal tetraoxa cage compounds **35a**−**c**, which possess an alkoxyl group directly on the skeleton. The structure of the novel triacetal trioxa cage compounds is proven for the first time by X-ray single-crystal analysis of the crystalline compound **36c**.

Conclusion

In summary, we have reported the first exclusive regioselective fragmentation of primary ozonides controlled by remote carbonyl groups on ozonolysis of norbornene derivatives. To account for the exclusive regioselective fragmentation of the primary ozonides, we propose that the conformation of the *endo* formyl and acyl groups may play an important role. The order of the preference of various carbonyl groups to control through space the fragmentation of the primary ozonides formed by ozonolysis of norbornene derivatives is as follows: aldehyde carbonyl > ketone carbonyl > thioester. The ability of an ester group to control the fragmentation of the primary ozonides may be compared to that of ketone carbonyl group. We have also demonstrated for the first time that reaction of final ozonide with triethylamine can act as a probe to determine the regiochemistry of carbonyl oxide formation from fragmentation of a primary ozonide. In reaction with the final ozonides, triethylamine is found to act as a base instead of a reducing agent, a different function from that of dimethyl sulfide. The synthesis of the tetraacetal oxa cages **35a**−**c**, which possess an alkoxyl group directly on the skeleton, has been accomplished. Ozonolysis of the *endo* esters **32b** and **32c** followed by reductive workup afforded the triacetal oxa cages **36b** and **36c** in addition to the tetraacetal oxa cages **35b** and **35c**, respectively. The structures of novel triacetal oxa cages are proven for the first time by X-ray analysis of the crystalline compound **36c**.

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 films between NaCl disks. ^{1}H NMR spectra were determined at 300 MHz, and ^{13}C NMR were determined at 75 MHz on 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. X-ray analyses 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.

General Procedure for the Preparation of 2-Alkylfurans 1b−d. To a solution of furan (2.0 g, 24.4 mmol) in dry THF (40 mL) was added *n*-BuLi (10.2 mL, 25.6 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added *n*-butyl bromide (4.1 g, 24.4 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 4 h. After addition of saturated NH_4Cl (20 mL) and extraction with ether (3 × 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 **1b**: pale yellow oil; yield 85%; IR (neat) 2980, 2940, 2880, 2870, 1610 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 1.0 Hz, 1H), 6.24 (dd, J = 2.7 Hz, J = 1.0 Hz, 1H), 5.94 (d, J = 2.7 Hz, 1H), 2.60 (t, J = 7.5 Hz, 2H), 1.66−1.56 (m, 2H), 1.42−1.31 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.53 (C), 140.57 (CH), 109.95 (CH), 104.44 (CH), 30.08 (CH_2), 29.76 (CH_2), 22.19 (CH_2), 13.77 (CH_3); LRMS *m*/*z* (rel inten) 124 (M^+, 100).

The same reaction conditions and procedure were applied to the preparation of **1c** and **1d**.

2-*n*-Octylfuran (1c): pale yellow oil; yield 90%; IR (neat) 2980, 2940, 2880, 2870, 1610 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (brs, 1H), 6.26 (brs, 1H), 5.96 (d, J = 2.1 Hz, 1H), 2.61 (t, J = 7.8 Hz, 2H), 1.65−1.60 (m, 2H), 1.42−1.15 (m, 10H), 0.97−0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.60 (C), 140.58 (CH), 109.98 (CH), 104.48 (CH), 31.84 (CH_2), 29.33 (CH_2), 29.22 (CH_2), 29.10 (CH_2), 28.02 (CH_2), 27.96 (CH_2), 22.66 (CH_2), 14.07 (CH_3); LRMS *m*/*z* (rel inten) 138 (M^+, 100).

2-Benzylfuran (1d): pale yellow oil; yield 89%; IR (neat) 3010, 2980, 2885, 1620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.21 (m, 6H), 6.28 (d, J = 1.5 Hz, 1H), 5.99 (brs, 1H), 3.97 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.53 (C), 141.45 (CH), 138.10 (C), 128.66 (2CH), 128.46 (2CH), 126.46 (CH), 110.22 (CH), 106.20 (CH), 34.43 (CH_2); LRMS *m*/*z* (rel inten) 180 (M^+, 100).

General Procedure for the Oxidation of 2-Alkylfurans 1a−d with *m*-Chloroperoxybenzoic Acid (*m*-CPBA). To a solution of 2-methylfuran (2.0 g, 24.4 mmol) in dichloromethane (180 mL) was added *m*-CPBA (4.2 g, 24.4 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. To this solution was added saturated Na_2CO_3 (50 mL). After separation, the water layer was extracted with dichloromethane (3 × 40 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated to give **2a** (0.9 g, 75%). Compounds **2a**−**d** were used for the next step, a Diels−Alder reaction, without purification, since **2a**−**d** were

sensitive to *cis*−*trans* isomerization upon heat or silica gel treatment. Spectral data for **2a**: IR ($CHCl_3$) 2920, 2860, 1770, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.19 (d, J = 7.2 Hz, 1H); 7.02 (d, J = 11.7 Hz, 1H), 6.18 (dd, J = 11.7 Hz, J = 7.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 198.21 (C=O), 192.29 (CHO), 140.31 (CH), 137.37 (CH), 30.47 (CH_3); LRMS *m*/*z* (rel inten) 98 (M^+, 18), 81 (57), 69 (100).

(*Z*)-2-Octene-1,4-dione (2b): IR ($CHCl_3$) 2930, 2870, 1770, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.21 (d, J = 7.2 Hz, 1H), 6.95 (d, J = 12.3 Hz, 1H), 6.16 (dd, J = 12.3 Hz, J = 7.2 Hz, 1H), 2.64 (t, J = 7.5 Hz, 2H), 1.73−1.42 (m, 4H), 0.91 (t, J = 5.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 200.61 (C=O), 192.30 (CHO), 140.28 (CH), 137.56 (CH), 43.61 (CH_2), 31.81 (CH_2), 24.15 (CH_2), 13.63 (CH_3); LRMS *m*/*z* (rel inten) 140 (M^+, 100).

(*Z*)-2-Dodecene-1,4-dione (2c): IR ($CHCl_3$) 2930, 2860, 1770, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.22 (d, J = 7.2 Hz, 1H), 6.96 (d, J = 12.6 Hz, 1H), 6.18 (dd, J = 12.6 Hz, J = 7.2 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 1.71−1.63 (m, 2H), 1.42−1.22 (m, 10H), 0.88 (t, J = 5.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 200.74 (C=O), 192.53 (CHO), 140.26 (CH), 137.75 (CH), 43.58 (CH_2), 31.69 (CH_2), 29.22 (CH_2), 29.13 (CH_2), 28.98 (CH_2), 23.53 (CH_2), 22.54 (CH_2), 13.98 (CH_3); LRMS *m*/*z* (rel inten) 196 (M^+, 15), 141 (100).

