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Metal-Catalyzed Organic Photoreactions. Chemo- and Regioselectivities in the $CuCl_2$-Induced Photooxidation of Olefins

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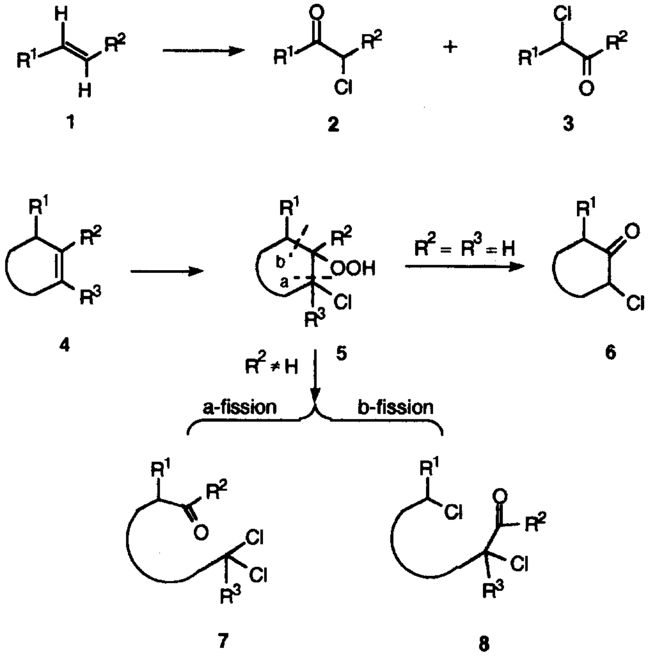
Abstract: Copper(II) chloride induced the chemo and regioselective chloro-hydroperoxidation, as well as the site-selective chlorination of olefins, under photooxygenation conditions.

As a series of an investigation on the metal-catalyzed photoreactions, we have developed several reactions which can be used as synthetic methodology.[1] Some time ago we reported that iron(III) chloride exhibited a characteristic effect on the photooxygenation of olefins in pyridine.[2] The reactions of acyclic olefins **1** afford α-chloro ketones **2** and **3**, while the reactions of cyclic olefins **4** afford either α-chloro ketones **6** or bond-cleavage products **7** or **8**, depending upon the nature of the substituents. It has been assumed, and in some cases confirmed, that the primary products of the photooxidation are β-chloro hydroperoxides **5**. The β-chloro hydroperoxides obtained from unsubstituted cycloalkenes (**4**, $R^2 = R^3 = H$) are secondary hydroperoxides, and they undergo dehydration to afford **6**. With unsymmetrically substituted cycloalkenes (R^2 or $R^3 \neq H$), the chloro-hydroperoxidation proceeds regioselectively to afford tertiary hydroperoxides, which undergo the C-C bond cleavage at either a or b position to afford **7** or **8**, respectively.

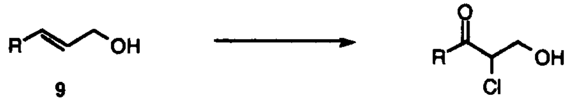
One plausible reaction mechanism for the chloro hydroperoxide formation would be a stepwise mechanism involving the following four steps: (i) the formation of a chlorine atom by the photolysis of $FeCl_3$, (ii) the addition of the chlorine atom to the less-substituted carbon atom of the double bond in the olefin, (iii) the combination of the radical thus formed with molecular oxygen, and (iv) hydrogen abstraction from the solvent to produce the β-chloro hydroperoxide. However, this reaction scheme was ruled out in view of the following observations: (i) molecular oxygen, as well as $FeCl_3$, is necessary to initiate the reaction, because any products suggesting the involvement of the chlorine atom was identified by irradiating olefin and $FeCl_3$ in the absence of molecular oxygen under the otherwise same conditions, resulting in only the recovery of the starting olefin, and (ii) the presence of radical scavengers did not exhibit any appreciable retarding effect on the major reaction pattern. In view of these considerations, we illustrated the formation of the β-chloro hydroperoxide as proceeding concertedly, involving a photo-induced interligand electron transfer from the



