Formal [2 + 2 + 2] Cycloaddition of Molecular Oxygen, 1,3-Diketone, and Olefin. Synthesis and Reactions of Cyclic Peroxides

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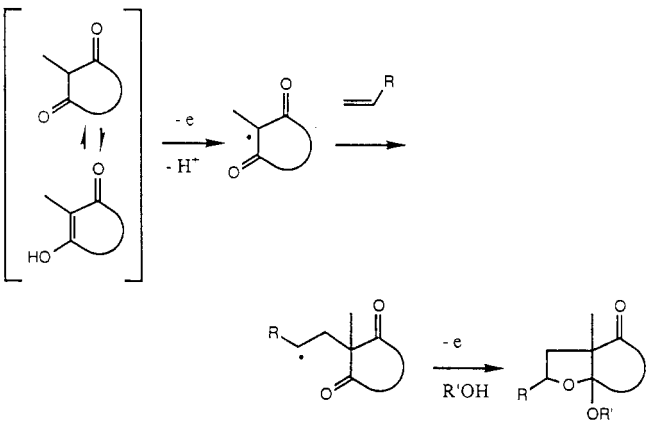
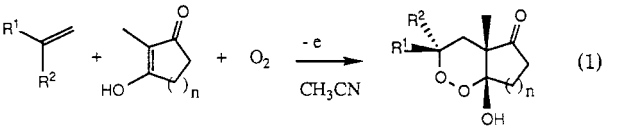
Formal [2 + 2 + 2] cycloaddition of molecular oxygen, 1,3-diketones, and olefins took place by electrochemical oxidation. A catalytic amount of electricity was sufficient for the reaction, and an electroinitiated radical chain mechanism was proposed. The reaction was also initiated by a radical initiator. The resulting cyclic peroxides reacted with acids and some reducing agents such as ferrous sulfate, thiourea, and copper(I) chloride to give oxygen–oxygen bond cleavage products.

Oxidation processes involving reactions with molecular oxygen are of considerable biological and industrial importance, and extensive studies have been performed on this subject.[1] Since the reactivity of triplet molecular oxygen toward organic molecule is generally low, activation of either the organic molecule or molecular oxygen is essential for accomplishing such processes under usual conditions. Much attention has been paid to the activation of molecular oxygen by metal complexes.[2] We have been interested in the activation of organic molecules, especially by electrochemical methods.[3] Carbon radical species are known to react with molecular oxygen spontaneously, and therefore generation of such species provides a useful method for activation of organic molecules. Among various methods developed so far, electrochemical methods provide a convenient and efficient access to carbon radical species. Recently we have found that the electrochemical oxidation of 1,3-diketones gives the corresponding carbon radical under neutral conditions and that this radical smoothly adds to olefins to give another carbon radical species, which is further oxidized electrochemically to give tetrahydrofuran derivatives (Scheme I). We envisioned that the carbon radical generated in this reaction can be trapped by molecular oxygen. It should be noted that the radical of 1,3-diketone is expected not to react with molecular oxygen because the radical carbon is flanked by two electron-withdrawing groups and therefore is very electron-deficient. Thus, molecular oxygen is expected to react selectively with the carbon radical formed by the addition to the olefin.[5] If so, the oxygenation reaction involving carbon–carbon bond formation can be achieved. On the

Scheme I



basis of this idea we have examined the electrochemical oxidation of 1,3-diketones in the presence of both olefins and molecular oxygen. The preliminary report from this laboratory disclosed that the reaction took place smoothly with an initializing amount of electricity to give the formal [2 + 2 + 2] cycloadducts (eq 1).[6] We report herein the full details of this novel type of oxygenation reaction together with some reactions of the resulting cyclic peroxides.



(1)

1 (n = 1)
2 (n = 2)

Results and Discussion

Reaction of Molecular Oxygen, 1,3-Diketone, and Olefin Initiated by Electrolysis. The electroinitiated oxygenations were carried out in acetonitrile using an undivided cell. The initiation was carried out by constant potential electrolysis (1.5 V vs Ag/AgCl) (see the Experimental Section). For example, the reaction of 2-methyl-1,3-cyclopentanedione and styrene gave 1-hydroxy-6-methyl-7-oxo-4-phenyl-2,3-dioxabicyclo[4.3.0]-nonane (**1a**: R^1 = Ph; R^2 = H) in 79% yield, which was identified by ^{1}H NMR, ^{13}C NMR, IR, mass spectrum, and elemental analyses. It is interesting to note that **1a** was obtained as a single stereoisomer. The structure of **1a** was also confirmed by X-ray crystallographic study. Figure 1 is a perspective drawing of the X-ray structure.[7]

(1) Recent works on oxygenation reactions, see, for example: (a) Feldman, K. S.; Simpson, R. E.; Parvez, M. *J. Am. Chem. Soc.* **1986**, *108*, 1328. (b) Roe, A. N.; McPhail, A. T.; Porter, N. A. *Ibid.* **1983**, *105*, 1199. (c) Nelsen, S. F.; Akaba, R. *Ibid.* **1981**, *103*, 2096. (d) Beckwith, A. L. J.; Wagner, R. D. *J. Chem. Soc., Chem. Commun.* **1980**, 485. (e) Saito, I.; Tamoto, K.; Matsuura, T. *Tetrahedron Lett.* **1979**, 2889. (f) Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055. The work on hydroperoxide cyclization related to the present work is also reported: (g) Bartlett, P. A.; Chapuis, C. *J. Org. Chem.* **1986**, *51*, 2799.

(2) For example: *The Role of Oxygen in Chemistry and Biochemistry*; Proceedings of an International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidations; Ando, W., Moro-oka, Y., Eds.; Elsevier: Amsterdam, 1988.

(3) Electro-initiated oxygenation: (a) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1978**, *100*, 5248. (b) Clennan, E. L.; Simmons, W.; Almgren, C. W. *J. Am. Chem. Soc.* **1981**, *103*, 2098.

(4) (a) Yoshida, J.; Sakaguchi, K.; Isoe, S. *Tetrahedron Lett.* **1986**, *27*, 6075. (b) Yoshida, J.; Sakaguchi, K.; Isoe, S. *J. Org. Chem.* **1988**, *53*, 2525.

(5) Light-induced homocoupling of olefins accompanied by dioxygen insertion reaction to give the corresponding 1,2-dioxane has been reported: (a) Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. *Aust. J. Chem.* **1978**, *31*, 1737. (b) Hisatome, M.; Hashiyama, T.; Yamakawa, K. *Tetrahedron Lett.* **1978**, 3759.

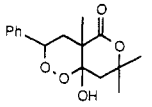
(6) Yoshida, J.; Sakaguchi, K.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 667.