(*Z*)-4-Benzyl-2-pentene-1,4-dione (2d): IR ($CHCl_3$) 2950, 2850, 1760, 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.98 (d, J = 7.3 Hz, 1H), 7.37−7.18 (m, 5H), 6.97 (d, J = 12.3 Hz, 1H), 6.21 (dd, J = 12.3 Hz, J = 7.3 Hz, 1H), 3.68 (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 200.50 (C=O), 193.15 (CHO), 141.32 (CH), 138.61 (CH), 134.65 (C), 129.51 (2CH), 128.41 (2CH), 127.67 (CH), 49.81 (CH_2); LRMS *m*/*z* (rel inten) 174 (M^+, 100).

General Procedure for the Diels−Alder Reaction of 2a−d with Cyclopentadiene. To a solution of **2a** (2.0 g, 20.4 mmol) in dichloromethane (3 mL) was added 1,3-cyclopentadiene (2.69 g, 40.8 mmol) at 25 °C. The reaction mixture was stirred at 25 °C for 2 h. The solvent was evaporated and the crude product was purified by column chromatography to give the *endo* adduct **3a** as major product (2.6 g, 14.6 mmol, 82%). Spectral data for **3a**: IR ($CHCl_3$) 2925, 2840, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.47 (d, J = 3.3 Hz, 1H), 6.41 (dd, J = 6.0 Hz, J = 2.7 Hz, 1H), 6.11 (dd, J = 6.0 Hz, J = 2.7 Hz, 1H), 3.68 (dd, J = 9.8 Hz, J = 3.6 Hz, 1H), 3.36 (brs, 1H), 3.17 (brs, 1H), 3.02−2.96 (m, 1H), 2.17 (s, 3H), 1.60−1.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 206.75 (C=O), 202.99 (CHO), 136.44 (CH), 133.70 (CH), 60.36 (CH), 55.73 (CH), 47.31 (CH), 45.53 (CH), 29.62 (CH_2), 28.75 (CH_3); LRMS *m*/*z* (rel inten) 164 (M^+, 4), 98 (36), 66 (100); HRMS (EI) calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0837.

Spectral data for **3b**: IR ($CHCl_3$) 2920, 2840, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.46 (d, J = 3.3 Hz, 1H), 6.40 (dd, J = 5.6 Hz, J = 2.7 Hz, 1H), 6.06 (dd, J = 5.6 Hz, J = 3.0 Hz, 1H), 3.68 (dd, J = 9.5 Hz, J = 3.9 Hz, 1H), 3.34 (brs, 1H), 3.17 (brs, 1H), 3.00−2.94 (m, 1H), 1.58−1.25 (m, 6H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 209.11 (C=O), 203.02 (CHO), 136.24 (CH), 133.79 (CH), 59.69 (CH), 55.76 (CH), 49.35 (CH2), 47.43 (CH), 45.45 (CH), 41.05 (CH_2), 25.63 (CH_2), 22.17 (CH_2), 13.74 (CH_3); LRMS *m*/*z* (rel inten) 206 (M^+, 7), 150 (100); HRMS (EI) calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1309.

Spectral data for **3c**: IR ($CHCl_3$) 2920, 2840, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.46 (d, J = 3.3 Hz, 1H), 6.40 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 6.06 (dd, J = 5.4 Hz, J = 2.7 Hz, 1H), 3.68 (dd, J = 9.3 Hz, J = 3.3 Hz, 1H), 3.34 (brs, 1H), 3.17 (brs, 1H), 3.00−2.94 (m, 1H), 2.44 (t, J = 6.9 Hz, 2H), 1.58−1.32 (m, 4H), 1.35−1.22 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 209.11 (C=O), 202.99 (CHO), 136.26 (CH), 133.82 (CH), 59.69 (CH), 55.79 (CH), 49.38 (CH_2), 47.46 (CH), 45.50 (CH), 41.40 (CH_2), 31.72 (CH_2), 29.30 (CH_2), 29.13 (CH_2), 29.04 (CH_2), 23.59 (CH_2), 22.54 (CH_2), 14.01 (CH_3); LRMS *m*/*z* (rel inten) 262 (M^+, 52), 141 (100); HRMS (EI) calcd for $C_{17}H_{26}O_2$ 262.1933, found 262.1942.

Spectral data for **3d**: IR ($CHCl_3$) 2980, 1775, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.44 (d, J = 3.0 Hz, 1H), 7.36−7.17 (m, 5H), 6.36 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 5.99 (dd, J = 5.7 Hz, J = 3.0 Hz, 1H), 3.76−3.68 (m, 3H), 3.28 (brs, 1H), 3.15 (brs, 1H), 2.98−2.92 (m, 1H), 1.53−1.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 206.40 (C=O), 202.70 (CHO), 136.09 (CH), 133.90 (CH), 133.61 (C), 129.27 (2CH), 128.60 (2CH), 127.03 (CH), 58.62 (CH), 55.88 (CH), 49.18 (CH_2), 48.68 (CH_2), 47.49 (CH), 45.36 (CH); LRMS *m*/*z* (rel inten) 240 (M^+, 30), 143 (65), 105 (100); HRMS (EI) calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1131.

Taking the ^1H and ^{13}C NMR Spectral Data of the Final Ozonides 4a−d. The solution of **3a** (0.050 g, 0.3 mmol) in $CDCl_3$ (1.0 mL) was cooled to −78 °C, and ozone was bubbled through it at −78 °C until the solution turned light blue. The solution was then transferred to an NMR tube, and the ^1H and ^{13}C NMR spectra were taken at −30 °C. Spectral data for **4a**: ^1H NMR (300 MHz, $CDCl_3$) δ 9.47 (s, 1H), 6.45 (s, 1H), 5.70 (s, 1H), 3.13−3.07 (m, 1H), 2.94 (dd, J = 7.8 Hz, J = 7.5 Hz, 1H), 2.83 (dd, J = 6.9 Hz, J = 7.2 Hz, 1H), 2.75−2.69 (m, 1H), 2.67−2.01 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 205.29 (C=O), 200.71 (CHO), 103.64 (CH), 101.55 (CH), 56.20 (CH), 52.82 (CH), 47.48 (CH), 44.99 (CH), 29.40 (CH_3), 28.19 (CH_2).

