Exceptionally Stable Ozonides. Influence of Methyl Substituents on the Course of Cyclopentene Ozonolyses and on the Reactivities of Ozonides

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Ozonolyses of 1,2,3,3,4,4,5,5-octamethyl- (**1a**), 1,2,3,3,4,4,5-heptamethyl- (**1b**), and 1,2,3,3,4,4-hexamethyl cyclopentenes (**1c**) in methanol did not yield the ordinary hemiperacetals but gave the corresponding ozonides **6a–c** instead. The ozonides **6a,b** were extremely stable and remained intact even when refluxed with triphenylphosphine in tetrahydrofuran. Cycloreversion of the primary ozonides from unsymmetrically substituted 1,2,3,3-tetramethylcyclopentene (**1d**) and 1,5,5-trimethylcyclopentene (**1g**) was highly regioselective to yield the intermediate ω-oxo carbonyl oxides with the geminal methyl groups remote from the carbonyl oxide groups.

The basic mechanism that describes the ozonolysis of an alkene to produce a 1,2,4-trioxolane (secondary ozonide) evolved during the 1950's and is known as the Criegee mechanism.[1] It consists of three steps. The first step is a [3 + 2] cycloaddition reaction of ozone with the alkene leading to formation of a primary ozonide (1,2,3-trioxolane). The second is a cycloreversion process of the primary ozonide to provide the transient carbonyl oxide and a stable carbonyl compound, which may proceed in two different ways in the case of unsymmetrically substituted alkenes. Finally, recombination of the carbonyl oxide and the carbonyl compound gives the 1,2,4-trioxolane. In alcohols, however, the carbonyl oxide is generally captured by the solvent to yield the corresponding hemiperacetals.[1] We report now that in ozonolyses of highly methylated cyclopentenes the methyl substituents exert a remarkable influence on the course of the reaction and also on the reactivity of the resulting ozonides toward triphenylphosphine.

Results and Discussion

Ozonolysis of Highly Methylated Cyclopentenes. Ozonolyses of octamethylcyclopentene (**1a**) in ether as well as in CF₃CH₂OH/CH₂Cl₂ (1:4, v/v) or MeOH/ether (1:2, v/v) gave the corresponding ozonide **6a** in isolated yields of 68–72%; no evidence for the formation of the corresponding epoxide **3a**[2a] or its sequential products such as octamethylcyclopentanone[2b] was obtained (Scheme 1). The structure of the monoozonide **6a** was unambiguously determined by X-ray analysis.[3]

In analogy to the ozonolysis of compound **1a**, Criegee and co-workers[4] reported that the reaction of 1,2-dimethylcyclopentene (**1e**) with ozone in pentane results in

Scheme 1
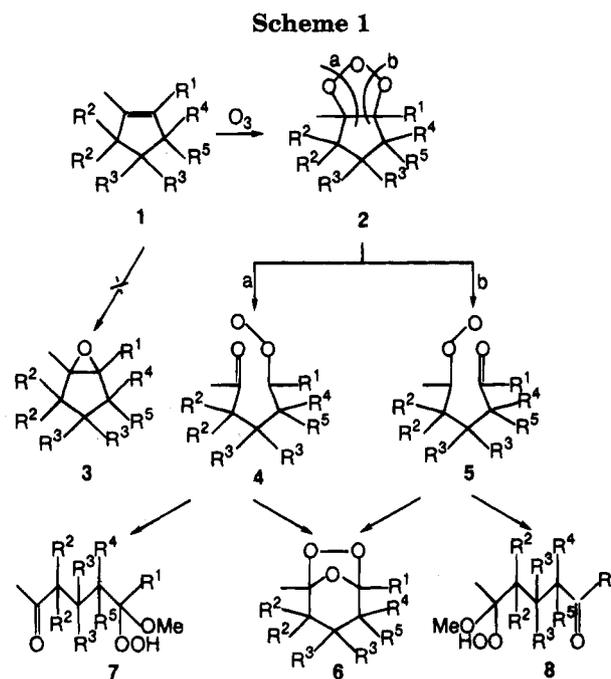
R¹	R²	R³	R⁴	R⁵	1-8	product ratio in MeOH		
						7	6	8
Me	Me	Me	Me	Me	a	—	100	—
Me	Me	Me	Me	H	b	—	100	—
Me	Me	Me	H	H	c	—	100	—
Me	Me	H	H	H	d	100	—	—
Me	H	H	H	H	e	100	—	—
H	Me	H	H	H	f	100	—	—
H	H	H	H	H	g	10	—	90[13]