0022-3263/89/1954-3383$01.50/0

Table I. Formal [2 + 2 + 2] Cycloaddition of Molecular Oxygen, 1,3-Diketone, and Olefin Initiated by Electrolysis[a]

1,3-diketone	olefin (equiv)[b]	electricity, F/mol[b]	product[c]	yield,[d] %
2-methyl-1,3-cyclopentanedione	$PhCH{=}CH_2$ (2.0)	0.018	**1a** (R^1 = Ph, R^2 = H)	79
		0.061		0[e]
		0.031		24[f]
	$PhC(Me){=}CH_2$ (2.0)	0.138	**1b** (R^1 = Ph, R^2 = Me) + **1c** (R^1 = Me, R^2 = Ph)	58
	$Me_3SiCH_2CH{=}CH_2$ (5.5)	0.043	**1d** (R^1 = CH_2SiMe_3, R^2 = H)	42
	$EtOCH{=}CH_2$ (7.5)	0.031	**1e** (R^1 = OEt, R^2 = H) + **1f** (R^1 = H, R^2 = OEt)	36
	isoprene (7.6)	0.024	**1g** (R^1 = $CH{=}CH_2$, R^2 = Me) + **1h** (R^1 = Me, R^2 = $CH{=}CH_2$)	54[g]
	2,3-dimethyl-1,3-butadiene (2.0)	0.173	**1i** (R^1 = $C(Me){=}CH_2$, R^2 = H) + **1j** (R^1 = H, R^2 = $C(Me){=}CH_2$)	25
1,3-cyclopentanedione	$PhCH{=}CH_2$ (2.0)	0.048	–	0
2-methyl-1,3-cyclohexanedione	$PhCH{=}CH_2$ (2.0)	0.150	**2** (R^1 = Ph, R^2 = H)	11
3-methyl-2,4-pentanedione	$PhCH{=}CH_2$ (2.0)	0.121	–	0
3,6,6-trimethyl-2,4-dioxotetrahydropyran	$PhCH{=}CH_2$ (2.1)	0.122	**3**[h]	44

[a] The reactions were normally carried out with 1.0 mmol of 1,3-diketone in 10–13 mL of 0.2 M Et_4NOTs/CH_3CN. Electric current was passed through the undivided cell equipped with a carbon rod anode (i.d. 6 mm) and a platinum plate cathode (20 × 30 mm) with bubbling of oxygen at room temperature. [b] Based upon the 1,3-diketone. [c] For the ratio of the products, see the Experimental Section. [d] Isolated yields based upon the 1,3-diketone. [e] The reaction was carried out under an atmosphere of argon. [f] Catechol (0.11 mmol) was added immediately after the electrolysis. [g] Noncyclized hydroperoxide **4** was formed as a byproduct (34% yield). [h] A mixture of three isomers.



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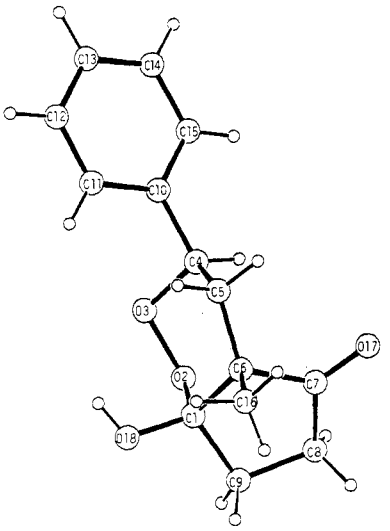


Figure 1.

Table I summarizes the results obtained with some other olefins and diketones. In some cases it was required to repeat the electrolysis several times to complete the reaction, but in all cases only a catalytic amount of electricity with respect to the 1,3-diketone was sufficient for the reaction. Although 1-alkenes such as 1-decene were inactive under the conditions, styrene derivatives, allyltrimethylsilane, and ethyl vinyl ether afforded the corresponding cyclic peroxide in moderate yields. 1,3-Dienes also served as good substrates for the present reaction, but 1,4-addition products (hydroperoxide) were also formed as byproducts. Although cyclic 1,3-diketones reacted smoothly to give the corresponding cyclic peroxides, acyclic 1,3-diketones did not give similar products under the conditions. The reason is not clear at present. The keto lactone (3,6,6-trimethyl-2,4-dioxotetrahdyropyran) also reacted with olefin and molecular oxygen to give the cyclic peroxide. Only

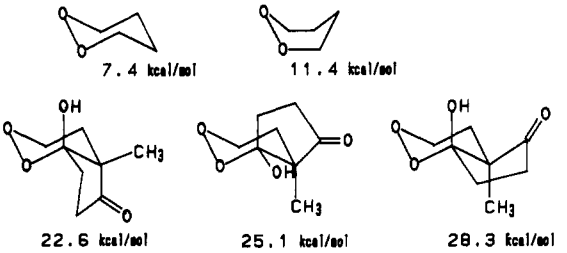
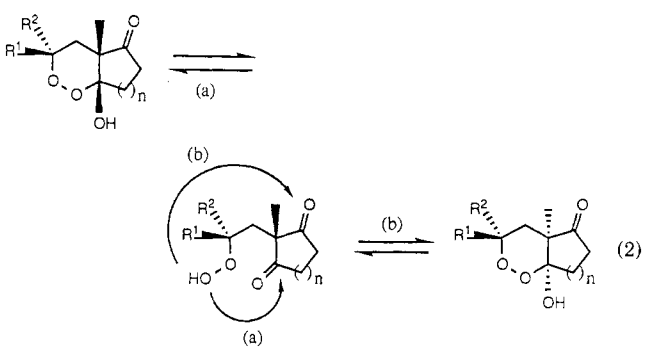


Figure 2.

the keto carbonyl group participated in the cyclization, presumably because of higher reactivity of keto carbonyl group for nucleophilic reactions than that of the ester carbonyl group.

The stereoselectivity of the present reaction seems to be interesting. Styrene and allyltrimethylsilane gave a single stereoisomer (**1a** and **1d**), but α-methylstyrene and ethyl vinyl ether (**1b** and **1c**, **1e** and **1f**) gave a mixture of isomers with respect to the stereochemistry at the carbon bearing the substituent R^1 and R^2. The stereoselectivity of the reaction can be rationalized in terms of the following possible equilibrium between the cyclic peroxide and the open keto hydroperoxide (eq 2). Since the hydroperoxide moiety of the open form can be cyclized with either carbonyl group of the cyclopentanedione part, the stereoselectivity should be determined by the relative thermodynamical stability of the cyclic products.



(2)

(7) Johnson, C. K. ORTEP, Oak Ridge National Laboratory Report, ORNL-TM-3794.

Table II. Formal [2 + 2 + 2] Cycloaddition of Molecular Oxygen, 1,3-Diketone, and Olefin Initiated by AIBN[a]

1,3-diketone	olefin (equiv)[c]	AIBN,[b] equiv[c]	product	yield,[d] %
2-methyl-1,3-cyclopentanedione	$PhCH{=}CH_2$ (2.0)	0.11	**1a**	66
	$PhC(Me){=}CH_2$ (2.0)	0.11	**1b** + **1c**	90
	$Me_3SiCH_2CH{=}CH_2$ (6.0)	0.14	**1d**	73
	$EtOCH{=}CH_2$ (19)	0.13	**1e** + **1f**	65
	isoprene (9.0)	0.12	**1g** + **1h**	12
	$ClCH_2C(Me){=}CH_2$ (8.0)	0.61	**1k** ($R^1 = CH_2Cl$, $R^2 = Me$) + **1l** ($R^1 = Me$, $R^2 = CH_2Cl$)	49
	$C_3H_7C(Me){=}CH_2$ (6.0)	0.43	**1m** ($R^1 = C_3H_7$, $R^2 = Me$) + **1n** ($R^1 = Me$, $R^2 = C_3H_7$)	19
2-methyl-1,3-cyclohexanedione	$PhCH{=}CH_2$ (3.0)	0.10	**2** ($R^1 = Ph$, $R^2 = H$)	40
3,6,6-trimethyl-2,4-dioxotetrahydropyran	$PhCH{=}CH_2$ (4.0)	0.21	**3**	60

[a] The reactions were normally carried out with 1.0 mmol 1,3-diketone in 10 mL of CH_3CN at 50–60 °C. [b] Azobis(isobutyronitrile). [c] Based upon the 1,3-diketone. [d] Isolated yields based upon the 1,3-diketone.