Spectral data for **4b**: ^1H NMR (300 MHz, $CDCl_3$) δ 9.45 (s, 1H), 6.50 (s, 1H), 5.74 (s, 1H), 3.20−3.15 (m, 1H), 2.95−2.72 (m, 3H), 2.57−2.16 (m, 4H), 1.61−1.51 (m, 2H), 1.28−1.22 (m, 2H), 0.85 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 208.70 (C=O), 201.91 (CHO), 103.43 (CH), 101.62 (CH), 54.51 (CH), 52.70 (CH), 46.61 (CH), 43.96 (CH), 41.34 (CH_2), 27.67 (CH_2), 25.60 (CH_2), 22.11 (CH_2), 14.07 (CH_3).

Spectral data for **4c**: ^1H NMR (300 MHz, $CDCl_3$) δ 9.47 (s, 1H), 6.48 (s, 1H), 5.69 (s, 1H), 3.05 (dd, J = 8.7 Hz, J = 2.1 Hz, 1H), 2.97 (dd, J = 7.8 Hz, J = 7.8 Hz, 1H), 2.83 (dd, J = 6.9 Hz, J = 7.4 Hz, 1H), 2.74−2.68 (m, 1H), 2.52−2.10 (m, 4H), 1.62−1.57 (m, 2H), 1.36−1.17 (m, 10H), 0.84 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 208.56 (C=O), 200.89 (CHO), 103.66 (CH), 101.62 (CH), 55.24 (CH), 52.82 (CH), 47.63 (CH), 44.95 (CH), 42.15 (CH_2), 31.78 (CH_2), 29.36 (CH_2), 29.16 (CH_2), 29.07 (CH_2), 28.25 (CH_2), 23.91 (CH_2), 22.57 (CH_2), 14.04 (CH_3).

Spectral data for **4d**: ^1H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.41−7.17 (m, 5H), 6.51 (s, 1H), 5.71 (s, 1H), 3.78 (ABq, J = 16.2 Hz, δ_A 3.85, δ_B 3.71, 2H), 3.12−3.00 (m, 2H), 2.79−2.66 (m, 2H), 2.26−2.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 205.61 (C=O), 201.27 (CHO), 134.02 (C), 129.36 (2CH), 128.72 (2CH), 127.14 (CH), 103.60 (CH), 101.59 (CH), 54.07 (CH), 52.79 (CH), 49.18 (CH_2), 47.54 (CH), 44.63 (CH), 28.05 (CH_2).

General Procedure for the Preparation of 2-Deuterio-5-alkylfurans 6a and 6b. To a solution of 2-octylfuran (2.0 g, 11.1 mmol) in dry THF (40 mL) was added 2.5 M *n*-BuLi (4.8 mL, 12.1 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added D_2O (0.3 g, 16.8 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 1 h. After addition of saturated NH_4Cl (20 mL) and extraction with ether (3 × 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 **6b**: Spectral data for **6b**: pale yellow oil; yield 87%; ^1H NMR (300 MHz, $CDCl_3$) δ 6.26 (d, J = 2.7 Hz, 1H), 5.96 (d, J = 2.7 Hz, 1H), 2.60 (t, J = 8.1 Hz, 2H), 1.68−1.58 (m, 2H), 1.40−1.22 (m, 10H), 0.96−0.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 156.51 (C), 139.75 (CD), 109.75 (CH), 104.45 (CH), 31.93 (CH_2), 31.84 (CH_2), 29.33 (CH_2), 29.22 (CH_2), 28.02 (CH_2), 27.96 (CH_2), 22.66 (CH_2), 14.07 (CH_3).

Formation of 7a and 7b. The same reaction conditions and procedure for the synthesis of **2a**−**d** from the oxidation of **1a**−**d** were applied to the oxidation of **6a** and **6b**. Compounds **7a** and **7b** were used for the next step, a Diels−Alder reaction, without purification, since **7a** and **7b** were sensitive to *cis*−*trans* isomerization upon heat or silica gel treatment. Spectral data for **7a**: pale yellow oil; yield 78%; IR ($CHCl_3$) 2925, 2860, 1770, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, J = 11.7 Hz, 1H), 6.19 (d, J = 11.7 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 198.56 (C=O), 192.31 (CDO), 140.20 (CH), 137.65 (CH), 30.47 (CH_3); LRMS *m*/*z* (rel inten) 99 (M^+, 21), 82 (59), 70 (100).

Spectral data for **7b**: pale yellow oil; yield 78%; IR ($CHCl_3$) 2930, 2860, 1770, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ

6.98 (d, J = 12.6 Hz, 1H), 6.19 (d, J = 12.6 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 1.73−1.63 (m, 2H), 1.42−1.21 (m, 10H), 0.88 (t, J = 5.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 200.53 (C=O), 192.63 (CDO), 140.14 (CH), 137.45 (CH), 43.19 (CH_2), 31.58 (CH_2), 29.32 (CH_2), 29.03 (CH_2), 28.77 (CH_2), 23.46 (CH_2), 22.38 (CH_2), 13.98 (CH_3); LRMS *m/z* (rel inten) 197 (M^+, 14), 142 (100).

Diels−Alder Reaction of 7a and 7b with Cyclopentadiene. The same reaction conditions and procedure as for the synthesis of **3a**−**d** from the Diels−Alder reaction of **2a**−**d** were applied to the Diels−Alder reaction of **7a** and **7b**. Spectral data for **8a**: pale yellow oil; yield 84%; IR ($CHCl_3$) 2920, 2840, 1710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42−6.39 (m, 1H), 6.12−6.09 (m, 1H), 3.69 (dd, J = 8.7 Hz, J = 3.6 Hz, 1H), 3.37 (brs, 1H), 3.17 (brs, 1H), 2.98 (dd, J = 8.8 Hz, J = 3.0 Hz, 1H), 2.17 (s, 3H), 1.59−1.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 206.83 (C=O), 202.75 (CDO), 136.44 (CH), 133.64 (CH), 60.36 (CH), 55.53 (CH), 49.35 (CH), 47.28 (CH), 45.47 (CH_2), 28.69 (CH_3); LRMS *m/z* (rel inten) 165 (M^+, 12), 139 (100); HRMS (EI) calcd for $C_{10}H_{11}DO_2$ 165.0897, found 165.0896.

