Reaction of Highly Methylated 2-Methylenecycloalkyl Hydroperoxides with $FeSO_4/CuCl_2$. Remarkably Efficient 5-*endo-trig* or 6-*endo-trig* Cyclization of the Intermediate Carbon Radicals

Yuji Nonami,[†] Janusz Baran,*[,‡] Jacek Sosnicki,[‡] Herbert Mayr,[§] Araki Masuyama,[†] and Masatomo Nojima*[,†]

Department of Materials Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan, Institute of Fundamental Chemistry, Technical University of Szczecin, Al. Piastów 42, PL-71065 Szczecin, Poland, and Institut für Organische Chemie, der Ludwig-Maximilians-Universität, München, Karlstrasse 23, D-80333 München, Germany

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Treatment of 1,3,3,4,4,5,5-heptamethyl-2-methylenecyclopentyl hydroperoxide, derived from a singlet oxygen ene reaction of 1,2,3,3,4,4,5,5-octamethylcyclopentene, with $FeSO_4/CuCl_2$ gave 1-chloro-2,2,3,3,4,4-hexamethylcyclopentyl methyl ketone in high yield, suggesting that the consecutive O−O and C−C bond fission is followed by a novel 5-*endo-trig* cyclization of the intermediate carbon radical to the activated C−C double bond. In the case of 1,3,3,6,6-pentamethyl-2-methylene-1-cyclohexyl hydroperoxide also, an efficient 6-*endo-trig* cyclization of the corresponding carbon radical was realized giving 1-chloro-2,2,5,5-tetramethylcyclohexyl methyl ketone in high yield.

A variety of allylic hydroperoxides have conveniently been prepared by the singlet oxygen ene reaction of unactivated olefins with allylic hydrogen atoms.[1] The allylic hydroperoxides thus prepared have proven to be synthetically useful intermediates.[2] While reduction leads to allylic alcohols, the reaction with Ti^{IV} complexes has been utilized to prepare epoxy alcohols.[3] Finally, dehydration provides convenient access to enones.[4] We report here that (1) the reaction of highly methylated cycloalkenes with singlet oxygen proceeds very rapidly providing the corresponding 2-methylenecycloalkyl hydroperoxides in high yield and (2) the subsequent treatment of the allylic hydroperoxides with $FeSO_4/CuCl_2$[5] affords 1-chlorocycloalkyl methyl ketones, indicating that the homolytic O−O and C−C bond fission is followed by efficient 5-*endo-trig*[6] or 6-*endo-trig*[7] cyclization of the intermediate carbon radicals.

Results and Discussion

Singlet Oxygen Ene Reaction of Highly Methylated Cycloalkenes. Octamethylcyclopentene (**1a**) was irradiated in CH_2Cl_2 in the presence of a small amount of tetraphenylporphine and $NaHCO_3$ under a slow stream of oxygen. By subsequent column chromatography on basic alumina, 1,3,3,4,4,5,5-heptamethyl-2-methylene-1-cyclopentyl hydroperoxide (**2a**) was isolated in 87% yield (Scheme 1**)**.[8] However, the hydroperoxide **2a** was very labile even in a refrigerator. In the absence of any initiator, **2a** dissolved in $CDCl_3$ (pretreated with $NaHCO_3$) completely rearranged to the regioisomeric hydroperoxide **5a** within 2 days. However, the presence of a small amount of methylhydroquinone, a radical scavenger, was found to retard the rearrangement completely, suggesting that the rearrangement of **2a** to **5a** proceeds via the corresponding peroxyl radical intermediates, **8a** and **9a** (Scheme 1).[9]

The reaction of 1,2,3,3,4,4-hexamethylcyclopentene (**1b**) with singlet oxygen may produce three different allylic hydroperoxides **2b**−**4b** (Scheme 1). When the reaction of **1b** was conducted under the reaction conditions described above, all three isomers **2b**−**4b** were

[†] Faculty of Engineering.
[‡] Technical University of Szczecin.
[§] Institut für Organische Chemie der Ludwig-Maximilians-Universität.

(1) (a) *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979. (b) Foote, C. S.; Clennan, E. L. In *Active Oxygen in Chemistry*; Foote, C. S., Valentine, J. S., A. Greenberg, A., Liebman, J. F., Eds.; Blackie Academic & Professional: London, 1995; Vol. 2.