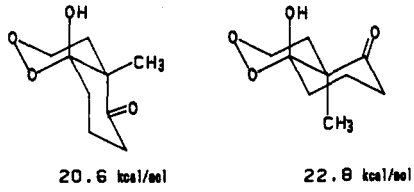
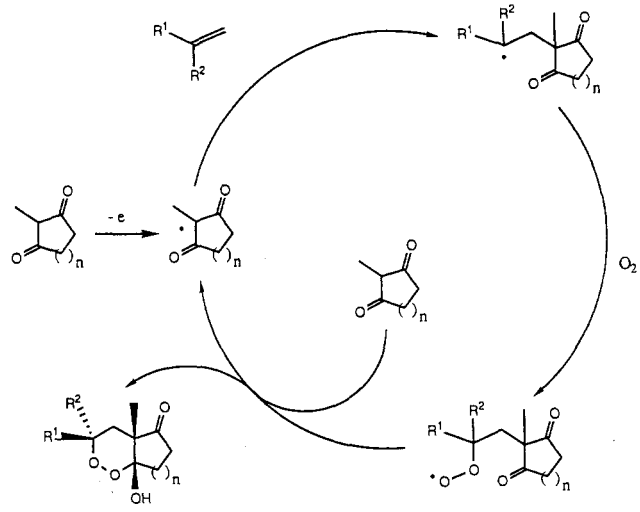


Figure 3.

MM2 calculations[8] were carried out to determine the relative stabilities of the possible stereoisomers of the products (Figure 2). The conformation of 1,2-dioxane ring was examined first, and the calculations indicated that the chair form is much more stable than the boat form. This is consistent with the X-ray structure of **1a**. So, hereafter we consider only the chair form of 1,2-dioxane ring. As for the stereochemistry of the ring junction of 2,3-dioxabicyclo[4.3.0]nonane system, the cis fused isomer is more stable than the trans fused one. The hydroxyl group at the ring junction occupies the axial position preferentially presumably because of the anomeric effect. The methyl group occupies the equatorial position preferentially. Stereochemistry at the carbon bearing the substituent R^1 and R^2 can be explained as follows. The 1,2-dioxane ring exists in the chair conformation. In the case where R^1 = Ph or Me_3SiCH_2 and R^2 = H (**1a** and **1d**), the equatorial isomer is much more stable than the axial one, and therefore the equilibrium lies to the left. This accommodates the X-ray data (Figure 1). In the case where R^1 = OEt and R^2 = H (or R^1 = H and R^2 = OEt) (**1e** and **1f**), however, both the equatorial and the axial isomers seem to be energetically comparable presumably due to the anomeric effect. Thus the product was obtained as a mixture of two stereoisomers. A mixture of two stereoisomers was also obtained in the case where two substituents were attached to the carbon.

The stereochemistry of 2,3-dioxabicyclo[4.4.0]decane derivative **2** warrants a comment. It is known that trans fused [4.4.0]decane is more stable than the cis fused one.[9] In the present case, however, MM2 calculations indicated that the cis fused isomer is more stable than the trans fused isomer. This can be ascribed not to the presence of 1,2-dioxane ring but to the presence of two substituents at the ring junction.[10] As a matter of fact the calculations indicated that *cis*-1-hydroxy-6-methyldecalin is more stable than the trans isomer. Thus the stereochemistry of **2** at the ring junction was determined to be cis.

Scheme II



The following features of the present reaction are important for the elucidation of the mechanism. (1) Under an atmosphere of argon only a trace amount of **1a** was formed, indicating that molecular oxygen is essential for the present reaction. (2) Without electrochemical activation the amount of **1a** produced was negligibly small in the similar range of reaction time. After prolonged reaction time, however, a significant amount of **1a** was formed. (3) The applied potential (1.50 V vs Ag/AgCl) was sufficient for the oxidation of 2-methyl-1,3-cyclopentanedione (E_p = 1.26 V vs Ag/AgCl), but less than the oxidation potential of styrene (E_p = 1.85 V vs Ag/AgCl). Therefore electrochemical oxidation of the 1,3-diketone occurred first, and this reaction seemed to initiate the whole process. (4) Addition of catechol to the reaction mixture immediately after the electrolysis decreased the yield of **1a** dramatically (24%). Therefore a radical chain mechanism is suggested.

On the basis of these facts it is reasonable to propose the following electroinitiated radical chain mechanism for the present reaction (Scheme II). One-electron oxidation of 1,3-diketone (presumably its enol form) followed by removal of proton affords the radical species. This ambident radical behaves as a carbon-centered radical[11] and adds to the olefin. Reaction of the resulting radical with molecular oxygen gives the peroxy radical.[12] Abstraction of hydrogen from another molecule of 1,3-diketone produces the hydroperoxide and regenerates the radical

(8) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.
(9) Chang, S.-J.; McNally, D.; Shary-Tehrany, S.; Hickey, S. M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109.
(10) (a) Allinger, N. L. *J. Org. Chem.* **1956**, *21*, 915. (b) Turner, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2118.
(11) Carbon-radical flanked by two carbonyl groups such as acetylacetonyl radical is known to behave primarily as a C radical in addition reaction with olefin, see: Chow, Y. L.; Buono-Core, G. E. *J. Am. Chem. Soc.* **1986**, *108*, 1234.
(12) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095.

Table III. Reactions of Cyclic Peroxides with Reducing Agents

cyclic peroxide	reducing agent (equiv)[a]	product	yield,[b] %
1a	$FeSO_4$[c] (3.0)	**6a** (R^1 = Ph)	100
	$FeSO_4$[d] (0.24)	**6a**	43
5	$FeSO_4$[c] (3.0)	many products[e]	–
1b + 1c	$FeSO_4$[c] (3.0)	**6b** (R^1 = Me)	25
		+ PhCOMe	44[f]
1d	$FeSO_4$[c] (3.0)	**6b**	24
1a	thiourea[g] (1.2)	**7a** (R^1 = Ph, R^2 = H)	71
5	thiourea[g] (1.1)	–[h]	–
1b + 1c	thiourea[g] (1.1)	**7b** (R^1 = Ph, R^2 = Me)	51
1d	thiourea[g] (1.1)	**7c** (R^1 = CH_2SiMe_3, R^2 = H)	58
1a	CuCl[i] (3.0)	**6a**	41
		+ **7a**	23
5	CuCl[i] (6.0)	**7a**	43
1b + 1c	CuCl[i] (3.0)	**7b**	52
		+ PhCOMe	21[f]
1d	CuCl[i] (3.0)	**7c**	55

[a] Based upon the cyclic peroxide. [b] Isolated yields based upon the cyclic peroxide. [c] The cyclic peroxide was allowed to react with $FeSO_4$ in methanol at room temperature for 1 h. [d] The cyclic peroxide was allowed to react with $FeSO_4$ in methanol at room temperature under N_2 atmosphere overnight. [e] Many products were observed by TLC, but they were not fully characterized. [f] Determined by VPC analysis. [g] The cyclic peroxide was allowed to react with thiourea in refluxing methanol. [h] The starting material was remained unchanged. [i] The cyclic peroxide was allowed to react with CuCl in CH_3CN.

species of the 1,3-diketone. The hydroperoxide cyclizes spontaneously to give the cyclic peroxide. Another possibility to be considered is that the peroxy radical cyclizes with the carbonyl group to give the alkoxyl radical, which abstracts hydrogen from another 1,3-diketone to give the cyclic peroxide. It seems to be difficult to distinguish these two mechanisms at present. In the case of the reaction of 2-methyl-1,3-cyclopentanedione and styrene the product was formed in 79% yield with consumption of 0.018 F/mol of electricity. Therefore turnover number is 44.