Spectral data for **8b**: pale yellow oil; yield 80%; IR ($CHCl_3$) 2920, 2840, 1720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (dd, J = 5.6 Hz, J = 2.4 Hz, 1H), 6.06 (dd, J = 5.1 Hz, J = 2.4 Hz, 1H), 3.68 (dd, J = 9.5 Hz, J = 3.9 Hz, 1H), 3.34 (brs, 1H), 3.16 (brs, 1H), 2.96 (dd, J = 9.5 Hz, J = 3.0 Hz, 1H), 2.45 (t, J = 7.2 Hz, 2H), 1.61−1.22 (m, 14H), 0.89−0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 209.11 (C=O), 202.64 (CDO), 136.29 (CH), 133.73 (CH), 59.69 (CH), 55.59 (CH), 49.35 (CH_2), 47.43 (CH), 45.42 (CH), 41.31 (CH_2), 31.69 (CH_2), 29.27 (CH_2), 29.07 (CH_2), 29.01 (CH_2), 23.53 (CH_2), 22.52 (CH_2), 13.98 (CH_3); LRMS *m/z* (rel inten) 263 (M^+, 38), 142 (100); HRMS (EI) calcd for $C_{17}H_{25}DO_2$ 263.1992, found 263.1988.

Taking the ^{1}H and ^{13}C NMR Spectral Data of the Final Ozonides 9a and 9b. The same reaction conditions and procedure as for the synthesis of **4a**−**d** from the ozonolysis of **3a**−**d** were applied to the ozonolysis of **8a** and **8b**. Spectral data for **9a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (s, 1H), 5.69 (s, 1H), 3.10−3.07 (m, 1H), 2.94 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H), 2.82 (dd, J = 7.5 Hz, J = 7.2 Hz, 1H), 2.74−2.71 (m, 1H), 2.19 (s, 3H), 2.23−2.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 205.52 (C=O), 200.89 (CHO), 103.63 (CH), 101.69 (CD), 56.08 (CH), 52.76 (CH), 47.22 (CH), 44.83 (CH), 29.33 (CH_3), 28.08 (CH_2).

Spectral data for **9b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (s, 1H), 5.69 (s, 1H), 3.11−2.69 (m, 4H), 2.51−2.08 (m, 4H), 1.64−1.56 (m, 2H), 1.30−1.20 (m, 10H), 0.90−0.76 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 208.09 (C=O), 200.92 (CHO), 103.69 (CH), 101.33 (CD), 55.18 (CH), 52.79 (CH), 47.49 (CH), 44.89 (CH), 42.09 (CH_2), 31.72 (CH_2), 29.30 (CH_2), 29.10 (CH_2), 29.04 (CH_2), 28.20 (CH_2), 23.88 (CH_2), 22.54 (CH_2), 14.01 (CH_3).

General Procedure for the Synthesis of the Tetraquinane Oxa Cage Compounds 16a−d. A solution of **3a** (0.30 g, 1.8 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 (0.28 g, 2.8 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 **16a** (0.34 g, 90%). Spectral data for **16a**: white waxy solid; mp 166−167 °C; IR ($CHCl_3$) 3500−3300, 2950, 1770 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (d, J = 6.3 Hz, 1H), 5.57 (brs, 1H), 5.17 (d, J = 2.4 Hz, 1H), 3.87−3.83 (m, 1H), 2.64 (dd, J = 11.1 Hz, J = 8.7 Hz, 1H), 3.24−3.18 (m, 1H), 2.75−2.68 (m, 1H), 2.42−2.37 (m, 2H), 1.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 178.79 (C=O), 119.61 (C), 107.32 (CH), 105.07 (CH), 59.41 (CH), 53.50 (CH), 53.06 (CH), 47.26 (CH), 36.95 (CH_2), 26.23 (CH_3); LRMS *m/z* (rel inten) 212 (M^+, 15), 195 (100); HRMS (EI) calcd for $C_{10}H_{12}O_5$ 212.0685, found 212.0688.

Spectral data for **16b**: white waxy solid; yield 87%; mp 114−115.5 °C; IR ($CHCl_3$) 3500−3300, 2950, 1770 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.07 (d, J = 6.6 Hz, 1H), 5.32 (d, J = 2.0 Hz, 1H), 3.73−3.64 (m, 2H), 3.39 (dd, J = 10.8 Hz, J = 8.7 Hz, 1H), 3.19 (dd, J = 9.0 Hz, J = 9.0 Hz, 1H), 2.77−2.70 (m, 1H), 2.62−2.36 (m, 2H), 2.05−1.83 (m, 2H), 1.48−1.32 (m, 4H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 178.31 (C=O), 121.84 (C), 106.69 (CH), 104.18 (CH), 57.36 (CH), 52.53 (CH), 51.83 (CH), 46.84 (CH), 38.34 (CH_2), 36.79 (CH_2), 26.16 (CH_2), 22.63 (CH_2), 13.92 (CH_3); LRMS *m/z* (rel inten) 254 (M^+, 11), 197 (49), 166 (100); HRMS (EI) calcd for $C_{13}H_{18}O_5$ 254.1154, found 254.1154.

Spectral data for **16c**: white waxy solid; yield 88%; mp 110−111 °C; IR ($CHCl_3$) 3500−3300, 2920, 1775 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00 (d, J = 5.7 Hz, 1H), 5.24 (d, J = 2.7 Hz, 1H), 3.68−3.59 (m, 1H), 3.33 (dd, J = 8.7 Hz, J = 8.7 Hz, 1H), 3.13 (dd, J = 9.6 Hz, J = 8.7 Hz, 1H), 2.71−2.30 (m, 3H), 1.98−1.76 (m, 2H), 1.46−1.14 (m, 13H), 0.83 (t, J = 5.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 178.54 (C=O), 121.70 (C), 106.75 (CH), 104.10 (CH), 57.22 (CH), 52.50 (CH), 51.83 (CH), 46.84 (CH), 38.57 (CH_2), 36.68 (CH_2), 31.75 (CH_2), 29.51 (CH_2), 29.39 (CH_2), 29.13 (CH_2), 24.00 (CH_2), 22.54 (CH_2), 13.98 (CH_3); LRMS *m/z* (rel inten) 310 (M^+, 2), 197 (100); HRMS (EI) calcd for $C_{17}H_{26}O_5$ 310.1780, found 310.1780.

Spectral data for **16d**: white waxy solid; yield 84%; mp 192−193 °C; IR ($CHCl_3$) 3500−3300, 1760, 1080 cm^{-1}; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.33−7.20 (m, 5H), 5.92 (d, J = 6.3 Hz, 1H), 4.99 (d, J = 3.0 Hz, 1H), 3.51−3.01 (m, 7H), 2.34−2.18 (m, 2H); ^{13}C NMR (75 MHz, CD_3COCD_3, DEPT) δ 178.98 (C=O), 136.41 (C), 130.55 (CH), 127.87 (2CH), 126.44 (2CH), 119.33 (C), 106.46 (CH), 103.66 (CH), 56.43 (CH), 52.09 (CH), 51.77 (CH), 46.61 (CH), 44.10 (CH_2), 35.60 (CH_2); LRMS *m/z* (rel inten) 288 (M^+, 2), 271 (100); HRMS (EI) calcd for $C_{16}H_{16}O_5$ 288.0998, found 288.0997.