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(8) The photolysis in the absence of $NaHCO_3$, followed by column chromatography on silica gel, afforded (2,3,3,4,4,5,5-heptamethyl-1-cyclopentenyl)methyl hydroperoxide (**5a**) in 25% yield, together with unidentified decomposition products. In this connection, allylic hydroperoxides are known to be labile toward acid catalysts. Schenck, G. O.; Schulte-Elte, K.-H. *Liebigs Ann. Chem.* **1958**, *618*, 185.

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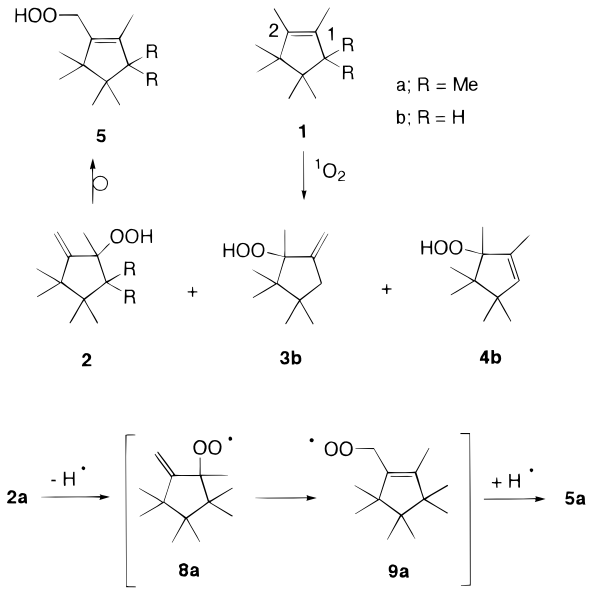
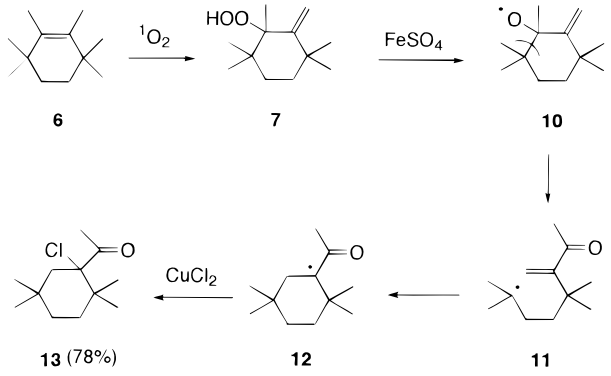
Scheme 1



Scheme 2

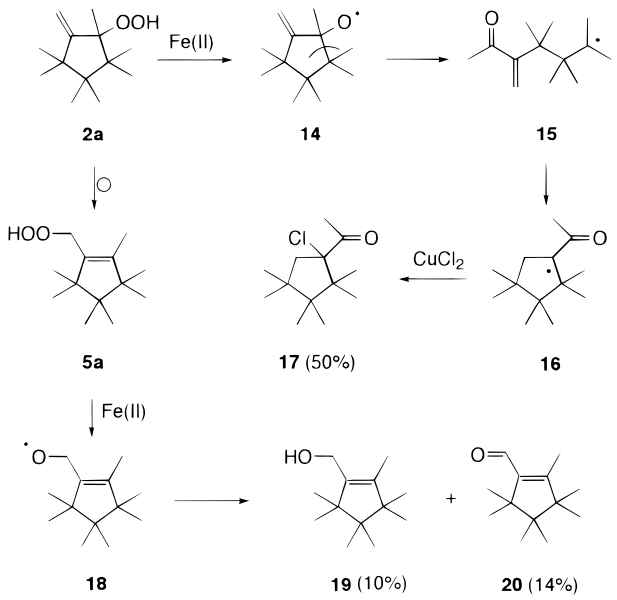


isolated. The ratio **2b**:**3b**:**4b** was determined by ^{1}H NMR spectroscopy of the crude reaction mixture to be ca. 78:9:13. The preferential formation of 1,3,3,4,4-pentamethyl-2-methylene-1-cyclopentyl hydroperoxide (**2b**) is consistent with the proposal by Orfanopoulos and co-workers[10] that a "large group nonbonding effect" plays an important role in determining the regioselectivity of Schenck ene reaction, thereby affording predominantly the corresponding allylic hydroperoxide **2b** derived from abstraction of hydrogen from the more shielded 2-methyl group. Compared with **2a**, the sterically less-congested allylic hydroperoxide **2b** was very stable and could be kept in a refrigerator for at least 1 month without notable rearrangement.