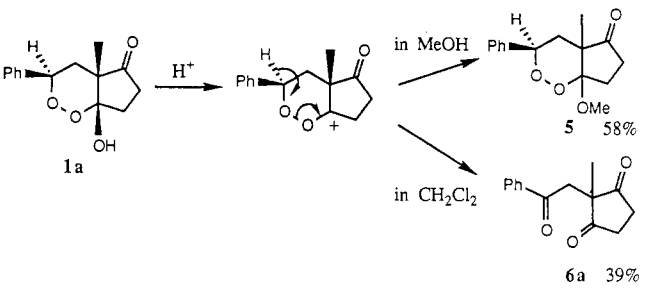
Reaction of Molecular Oxygen, 1,3-Diketone, and Olefin Initiated by Radical Initiator. The success of the electroinitiated oxygenation and radical chain mechanisms proposed above prompted us to examine the use of a radical initiator instead of the electrolysis for the initiation of the oxygenation. Azobis(isobutyronitrile) (AIBN) was found to be an effective initiator for the present cycloaddition reaction (See the Experimental Section). Table II summarizes the results obtained for AIBN-initiated oxygenation of some 1,3-diketones with olefins.

The hydrogen abstraction of 1,3-diketone by the radical derived from AIBN seems to be the initiation step, and after the radical of 1,3-diketone is formed, the reaction may proceed by essentially the same radical chain mechanism as that for the electroinitiated reaction.

Reactions of Cyclic Peroxides. Since decomposition of cyclic peroxides, especially the cleavage of the oxygen–oxygen bond, receives significant research interest,[13] the reactions of the cyclic peroxides that were obtained by the present oxygenation were investigated under various conditions.

The treatment of **1a** with *p*-toluenesulfonic acid in refluxing methanol did not cleave the oxygen–oxygen bond, but gave the methoxylated product (Scheme III). However, the treatment of **1a** with camphorsulfonic acid in refluxing dichloromethane caused the cleavage of the oxygen–oxygen bond. These acid-promoted reactions can be explained as follows. Acid-catalyzed elimination of the hydroxyl group gives the carbocation. In methanol this cation reacts with methanol to give the methoxylated product. In dichloromethane, however, there is no good nucleophile to attack the carbon, and therefore the elimination of the proton takes place to give the triketone.

Scheme III



Some reducing agents were found to cleave the oxygen–oxygen bond of the cyclic peroxides, but the mode of the cleavage depends on the nature of the reducing reagent.

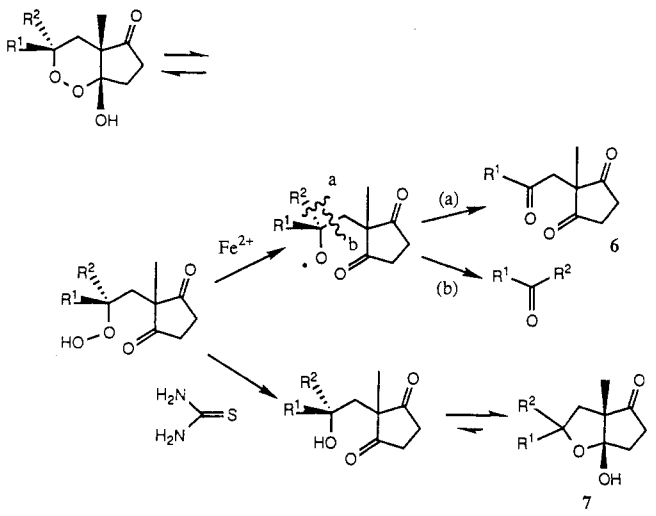
Since the reaction of hydroperoxide with ferrous sulfate is well known,[14] we first examined the reaction of the cyclic peroxide with ferrous sulfate. Treatment of **1a** with 0.24 equiv of ferrous sulfate in methanol at room temperature gave the triketone **6a** in 43% yield (Table III). Therefore the reaction is catalytic with respect to ferrous sulfate, but use of 3 equiv of ferrous sulfate resulted in much higher yield of **6a** with shorter reaction time. Treatment of the methoxylated peroxide **5** with ferrous sulfate did not give the corresponding triketone but gave a complex mixture. Therefore the presence of the free hydroxyl group seems to be essential for the reaction. The carbon–carbon bond cleavage took place in the reaction of the cyclic peroxide derived from α-methylstyrene (**1b** + **1c**) with ferrous sulfate, and acetophenone and **6b** were obtained in 44% and 25% yields, respectively. The former product was produced by the cleavage of the carbon–carbon bond. This mode of cleavage seems to be interesting because similar cleavage of the carbon–carbon bond also takes place during the transformation of prostaglandins to thromboxanes in biological systems.[15] The reaction of **1d** gave the triketone in which the silyl group is lost. Presumably the initially

(13) For example: Saito, I.; Nittala, S. S. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: Chichester, 1983.

(14) (a) Cekovic, Z.; Dimitrijevic, L.; Djokic, G.; Srnic, T. *Tetrahedron* **1979**, *35*, 2021. (b) Schreiber, S. L.; Hulin, B.; Liew, W.-F. *Tetrahedron* **1986**, *42*, 2945 and references cited therein. Fe promoted cleavage of O–O bond in cyclic peroxides have also been reported, see: (c) Yoshida, M.; Miura, M.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1983**, *105*, 6279. (d) Bascetta, E.; Gunstone, F. D.; Scrimgeour, C. M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2199.

(15) For example: (a) Salomon, R. G. *Acc. Chem. Res.* **1985**, *18*, 294. (b) Takahashi, K.; Kishi, M. *J. Chem. Soc., Chem. Commun.* **1987**, 722. (c) Kishi, M. *J. Chem. Soc., Chem. Commun.* **1986**, 885.

Scheme IV



formed α-silyl ketone was desilylated under the acidic condition.

The present Fe(II)-promoted reaction can be rationalized as follows (Scheme IV). There seems to exit an equilibrium between the cyclic peroxide and the keto hydroperoxide as mentioned before (eq 2). In the open form the hydroperoxide moiety is considered to be reduced by ferrous sulfate to give the alkoxyl radical. The fact that the methoxylated cyclic peroxide (**5**) did not react in a similar fashion is consistent with this hypothesis. If the α-position of the alkoxyl radical is substituted by hydrogen, C–H bond cleavage takes place to give the triketone. Ferric ion may be reduced to ferrous ion under the conditions, and thus the reaction is catalytic with respect to the ferrous sulfate. If there is no hydrogen at the α-position, the C–C bond cleavage takes place. Ph–C bond cleavage gives **6b**, and the cleavage of the C–C bond in the peroxide ring gives acetophenone, but the counterpart of these products were not detected.

Thiourea[16] reacted with the cyclic peroxides in refluxing methanol to give the corresponding tetrahydrofuran derivatives (Table III). The methoxylated compound **5** did not react under the same conditions. A possible mechanism for this reaction involves the reduction of hydroperoxide moiety of the open form to give the hydroxy diketone, which cyclizes to the tetrahydrofuran derivative (Scheme IV).

Copper(I) chloride also reacted with the cyclic peroxides. In this case both $FeSO_4$-type of products and thiourea-type of products were obtained (Table III). Presumably both modes of the cleavage took place simultaneously.