Synthesis of the Tetraquinane Oxa Cage Compounds 19a and 19b. The same reaction conditions and procedure as for the synthesis of **16a**−**d** from the ozonolysis of **3a**−**d** were applied to the ozonolysis of **8a and 8b**. Spectral data for **19a**: white waxy solid; yield 89%; mp 170−171 °C; IR (KBr) 3500−3300, 2950, 1770 cm^{-1}; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 5.46 (d, J = 4.5 Hz, 1H), 5.15 (dd, J = 4.5 Hz, J = 3.3 Hz, 1H), 3.83 (dd, J = 10.2 Hz, J = 10.2 Hz, 1H), 3.40 (dd, J = 10.2 Hz, J = 8.7 Hz, 1H), 3.22−3.15 (m, 1H), 2.71−2.66 (m, 1H), 2.40−2.36 (m, 2H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 179.00 (C=O), 119.86 (C), 106.45 (CD), 105.32 (CH), 59.69 (CH), 53.63 (CH), 53.34 (CH), 47.51 (CH), 30.57 (CH_2), 26.49 (CH_3); LRMS *m/z* (rel inten) 213 (M^+, 7), 167 (100); HRMS (EI) calcd for $C_{10}H_{11}DO_5$ 213.0744, found 213.0741.

Spectral data for **19b**: white waxy solid; yield 88%; mp 110−112 °C; IR ($CHCl_3$) 3500−3300, 2980, 1770 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.30 (brs, 1H), 3.81 (brs, 1H), 3.68 (dd, J = 10.5 Hz, J = 10.8 Hz, 1H), 3.39 (dd, J = 10.5 Hz, J = 9.6 Hz, 1H), 3.18 (dd, J = 9.6 Hz, J = 9.6 Hz, 1H), 2.78−2.35 (m, 3H), 1.95−1.84 (m, 2H), 1.44−1.20 (m, 12H), 0.91−0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 178.45 (C=O), 121.75 (C), 106.32 (CD), 104.10 (CH), 57.25 (CH), 52.38 (CH), 51.74 (CH), 46.81 (CH), 38.57 (CH_2), 36.73 (CH_2), 31.75 (CH_2), 29.51 (CH_2), 29.39 (CH_2), 29.16 (CH_2), 24.00 (CH_2), 22.54 (CH_2), 14.01 (CH_3); LRMS *m/z* (rel inten) 311 (M^+, 7), 198 (100); HRMS (EI) calcd for $C_{17}H_{25}DO_5$ 311.1836, found 311.1842.

General Procedure for the Ozonolysis of 3a−d. Formation of the Tetraacetal Oxa Cage Compounds 21a−d. A solution of **3a** (0.5 g, 3.0 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 (0.56 g, 9.0 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 tetraacetal oxa cage compound **21a** (0.5 g, 85%). Spectral data for **21a**: white waxy solid; mp 127.5−128.5 °C; IR ($CHCl_3$) 2970, 1060 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (d, J = 5.4 Hz, 1H), 5.50 (d, J = 6.3 Hz, 2H), 3.52−3.47 (m, 1H), 3.10 (dd, J = 10.8 Hz, J = 7.2 Hz, 1H), 2.94−2.88 (m, 1H), 2.83−2.76 (m, 1H), 2.00−1.83 (m, 2H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 117.59 (C), 109.46 (CH), 103.25 (CH), 102.82 (CH), 56.52 (CH), 54.19 (CH), 45.82 (CH), 45.30 (CH), 29.36 (CH_2), 24.70 (CH_3); LRMS *m/z* (rel inten) 196 (M^+, 39), 79 (76), 43 (100); HRMS (EI) calcd for $C_{10}H_{12}O_4$ 196.0736, found 196.0736.

1-Butyl-2,4,6,13-tetraoxapentacyclo[5.5.1.0.^{3,11}0.^{5,9}0^{8,12}]-tridecane (21b): pale yellow oil; yield 87%; IR ($CHCl_3$) 2975, 1060 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (d, J = 5.4 Hz, 1H), 5.35 (d, J = 6.6 Hz, 2H), 3.44 (ddd, J = 10.4 Hz, J = 7.4

Hz, J = 5.4 Hz, 1H), 3.10 (dd, J = 10.4 Hz, J = 7.5 Hz, 1H), 2.87−2.78 (m, 2H), 2.00−1.72 (m, 4H), 1.43−1.27 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 119.74 (C), 109.43 (CH), 103.19 (CH), 102.82 (CH), 54.83 (CH), 53.87 (CH), 46.00 (CH), 45.36 (CH), 37.26 (CH_2), 29.45 (CH_2), 26.30 (CH_2), 22.66 (CH_2), 13.92 (CH_3); LRMS m/z (rel inten) 238 (M^+, 4), 209 (41), 196 (100); HRMS (EI) calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1203.

1-Octyl-2,4,6,13-tetraoxapentacyclo[5.5.1.0.^{3,11}0.^{5,9}0^{8,12}]-tridecane (21c): white waxy solid; yield 86%; mp 74−75 °C; IR ($CHCl_3$) 2970, 1065 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (d, J = 5.4 Hz, 1H), 5.37 (d, J = 6.6 Hz, 1H), 5.35 (d, J = 6.0 Hz, 1H), 3.38−3.30 (m, 1H), 2.99 (dd, J = 10.7 Hz, J = 8.1 Hz, 1H), 2.76−2.67 (m, 2H), 1.93−1.58 (m, 4H), 1.35−1.12 (m, 12H), 0.77 (t, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 119.48 (C), 109.20 (CH), 102.99 (CH), 102.61 (CH), 54.59 (CH), 53.63 (CH), 45.77 (CH), 45.13 (CH), 37.35 (CH_2), 31.35 (CH_2), 29.33 (CH_2), 29.19 ($2CH_2$), 28.90 (CH_2), 23.91 (CH_2), 22.31 (CH_2), 13.77 (CH_3); LRMS m/z (rel inten) 294 (M^+, 7), 265 (33), 196 (100); HRMS (EI) calcd for $C_{17}H_{26}O_4$ 294.1831, found 294.1823.