From 1,2,3,3,6,6-hexamethylcyclohexene (**6**) also, the ene product **7** was obtained in 76% yield (Scheme 2).

Treatment of Allylic Hydroperoxides with $FeSO_4$/$CuCl_2$. With the highly methylated allylic hydroperoxides **2a**,**b** and **7** in hand, we then conducted the Fe(II)-catalyzed decomposition.[5] Treatment of a solution of the hydroperoxide **7** in MeCN with a solution of iron(II) sulfate (1 equiv) and copper(II) chloride (3 equiv) in water at room temperature gave the acetyl-substituted cyclohexyl chloride **13** selectively (78%) (Scheme 2).

Scheme 3



This result indicates that oxy radical **10**, generated by fragmentation of the O−O bond, undergoes selective β-scission of one of the C−C bonds to give the acyclic radical **11**. Successive intramolecular cyclization gives **12**, which in turn reacts with copper(II) chloride to provide the chlorinated cyclohexane **13**. This efficient 6-*endo-trig* cyclization is explained by the directing effect of the α,β-unsaturated carbonyl group in the intermediate **11**.[7]

It was of interest to see that the highly methylated acyclic carbon radical **15** undergoes the novel 5-*endo-trig* cyclization. Treatment of the allylic hydroperoxide **2a** with $FeSO_4$/$CuCl_2$ in aqueous CH_3CN gave acetyl-substituted cyclopentyl chloride **17** (50%), together with cyclopentenylmethanol **19** (10%) and aldehyde **20** (14%) (Scheme 3). It is reasonable to assume that an analogous mechanism as suggested for the compound **7** accounts for the formation of **17** (Scheme 3). In this reaction sequence the tertiary carbon radical **15** undergoes an efficient 5-*endo-trig* cyclization.

The reaction sequence proposed for the production of **19** and **20** from **2a** is based on the former observation that the allylic hydroperoxide **2a** is very labile. Under the above reaction conditions in which the oxy radical **14** is produced, it is reasonable to expect that isomerization of **2a** to **5a** competes with the reduction leading to **17**. Consistent with this, treatment of the pure allylic hydroperoxide **5a** with $FeSO_4$/$CuCl_2$ gave the expected mixture of **19** (38%) and **20** (46%).

In marked contrast to the efficient formation of the cyclopentyl chloride **17** from **2a**, the reaction of 1,3,3,4,4-pentamethyl-2-methylene-1-cyclopentyl hydroperoxide (**2b**) under the same conditions yielded the corresponding alcohol **22** (76%) (Scheme 4). Obviously, the β-scission in the intermediate **21** leading to the primary carbon radical **23** does not occur.[11]

The following observation would suggest that 5-*endo-trig* cyclization is a difficult process. Treatment of the allylic hydroperoxide **24**, derived from singlet oxygen ene

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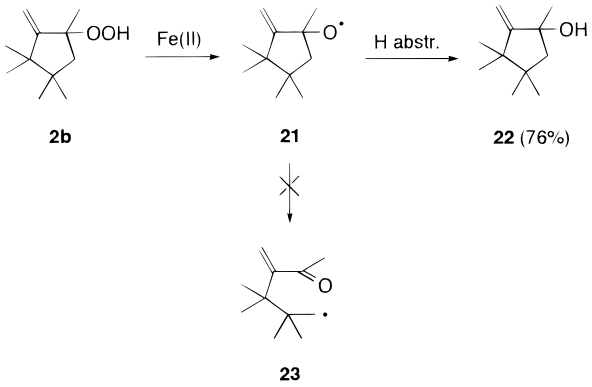
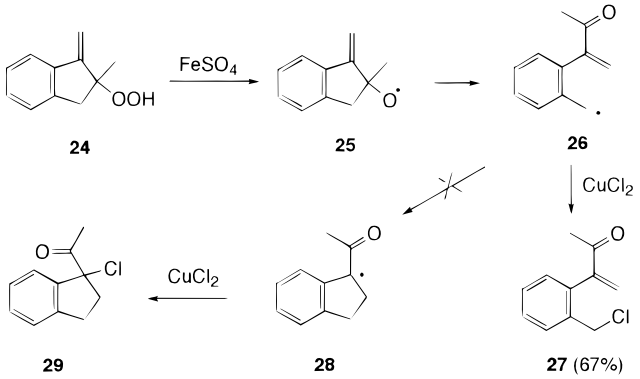
(11) β-Scission is a well-established reaction of many alkoxyl radicals. The extent to which β-scission occurs is determined by a number of factors, one of which is the stability of the organic radical generated: Labeque, R.; Marnett, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 2828.