Concluding Remarks

The electro- and radical-initiated formal [2 + 2 + 2] cycloadditions of molecular oxygen, 1,3-diketones, and olefins provide a new aspect to oxygenation reactions. Facile reactions of the cyclic peroxides with acids and some reducing agents under mild conditions and the mode of cleavage of the oxygen–oxygen bond which depends upon the nature of the reagent also provide valuable information to the chemistry of cyclic peroxides.

Experimental Section

General Comments. Glass-support precoated (Merk Silica gel 60 F_{254}, 0.25 mm) plates were employed for analytical TLC. Vapor-phase chromatography (VPC) was performed on a Shimadzu gas chromatograph equipped with 2 m × 3 mm column packed with Silicone OV-1 (2%) on Chromosorb WAW DMCS. Proton NMR spectra were determined on a Hitachi R-90H spectrometer (90 MHz) or a JEOL JNM-GX-400 spectrometer (400 MHz). Carbon NMR spectra were determined on a JEOL JNM-GX-400 spectrometer. The sign (+) indicates the positive signal and (–) indicates the negative signal obtained in the INEPTR method. Infrared (IR) spectra were determined on a JASCO A-102 diffraction grating spectrophotometer. Mass spectra were obtained on a JEOL JMS-D300 mass spectrometer. Ionization potential was 70 eV. Cyclic voltammetry was performed on a Hokuto Potetiostat/Garvanostat HA-301 connected to a function generator HB-104 and Graphtec WX1000 X-Y plotter. Constant potential electrolyses were performed by using Hokuto Potentiostat/Garvanostat HA-301.

Tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) was prepared according to the literature,[17] and its solution in acetonitrile was dried over 4A molecular sieves at least overnight before use. Styrene was washed with aqueous NaOH, dried over Na_2SO_4, and distilled under reduced pressure before use. 2-Methyl-1,3-cyclohexanedione[18] and 3,6,6-trimethyl-2,4-dioxotetrahydropyran[19] were prepared according to the literature. Other chemicals were used as obtained commercially.

General Procedure for the Reaction of Molecular Oxygen, 1,3-Diketone, and Olefin Initiated by Electrolysis. The reaction was carried out in an undivided cell equipped with carbon rod anode (i.d. = 6 mm) and platinum plate cathode (20 × 30 mm). 1,3-Diketone (1.0 mmol) and olefin were dissolved in 0.2 M Et_4NOTs/CH_3CN (10 mL), and oxygen gas was bubbled through the cell with magnetical stirring. The constant potential electrolysis (1.5 vs Ag/AgCl) was carried out for 1 min. After the reaction was initiated, the reaction mixture was stirred with bubbling of oxygen at room temperature. Usually the reaction was completed in 1 h. But sometimes the reaction did not complete by the procedure described above. In such a case the electrolysis was repeated several times until the most of the 1,3-diketone was consumed. After the reaction was completed, the reaction mixture was partitioned between ether and brine. The ether layer was separated, and the aqueous layer was extracted with ether several times. The combined ether layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography to obtain the corresponding cyclic peroxide.

General Procedure for the Reaction of Molecular Oxygen, 1,3-Diketone, and Olefin Initiated by AIBN. 1,3-Diketone (1.0 mmol) and olefin were dissolved in CH_3CN (10 mL), and oxygen gas was bubbled. AIBN (about 0.1 mmol) was added, and the mixture was heated at 50–60 °C for 1 h. Sometimes the reaction did not complete, and in such a case the addition of AIBN and heating were repeated several times until the most of the 1,3-diketone was consumed. After the reaction was completed, similar workup and purification as described above afforded the corresponding cyclic peroxide.

1-Hydroxy-6-methyl-7-oxo-4-phenyl-2,3-dioxabicyclo-[4.3.0]nonane (1a): TLC R_f 0.60 (hexane/ethyl acetate, 1:1); VPC t_R 7.6 min (180 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 3 H), 1.92–2.61 (m, 6 H), 4.86 (dd, J = 11.97 and 2.45 Hz, 1 H), 7.25–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 215.75, 136.96, 128.60, 128.30, 126.66, 106.90, 80.87, 50.69, 34.78, 33.92, 28.98, 20.48; INEPTR ($CDCl_3$) δ 128.62 (+), 128.30 (+), 126.66 (+), 80.87 (+), 50.69 (+), 34.78 (–), 33.91 (–), 28.98 (–), 20.48 (+); IR ($CHCl_3$) 3600–3100 (br), 3550 (m), 2950 (m), 2925 (m), 2875 (m), 1735 (s), 1495 (w), 1450 (m), 1400 (m), 1375 (m), 1305 (m), 1265 (m), 1180 (m), 1105 (m), 1060 (s), 985 (m), 890 (m), 870 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 230 (16), 172 (4), 161 (2), 125 (28), 106 (18), 105 (100), 97 (6). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.72; H, 6.47.

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(18) Meklier, A. B.; Ramachandran, S.; Swaminathan, S.; Newman, M. S. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 743.

(19) Prepared by the reaction condensation of acetone with the dianion of methyl 2-methyl-3-oxobutanoate followed by cyclization by the treatment with NaOH, see: Arnett, E. M.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 809.

1-Hydroxy-4,6-dimethyl-7-oxo-4-phenyl-2,3-dioxabicyclo[4.3.0]nonane (1b and 1c). Compounds **1b** and **1c** were characterized as a mixture (1:1): TLC R_f 0.50 (hexane/ethyl acetate, 1:1); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.05 (s), 1.07 (s) (total 3 H), 1.35 (s), 1.45 (s) (total 3 H), 1.60–3.00 (m, 6 H), 3.85 (br, 1 H), 7.10–7.40 (m, 5 H); IR ($CHCl_3$) 3600–3100 (br), 3550 (m), 2970 (m), 2920 (m), 1735 (s), 1495 (w), 1440 (m), 1400 (w), 1365 (w), 1300 (m), 1270 (w), 1170 (w), 1160 (m), 1085 (s), 1065 (m), 1025 (w), 980 (w), 890 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 262 (M, 0.9), 247 (2.5), 229 (23), 169 (16), 105 (100); high-resolution MS calcd for $C_{15}H_{18}O_4$ 262.1204, found 262.1179.

1-Hydroxy-6-methyl-4-[(trimethylsilyl)methyl]-7-oxo-2,3-dioxabicyclo[4.3.0]nonane (1d): VPC t_R 3.6 min (100–200 °C, 10 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 0.66 (dd, J = 14.16 and 8.79 Hz, 1 H), 0.83 (dd, J = 14.16 and 5.86 Hz, 1 H), 1.04 (s, 3 H), 1.40 (dd, J = 13.67 and 11.47 Hz, 1 H), 3.50 (br, 1 H), 3.88–3.95 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 215.59, 106.61, 96.06, 77.73, 50.50, 36.52, 34.68, 34.52, 28.86, 22.37, 20.61, –0.39; INEPTR ($CDCl_3$) δ 77.72 (+), 36.49 (–), 34.67 (–), 28.84 (–), 22.34 (–), 20.60 (+), –0.39 (+); IR ($CHCl_3$) 3550 (w), 3600–3100 (br), 2930 (m), 1740 (s), 1445 (w), 1405 (w), 1365 (w), 1305 (m), 1250 (m), 1190 (m), 1150 (m), 1080 (m), 1055 (m), 970 (w), 890 (m), 855 (s), 840 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 258 (M, 0.09), 243 (3), 226 (10), 225 (51), 198 (3), 183 (9), 153 (9), 125 (11), 101 (26), 75 (56), 73 (100); high-resolution MS (M – Me) calcd for $C_{11}H_{19}O_4Si$ 243.1052, found 243.1057. Anal. Calcd for $C_{12}H_{22}O_4Si$: C, 55.78; H, 8.58. Found: C, 55.89; H, 8.43.