1-Benzyl-2,4,6,13-tetraoxapentacyclo[5.5.1.0.^{3,11}0.^{5,9}0^{8,12}]-tridecane (21d): white waxy solid; yield 83%; mp 90−90.5 °C; IR ($CHCl_3$) 2970, 1500, 1050 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.21 (m, 5H), 5.82 (d, J = 5.7 Hz, 1H), 5.47 (d, J = 6.3 Hz, 1H), 5.40 (d, J = 6.3 Hz, 1H), 3.35 (ddd, J = 10.8 Hz, J = 7.5 Hz, J = 5.7 Hz, 1H), 3.18 (d, J = 13.5 Hz, 1H), 3.07 (dd, J = 10.8 Hz, J = 7.5 Hz, 1H), 2.97 (d, J = 13.5 Hz, 1H), 2.97−2.72 (m, 1H), 2.34−2.23 (m, 1H), 2.04−1.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 136.03 (C), 130.17 (2CH), 127.87 (2CH), 126.47 (CH), 119.10 (C), 109.43 (CH), 103.19 (CH), 102.76 (CH), 54.07 (CH), 53.57 (CH), 45.74 (CH), 45.15 (CH), 43.00 (CH_2), 29.19 (CH_2); LRMS m/z (rel inten) 272 (M^+, 39), 181 (100); HRMS (EI) calcd for $C_{16}H_{16}O_4$ 272.1049, found 272.1043.

Ozonolysis of 8a and 8b. Formation of the Tetraacetal Oxa Cage Compounds 23a and 23b. The same reaction conditions and procedure as for the synthesis of **21a**−**d** from the ozonolysis of **3a**−**d** were applied to the ozonolysis of **8a and 8b**. Spectral data for **23a**: white waxy solid; yield 87%; mp 122.5−123 °C; IR ($CHCl_3$) 2970, 1065 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (d, J = 6.6 Hz, 2H), 3.48 (dd, J = 10.2 Hz, J = 7.2 Hz, 1H), 3.09 (dd, J = 10.2 Hz, J = 7.2 Hz, 1H), 2.94−2.78 (m, 2H), 2.00−1.82 (m, 2H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 117.59 (C), 109.72 (CD), 103.25 (CH), 102.82 (CH), 56.55 (CH), 54.07 (CH), 45.82 (CH), 45.30 (CH), 29.36 (CH_2), 24.67 (CH_3); LRMS m/z (rel inten) 197 (M^+, 49), 108 (93), 80 (100); HRMS (EI) calcd for $C_{10}H_{11}DO_4$ 197.0795, found 197.0809.

1-Deuterio-7-octyl-2,4,6,13-tetraoxapentacyclo-[5.5.1.0^{3,11}0.^{5,9}0^{8,12}]tridecane (23b): white waxy solid; yield 88%; mp 110−112 °C; IR ($CHCl_3$) 2970, 1065 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (d, J = 6.0 Hz, 2H), 3.44 (dd, J = 10.5 Hz, J = 7.5 Hz, 1H), 3.10 (dd, J = 10.4 Hz, J = 7.8 Hz, 1H), 2.87−2.76 (m, 2H), 2.05−1.67 (m, 4H), 1.44−1.20 (m, 12H), 0.94−0.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 119.66 (C), 109.05 (CD), 103.11 (CH), 102.76 (CH), 54.74 (CH), 53.66 (CH), 45.91 (CH), 45.27 (CH), 37.49 (CH_2), 31.69 (CH_2), 29.51 (CH_2), 29.33 ($2CH_2$), 29.07 (CH_2), 24.09 (CH_2), 22.49 (CH_2), 13.95 (CH_3); LRMS m/z (rel inten) 295 (M^+, 8), 197 (100); HRMS (EI) calcd for $C_{17}H_{25}DO_4$ 295.1887, found 295.1869.

Taking the ^{1}H and ^{13}C NMR Spectral Data of the Final Ozonides 27a and 27b. The same reaction conditions and procedure as for the synthesis of **4a**−**d** from the ozonolysis of **3a**−**d** were applied to the ozonolysis of **24a** and **24b**. Spectral data for **27a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1H), 6.45 (s, 1H), 5.79 (s, 1H), 3.39 (dd, J = 8.1 Hz, J = 8.1 Hz, 1H), 3.10−2.92 (m, 2H), 2.80−2.68 (m, 1H), 2.34 (s, 3H), 2.26−2.02 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 201.15 (CHO), 197.77 (COS), 103.66 (CH), 101.13 (CH), 54.59 (CH), 52.79 (CH), 47.83 (CH), 45.10 (CH), 28.05 (CH_2), 11.94 (CH_3).

Spectral data for **27b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 5.83 (s, 1H), 3.51 (dd, J = 8.4 Hz, J = 8.0 Hz, 1H), 3.29 (dd, J = 8.4 Hz, J = 7.8 Hz, 1H), 3.02−2.94 (m, 2H), 2.43 (s, 3H), 2.40−2.10 (m, 2H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 202.55 (CHO), 198.18 (COS), 109.98 (C), 104.56 (CH), 56.11 (CH), 52.18 (CH), 51.48 (CH), 46.79 (CH), 28.93 (CH_2), 13.72 (CH_3), 12.06 (CH_3).

Formation of 31b and 31c. The commercially available compound **30b** (1.0 g, 7.8 mmol) was dissolved in absolute ethanol (50 mL) with heating in a Pyrex tube. The mixture was irradiated with ultraviolet light (300 nm) at 25 °C for 8 h. Then, the solvent was evaporated and the crude product was purified by column chromatography to give **31b** (0.56 g, 4.4 mmol, 56%). Spectral data of **31b**: pale yellow oil; IR ($CHCl_3$) 2980, 1770, 1725 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (d, J = 12.0 Hz, 1H), 5.95 (d, J = 12.0 Hz, 1H), 3.67 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 201.21 (C═O), 165.55 (C═O), 141.83 (CH), 124.03 (CH), 51.88 (CH_3), 29.74 (CH_3).

Spectra data of **31c**: pale yellow oil; yield 76%; IR ($CHCl_3$) 2980, 1725, 1675 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95−7.92 (m, 2H), 7.60−7.43 (m, 3H), 6.89 (d, J = 11.7 Hz, 1H), 6.27 (d, J = 11.7 Hz, 1H), 4.02 (q, J = 6.9 Hz, 2H), 1.05 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 193.87 (C═O), 164.53 (C═O), 140.81 (CH), 135.59 (C), 133.38 (CH), 128.57 (2CH), 128.46 (2CH), 125.78 (CH), 60.74 (CH_2), 13.42 (CH_3); LRMS m/z (rel inten) 204 (M^+, 19), 159 (15), 105 (100).

