Table VI. Kinetic Data for Thermal Rearrangement of 7

T, K	$k \times 10^3$	ln k	R^2
703.0	4.4526	−5.41426	0.995
710.5	7.0403	−4.95610	0.999
716.5	9.8611	−4.61916	0.999
722.3	16.5136	−4.10357	0.995
730.0	19.9017	−3.91695	0.997
736.0	36.2569	−3.31713	0.984

Table VII. Kinetic Data for Thermal Rearrangement of 9

T, K	$k \times 10^3$	ln k	R^2
548.0	3.3525	−5.69851	0.847
554.4	4.2474	−5.46145	0.979
562.5	7.5062	−4.89203	0.960
572.5	11.6534	−4.45216	0.992
577.0	16.2270	−4.12107	0.995
581.5	23.0012	−3.77221	0.996
587.5	34.4480	−3.36830	0.997
593.5	53.1226	−2.93515	0.981

0.25 in. 20% Dow Corning 710 silicon oil on Chromosorb P) on a Varian Aerograph 90-P. All pyrolyses on the stirred-flow apparatus were extremely clean, yielding only a starting material and a product peak, except for **5** (containing a 3% impurity in the starting material) which pyrolyzed to *exo*- and *endo*-**6**. Compound **9** thermalized to **10** with very minor traces of **11** present. Peak areas were determined by disk integration. The flow rates were measured with a soap-film flow meter at 25 °C and cross checked with an electronic flow meter and by the position of the set screw on the carrier gas needle valve which had previously been calibrated with flow rate. Tables IV-VII summarize the specific kinetic data and Table I summarizes the activation parameters calculated from the Arrhenius and Eyring plots.[14]

Acknowledgment. We thank Professor E. Vedejs for allowing us to use his micro stirred flow apparatus for these studies. We also thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs. We thank the National Science Foundation for contributions toward the purchase of major departmental instrumentation utilized throughout this work.

Registry No. **3**, 39834-22-5; **4**, 39834-25-8; **5**, 75751-13-2; **6** (isomer 1), 75751-14-3; **6** (isomer 2), 75751-15-4; **7**, 42161-96-6; **8**, 19980-43-9; **9**, 75751-16-5; **10**, 75751-17-6; **12**, 693-86-7; **13**, 16906-27-7; **14**, 49785-10-6; **15**, 24560-57-4; **16**, 75751-18-7; **17**, 19159-61-6; **18**, 75751-19-8; **19**, 694-89-3; **20**, 822-93-5; **21**, 4663-22-3; **22**, 3422-07-9; **23**, 54159-22-7; **24**, 1003-33-4.

Supplementary Material Available: Spectral data for compounds **4**, **5**, **6**, **9**, and **10** (3 pages). Ordering information is given on any current masthead page.

Metal-Catalyzed Organic Photoreactions. One-Step Synthesis of Chlorinated Ketones from Olefins by Photooxidation in the Presence of Iron(III) Chloride[1]

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Received September 17, 1980

Under photooxidation in pyridine in the presence of $FeCl_3$, mono- and disubstituted olefins gave α-chloro ketones, while tri- and tetrasubstituted olefins gave dichloro ketones with a C–C bond cleavage. The reaction was interpreted in terms of an electron-transfer mechanism occurring within the coordination sphere of the iron ion.

In our preceding paper,[2] we reported that $UO_2(OAc)_2$ caused the photoreactions of olefins to produce β-hydroxy hydroperoxides or bromohydrins as main products by reaction of molecular oxygen or polyhalomethanes, respectively. It was further revealed that the reaction proceeded by an entirely different mechanism from those known for the photoreaction of olefins, and we proposed a mechanism termed long-range electron transfer for the reaction. Our rationale for this mechanism was inter alia the findings that polyhalomethanes, as well as molecular oxygen, functioned as an electron acceptor and played an important role in initiating the reaction and that there existed a good correlation between reduction potentials of the halomethanes and their reactivities for the formation of the bromohydrins.

In our preliminary paper,[1] we reported that the photooxidation of olefins in the presence of $FeCl_3$ afforded α-chloro ketones or dichloro ketones, depending upon the type of the substrate olefins. In the present study, we investigated the photooxidation under various conditions with several types of olefin and found that the reaction could also be interpreted in terms of the long-range electron-transfer mechanism.

Results

Pyridine solutions of mono- and disubstituted olefins **1–16**, containing an appropriate amount of $FeCl_3$ and other additives as specified in Table I, were irradiated with Pyrex-filtered light for 30–180 min while oxygen gas was bubbled through. The evaporation of the solvent followed by extraction (workup I) gave α-chloro ketones or vinylogs **19–37** as the almost exclusive products (type A). On the other hand, tri- and tetrasubstituted olefins **17** and **18** afforded dichloro ketones **38** and **39**, respectively, under the same conditions. The reaction conditions and yields are summarized in the Table I. The structures of the most of the products were determined definitely on the isolated pure samples by comparison with the authentic samples, by chemical reactions, or by spectroscopic data. However, complete isolation was not accomplished with **24**, **30**, and *trans*-**35**, and these structures are speculative.