4-Ethoxy-1-hydroxy-6-methyl-7-oxo-2,3-dioxabicyclo[4.3.0]nonane (1e and 1f). Compounds **1e** and **1f** were characterized as a mixture (1:1): VPC t_R 5.0 min (100–200 °C, 10 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97–1.19 (m, 6 H), 1.59 (dd, J = 13.43 and 9.77 Hz), 1.80 (dd, J = 14.04 and 4.27 Hz) (total 1 H), 2.00–2.55 (m, 5 H), 5 3.35–3.85 (m, 2 H), 4.35 (br, 1 H), 4.50–4.81 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 215.94, 215.07, 106.96, 106.94, 101.79, 98.72, 66.26, 62.82, 52.70, 46.11, 35.19, 34.48, 33.65, 31.62, 30.62, 28.51, 20.50, 20.23, 15.51, 14.97; INEPTR ($CDCl_3$) δ 101.81 (+), 98.72 (+), 66.28 (–), 62.82 (–), 35.21 (–), 34.48 (–), 33.63 (–), 31.62 (–), 30.62 (–), 28.52 (–), 20.51 (+), 20.23 (+), 15.52 (+), 14.98 (+); IR (neat) 3050–3600 (br), 2960 (m), 2920 (m), 2880 (m), 1780 (w), 1735 (s), 1445 (m), 1375 (m), 1305 (m), 1265 (m), 1170 (s), 1100 (s), 1040 (s), 885 (m), 860 (m), 810 (w), 745 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 199 (3), 198 (22), 170 (13), 152 (6), 126 (8), 125 (100), 124 (31), 97 (17), 69 (28); high-resolution MS (M – H_2O) calcd for $C_{10}H_{14}O_4$ 198.0890, found 198.0882.

1-Hydroxy-4,6-dimethyl-7-oxo-4-vinyl-2,3-dioxabicyclo[4.3.0]nonane (1g and 1h). Compounds **1g** and **1h** were characterized as a mixture. It was difficult to determine their ratio by NMR: TLC R_f 0.55 (hexane/ethyl acetate, 1:1); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.03 (s), 1.05 (s) (total 3 H), 1.20 (s), 1.23 (s) (total 3 H), 1.58–2.61 (m, 6 H), 4.01 (br, 1 H), 4.95–5.93 (m, 3 H); IR ($CHCl_3$) 3650 (w), 3600–3100 (br), 2960 (m), 2920 (m), 2450 (w), 1860 (w), 1780 (w), 1725 (s), 1445 (m), 1400 (m), 1370 (m), 1305 (m), 1270 (m), 1180 (m), 1150 (m), 1100 (m), 1080–1000 (br), 990 (m), 925 (m), 890 (m), 840 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 212 (M, 0.8), 197 (0.7), 194 (0.6), 179 (63), 151 (11), 119 (31), 69 (100), 55 (84); high-resolution MS calcd for $C_{11}H_{16}O_4$ 212.1047, found 212.1046.

1-Hydroxy-4,6-dimethyl-7-oxo-4-(2-propenyl)-2,3-dioxabicyclo[4.3.0]nonane (1i and 1j). Nonanes **1i** and **1j** were characterized as a mixture (2:1 or 1:2): TLC R_f 0.48 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s), 1.03 (s) (total 3 H), 1.19 (s), 1.23 (s) (total 3 H), 1.74 (d, J = 0.49 Hz), 1.75 (d, J = 0.74 Hz) (total 3 H), 2.00–2.64 (m, 6 H), 3.51 (br), 3.60 (br) (total 1 H), 4.81–4.96 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 216.71, 147.77, 144.81, 113.36, 110.28, 82.94, 49.30, 48.47, 36.40, 35.36, 35.32, 34.69, 29.70, 29.06, 27.64, 27.19, 22.37, 21.71, 21.35, 18.91; INEPTR ($CDCl_3$) δ 113.36 (–), 110.28 (–), 36.40 (–), 35.36 (–), 35.32 (–), 34.69 (–), 29.70 (–), 29.06 (–), 27.64 (+), 27.19 (+), 22.37 (+), 21.71 (+), 21.35 (+), 18.91 (+); IR ($CHCl_3$) 3660 (w), 3570 (m), 3500–3100 (br), 2960 (m), 2920 (m), 2420 (w), 1735 (s), 1640 (w), 1445 (m), 1400 (w), 1370 (m), 1305 (m), 1265 (w), 1175 (w), 1135 (m), 1095 (m), 1065 (w), 985 (w), 900 (m), 835 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 211 (2), 193 (79), 175 (7), 169 (7), 151 (6), 147 (7), 137 (9), 133 (34), 125 (30), 123 (9), 113 (16), 109 (30), 99 (25), 85 (13), 69 (100), 55 (6); high-resolution MS (M – Me) calcd for $C_{11}H_{15}O_4$ 211.0969, found 211.0964.

4-(Chloromethyl)-1-hydroxy-4,6-dimethyl-7-oxo-2,3-dioxabicyclo[4.3.0]nonane (1k and 1l). Compounds **1k** and **1l** were characterized as a mixture (2.5:1 or 1:2.5): TLC R_f 0.50 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s), 1.06 (s) (total 3 H), 1.24 (s), 1.28 (s) (total 3 H), 1.64–2.58 (m, 6 H), 3.03, 3.20, 3.25, 3.28, 3.43, 3.51, 3.54 (7 peaks, total 2 H); ^{13}C NMR ($CDCl_3$) δ 217.16, 217.00, 106.82, 106.40, 79.29, 79.07, 51.68, 50.13, 50.07, 48.96, 48.82, 47.10, 47.04, 46.96, 34.66, 34.60, 34.51, 34.41, 34.11, 29.11, 28.37, 23.76, 21.01, 20.93, 20.78; INEPTR ($CDCl_3$) δ 51.68 (–), 50.13 (–), 50.07 (–), 48.96 (–), 48.82 (–), 47.10 (–), 47.04 (–), 46.96 (–), 34.66 (–), 34.60 (–), 34.51 (–), 34.41 (–), 34.11 (–), 29.11 (–), 28.37 (–), 23.76 (+), 21.01 (+), 20.93 (+), 20.78 (+); IR ($CHCl_3$) 3650 (w), 3550 (m), 3500–3100 (br), 2950 (m), 2910 (m), 2430 (w), 1860 (w), 1785 (m), 1735 (s), 1450 (m), 1400 (w), 1375 (m), 1310 (m), 1265 (m), 1180 (m), 1140 (w), 1120 (w), 1090 (m), 1060 (m), 1040 (m), 990 (m), 945 (w), 905 (m), 890 (m), 840 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 238 (0.2), 220 (0.2), 218 (0.6), 203 (3), 201 (7), 125 (68), 114 (18), 111 (10), 101 (9), 97 (13), 83 (5), 73 (12), 69 (100), 55 (6); high-resolution MS calcd for $C_{10}H_{15}O_4Cl$ 234.0659, found 234.0664.