Preparation of 32a. To a solution of 2-methoxyfuran (1.0 g, 10.2 mmol) in dichloromethane (80 mL) was added PCC (3.3 g, 15.3 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 1 h. Cyclopentadiene (1.4 g, 20.4 mmol) was added to the solution, and the reaction mixture was stirred at 25 °C for 10 h. Then, ether (30 mL) was added, and the reaction mixture was filtered through silical gel and Celite. After filtration, the solution was evaporated, and the residue was purified by flash column chromatography to give the *endo* adduct **32a** (0.91 g, 50%): pale yellow oil; IR ($CHCl_3$) 2950, 2940, 1770, 1730 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.30 (d, J = 3.9 Hz, 1H), 6.28−6.23 (m, 2H), 3.76−3.60 (m, 1H), 3.59 (s, 3H), 3.40 (dd, J = 9.8 Hz, J = 3.6 Hz, 1H), 3.27 (brs, 1H), 3.14−3.05 (m, 1H), 1.52−1.50 (m, 1H), 1.37−1.35 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 203.13 (CHO), 172.60 (C═O), 136.03 (CH), 134.98 (CH), 55.38 (CH), 51.80 (CH_3), 49.32 (CH), 49.18 (CH_2), 46.47 (CH), 46.14 (CH); LRMS m/z (rel inten) 180 (M^+, 2), 119 (19), 66 (100); HRMS (EI) calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0780.

General Procedure for the Diels−Alder Reaction of 31b and 31c with Cyclopentadiene. The same reaction conditions and procedure as for the synthesis of **3a**−**d** from the Diels−Alder reaction of **2a**−**d** were applied to the Diels−Alder reaction of **31b** and **31c** with cyclopentadiene to give the *endo* adducts **32b** and **32c** in 80% yield, respectively. Spectral data for **32b**: pale yellow oil; IR ($CHCl_3$) 2970, 1740, 1720, 1200 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.25 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 6.01 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 3.52 (s, 3H), 3.41 (dd, J = 9.9 Hz, J = 3.3 Hz, 1H), 3.14−3.06 (m, 3H), 2.04 (s, 3H), 1.41−1.37 (m, 1H), 1.29−1.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 206.16 (C═O), 173.36 (C═O), 135.77 (CH), 133.26 (CH), 56.05 (CH), 51.24 (CH_3), 48.42 (CH_2), 47.75 (CH), 46.55 (CH), 46.09 (CH), 30.03 (CH_3); LRMS m/z (rel inten) 194 (M^+, 2), 162 (27), 119 (68), 66 (100); HRMS (EI) calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0942.

Spectral data for **32c**: pale yellow oil; yield 78%; IR ($CHCl_3$) 3040, 2945, 1730, 1680 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93−7.90 (m, 2H), 7.57−7.41 (m, 3H), 6.29 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 6.22 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 4.20 (dd, J = 9.9 Hz, J = 3.0 Hz, 1H), 3.93−3.86 (m, 2H), 3.44 (dd, J = 9.9 Hz, J = 3.0 Hz, 1H), 3.24 (brs, 2H), 1.54−1.47 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 193.15 (C═O), 172.54 (C═O), 137.63 (C), 134.66 (2CH), 132.45 (CH), 128.43 (2CH), 127.73 (2CH), 60.10 (CH_2), 51.74 (CH), 49.23 (CH), 48.50 (CH_2), 47.34 (CH), 46.79 (CH), 13.83 (CH_3); LRMS m/z (rel inten) 270 (M^+, 5), 197 (35), 159 (57), 105 (100); HRMS (EI) calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1258.

Taking the ^{1}H and ^{13}C NMR Spectral Data of the Final Ozonides 33a + 34a, 33b + 34b, and 33c + 34c. The same reaction conditions and procedure as for synthesis of **4a**−**d** from the ozonolysis of **3a**−**d** were applied to the ozonolysis of **32a**−**c**. Spectral data for **33a** + **34a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.93 (s, 15% of 1H), 9.86 (s, 15% of 1H), 9.59 (s, 85% of 1H), 6.52 (s, 85% of 1H), 5.88 (s, 85% of 1H), 5.72 (s, 15% of

1H), 3.79 (s, 85% of 3H), 3.69 (s, 15% of 3H), 3.48−2.78 (m, 4H), 2.32−2.16 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 201.38 (15% of CHO), 200.83 (85% of 1CHO), 200.04 (15% of 1CHO), 171.52 (85% of 1C═O), 124.03 (15% of 1C), 103.89 (15% of 1CH), 103.49 (85% of 1CH), 101.50 (85% of 1CH), 55.03 (15% of 1CH), 53.89 (15% of $1CH_3$), 52.55 (85% of 1CH), 52.23 (85% of CH_3), 51.65 (15% of 1CH), 48.94 (15% of 1CH), 48.07 (15% of 1CH), 47.43 (85% of 1CH), 46.12 (85% of 1CH), 45.01 (85% of 1CH), 27.82 (15% of $1CH_2$), 27.82 (85% of $1CH_2$).

Spectral data for **33b** + **34b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 70% of 1H), 9.90 (s, 30% of 1H), 5.76 (s, 30% of 1H), 5.65 (s, 70% of 1H), 3.81 (s, 30% of 3H), 3.63 (s, 70% of 3H), 3.48−2.80 (m, 4H), 2.37 (s, 70% of 3H), 2.29−2.00 (m, 2H), 1.68 (s, 30% of 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 206.08 (70% of 1C═O), 204.53 (70% of 1CHO), 202.58 (30% of 1CH), 171.02 (30% of 1C═O), 124.17 (70% of 1C═O), 110.07 (30% of 1C), 104.74 (30% of 1CH), 103.86 (70% of 1CH), 55.96 (70% of 1CH), 54.01 (70% of $1CH_3$), 52.15 (30% of 1CH), 50.31 (30% of 1CH), 49.64 (70% of 1CH), 49.52 (30% of $1CH_3$), 48.13 (70% of 1CH), 47.78 (70% of 1CH), 47.02 (30% of 1CH), 46.14 (30% of 1CH), 29.94 (70% of $1CH_3$), 29.77 (70% of $1CH_2$), 28.46 (30% of $1CH_2$), 13.63 (30% of $1CH_3$).