Scheme 4



Scheme 5



reaction of 2,3-dimethylindene,[12] with $FeSO_4/CuCl_2$ gave exclusively the benzyl chloride **27** (Scheme 5). This implies that β-scission in the oxy radical **25** occurs. However, chlorine atom transfer from $CuCl_2$ is much faster than 5-*endo-trig* cyclization, thereby providing exclusively the acyclic product **27**.[13]

Conclusion. The singlet oxygen ene reaction of highly methylated cycloalkenes proceeds well providing the corresponding 2-methylenecycloalkyl hydroperoxides in good yield. In the case of the unsymmetrically substituted **1b**, the regioselectivity is notable, affording predominantly the corresponding allylic hydroperoxide derived from abstraction of hydrogen from the more shielded 2-methyl group. As a new and attractive transformation of allylic hydroperoxide, treatment of **2a** and **7** with $FeSO_4/CuCl_2$ gives the corresponding 1-chlorocycloalkyl methyl ketones in high yield.

Experimental Section

Materials. 1,2,3,3,4,4,5,5-Octamethylcyclopentene (**1a**),[14] 1,2,3,3,4,4-hexamethylcyclopentene (**1b**),[14] 1,2,3,3,6,6-hexamethylcyclohexene (**6**),[15] and 2-methyl-1-methylene-2-indenyl hydroperoxide (**24**) (63% yield; an oil; ^{1}H NMR δ 1.14 (s, 3 H), 2.88 (d, J = 17.2 Hz, 1 H), 3.38 (d, J = 17.2 Hz, 1 H), 5.21 (s, 1 H), 5.62 (s, 1 H), 7.1−7.4 (m, 4 H), 7.65 (s, 1 H); ^{13}C NMR δ 23.76, 41.58, 90.26, 105.39, 121.01, 125.25, 126.85, 129.22, 138.56, 142.16, 151.52)[12] were prepared by the reported methods. NMR spectra were measured in $CDCl_3$ pretreated with $NaHCO_3$.

Caution. Since organic peroxides are potentially hazardous compounds, they must be handled with due care; avoid exposure to strong heat or light, mechanical shock, oxidizable organic materials, or transition metal ions. No particular difficulties were experienced in handling any of the new peroxides synthesized in this work using the reaction scales and procedures described below together with the safeguard mentioned above.

Photooxygenation. A tube containing 20 mL of a CH_2Cl_2 solution of a cyclopentene **1** (1−2 mmol), tetraphenylporphine (1 mg), and $NaHCO_3$ (5 mg) was irradiated at 0 °C for 1.5 h (the reaction was followed by TLC) with a 300 W high-pressure mercury lamp through an aqueous $CuSO_4$ filter solution (>400 nm) under an oxygen stream. After ether (50 mL) was added, the organic layer was washed with aqueous $NaHCO_3$ and then with saturated brine and the solvent was evaporated (room temperature, 15 mmHg). The residue was separated by column chromatography (column 2.0 × 60 cm; 40 g of basic alumina; elution with ether−hexane).

Photooxygenation of 1,2,3,3,4,4,5,5-Octamethylcyclopentene (1a). The photooxygenation of **1a** (180 mg, 1 mmol) was conducted as described above. The ^{1}H NMR spectrum of the crude product showed the presence of only **2a**. Column chromatography of the residue (elution with ether−hexane, 5:95) gave **2a** (184 mg, 87%).

1,3,3,4,4,5,5-Heptamethyl-2-methylene-1-cyclopentyl hydroperoxide (2a): mp 58−62 °C; ^{1}H NMR δ 0.82 (s, 3 H), 0.85 (s, 3 H), 0.89 (s, 3 H), 1.03 (s, 3 H), 1.08 (s, 3 H), 1.13 (s, 3 H), 1.32 (s, 3 H), 5.20 (s, 1 H), 5.23 (s, 1 H), 6.96 (s, 1 H); ^{13}C NMR δ 15.58, 16.89, 22.41, 24.64, 26.27, 29.89, 30.68, 44.96, 46.11, 49.89, 94.52, 110.51, 162.57. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.58; H, 11.49.