Scheme 1

chloride ligand to molecular oxygen through the metal ion and olefin molecule, which we termed "long range electron transfer mechanism".[3] In view of the characteristic feature and reasonable yields of the ring cleavage reaction of cyclic olefins, we have utilized the reaction for some natural product syntheses, in order to demonstrate the applicability of the reaction.[4] With a view to define the limitation for the potentiality as a synthetic methodology, we now investigated the reactions with functionalized olefins under various conditions.

It has been established that the terminal olefins (**1**, $R^2 = H$) afford **2** as sole products, while no regioselectivity is observed with internal olefins (**1**, $R^2 \neq H$), such as 2-octene, affording a mixture of **2** and **3** in about equal amounts.[3] On the other hand, when hydroxyl group is present at allylic position, the regiochemistry of the reaction of the internal olefin is controlled by the functional group, as exemplified by the reaction of **9a** affording **10a** as a single product. We rationalized the selectivity in terms of the preliminary complexation of iron ion with hydroxyl group. Due to the low mass balance of the reaction (32% yield), however, the argument on the regioselectivity is ambiguous, and therefore, we tried to optimize the conditions to achieve a good mass balance.



9 **10**

a: R = Me; b: R = *n*-Pr

In our previous report of the iron(III) ion-induced photodegradation of carbohydrates,[5] we found that iron(III) triflate is an effective catalyst even with 0.01 equivalent amount. Since we have also observed that $CHCl_3$ and CCl_4 can be chlorine sources for the present reaction,[3] we examined the reaction of **9b** in various

Table 1. $Fe(OTf)_3$-Catalyzed Photooxidation of **9b**.[a)]

Run	Solvent		Additive	Yield (%) of **10b**[b)]
1	Pyridine			No reaction
2	Pyridine-CCl_4	(1 : 1)		41
3	"	(1 : 7)		34
4	CCl_4			No reaction
5	Pyridine-$CHCl_3$	(1 : 7)		26
6	"		LiCl (3 eq)	34
7	"		$CuCl_2$ (0.25 eq)	45
8	$CHCl_3$			No reaction
9	Pyridine-CH_2Cl_2	(1 : 7)		No reaction
10	"		$CuCl_2$ (0.25 eq)	47

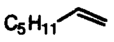
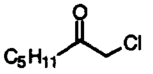
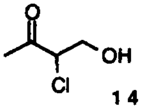
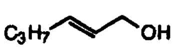
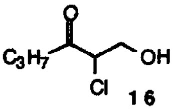
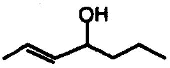
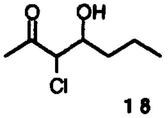
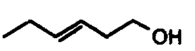
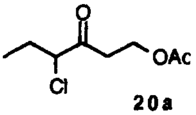
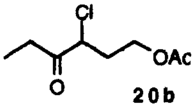
a) Irradiation of 0.025 M solution of olefin in the presence of 0.01 eq $Fe(OTf)_3$ for 2 h.
b) The yields were determined from ^1H NMR spectra using 1,1,2,2-tetrachloroethane (TCE) as an internal reference.

solvent systems using 0.01 equiv of $Fe(OTf)_3$. The results are shown in Table 1. The characteristic points of the results are as follows: (i) iron(III) triflate is an effective catalyst for the reaction, if appropriate chlorine sources are present, (ii) the reaction proceeds only in the presence of pyridine (runs 4 and 8), (iii) while CCl_4 and $CHCl_3$ can be chlorine sources in the presence of pyridine (runs 2, 3, and 5), CH_2Cl_2 can not be a chlorine source (run 9), and (iv) $CuCl_2$ can be a chlorine source in pyridine-CH_2Cl_2 solvent system (run 10). The result of (ii) is consistent with our previous findings that the present reaction proceeds well in pyridine, pyridine-CCl_4, or pyridine-benzene but not at all in other ordinary solvent systems containing no pyridine. The reaction in run 10 proceeded cleanly with 48% recovery of the starting material, as well as 47% yield of the product, achieving the high mass balance of 95%.