1-Hydroxy-4,6-dimethyl-7-oxo-4-propyl-2,3-dioxabicyclo[4.3.0]nonane (1m and 1n). Nonanes **1m** and **1n** were characterized as a mixture (1:1): TLC R_f 0.62 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85–0.93 (m, 3 H), 1.016 (s), 1.022 (s) (total 3 H), 1.10 (s), 1.11 (s) (total 3 H), 1.25–1.45 (m, 4 H), 2.07–2.56 (m, 6 H); IR ($CHCl_3$) 3650 (w), 3550 (m), 3500–3100 (br, m), 3020 (sh), 2950 (m), 2930 (m), 2860 (m), 1735 (s), 1655 (w), 1450 (m), 1400 (m), 1375 (m), 1310 (m), 1265 (m), 1175 (s), 1125 (s), 1100 (m), 1050 (s), 1010 (w), 985 (m), 945 (w), 890 (m), 835 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 228 (M, 0.8), 212 (1), 210 (0.6), 195 (30), 139 (10), 125 (100), 113 (89), 111 (14), 97 (15), 86 (25), 83 (14), 73 (24), 71 (33), 69 (72), 58 (40), 55 (11); high-resolution MS calcd for $C_{12}H_{20}O_4$ 228.1360, found 228.1360.

1-Hydroxy-6-methyl-7-oxo-4-phenyl-2,3-dioxabicyclo[4.4.0]decane (2): TLC R_f 0.72 (hexane/ethyl acetate, 1:1); VPC t_R 12.6 min (100–220 °C, 10 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 3 H), 1.79–2.67 (m, 8 H), 3.66 (br, 1 H), 5.14 (dd, J = 11.72 and 1.95 Hz), 7.20–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 210.54, 137.24, 128.56, 128.30, 126.79, 102.92, 81.03, 52.38, 36.70, 33.91, 31.27, 23.24, 18.51; INEPTR ($CDCl_3$) δ 128.57 (+), 128.32 (+), 126.84 (+), 81.04 (+), 36.72 (–), 33.92 (–), 31.27 (–), 23.30 (+), 18.56 (–); IR ($CHCl_3$) 3600–3150 (br), 2950 (m), 1705 (s), 1455 (w), 1315 (w), 1175 (w), 1110 (m), 1020 (m), 910 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 245 (7), 244 (36), 226 (2), 171 (2), 139 (19), 111 (23), 105 (100), 77 (14), 69 (8). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.70; H, 6.90.

1-Hydroxy-6,9,9-trimethyl-7-oxo-4-phenyl-2,3,8-trioxabicyclo[4.4.0]decane (3). The peroxide **3** was a mixture of three stereoisomers (58:29:13), and they were characterized as a mixture: TLC R_f 0.60 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s), 1.43 (s), 1.46 (s), 1.48 (s), 1.50 (s), 1.53 (s), 1.55 (s), 1.56 (s), 1.58 (s) (total 9 H), 1.91–3.09 (m, 4 H), 5.14 (dd, J = 10.25 and 1.50 Hz), 5.28 (dd, J= 9.52 and 3.66 Hz), 5.42 (dd, J = 10.52 and 1.75 Hz) (total 1 H), 7.27–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 206.24, 136.89, 136.78, 128.95, 128.64, 128.49, 128.45, 127.08, 126.54, 100.35, 100.12, 81.79, 78.88, 45.23, 43.91, 40.27, 39.32, 35.03, 31.92, 30.33, 29.67, 23.28; INEPTR ($CDCl_3$) δ 128.96 (+), 128.64 (+), 128.54 (+), 128.51 (+), 128.46 (+), 127.12 (+), 126.55 (+), 81.80 (+), 78.87 (+), 40.25 (–), 39.27 (–), 35.00 (–), 31.93 (+), 30.33 (+), 29.67 (+), 23.29 (+); IR ($CHCl_3$) 3650 (w), 3550 (m), 3500–3110 (br), 2970 (m), 2930 (m), 1705 (s), 1445 (m), 1370 (m), 1340 (m), 1320 (m), 1290 (m), 1140 (s), 1070 (m), 1000 (m), 970 (m), 910 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 272 (15), 256 (15), 218 (5), 190 (3), 174 (26), 169 (46), 120 (5), 105 (100), 83 (38), 69 (11); high-resolution MS calcd for $C_{16}H_{18}O_4$ (M – H_2O) 274.1204, found 274.1194.

2-(4-Hydroperoxy-2-methyl-2-butenyl)-2-methyl-1,3-cyclopentanedione (4). A mixture of two isomers with respect to the stereochemistry of the carbon–carbon double bond: TLC R_f 0.37 (hexane/ethyl acetate, 1:1); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.13 (s, 3 H), 1.62 (s), 1.63 (s) (total 3 H), 2.43 (s, 2 H), 2.76 (s, 4 H), 4.43 (d, J = 6.81 Hz, 2 H), 5.20–5.39 (m, 1 H); IR ($CHCl_3$) 3650 (w), 3600–3100 (br), 3025 (w), 2950 (w), 2920 (m), 2870 (w), 1860 (m), 1780 (m), 1705 (s), 1665 (m), 1420 (w), 1410 (m), 1395

(m), 1370 (m), 1305 (m), 1265 (w), 1230–1200 (br), 1185 (m), 1140 (m), 1110 (w), 1060 (m), 1040 (m), 990 (m), 905 (m), 865 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 194 (12), 179 (19), 177 (10), 151 (14), 149 (12), 137 (18), 135 (22), 123 (33), 113 (100), 109 (47), 99 (44), 95 (51), 82 (86), 79 (39), 55 (72); high-resolution MS ($M - H_2O$) calcd for $C_{11}H_{14}O_3$ 194.0941, found 194.0930.

Reaction of 1a with *p*-Toluenesulfonic Acid in Methanol. The cyclic peroxide **1a** (167 mg, 0.67 mmol) was dissolved in 10 mL of methanol. *p*-Toluenesulfonic acid monohydrate (26 mg, 0.14 mmol) was added, and the solution was refluxed for 12.5 h. The reaction mixture was partitioned between aqueous $NaHCO_3$ and ether. The ether layer was separated, and the aqueous layer was extracted with ether several times. The combined ether layer was dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 4:1) to give **5** in 58% yield.

1-Methoxy-6-methyl-7-oxo-4-phenyl-2,3-dioxabicyclo[4.3.0]nonane (5): TLC R_f 0.59 (hexane/ethyl acetate, 2:1); VPC decomposition; ^1H NMR (400 MHz, $CDCl_3$) δ 1.068 (s), 1.11 (s) (total 3 H), 1.93–2.58 (m, 6 H), 3.473 (s), 3.475 (s), 3.497 (s), 3.500 (s) (total 3 H), 4.84 (dd, J = 11.96 and 2.2 Hz), 5.23 (br d, J = 4.88 Hz) (total 1 H), 7.26–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 215.80, 137.36, 128.28, 126.84, 126.11, 109.06, 80.68, 50.82, 50.03, 34.94, 34.13, 25.93, 20.21; INEPTR ($CDCl_3$) δ 128.27 (+), 126.84 (+), 126.08 (+), 109.03 (+), 80.65 (+), 50.79 (+), 50.02 (+), 34.93 (–), 34.07 (–), 25.88 (–), 20.19 (+); IR (neat) 2920 (m), 1740 (s), 1490 (w), 1450 (m), 1400 (w), 1370 (w), 1260 (w), 1205 (m), 1170 (m), 1125 (m), 1095 (m), 1065 (m), 1035 (m), 985 (w), 885 (w), 750 (w), 695 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 262 (M, 0.5), 244 (2), 230 (7), 142 (8), 125 (29), 105 (100); high-resolution MS calcd for $C_{15}H_{18}O_4$ 262.1204, found 262.1202.