a quantitative formation of the corresponding ozonide **6e**. We observed that ozonide **6e** was also obtained in ether in 84% yield. In contrast, capture of the carbonyl oxide intermediate **4e** by the solvent predominated in methanol, and the expected α-methoxyalkyl hydroperoxide **7e** was obtained in 86% yield (Scheme 1).[5,6]

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® Abstract published in *Advance ACS Abstracts*, July 15, 1994.
(1) (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.
(2) (a) Bailey, P. S.; Hwang, H. H.; Chiang, C.-Y. *J. Org. Chem.* **1985**, *50*, 231. (b) Mayr, H.; Koschinsky, R.; Will, E.; Bäuml, E. *J. Org. Chem.* **1987**, *52*, 1342.
(3) Jerzykiewicz, L. B.; Dziewońska-Baran, D.; Baran, J.; Lis, T. *Acta Crystallogr.* **1993**, *C49*, 400.

(4) Criegee, R.; Blust, G.; Lohaus, G. *Liebigs Ann. Chem.* **1953**, *583*, 2.

In order to understand the remarkably different behavior of the carbonyl oxide intermediates, **4a** and **4e**, toward methanol, we investigated the ozonolyses of 1,2,3,3,4,4,5-heptamethyl- (**1b**), 1,2,3,3,4,4-hexamethyl- (**1c**), and 1,2,3,3-tetramethyl cyclopentenes (**1d**) (Scheme 1). Ozonolyses in ether at −70 °C gave the corresponding ozonides **6b–d** in yields of 75%, 72%, and 73%, respectively. Also, in MeOH–ether (1:2, v/v) the reactions of the cyclopentenes **1b** and **1c** with ozone at −70 °C resulted in the formation of ozonides **6b** (79%) and **6c** (77%), respectively. In marked contrast, ozonolysis of tetramethylcyclopentene (**1d**) under the same conditions led to the formation of the methanol-derived product **7d**. The hydroperoxide **7d** was labile; however, and evaporation of the solvent was accompanied by partial decomposition to diketone **10d**. The ozonolysis of **1d** was, therefore, performed in CD$_3$OD and the ^{1}H- and ^{13}C-NMR spectra of the CD$_3$OD solution obtained in this way indicated the presence of hydroperoxide **7d**-d_4 as the sole detectable product.

Thus, carbonyl oxide intermediates, **4a–c** and/or **5b,c**, seem to undergo intramolecular cycloaddition even in methanol, while the sterically less-congested carbonyl oxides **4d,e** can be efficiently captured by the solvent. Of particular interest is the different behavior of the substrates **1c** and **1d**, which suggests that the presence of the methyl substituents at the 4-position is also indispensable for the formation of ozonide in methanol.

The formation of ozonides **6a–c** in methanol[7,8] is explained by the *gem*-dimethyl effect[9] which obviously accelerates intramolecular cycloaddition to such an extent that capture of the carbonyl oxide by methanol cannot compete. Two modes of cycloreversion of the unsymmetrically substituted primary ozonide **2d** are possible. Each pathway leads to a different carbonyl oxide, **4d** (path a in Scheme 1) or **5d** (path b in Scheme 1). Exclusive formation of the methanol-derived product **7d** from **1d**, however, implies that presence of two methyl groups in one allylic position of the substrate olefin causes a regioselective cleavage of the primary ozonide **2d** to give the carbonyl oxide intermediate **4d** with the *geminal* methyl groups remote from the carbonyl oxide fragment.[10,11]

In order to estimate the extent of the directive effect of the allylic *gem*-dimethyl group on the regioselectivity of the cleavage of the primary ozonide, we studied the ozonolysis of 1,5,5-trimethylcyclopentene (**1f**). It is well-established that trialkyl-substituted alkenes react with ozone to produce an aldehyde and a ketone O-oxide predominantly, since electron-donating alkyl substituents stabilize the carbonyl oxide.[1a,12] Consistent with this, Griesbaum and Kiesel[13] have found that ozonolysis of 1-methylcyclopentene (**1g**) in methanol proceeds mainly

(5) Consistent with this, ozonolysis of 3,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide in methanol gives the corresponding hemiperacetal in high yield.[6]

(6) Criegee, R.; Lohaus, G. *Liebigs Ann. Chem.* **1953**, *583*, 12.