We further found that $CuCl_2$ served not only as a chlorine source, but also as an effective reagent for the present reaction: the reaction proceeded fairly clean even in the absence of any iron(III) compounds. It was found that the irradiation of **9b** (0.013 M) in pyridine-CH_2Cl_2 (1 : 7 vol ratio) in the presence of 0.5 equivalent of $CuCl_2$ for 4 h gave **10b** in 84% yield with 13% recovery of the starting material. Evidently the reaction proved to proceed with complete regioselectivity.

Although the presence of pyridine is requisite for the present reaction, it is desirable to reduce its amount as much as possible from the technical viewpoint. We found that we could reduce the amount of pyridine to one-eighth volume in CH_2Cl_2 without any decrease in the yields of the products. With less amount of pyridine, however, $CuCl_2$ did not dissolve completely, and the yields of the product decreased remarkably. While the role of pyridine has not been clarified, it is highly probable that the coordination ability to $CuCl_2$ could be an important factor, since it has been known that $CuCl_2$-pyridine complex induces oxidative C-C bond cleavage of catechol by molecular oxygen.[6] We carried out the photoreaction of some other substrates under the optimized conditions as shown in Table 2. Comparing with the results by $FeCl_3$-induced reactions (yields

Table 2. Comparison between $CuCl_2$- and $FeCl_3$-Induced Photooxidation of Olefins.[a)]

Run	Starting material	Product	Yield (%)[b)]
11	 **11**	 **12**	68 (58)
12	 **13**	 **14**	57 (32)
13	 **15**	 **16**	84 (41)
14	 **17**	 **18**	55 (41)[c)]
15[d)]	 **19**	 **20a**	35 (23)
		 **20b**	30 (21)

a) Irradiation of 0.013 M of olefin in the presence of 0.5 eq $CuCl_2$ or 1 eq $FeCl_3$ for 4 h.

b) The yields were determined from ^1H NMR spectra using TCE as an internal reference. The yields in the parentheses are those of the $FeCl_3$-catalyzed reactions.

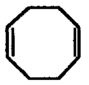
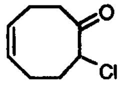
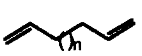
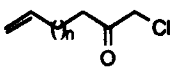
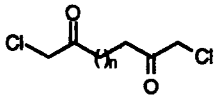
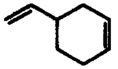
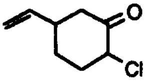
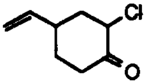
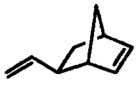
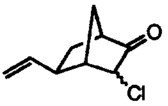
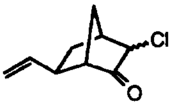
c) 1 : 1 Diastereomer mixture.

d) Products were identified after acetylation.

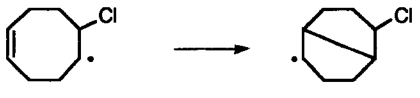
in parentheses), it is obvious that better yields have been obtained with $CuCl_2$. Notably both of the regio isomers were identified with homoallyl alcohol **19** (run 15), in contrast to the excellent regioselectivity with allyl alcohols **13**, **15**, and **17** (runs 12-14).

In our previous paper,[3] we reported that the iron(III) chloride-induced reaction of **21** afforded **22** in 29% yield. Further irradiation induced the secondary reactions from **22**, resulting in only 9% yield of the product, accompanied by much amounts of unidentified byproducts. On the other hand, the reaction induced by 0.5 eq of $CuCl_2$ afforded **22** in 37% yield with 40% recovery of the starting material, without producing any other products. The yield increased to 68% with 10% recovery of the starting material, when 1 eq of $CuCl_2$ was used. Despite the presence of 2 eq of chlorine atom, the amounts of the secondary reaction products were negligible. Presumably, once the α-chloro carbonyl moiety is created by the first-stage reaction, the reactivity of the copper ion for the second-stage reaction is diminished due to chelation. The absence of any products suggestive of the involvement of annulated intermediate 33 could be an another support in favor of the concerted mechanism rather than the stepwise mechanism involving free radical species such as 32. Inspired by these results we investigated several diolefins under these conditions. The results are shown in Table 3.