Spectral data for **33c** + **34c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.11 (s, 75% of 1H), 10.02 (s, 25% of 1H), 7.95−7.43 (m, 5H), 6.08 (s, 25% of 1H), 5.69 (s, 75% of 1H), 4.22−4.15 (m, 25% of 2H), 3.85−3.67 (m, 75% of 2H), 3.64−2.78 (m, 4H), 2.60−2.10 (m, 2H), 0.94−0.81 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 204.30 (75% of 1CH), 202.49 (25% of 1CH), 198.12 (75% of 1C═O), 170.03 (25% of 1C═O), 136.96 (75% of 1C), 133.00 (75% of 1CH), 130.47 (25% of 1CH), 128.43 (75% of 1CH), 128.28 (25% of 1CH), 128.22 (75% of 1CH), 127.96 (25% of 1CH), 126.82 (25% of 1C), 123.91 (75% of 1C), 110.80 (25% of 1C), 104.83 (25% of 1CH), 103.72 (75% of 1CH), 62.67 (75% of $1CH_2$), 60.57 (25% of $1CH_2$), 53.57 (25% of 1CH), 51.94 (75% of 1CH), 51.01 (75% of 1CH), 50.81 (25% of 1CH), 49.76 (75% of 1CH), 48.68 (75% of 1CH), 47.60 (25% of 1CH), 46.52 (25% of 1CH), 29.86 (75% of $1CH_2$), 28.37 (25% of $1CH_2$), 14.04 (75% of $1CH_3$), 13.25 (25% of $1CH_3$).

Formation of Tetraacetal Tetraoxa Cage Compounds 35a−c and Triacetal Trioxa Cages 36b and 36c. The same reaction conditions and procedure as for the synthesis of **21a−d** from the ozonolysis of **3a−d** were applied to the ozonolysis of **32a−c**. Spectral data of **35a**: white waxy solid; yield 80% mp 77−78 °C; IR ($CHCl_3$) 2970, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (d, J = 5.7 Hz, 1H), 5.59 (d, J = 6.3 Hz, 1H), 5.46 (d, J = 6.3 Hz, 1H), 3.72−3.63 (m, 1H), 3.46 (s, 3H), 3.13 (dd, J = 10.7 Hz, J = 7.5 Hz, 1H), 3.00−3.63 (m, 1H), 2.80−2.76 (m, 1H), 1.95−1.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 131.60 (C), 108.67 (CH), 103.19 (CH), 102.47 (CH), 53.40 (CH), 52.35 (CH_3), 51.86 (CH), 45.04 (CH), 44.60 (CH), 29.33 (CH_2); LRMS m/z (rel inten) 212 (M^+, 13), 183 (100); HRMS (EI) calcd for $C_{10}H_{12}O_2$ 212.0685, found 212.0693.

Spectral data for **35b**: pale yellow oil; yield 66%; IR ($CHCl_3$) 2970, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (d, J = 6.3 Hz, 1H), 5.50 (d, J = 6.3 Hz, 1H), 3.48 (s, 3H), 3.25−3.16 (m, 2H), 2.99−2.88 (m, 2H), 1.95−1.75 (m, 2H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 131.02 (C), 116.60 (C), 102.82 (CH), 102.55 (CH), 55.88 (CH), 54.36 (CH), 51.68 (CH_3), 45.53 (CH), 44.60 (CH), 29.19 (CH_2), 24.96 (CH_3); LRMS m/z (rel inten) 226 (M^+, 6), 195 (100); HRMS (EI) calcd for $C_{11}H_{14}O_5$ 226.0841, found 226.0822.

Spectral data for **35c**: white waxy solid; yield 67%; mp 123−124.5 °C; IR ($CHCl_3$) 2980, 1330, 1050 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52−7.48 (m, 2H), 7.38−7.30 (m, 3H), 5.73 (d, J = 6.3 Hz, 1H), 5.69 (d, J = 6.6 Hz, 1H), 3.95−3.87 (m, 2H), 3.43−3.28 (m, 2H), 3.07−2.93 (m, 2H), 1.98−1.94 (m, 1H), 1.84−1.76 (m, 1H), 1.27 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 140.61 (C), 131.28 (C), 128.19 (CH), 127.99 (2CH), 125.22 (2CH), 116.68 (C), 103.17 (CH), 102.93 (CH), 60.25 (CH_2), 58.76 (CH), 54.62 (CH), 45.62 (CH), 44.66 (CH), 29.10 (CH_2), 15.29 (CH_3); LRMS m/z (rel inten) 302 (M^+, 2), 197 (29), 105 (100); HRMS (EI) calcd for $C_{17}H_{18}O_5$ 302.1154, found 302.1150.

Spectral data for **36b**: pale yellow oil; yield 9%; IR ($CHCl_3$) 2970, 1680, 1150 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (d, J = 4.8 Hz, 1H), 5.44 (d, J = 6.9 Hz, 1H), 3.70 (s, 3H), 3.14−2.97 (m, 3H), 2.51 (dd, J = 5.3 Hz, J = 2.4 Hz, 1H), 1.62−1.58 (m, 1H), 1.55 (s, 3H), 1.29−1.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 172.25 (C═O), 107.27 (C), 100.46 (CH), 95.71 (CH), 51.59 (CH_3), 47.11 (CH), 45.56 (CH), 44.80 (CH), 40.49 (CH), 24.76 (CH_2), 22.66 (CH_3); LRMS m/z (rel inten) 226 (M^+, 3), 180 (36), 127 (94), 99 (100); HRMS (EI) calcd for $C_{11}H_{14}O_5$ 226.0841, found 226.0872.

Spectral data for **36c**: white waxy solid; yield 8%; mp 120−121 °C; IR ($CHCl_3$) 2990, 1730, 1225, 1050 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.32 (m, 5H), 5.70 (d, J = 6.9 Hz, 1H), 5.67 (d, J = 4.8 Hz, 1H), 3.96−3.87 (m, 1H), 3.54−3.42 (m, 2H), 3.29−3.16 (m, 2H), 2.55−2.50 (m, 1H), 1.72−1.68 (m, 1H), 1.37−1.30 (m, 1H), 0.69 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 171.40 (C═O), 138.36 (C), 128.51 (CH), 127.84 (2CH), 125.02 (2CH), 106.78 (C), 101.13 (CH), 95.82 (CH), 60.04 (CH_2), 48.83 (CH), 45.56 (CH), 44.95 (CH), 40.26 (CH), 24.85 (CH_2), 13.16 (CH_3); LRMS m/z (rel inten) 302 (M^+, 7), 197 (100); HRMS (EI) calcd for $C_{17}H_{18}O_5$ 302.1154, found 302.1153.[11]

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **4a−d**, **9a**, **9b**, **16a−d, 19a**, **19b**, **27a**, **27b**, **35a−c**, **36b** and **36c** and ORTEP diagram of **36C** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.