(7) A similar trend has been observed for the ozonolyses of highly-substituted cyclobutene derivatives, hexamethyldewarbenzene,[8a] and 3,3,4-trisubstituted 1,2-diphenylcyclobutenes in methanol.[8b]

(8) (a) Junker, H.-N.; Schäfer, W.; Niedenbrück, H. *Chem. Ber.* **1967**, *100*, 2508. (b) Reinhardt, H. G.; Doorakian, G. A.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 5934.

(9) (a) Smith, S. W.; Newman, M. S. *J. Am. Chem. Soc.* **1968**, *90*, 1249, 1253. (b) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976.

(10) Criegee reported a similar directing effect of the methyl groups during ozonolysis of 1,2,3,3-tetramethyl-4-acetylcyclohexene.[11a]

(11) (a) Criegee, R. *Chem. Ber.* **1975**, *108*, 743. (b) For the steric effects see also: Griesbaum, K.; Volpp, W. *Chem. Ber.* **1988**, *121*, 1795.

Scheme 2

a; R^1 = R^2 = R^3 = R^4 = Me   **b**; R^1 = R^2 = R^3 = Me, R^4 = H

c; R^1 = R^2 = Me, R^3 = R^4 = H   **d**; R^1 = Me, R^2 = R^3 = R^4 = H

e; R^1 = R^2 = R^3 = R^4 = H

by the ketone O-oxide **5g** (the ratio of contribution of **4g** and **5g** is ca. 1:9) (Scheme 1). Thus, in the case of compound **1f**, the electronic effect of the methyl substituent at the 1-position and the steric effect of the *geminal* methyl groups at the 5-position should direct in opposite sense and both of the possible carbonyl oxide intermediates, **4f** and **5f**, may competitively participate.

The sole isolable product obtained from the ozonolysis of **1f** in MeOH–ether was hydroperoxide **7f**, however, which is derived from capture of **4f** by methanol (Scheme 1). It is thus suggested that in the cycloreversion of the primary ozonide **2f**, the directive effect of the allylic methyl groups is still decisive, thereby producing the less-hindered carbonyl oxide **4f** predominantly. However, the reason for this strong directive effect of the allylic methyl substituents is obscure.

Reduction of Cyclopentene Ozonides. Ozonides are well known to be easily reduced by various reductants.[1] Treatment of ozonide **6a** with Zn/acetic acid in ether at 20 °C[14] resulted in the recovery of ozonide **6a**. In refluxing ether, however, ozonide **6a** was efficiently reduced to diketone **10a** with Zn/CH$_3$CO$_2$H during 3 h. Under the latter conditions, the diketones **10b,c** were obtained from the ozonides **6b,c**. Hydrogenation catalyzed by palladium on activated carbon under atmospheric pressure gave also diketone **10a** quantitatively.

Surprisingly, ozonides **6a,b** could not be reduced by triphenylphosphine in CDCl$_3$ at 20 °C, in refluxing ether during several days, or in refluxing tetrahydrofuran. Under similar conditions the sterically-congested monoozonide from hexamethyldewarbenzene and also 1,2,3-triphenylindene ozonide were reduced to the corresponding diketones. Compounds **6a,b** are, therefore, the least reactive ozonides toward triphenylphosphine presently known.

In contrast to **6a,b**, hexamethylcyclopentene ozonide (**6c**) was efficiently reduced to the corresponding diketone **10c** by triphenylphosphine in refluxing tetrahydrofuran. The reaction of the less-hindered ozonides **6d,e** with triphenylphosphine was very fast; in CDCl$_3$ the ozonides **6d,e** were rapidly deoxygenated at 20 °C to give the corresponding diketones **10d,e** (Scheme 2). Competitive

(12) (a) Bunnelle, W. H.; Isbell, T. A. *J. Org. Chem.* **1992**, *57*, 729. (b) Sugiyama, T.; Yamakoshi, H.; Nojima, M. *J. Org. Chem.* **1993**, *58*, 4212.