Table 3. $CuCl_2$-Induced Photooxidation of Diolefins.[a)]

Run	Starting material	Product and yield (%)[b)]	
16	 21	 22 68%	
17	 23 a: n = 3 b: n = 5	 24 83% 58%	 25 ~7% 7%
18	 26	 27 1.4	 : 1 28
		80%	
19	 29	 30	 31
		57%	

a) Irradiation of 0.013 M of olefin in the presence of 1 eq $CuCl_2$ or 1 eq $FeCl_3$ for 4 h.
b) The yields were determined from ^1H NMR spectra using TCE as an internal reference.

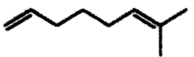
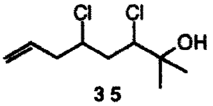
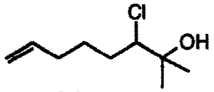
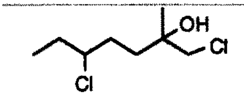
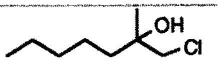


32 33

As obvious from run 17, the reactions of **23a** and **23b** terminated mainly at the first stage. The reactions of **26** and **29** proceeded also with complete chemoselectivity, although the regio- and stereoselectivities were poor. The products from **26**, isolated in 80% yield, showed a single spot on TLC, but four peaks on GLC in a ratio of 56 : 24 : 13 : 7. When the product mixture was treated with Zn-Cu, and then hydrogenated, a mixture of 3-ethylcyclohexanone and 4-ethylcyclohexanone in a ratio of 1.4 : 1.0 was obtained. Both compounds were identified by comparing the GC-MS data with those of the authentic samples. Consequently we concluded that the products of the photooxidation is a mixture of two regioisomers **27** and **28** of unknown stereochemistry. The product from **29** also showed a single spot on TLC, but showed a shoulder on the GC analysis. Since the products showed ^1H NMR signals typical of vinyl protons, it was concluded that the reaction proceeded at the cyclic olefin. Since the ^{13}C NMR spectrum showed four pairs of olefinic carbons with relative peak heights of 48 : 33 : 12 : 7, and the ^1H NMR showed three doublets of protons at the chlorine-bearing carbon with relative signal area of 45 : 33 : 22, we tentatively assigned the product as a mixture of regio and stereoisomers of **30** and **31**.

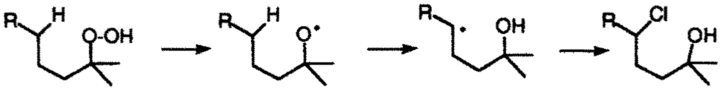
We next investigated the reaction of branched diolefins. As described above, cyclic olefins having substituents at the olefinic carbon undergo the ring cleavage to produce dichloro ketones. On the other hand, the reaction in acyclic system proceeded in different ways, as shown in Table 4. The major products from **34** and **37** were **35** and **38**, accompanied by minor products **36** and **39**, respectively. 400 MHz ^1H NMR spectrum of **35** revealed that the product is a diastereomer mixture in a ratio of 83 : 17. The splitting patterns of two methylene group of the major isomer were completely assignable (see Experimental Section), thus establishing the positions of the chlorine atoms. The structures of these products were further confirmed by deriving into the corresponding oxiranes **40** and **41** by treating the oxidation products with $Ca(OH)_2$. The δ-position of the chlorine atom from the branched carbon was also confirmed by the doublet splitting pattern of methyl signal of **43**, obtained by the photooxidation of **42** followed by $Ca(OH)_2$ treatment. Obviously the