Reaction of 1a with Camphorsulfonic Acid in Dichloromethane. The cyclic peroxide **1a** (41 mg, 0.17 mmol) was dissolved in 1.5 mL of dichloromethane. Camphorsulfonic acid (127 mg, 0.55 mmol) was added, and the mixture was refluxed for 31 h. The reaction mixture was partitioned between aqueous $NaHCO_3$ and ether. The ether layer was separated, and the aqueous layer was extracted with ether several times. The combined ether layer was dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by preparative TLC on silica gel (dichloromethane/ethyl acetate, 9:1) to give **6a** in 39% yield.

2-Methyl-2-(2-phenyl-2-oxoethyl)-1,3-cyclopentanedione (6a): TLC R_f 0.65 (dichloromethane/ethyl acetate, 9:1); ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 3 H), 2.86–3.10 (m, 4 H), 3.72 (s, 2 H), 7.42–7.89 (m, 5 H); IR ($CHCl_3$) 3660 (w), 3620–3100 (br, m), 3030 (sh), 3000 (sh), 2960 (sh), 2920 (w), 2870 (sh), 1720 (s), 1670 (m), 1600 (w), 1450 (w), 1345 (w), 1290 (w), 1180 (m), 1070 (m), 1050 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 230 (M, 8), 174 (2), 125 (15), 105 (100), 77 (9); high-resolution MS calcd for $C_{14}H_{14}O_3$ 230.0943, found 230.0955.

General Procedure for the Reaction of the Cyclic Peroxide with Ferrous Sulfate. To a solution of the cyclic peroxide (0.1–0.17 mmol) in 1.0 mL of methanol was added $FeSO_4 \cdot 7H_2O$ (3.0 equiv) at room temperature. The mixture was stirred at this temperature for 1 h. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel to give the corresponding products.

2-Methyl-2-(2-oxopropyl)-1,3-cyclopentanedione (6b): TLC R_f 0.45 (dichloromethane/ethyl acetate, 9:1); ^1H NMR (90 MHz, $CDCl_3$) δ 1.04 (s, 3 H), 2.06 (s, 3 H), 2.87–2.88 (m, 4 H), 3.15 (s, 2 H); IR ($CHCl_3$) 3670 (w), 3610–3130 (br, w), 3030 (sh), 3000 (sh), 2910 (m), 2850 (sh), 1710 (s), 1675 (w), 1390 (w), 1360 (w), 1285 (w), 1175 (m), 1150 (w), 1070 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 168 (M, 20), 125 (100), 97 (22), 69 (14); high-resolution MS calcd for $C_9H_{12}O_3$ 168.0785, found 168.0775.

General Procedure for the Reaction of the Cyclic Peroxide with Thiourea. The cyclic peroxide (0.13–0.21 mmol) and thiourea (1.1 equiv) were dissolved in 1.5–2.0 mL of methanol, and the solution was refluxed for 7.5 h. After removal of methanol under reduced pressure, the residue was partitioned between ether and brine. The ether layer was separated, and the aqueous layer was extracted with ether several times. The combined ether layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by preparative TLC to give the corresponding product.

Compound **7a** was identified by comparison of its spectral data with those of an authentic sample.[4]

1-Hydroxy-3,5-dimethyl-6-oxo-3-phenyl-2-oxabicyclo[3.3.0]octane (7b). The tetrahydrofuran derivative **7b** was obtained as a mixture of two stereoisomers and characterized as a mixture: TLC R_f 0.55 (hexane/ethyl acetate, 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (s), 1.11 (s) (total 3 H), 1.33 (s), 1.36 (s) (total 3 H), 1.87–2.98 (m, 6 H), 7.16–7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 220.34, 219.23, 128.48, 128.32, 128.14, 127.69, 126.95, 126.73, 126.17, 124.33, 124.25, 124.06, 112.39, 111.94, 85.34, 84.97, 59.60, 59.31, 48.20, 36.25, 36.11, 34.30, 32.22, 32.18, 30.19, 16.34, 16.27; IR ($CHCl_3$) 3660 (w), 3590 (m), 3500–3150 (br), 2960 (m), 2930 (m), 2860 (w), 1740 (s), 1600 (w), 1490 (m), 1440 (m), 1400 (m), 1370 (m), 1300 (m), 1260 (w), 1180 (w), 1120 (w), 1080 (m), 1060 (s), 980 (w), 960 (m), 940 (m), 900 (w), 860 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 247 (M + 1, 13), 246 (M, 65), 231 (59), 228 (35), 203 (24), 185 (32), 173 (34), 171 (20), 169 (29), 157 (10), 145 (100), 143 (15), 129 (13), 121 (25), 118 (26), 105 (76), 91 (10); high-resolution MS calcd for $C_{15}H_{18}O_3$ 246.1254, found 246.1254.

1-Hydroxy-5-methyl-6-oxo-3-[(trimethylsilyl)methyl]-2-oxabicyclo[3.3.0]octane (7c). The tetrahydrofuran derivative **7c** was obtained as a mixture of two stereoisomers and characterized as a mixture: TLC R_f 0.38 (hexane/ethyl acetate, 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (s), 0.05 (s) (total 9 H), 0.63–0.85 (m, 2 H), 1.03 (s, 3 H), 1.99–2.53 (m, 6 H), 3.90–3.93 (m, 1 H); IR ($CHCl_3$) 3650 (w), 3550 (m), 3500–3100 (br), 2950 (m), 2920 (sh), 1740 (s), 1450 (m), 1365 (m), 1305 (m), 1250 (m), 1190 (m), 1150 (w), 1060 (m), 970 (m), 890 (w), 855 (s), 840 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 242 (M, 6), 227 (14), 209 (5), 185 (13), 169 (32), 152 (23), 137 (13), 124 (17), 110 (16), 109 (28), 97 (19), 95 (15), 93 (22), 77 (17), 75 (83), 73 (100); high-resolution MS calcd for $C_{12}H_{22}O_3Si$ 242.1339, found 242.1356.

General Procedure for the Reaction of the Cyclic Peroxide with Copper(I) Chloride. To a solution of the cyclic peroxide (0.12–0.21 mmol) in 1.0–1.5 mL of acetonitrile was added copper(I) chloride (3 equiv), and the mixture was stirred at room temperature overnight. The reaction mixture was filtered through a short column of silica gel (elution by ether), and the eluent was concentrated under reduced pressure. The residue was purified by preparative TLC to give the corresponding products.

MM2 Calculations. Allinger's MM2 program (QCMP 004) modified by E. Osawa and M. Mochizuki, Hokkaido University, was used for the calculation. The parameters supplied with QCMP program was used for the calculations. Throughout the MM2 calculations, care was used in the search for initial conformations, but we cannot be sure that other low-energy conformers were not overlooked in some instances.

X-ray Crystallographic Analysis. Crystal data: $C_{14}H_{16}O_4$, monoclinic, space group $p2_1/n$, a = 13.858 (7) Å, b = 6.676 (3) Å, c = 13.858 (7) Å, β = 112.8 (3), z = 4, D_c = 1.30 g cm^{-3}. A total of 1773 reflections with $2\theta < 46$ were recorded on a four circle diffractometer using graphite monochromated Mo Kα radiation. Of these 1232 [with $I > 3\sigma(I)$] were judged observed. The structure was solved using MULTAN.[20] Full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms converged to R = 0.038.[21]

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Supplementary Material Available: Atomic coordinates, bond distances, and bond angles for **1a** (3 pages). Ordering information is given on any current masthead page.

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