(13) Griesbaum, K.; Kiesel, G. *Chem. Ber.* **1989**, *122*, 145.

(14) Harries, C.; Haarmann, R. *Chem. Ber.* **1915**, *48*, 32.

Scheme 3

Table 1. Heats of Formation of Ozonides 6a–e, Phosphoranes 9a–e, and 1,6-Dipoles 11a–e Calculated by PM3 Semiempirical Method (kcal/mol)[a]

	$\Delta H_f(6)$	$\Delta H_f(9)$	$\Delta H_f(11)$	ΔH_r 6 + Ph₃P → 9	ΔH_r 6 + Ph₃P → 11
a	−96.82	−57.57	−27.98	−50.78	−21.19
b	−96.20	−57.46	−28.58	−51.29	−22.41
c	−94.93	−58.27	−32.47	−53.37	−27.57
d	−88.45	−56.39	−29.28	−57.97	−30.86
e	−81.78	−49.26	−22.35	−57.51	−30.60

[a] The heat of formation of triphenylphosphine was 90.03 kcal/mol.

experiments showed the reactivity of ozonides toward triphenylphosphine to follow the sequence **1a,1b** < **1c** < **1d,1e**.

For the deoxygenation of ozonides with triphenylphosphine the mechanisms depicted in Schemes 2[15] and 3[16] are conceivable. According to semiempirical PM3 calculations the reaction of triphenylphosphine with ozonide **6** is exothermic to give either the phosphorane **9** or the zwitterionic intermediate **11**. Since the calculations refer to the gas phase, the difference of enthalpy calculated for the first step of the two different pathways is irrelevant, as the solvent will considerably stabilize the dipolar intermediate **11** relative to **9**. Table 1 shows, however, that for both mechanisms a decrease of exothermicity with increasing number of methyl groups is calculated. The differences in reaction enthalpies thus reflect the relative heights of the barriers of the reductions with triphenylphosphine.

Conclusion. The stabilities of 6,7,8-trioxabicyclo-[3.2.1]octanes **6** (cyclopentene ozonides) are highly increased by methyl substitution as seen from their rates of reduction. The *gem*-dimethyl effect is suggested to be responsible for fast cyclization of the highly-methylated intermediate carbonyl oxides and the failure to trap **4a–c** or **5b,c** by methanol. The semiempirical calculations suggest that the increase of conformational strain during lengthening the O–O bond is greater in the highly methyl-substituted compounds **6**. As a result, the ozonides **6a** and **6b** are so stable that they do not react even with triphenylphosphine in refluxing THF.

Experimental Section

General. ¹H and ¹³C NMR spectra were obtained in CDCl₃ (unless otherwise noted) with SiMe₄ as standard. 1,2,3,3,4,4,5,5-Octamethylcyclopentene (**1a**),[17] 1,2,3,3,4,4,5-heptamethylcyclopentene (**1b**),[17] 1,2,3,3,4,4-hexamethylcyclopentene (**1c**),[17] 1,2,3,3-tetramethylcyclopentene (**1d**),[18] 1,2-dimethylcyclopentene (**1e**) (in admixture with 7% of 2,3-dimethylcyclopentene),[19]

(15) (a) Carles, J.; Fliszär, S. *Can. J. Chem.* **1970**, *48*, 1309. (b) In this connection, the corresponding phosphorane is certainly produced in the reduction of dioxetane with triphenylphosphine. On warming, the phosphorane eliminates the phosphine oxide to yield the epoxide: Bartlett, P. D.; Baumstark, A. L.; Landis, M. E.; Lerman, C. L. *J. Am. Chem. Soc.* **1974**, *96*, 5267.

(16) A reviewer has kindly suggested this alternative mechanism.

(17) Klein, H.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1027.