Table 4. $CuCl_2$-Induced Photooxygenation of Branched Olefins.[a)]

Run	Starting olefin	Additive	Product and yield (%)[b)]	
	 **34**		 **35**	 **36**
20		none	43	37
	 **37**		 **38**	 **39**
21		none	60	27
22		CCl_4	48	38
23		LiCl	61	25
24		NCS	0	75

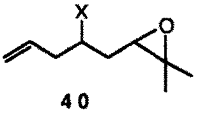
a) b) Same as the corresponding footnotes in Table 3.

tertiary hydroperoxide in the acyclic system undergoes the δ-hydrogen abstraction after the homolytic O-O bond cleavage. (Scheme 2). Although the Fe(II)-Cu(II) ion-catalyzed decomposition of hydroperoxides is known to afford unsaturated alcohols via the δ-hydrogen abstraction,[7] no such products were identified in the present reaction.



Scheme 2

In contrast to the relatively high diastereomer ratio of **35**, the products **38**, **41a**, and **43** were mixtures of two diastereomers of almost equal amounts as revealed by ^{13}C NMR analyses. The poor selectivity is probably due to the presence of two methylene units between two stereogenic centers, in contrast to only one methylene unit in **35**. Since the site-selective chlorination to give **35**, **38**, and **43** are interesting from the synthetic viewpoint, we carried out the reaction of **37** under several conditions (runs 21-24) with a view to improve the dichlorination ratio. However the additions of several chlorine sources, particularly N-chlorosuccinimide resulted in the decrease of the dichlorination ratio. The reaction in run 24 is remarkable in that the photoreaction of **37** and NCS in the absence of $CuCl_2$ and oxygen gave dichloro compound **44** as the sole product.



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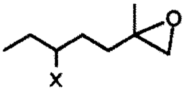
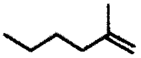
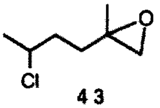


41

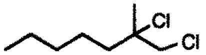
a: X = Cl; b: X = H



42



43



44

Experimental

Starting Materials. All the starting materials except **17** are commercially available. The allyl alcohol **17** was prepared according to the literature.[8]

General Procedure for the Photooxidation. The irradiation was carried out on a solution of olefin containing an appropriate amount of the additives as specified in the tables, in Pyrex test tubes while oxygen gas was bubbled through. A high-pressure mercury lamp [Ushio UM 452 (450 W)] was used as a light source. The irradiated solution was conventionally worked up in the following way (work-up I). The solvent was removed in vacuo, and the reaction products were extracted with ether from the residue. The extract was passed through a short column of Florisil, and the solvent was removed in vacuo. The material that remained after the evaporation of the solvent was almost pure and was directly analyzed by GLC or NMR techniques. 1,1,2,2-Tetrachloroethane was used as an internal reference for the NMR analysis. In particular cases, the irradiated solution was neutralized with 4 M HCl and shaken with ether. The extract was dried and the solvent was removed in vacuo (work-up II). No essential difference was observed between both methods.

Unless otherwise stated, all the spectroscopic data were determined on a sample purified by column chromatography (silica gel; Et_2O : hexane = 1 : 5, or CH_2Cl_2 : CCl_4 = 1 : 5).

Photooxidation of 11 (run 11). The product **12** showed identical spectroscopic data with those of the reported.[3]

Photooxidation of 13 (run 12). The product **14** showed identical spectroscopic data with those of the reported.[3]

Photooxidation of 15 (run 13). The product was **16**. Bp. 75-78 °C/25 mmHg, IR (neat), 3460, 2964, 2934, 2876, 1703, 1434, 1164, 776 cm^{-1}. ^1H NMR, δ 0.98 (t, *J* = 7 Hz, 3H), 1.22-1.97 (m, 2H), 2.68 (t, *J* = 6.4 Hz, 2H), 3.8-4.4 (m, 4H). ^{13}C NMR, δ 13.52, 16.95, 41.88, 61.82, 63.49, 205.16.