Rearrangement of 2a. The ^{1}H NMR spectra of a solution of **2a** (22 mg, 0.1 mmol) in $CDCl_3$ was periodically measured, which demonstrated that in 2 days **2a** rearranged to **5a** completely. Column chromatography on silica gel (elution with ether−hexane, 5:95) gave the rearranged allylic hydroperoxide **5a** quantitatively. When the same reaction was repeated in the presence of 0.05 equiv of methylhydroquinone, the rearrangement was completely suppressed.

(2,3,3,4,4,5,5-Heptamethyl-1-cyclopentenyl)methyl hydroperoxide (5a): an oil; ^{1}H NMR δ 0.78 (s, 6 H), 0.92 (s, 6 H), 0.96 (s, 6 H), 1.66 (s, 3 H), 4.55 (s, 2 H), 8.09 (s, 1 H); ^{13}C NMR δ 10.44, 21.44, 23.99, 24.91, 46.08, 49.04, 52.21, 71.40, 133.15, 147.60. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.58; H, 11.59.

Photooxygenation of 1,2,3,3,4,4-Hexamethylcyclopentene (1b). The photooxygenation of **1b** (280 mg, 1.84 mmol) was conducted as described above. The ^{1}H NMR spectrum of the crude product showed the presence of three allylic hydroperoxides, **2b**−**4b**. By comparing the peak areas of the characteristic signals of **2b** (δ 2.04), **3b** (δ 2.37), and **4b** (δ 5.40), the product ratio was determined to be 78:9:13. Column chromatography of the residue (elution with ether−hexane. 5:95) gave first **4b** (34 mg, 10%). From the second fraction, **3b** was obtained (27 mg, 8%). Elution with ether−hexane (8:92) gave **2b** (226 mg, 67%).

1,3,3,4,4-Pentamethyl-2-methylene-1-cyclopentyl hydroperoxide (2b): an oil; ^{1}H NMR δ 0.84 (s, 3 H), 0.92 (s, 3 H), 0.94 (s, 3 H), 1.00 (s, 3 H), 1.49 (s, 3 H), 1.64 (d, J = 14.2 Hz, 1 H), 2.04 (d, J = 14.2 Hz, 1 H), 5.05 (s, 1 H), 5.18 (s, 1 H), 7.81 (s, 1 H); ^{13}C NMR δ 23.87, 23.92, 24.42, 24.93, 25.11, 41.02, 47.71, 49.20 (CH_2), 88.92, 108.88 (CH_2), 162.81. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.54; H, 10.56.

1,4,4,5,5-Pentamethyl-2-methylene-1-cyclopentyl hydroperoxide (3b): an oil; ^{1}H NMR δ 0.81 (s, 3 H), 0.88 (s, 3 H), 0.91 (s, 3 H), 1.08 (s, 3 H), 1.33 (s, 3 H), 2.36 (m, 2 H), 5.15 (br s, 2 H), 7.14 (s, 1 H); ^{13}C NMR δ 15.65, 16.3, 23.51, 25.77, 28.21, 41.01, 45.77 (CH_2), 49.92, 94.39, 111.34 (CH_2), 151.14. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.64; H, 10.58.

(12) Fenical, W.; Kearns, D. R.; Radlick, P. *J. Am. Chem. Soc.* **1969**, *91*, 3396.

(13) Compared with 5-*endo* cyclization, 6-*endo* cyclization is a more facile process. Consistent with this, the reaction of 2-methylene-1-methylcyclohexyl hydroperoxide with $FeSO_4/CuCl_2$ gives 1-chlorocyclohexyl methyl ketone in 55% yield. Masuyama, A.; Sugawara, T.; Nojima, M. Unpublished result.

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

(15) Mayr, H.; Klein, H.; Sippel, E. *Chem. Ber.* **1983**, *116*, 3624.