(18) Horn, D. E.; Krapcho, A. P.; Grenon, B. Y. *J. Org. Chem.* **1979**, *44*, 454.

and 1,5,5-trimethylcyclopentene (**1f**),[20] were prepared by the reported methods. The method of ozonolysis was previously described.[12b]

Ozonolyses of Cyclopentenes 1a–c in MeOH–Ether. Ozonolysis of compound **1a** is representative. A MeOH–ether solution (15 mL, 1:2 v/v) of compound **1a** (235 mg, 1.30 mmol) was treated with ozone (2.61 mmol, 2 equiv) at −70 °C. After ether (50 mL) was added, the organic layer was washed with aqueous NaHCO₃ and then with saturated brine, and the solvent was evaporated (rt, 15 mmHg). The ¹H NMR spectra of the crude products showed the formation of small amounts of a methanol-derived product (δ 3.37). The residue was separated by column chromatography (column 2.0 × 60 cm; 40 g of silica gel). Elution with ether–hexane (5:95) gave ozonide **6a** (215 mg, 72% yield). Further elution with ether–hexane (1:4 to 1:1) yielded 24 mg of a complex mixture of unidentified products.

1,2,2,3,3,4,4,5-Octamethyl-6,7,8-trioxabicyclo[3.2.1]-octane (6a): mp 101–103 °C (from hexane); ¹H NMR (CCl₄) δ 0.79 (s, 3 H), 0.90 (s, 6 H), 1.08 (s, 6 H), 1.18 (s, 3 H), 1.38 (s, 6 H); ¹³C NMR δ 17.86, 21.98, 22.76, 24.61, 25.31, 41.18, 43.19, 114.34; MS *m/z* 228 (M⁺). Anal. Calcd for C₁₃H₂₄O₃: C, 68.38; H, 10.60. Found: C, 68.22; H, 10.71.

1,2,2,3,3,4,5-Heptamethyl-6,7,8-trioxabicyclo[3.2.1]-octane (6b): mp 55–60 °C; ¹H NMR (CCl₄) δ 0.80 (s, 3 H), 0.87 (s, 3 H), 0.92 (d, *J* = 7 Hz, 3 H), 0.97 (s, 3 H), 1.10 (s, 3 H), 1.35 (s, 3 H), 1.38 (s, 3 H), 1.78 (q, *J* = 7 Hz, 1 H); ¹³C NMR δ 11.10, 17.88, 19.74, 19.81, 20.10, 22.81, 25.36, 38.92, 42.68, 43.82, 110.67, 113.98. Anal. Calcd for C₁₂H₂₂O₃: C, 67.26; H, 10.35. Found: C, 66.94, H, 10.45.

1,2,2,3,3,5-Hexamethyl-6,7,8-trioxabicyclo[3.2.1]-octane (6c): oil; ¹H NMR (CCl₄) δ 0.88 (s, 3 H), 0.95 (s, 3 H), 1.04 (s, 3 H), 1.37 (s, 3 H), 1.50 (s, 6 H), 1.63 (d, *J* = 14 Hz, 1 H), 1.93 (d, *J* = 14 Hz, 1 H); ¹³C NMR δ 17.67, 19.09, 21.05, 22.99, 28.02, 28.10, 35.42, 41.57, 46.37, 108.18, 114.29. Anal. Calcd for C₁₁H₂₀O₃: C, 65.97; H, 10.06. Found: C, 66.19; H, 10.10.

Ozonolysis of 1,2,3,3-Tetramethylcyclopentene (1d) in Ether. A slow stream of ozone (4 mmol) was passed into a solution of **1d** (496 mg, 3.99 mmol) in ether (15 mL) at −70 °C. After evaporation of the solvent, ozonide **6d** (499 mg, 73%) was isolated by column chromatography on silica gel (elution with ether–hexane, 3:97).

1,2,2,5-Tetramethyl-6,7,8-trioxabicyclo[3.2.1]octane (6d): oil; ¹H NMR (CCl₄) δ 0.91 (s, 3 H), 1.03 (s, 3 H), 1.31 (s, 3 H), 1.38 (s, 3 H), 1.5–2.3 (m, 4 H); ¹³C NMR δ 16.47, 20.86, 23.01, 25.26, 31.92, 31.94, 36.62, 108.56, 113.37. Anal. Calcd for C₉H₁₆O₃: C, 62.77; H, 9.36. Found: C, 62.99; H, 9.56.