Photooxidation of 17 (run 14). The product was a mixture of two diastereoisomers of **18** in a ratio of 1 : 1, as revealed from ^{13}C NMR data. IR (neat), 3445, 2961, 2934, 2874, 1716, 1358, 789, 765 cm^{-1}. ^1H NMR, δ 0.91, (bt, 3H), 1.10-1.79 (m, 4H), 2.32 (s, 3H), 3.71 (bs, 1H), 3.80-4.21 (m, 2H). ^{13}C NMR,[9] δ [13.84*, 13.90], [18.44, 18.72*], [27.56, 28.00*], [35.14, 36.13*], [68.33*, 68.54], [71.24*, 71.30], [203.35, 203.96*] (1 : 1).

Photooxidation of 19 (run 15). Acetic anhydride (2.5 ml, 25 mmol) was added to the irradiated solution, and stirred for 14 h at room temperature prior to the workup. Column chromatography afforded two fractions. The fraction I was pure **20a**, while the fraction II was a mixture of **20a** and **20b**. The spectroscopic data of **20b** was assigned by subtracting the data of **20a** from those of the mixture. For **20a**: MS (CI), m/z 193 (M^+ + 1, with isotope peaks of chlorine at M^+ + 3, 34%), 133, 115 (base), 97, 77, 69, 55. IR, 1741, 1368, 1239, 789 cm^{-1}. ^1H NMR, δ 1.04 (t, *J* = 6.2 Hz, 3H), 2.00 (s, 3H), 1.65-2.37 (m, 2H), 2.95 (t, *J* = 6.2 Hz, 2H), 4.13 (bt, *J* = 6.2 Hz, 1H), 4.28 (t, *J* = 7 Hz, 2H). ^{13}C NMR, δ 20.40, 26.85, 32.31, 37.37, 58.96, 65.05, 170.41, 202.09. Exact mass (CI): calcd for $C_8H_{14}O_3Cl$ (M^+ + 1): 193.0631, obsd, 193.0652. For **20a**: IR, 2677, 1742, 1367, 1238, 1043, 789 cm^{-1}. ^1H NMR, δ 1.10 (t, *J* = 7 Hz, 3H), 2.00 (s, 3H), 1.65-2.37 (m, 2H), 2.45-2.85 (m, 2H), 3.78-4.24 (m, 3H). ^{13}C NMR, δ 20.78, 32.36, 32.56, 59.44, 60.46, 65.18, 170.46, 204.67.

Photooxidation of 21 (run 16). The product was **22** which showed identical spectroscopic data with those of the reported.[3]

Photooxidation of 23a (run 17). The major product was **24a**. Due to the small amount of the minor product, the structure **25a** was speculated only from the ^1H NMR data. For **24a**: MS, m/z 160 (M^+, with isotope peaks of chlorine at M^+ + 2, 34%), 125, 118, 111, 105, 93 (base), 83, 77, 69, 54. IR, 2933, 2859, 1734, 1404, 913, 787 cm^{-1}. ^1H NMR, δ 1.11-1.79 (m, 4H), 1.80-2.32 (m, 2H), 2.59 (bt, *J* = 6.5 Hz, 2H), 3.91 (s, 2H), 4.71-5.18 (m, 2H), 5.38-6.12 (m, 1H). Exact mass : calcd for $C_8H_{13}OCl$ (M^+): 160.0655, obsd, 160.0641. For **25a**: ^1H NMR, δ 1.35-1.85 (m, 4H), 2.42-2.85 (m, 4H), 4.02 (s, 4H).