1,2,4,4,5,5-Hexamethyl-2-cyclopenten-1-yl hydroperoxide (4b): an oil; ^{1}H NMR δ 0.82 (s, 3 H), 0.86 (s, 3 H), 0.96 (s, 3 H), 1.05 (s, 3 H), 1.58 (s, 3 H), 1.70 (s, 3H), 5.40 (s, 1 H), 7.16 (s, 1 H); ^{13}C NMR δ 13.87, 16.37, 17.97, 23.38, 23.84, 27.44, 46.88, 49.49, 98.08, 137.07, 141.26 (CH). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.66; H, 10.49.

Photooxygenation of 1,2,3,3,6,6-Hexamethylcyclohexene (6). The photooxygenation of **6** (120 mg, 0.73 mmol) was conducted as described above. Column chromatography of the residue (elution with ether−hexane, 5:95) gave **7** (109 mg, 76%).

1,3,3,6,6-Pentamethyl-2-methylene-1-cyclohexyl hydroperoxide (7): mp 60−61 °C; ^{1}H NMR δ 0.83 (s, 3 H), 1.01 (s, 3 H), 1.0−1.1 (m, 1 H), 1.14 (s, 3 H), 1.2−1.3 (m, 1 H), 1.29 (s, 3 H), 1.38 (s, 3 H), 1.53 (td, J = 13.9 and 4.3 Hz, 1 H), 2.06 (td, J = 13.9 and 4.3 Hz, 1 H), 5.20 (s, 1 H), 5.30 (s, 1 H), 6.80 (s, 1 H); ^{13}C NMR δ 16.32, 24.44, 24.71, 28.36, 28.65, 32.01, 32.69, 36.07, 38.62, 88.90, 114.43, 153.17. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.67; H, 11.18. Found: C, 73.18; H, 11.47.

Reaction of Allylic Hydroperoxide with $FeSO_4$/$CuCl_2$. To a solution of $FeSO_4$ (1 equiv) and $CuCl_2$ (3 equiv) in H_2O (15 mL) was added dropwise a solution of an allylic hydroperoxide (0.7−1.2 mmol) in CH_3CN (15 mL) during 30 min, and the mixture was stirred at room temperature for an additional 15 min. Then, the mixture was extracted with ether and the extract was dried over anhydrous $MgSO_4$ and evaporated. The residue was separated by column chromatography (column 2.0 × 60 cm; 40 g of silica gel; elution with ether−hexane, 1:99).

Reaction of 1,3,3,6,6-Pentamethyl-2-methylene-1-cyclohexyl Hydroperoxide (7) with $FeSO_4$/$CuCl_2$. The reaction of **7** (142 mg, 0.71 mmol) was conducted as described above. The ^{1}H NMR spectrum of the crude product showed the presence of only **13**. Column chromatography of the residue gave **13** (121 mg, 78%).

1-Chloro-2,2,5,5-tetramethylcyclohexyl methyl ketone (13): an oil; ^{1}H NMR δ 0.92 (s, 3 H), 1.02 (s, 3 H), 1.10 (s, 3 H), 1.19 (s, 3 H), 1.3−1.5 (m, 3 H), 1.74 (d, J = 15.2 Hz, 1 H), 1.83 (ddd, J = 13.8, 9.5, and 4.6 Hz, 1 H), 2.27 (d, J = 15.2 Hz, 1 H), 2.39 (s, 3 H); ^{13}C NMR δ 23.92 (CH_3), 27.68 (CH_3), 28.12 (CH_3), 29.80 (CH_3), 31.36, 32.05 (CH_3), 34.09 (CH_2), 34.15 (CH_2), 37.87, 45.09 (CH_2), 83.62, 205.53; HRMS calcd for $C_{12}H_{21}ClO$ (M^+) 216.1281, found 216.1274.

Reaction of 1,3,3,4,4,5,5-Heptamethyl-2-methylene-1-cyclopentyl Hydroperoxide (2a) with $FeSO_4$/$CuCl_2$. The reaction of **2a** (207 mg, 0.98 mmol) was conducted as described above. Column chromatography of the residue (elution with ether−hexane, the ratio was changed gradually from 1:99 to 1:9) gave first **17** (113 mg, 50%). From the second fraction, aldehyde **20** was isolated (27 mg, 14%). The final fraction contained alcohol **19** (19 mg, 10%).