Ozonolysis of Compound 1d in MeOH–Ether. A slow stream of ozone (1.67 mmol) was passed into a solution of **1d** (207 mg, 1.67 mmol) in MeOH–ether (13 mL, 10:3) at −70 °C. After evaporation of the solvent, the products were separated by column chromatography on silica gel. Elution with ether–hexane (2:3) gave a 2:1 mixture of hydroperoxide **7d** and diketone **10d** (124 mg), which could not be separated from each other.

3,3-Dimethyl-6-hydroperoxy-6-methoxy-2-heptanone (7d) (in admixture with 30% of diketone 10d): oil; ¹H NMR (CCl₄) δ 0.9–1.2 (m, 4 H), 1.13 (s, 3 H), 1.23 (s, 3 H), 1.53 (s, 3 H), 2.13 (s, 3 H), 3.23 (s, 3 H), 8.98 (br s, 1 H); IR 3600–3100, 2960, 1690, 1360, 1200, 1100, 840 cm⁻¹.

Ozonolysis of Compound 1d in CD₃OD. In a NMR tube compound **1d** (31 mg, 0.25 mmol) dissolved in CD₃OD (1 mL) was treated with 1.2 equiv of ozone at -70 °C. The ¹H- and ¹³C-NMR spectra indicated a quantitative formation of hydroperoxide **7d-*d₄***: ¹H NMR δ 0.9–1.2 (m, 4 H), 1.13 (s, 3 H), 1.27 (s, 3 H), 1.57 (s, 3 H), 2.13 (s, 3 H); ¹³C NMR δ 20.16, 25.39, 25.60, 26.11, 32.48, 35.79, 108.03, 217.30 (the signal attributable to the CD₃O–carbon could not be defined due to the presence of CD₃OD). A solution of triphenylphosphine (100 mg, 1.5 equiv) in CDCl₃ (0.5 mL) was added, and the mixture was kept at room temperature for 1 h. The ¹H NMR spectrum indicated a quantitative formation of diketone **10d**, which was

(19) Büchi, G.; Chu, P.-S. *Tetrahedron* **1981**, *37*, 4509.

(20) Fadel, A.; Salaün, J. *Tetrahedron* **1985**, *41*, 413.

isolated by column chromatography on silica gel (elution with ether–hexane, 1:1). 3,3-Dimethyl-2,6-heptanedione (**10d**)[21] was an oil: ^{1}H NMR (CCl₄) δ 1.08 (s, 6 H), 1.5–1.9 (m, 2 H), 2.05 (s, 6 H), 2.1–2.4 (m, 2 H); ^{13}C NMR δ 24.21, 24.99, 29.88, 32.77, 38.92, 46.86, 208.05, 213.33; IR 1700, 1350, 1150, 1120 cm⁻¹.

Ozonolysis of 1,2-Dimethylcyclopentene (1e) in Ether. A slow stream of ozone (1 equiv) was passed into an ether solution (15 mL) of **1e** (93% pure, 205 mg, 1.98 mmol) at −70 °C. After evaporation of the solvent, the residue was separated by column chromatography on silica gel. Elution with ether–hexane (1:9) gave 1,5-dimethyl-6,7,8-trioxabicyclo[3.2.1]octane (**6e**)[4] as an oil (241 mg, 84%): ^{1}H NMR δ 1.38 (s, 6 H), 1.5–1.9 (m, 6 H).

Ozonolysis of Compound 1e in MeOH–Ether. A MeOH–ether solution (15 mL, 1:3) of **1e** (93% pure, 192 mg, 1.86 mmol) was treated with 1 equiv of ozone at −70 °C. After evaporation of the solvent, the residue was separated by column chromatography on silica gel. Elution with ether–hexane (1:1) gave 6-hydroperoxy-6-methoxy-2-heptanone (**7e**) (281 mg, 86%). Treatment of **7e** with 1 equiv of triphenylphosphine in CH₂Cl₂ at rt for 2 h, followed by column chromatography on silica gel (elution with ether–hexane, 2:3) gave heptane-2,6-dione (**10e**) (189 mg, 94% yield). Heptane-2,6-dione (**10e**): mp 27–30 °C (lit.[22] mp 29–32 °C); ^{1}H NMR δ 1.5–2.0 (m, 2 H), 2.05 (s, 6 H), 2.2–2.5 (m, 4 H); IR 2930, 1705, 1350, 1155, 960 cm⁻¹.