Photooxidation of 23b (run 17). The major product was **24b**. Due to the small amount of the minor product, the structure **25b** was speculated only from the ^1H NMR data. For **24b**: IR, 2929, 2856, 1733, 1721, 1404, 911, 738 cm^{-1}. ^1H NMR, δ 1.10-1.76 (m, 8H), 1.77-2.30 (m, 2H), 2.57 (bt, *J* = 6.5 Hz, 2H), 3.91 (s, 2H), 4.69-5.14 (m, 2H), 5.38-6.13 (m, 1H). Exact mass (CI): calcd for $C_{10}H_{18}OCl$ (M^+ + 1): 189.1046, obsd, 189.1040. For **25b**: ^1H NMR, δ 1.06-1.90 (m, 8H), 2.60 (bt, *J* = 6.0 Hz, 4H), 4.05 (s, 4H).

Photooxidation of 26 (run 18). The product was a mixture of **27** and **28**, which could not be separated. MS, m/z 158 (M^+, with isotope peaks of chlorine at $M^+ + 2$, 34%), 96, 81 (base), 67, 55, 54. IR, 2941, 1728, 920 cm^{-1}. ^{1}H NMR, δ 1.60-3.32 (m, 7H), 4.00-4.30 (m, 1H), 4.81-5.36 (m, 2H), 5.47-6.17 (m, 1H). Exact mass : calcd for $C_8H_{11}OCl$ (M^+): 158.0498, obsd, 158.0498.

Dechlorination and Hydrogenation of a mixture of 27 and 28. A solution of the mixture (0.048 g, 0.3 mmol) and Cu-Zn (0.391 g, 6 mmol) in NH_4Cl-saturated methanol (7 ml) was stirred at room temperature for 10 min. Ethyl acetate (15 ml) was added and the solid materials were filtered off. After removal of the solvent in vacuo, a mixture of ethyl acetate and hexane (1 : 1) was added. A column chromatography (silica gel, ether-hexane (1 : 5)) gave a mixture of 3-vinylcyclohexanone and 4-vinylcyclohexanone (0.030 g, 81%). The mixture (0.023 g, 0.19 mmol) was hydrogenated (1 atm) under Pd-carbon catalyst (0.07 g) in ethyl acetate (5 ml) at room temperature for 24 h. The product was a mixture of 3-ethylcyclohexanone and 4-ethylcyclohexanone in a ratio of 1.4 : 1, as revealed by comparison with the authentic samples on GC-MS analysis.

Photooxidation of 29 (run 19). The product was a mixture of **30** and **31**, which could not be separated. MS, m/z 170 (M^+, with isotope peaks of chlorine at $M^+ + 2$, 34%), 135, 107, 91, 79, 67 (base). ^{1}H NMR, δ 1.03-3.01 (m, 7H), 3.56 (d, $J = 3.4$ Hz, 0.45 x 1H), 3.67 (d, $J = 3.1$ Hz, 0.22 x 1H), 3.90 (d, $J = 3.0$ Hz, 0.33 x 1H), 4.84-6.23 (m, 3H). Exact mass (CI): calcd for $C_9H_{12}OCl$ ($M^+ + 1$): 171.0577, obsd, 171.0616.

Photooxidation of 34 (run 20). The product was a mixture of **35** and **36**, which were separated on a column chromatography. For **35** (diastereomer mixture of 83 : 17): IR, 3437, 2980, 1375, 1125, 922, 786 cm^{-1}. ^{1}H NMR (400 MHz), δ 1.31 (s, 0.83 x 3H), 1.34 (s, 0.83 x 3H), 1.30 (s, 0.17 x 3H), 1.33 (s, 0.17 x 3H), 2.04 and 2.11 (dd of ABq, $J = 15.0$, 10.7, 2.3 Hz, 0.83 x 2H), 2.21 and 2.31 (dd of ABq, $J = 15.2$, 10.5, 3.0 Hz, 0.17 x 2H), 2.06-2.11 (b, 1H), 2.47 and 2.66 (m, 0.17 x 2H), 2.56 (ddd, $J = 6.8$, 6.5, 1.0 Hz, 0.83 x 2H), 3.88-3.92 (m, 0.17 x 2H), 4.20 (dd, $J = 11.0$, 2.3 Hz, 0.83 x 1H), 4.22-4.32 (m, 0.83 x 1H), 5.13-5.20 (m, 2H), 5.75-5.95 (m, 1H). ^{13}C NMR,[9] δ [25.61, 25.89*], [26.25, 26.86*], [40.08, 41.31*], [41.09, 43.10*], [58.83, 59.82*], [69.15, 70.45*], [72.46*, 72.80], [118.42*, 118.64], [133.05, 133.42*] (1 : ~5). For **36**: IR, 3426, 2978, 2930, 1375, 1129, 910, 780 cm^{-1}. ^{1}H NMR (90 MHz), δ 1.24 (s, 3H), 1.28 (s, 3H), 1.37-2.22 (m, 7H), 3.75-3.93 (bd, 2H), 4.87-5.20 (m, 2H), 5.67-6.00 (m, 1H).