1-Chloro-2,2,3,3,4,4,-hexamethyl-1-cyclopentyl methyl ketone (17): an oil; ^{1}H NMR δ 0.79 (s, 3 H), 0.89 (s, 3 H), 1.04 (s, 3 H), 1.12 (s, 3 H), 1.13 (s, 3 H), 1.25 (s, 3 H), 1.99 (d, J = 15.8 Hz, 1 H), 2.35 (s, 3 H), 3.00 (d, J = 15.8 Hz, 1 H); ^{13}C NMR δ 22.64 (CH_3), 23.78 (CH_3), 24.69 (CH_3), 25.09 (CH_3), 27.61 (CH_3), 29.02 (CH_3), 30.48 (CH_3), 40.69, 49.23, 51.35, 52.69 (CH_2), 88.12, 202.91; HRMS (EI) calcd for $C_{13}H_{23}ClO$ (M^+) 230.1437, found 230.1452.

(2,3,3,4,4,5,5-Heptamethyl-1-cyclopentenyl)methanol (19): an oil; ^{1}H NMR δ 0.80 (s, 6 H), 0.92 (s, 6 H), 0.98 (s, 6 H), 1.64 (s, 3 H), 1.6−1.7 (br s, 1 H), 4.12 (s, 2 H); ^{13}C NMR δ 10.10, 21.46 (2 C), 24.01 (2 C), 25.08 (2 C), 45.99, 49.31, 49.92, 56.96, 138.90, 142.91. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.24; H, 12.29.

1-Formyl-2,3,3,4,4,5,5-heptamethylcyclopentene (20): an oil; ^{1}H NMR δ 0.81 (s, 6 H), 1.01 (s, 6 H), 1.14 (s, 6 H), 2.01 (s, 3 H), 10.04 (s, 1 H); ^{13}C NMR δ 10.42, 20.99 (2 C), 23.65 (2 C), 24.20 (2 C), 46.31, 48.43, 52.13, 132.54, 141.13, 190.22. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.48; H, 11.65.

Reaction of (2,3,3,4,4,5,5-Heptamethyl-1-cyclopentenyl)methyl Hydroperoxide (5a) with $FeSO_4$/$CuCl_2$. The reaction of **5a** (180 mg, 0.85 mmol) was conducted as described above. By column chromatography on silica gel (elution with ether−hexane, 1:99), aldehyde **20** was isolated (76 mg, 46%). Subsequent elution with ether−hexane (2:8) gave alcohol **19** (63 mg, 38%).

Reaction of 1,3,3,4,4-Pentamethyl-2-methylene-1-cyclopentyl Hydroperoxide (2b) with $FeSO_4$/$CuCl_2$. The reaction of **2b** (150 mg, 0.81 mmol) was conducted as described above. By column chromatography on silica gel, alcohol **22** was isolated (104 mg, 76%). The physical properties of **22** were the same as those obtained by the reaction of the allyl hydroperoxide **2b** with 1 equiv of triphenylphosphine in $CDCl_3$.

2-Methylene-1,3,3,4,4-pentamethylcyclopentanol (22): an oil; ^{1}H NMR δ 0.85 (s, 3 H), 0.92 (s, 3 H), 0.95 (s, 3 H), 1.02 (s, 3 H), 1.42 (s, 3 H), 1.6−1.8 (br s, 1H), 1.83 (s, 2 H), 4.92 (s, 1 H), 5.13 (s, 1 H); ^{13}C NMR δ 23.25, 23.70, 24.80, 25.31, 31.25, 41.53, 47.96, 53.84, 76.87, 105.28, 170.08. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.41; H, 12.06.

Reaction of 2-Methyl-1-methylene-2-indenyl Hydroperoxide (24) with $FeSO_4$/$CuCl_2$. The reaction of **24** (202 mg, 1.15 mmol) was conducted as described above. By column chromatography on silica gel (elution with ether−hexane, 8:92), chloride **27** was isolated (149 mg, 67%).

3-(2-Chloromethylphenyl)-3-buten-2-one (27): an oil; ^{1}H NMR δ 2.33 (s, 3 H), 4.37 (s, 2 H), 5.89 (s, 1 H), 6.37 (s, 1 H), 7.0−7.4 (m, 4 H); ^{13}C NMR δ 26.70, 46.37, 128.39, 128.52, 128.79, 129.92, 130.01, 135.24, 137.39, 147.78, 198.47. Anal. Calcd for $C_{11}H_{11}ClO$: C, 67.87; H, 5.70. Found: C, 67.62; H, 5.86.

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