6-Hydroperoxy-6-methoxy-2-heptanone (7e): oil; ^{1}H NMR δ 1.23 (s, 3 H), 1.5–1.9 (m, 4 H), 2.10 (s, 3 H), 2.2–2.6 (m, 2 H), 3.24 (s, 3 H), 8.33 (s, 1 H); ^{13}C NMR δ 16.86, 17.52, 21.33, 32.99, 42.31, 50.54, 108.92, 208.63; IR 3600–3100, 2950, 1700, 1365, 1100, 1060 cm⁻¹. Anal. Calcd for C₈H₁₆O₄: C, 54.53; H, 9.15. Found: C, 54.28; H, 8.92.

Ozonolysis of 1,5,5-Trimethylcyclopentene (1f) in Ether. A slow stream of ozone was passed into an ether (15 mL) solution of **1f** (78 mg, 0.71 mmol) at −70 °C. After evaporation of the solvent, the residue was separated by column chromatography on silica gel. Elution with ether–hexane (5:95) gave the ozonide **6f** (65 mg, 58%).

1,2,2-Trimethyl-6,7,8-trioxabicyclo[3.2.1]octane (6f): oil; ^{1}H NMR (CCl₄) δ 0.93 (s, 3 H), 1.07 (s, 3 H), 1.38 (s, 3 H), 1.5–2.3 (m, 4 H), 5.58 (br s, 1 H); ^{13}C NMR δ 16.15, 23.15, 25.67, 27.81, 30.80, 37.59, 102.62, 112.48. Anal. Calcd for C₈H₁₄O₃: C, 60.74; H, 8.92. Found: C, 60.55; H, 9.00.

Ozonolysis of 1,5,5-Trimethylcyclopentene (1f) in MeOH–Ether. A slow stream of ozone was passed into a solution of **1f** (78 mg, 0.71 mmol) in MeOH–ether (15 mL, 1:2) at −70 °C. Ether (50 mL) was added, and the reaction mixture was washed with aqueous NaHCO₃ and saturated brine and dried over anhydrous MgSO₄. After evaporation of the solvent, the residue was separated by column chromatography on silica gel. Elution with ether–hexane (2:3) gave the hydroperoxide **7f** (87 mg, 64%).

3,3-Dimethyl-6-hydroperoxy-6-methoxy-2-hexanone (7f): oil; ^{1}H NMR (CCl₄) δ 1.10 (s, 6 H), 1.4–1.7 (m, 4 H), 2.10 (s, 3 H), 3.44 (s, 3 H), 4.5–4.7 (m, 1 H), 9.60 (br s, 1 H); ^{13}C NMR δ 24.26, 24.79, 25.29, 27.22, 34.23, 47.52, 56.12, 108.62, 214.85; IR 3600–3100, 1700, 1460, 1360, 1100 cm⁻¹. Anal. Calcd for C₉H₁₈O₄: C, 56.82; H, 9.54. Found: C, 57.02; H, 9.43.

Reduction of Ozonides 6a–c with Zn/CH₃CO₂H. The reduction of **6a** is representative. An ether (10 mL)–acetic acid (2 mL) solution of **6a** (0.5 g, 2.19 mmol) and Zn (3.0 g) was refluxed for 3 h. After filtration of Zn, the organic layer was washed with water and aqueous NaHCO₃, and dried over

anhydrous MgSO₄. After evaporation of the solvent in *vacuo*, 373 mg (80%) of diketone **10a** was left.

3,3,4,4,5,5-Hexamethylheptane-2,6-dione (10a): mp 67–71 °C; ^{1}H NMR δ 1.17 (s, 18 H), 2.14 (s, 6 H); ^{13}C NMR δ 22.54, 24.51, 29.46, 45.47, 53.97, 214.95; IR 3000, 2980, 2950, 2925, 1695, 1480, 1385, 1355, 1135, 1115, 1105, 1095, 965, 795 cm⁻¹. Anal. Calcd for C₁₃H₂₄O₂: C, 73.54; H, 11.39. Found: C, 73.21; H, 11.37.