Photooxidation of 37 (run 21). The product was a mixture of **38** and **39**, which were separated on a column chromatography. For **38** (diastereomer mixture): ^{1}H NMR (90 MHz), δ 0.98 (t, $J = 6.3$ Hz, 3H), 1.13-1.40 (m, 5H), 1.52-1.93 (m, 4H), 2.13 (bs, 1H), 3.48 (s, 2H), 3.75-4.00 (m, 1H). For **39**: IR, 3417, 2956, 2871, 1463, 1376, 785 cm^{-1}. ^{1}H NMR (60 MHz), δ 0.91 (bt, 3H), 1.23 (s, 3H), 1.10-1.73 (m, 8H), 3.55 (s, 2H), 7.50 (bs, 1H).

General Procedure for Cyclization of Chlorohydrins into Oxiranes. Chlorohydrins were stirred with 2 equivalents of $Ca(OH)_2$ in water for 10-20 min at room temperature, and the products were extracted with ether. The products were purified by column chromatography. For **40a**: ^{1}H NMR (90 MHz), δ 1.27 (s, 3H), 1.34 (s, 3H), 2.00 (t, $J = 6.1$ Hz, 2H), 2.59 (t, $J = 6.8$ Hz, 2H), 2.97 (t, $J = 6.1$ Hz, 1H), 4.10 (dist. quintet, 1H), 5.01-5.31 (m, 2H), 5.63-6.25 (m, 1H). Exact mass (CI): calcd for $C_9H_{16}OCl$ ($M^+ + 1$): 175.0890, obsd, 175.0907. For **40b**: Exact mass (CI): calcd for $C_9H_{17}O$ ($M^+ + 1$): 141.1279, obsd, 141.1290. For **41a**: IR, 2966, 2936, 1456, 1391, 803 cm^{-1}. ^{1}H NMR (60 MHz), δ 1.03 (t, $J = 7.0$ Hz, 3H), 1.32 (s, 3H), 1.50-2.80 (m, 6H), 2.60 (s, 2H), 3.84 (broad quintet, 1H). ^{13}C NMR,[9] δ 11.0, [20.95*, 21.31], [31.56, 31.67*], [33.30*, 33.41], [33.64*, 33.86], [53.44*, 54.00], [56.27, 56.49*], [65.13, 65.37*] (1 : 1). Exact mass (CI): calcd for $C_8H_{16}OCl$ (M^+ + 1): 163.0890, obsd, 163.0928. For **43**: ^1H NMR (60 MHz), δ 1.31 (s, 3H), 1.53 (d, J = 6.0 Hz, 3H), 1.76-1.92 (m, 4H), 2.60 (s, 2H), 3.80-4.30 (m, 1H). ^{13}C NMR,[9] δ [20.95*, 21.26], [25.32, 25.43*], [33.41, 33.90*], [35.64*, 35.86], [53.44, 53.89*], [56.22, 56.42*], [58.25*, 58.45] (1 : 1).

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9. Signals shown in the brackets appear as a pair, with asterisk on the stronger peaks. The average ratio of each pair is shown in parenthesis.

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