3,3,4,4,5-Pentamethylheptane-2,6-dione (10b): oil; ^{1}H NMR (CCl₄) δ 1.08 (s, 3 H), 1.12 (d, *J* = 7 Hz, 3 H), 1.25 (s, 9 H), 2.10 (s, 6 H), 3.05 (q, *J* = 7 Hz, 1 H); ^{13}C NMR δ 14.20, 20.67, 21.74, 22.07, 22.35, 29.45, 31.40, 41.09, 48.92, 53.46, 213.14, 215.07; IR 1720, 1700, 1480, 1360, 1260, 1120, 970 cm⁻¹. Anal. Calcd for C₁₂H₂₂O₂: C, 72.68; H, 11.19. Found: C, 72.44; H, 11.32.

3,3,4,4-Tetramethylheptane-2,6-dione (10c): oil; ^{1}H NMR (CCl₄) δ 1.07 (s, 6 H), 1.12 (s, 6 H), 2.12 (s, 3 H), 2.17 (s, 3 H), 2.50 (s, 2 H); ^{13}C NMR δ 21.32, 22.45, 29.76, 33.05, 38.49, 49.12, 52.93, 209.13, 214.81. Anal. Calcd for C₁₁H₂₀O₂: C, 71.70; H, 10.94. Found: C, 71.64; H, 11.17.

Hydrogenation of Ozonide 6a. Ozonide **6a** (1.50 g, 6.57 mmol) and Pd suspended on carbon (120 mg) was dissolved in 15 mL of methanol. Then, the hydrogenation was conducted under a normal pressure at 20 °C for 30 min. After filtration of Pd/C, the solvent was evaporated to leave diketone **10a** (1.30 g, 93%).

Treatment of a Mixture of Two Ozonides, 6a and 6c, with PPh₃. A THF solution (20 mL) of **6a** (19 mg, 0.085 mmol), **6c** (17 mg, 0.083 mmol), and triphenylphosphine (22 mg, 0.084 mmol) was refluxed for 3 h. After evaporation of the solvent, the residue was separated by column chromatography on silica gel. Elution with ether–hexane (1:20) gave the unreacted ozonide **6a** (19 mg, 100%). Subsequent elution with ether–hexane (1:5) gave diketone **10c** (15 mg, 96%).

Treatment of a Mixture of Two Ozonides, 6a and 6e, with PPh₃. A CDCl₃ solution (0.3 mL) of **6a** (40 mg, 0.18 mmol) and **6e** (25 mg, 0.17 mmol) was admixed with 0.2 mL of a CDCl₃ solution containing PPh₃ (46 mg, 0.18 mmol) in a NMR tube and kept at 20 °C. After 3 h ^{1}H NMR analysis showed the disappearance of the signals attributable to **6e** with concomitant appearance of diketone **10e**. After 24 h the crude products were separated by column chromatography on silica gel. The first fraction (elution with ether–hexane, 5:95) contained the unreacted ozonide **6a** (40 mg, 100%). From the second fraction (elution with ether–hexane, 1:1) was obtained diketone **10e** (10 mg, 46%).

Treatment of a Mixture of Two Ozonides, 6d and 6e, with PPh₃. A solution of **6d** (292 mg, 1.7 mmol), **6e** (245 mg, 1.7 mmol), and triphenylphosphine (450 mg, 1.7 mmol) in benzene (10 mL) was stirred at 20 °C for 1 day. After evaporation of the solvent, the crude products were separated by column chromatography on silica gel. Elution with ether–hexane (1:20) gave a ca. 2:1 mixture of **6d** (^{1}H NMR δ 0.91 (s, 3 H), 1.38 (s, 3 H)) and **6e** (^{1}H NMR δ 1.38 (s, 6 H)) (220 mg). Subsequent elution with ether–hexane (15:85) gave a ca. 1:2 mixture of diketones, **10d** (^{1}H NMR δ 1.08 (s, 6 H), 2.05 (s, 6 H)), and **10e** (^{1}H NMR δ 2.05 (s, 6 H)) (195 mg).

Theoretical Calculations. The theoretical studies were performed by PM3 molecular orbital method.[23] The MOPAC program (QCPE No. 455), which was revised as OS/2 Version 5.01 to adapt for the use of a NECPC computer, was obtained through the Japan Chemistry Program Exchange (JCPE).[24] Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables.

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