Most of these reactions are quite clean, and the amounts of byproducts are very small. We ascribe the unsatisfactory mass balance of the reaction to the escape of the starting olefins during the irradiation or workup proce-

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[1] Preliminary report: E. Murayama, A. Kohda, and T. Sato, *Chem. Lett.*, 161 (1978).

[2] E. Murayama, A. Kohda, and T. Sato, *J. Chem. Soc., Perkin Trans. 1*, 947 (1980).

0022-3263/81/1946-0509$01.00/0

Table I. Reaction Conditions and Yields of the Products[a]

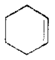
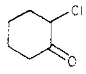
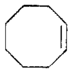
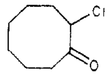
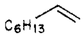
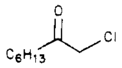
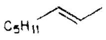
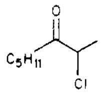
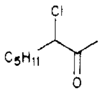
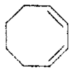
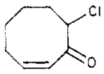
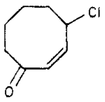
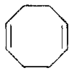
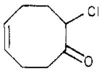
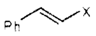
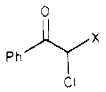
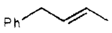
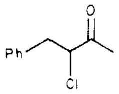
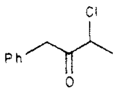
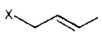
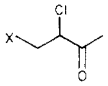
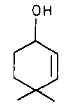
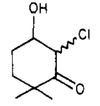
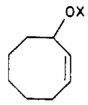
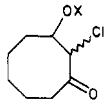
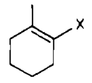
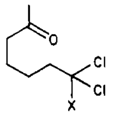
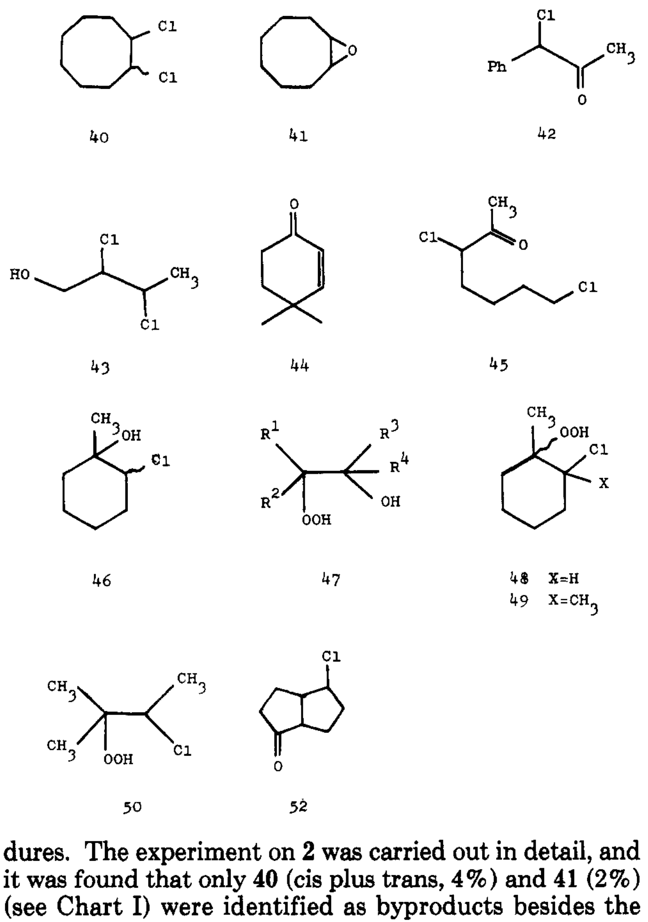
starting olefin	product	solvent	reaction time, min	additive	yield, %	run
 **1**	 **19**	Py[b]	60		54	1
 **2**	 **20**	Py	60		57	2
		Py	60	TTBP[c] (1 equiv)	56	3
 **3**	 **21**	Py	60		32	4
		Py-CCl$_4$ (1:1)	60		57	5
		Py-Bz[d] (1:1)	60		52	6
 **4**	 **22**	Py	60		28 (**22**), 23 (**23**)	7
		Py	60	TTBP (0.5 equiv)	21 (**22**), 29 (**23**)	8
		Py-Bz (3:2)	60		29 (**22**), 29 (**23**)	9
		Py-CCl$_4$ (1:1)	60		28 (**22**), 32 (**23**)	10
	 **23**	Py-CCl$_4$ (1:1)[e]	60		5 (**22**), 4 (**23**)	11
		Py-CCl$_4$ (1:1)[e]	60	TTBP (1 equiv)	0 0	12
		Py-CCl$_4$ (1:1)[f]	60		17 (**22**), 15 (**23**)	13
		Py-CCl$_4$ (1:1)[f]	60	TTBP (1 equiv)	25 (**22**), 16 (**23**)	14
 **5**	 **24**  **25**	Py-CCl$_4$ (1:1)	140		8 (**24**), 21 (**25**)	15
 **6**	 **26**	Py-CCl$_4$ (1:1)	120		29	16
						
7, X = Ph	**27**, X = Ph	Py	30		35	17
		Py	30	DTBN[g] (0.1 equiv)	33	18
		Py	30	DTBN (0.5 equiv)	10	19
		Py	30	DTBN (1 equiv)	5	20
8, X = CH$_3$	**28**, X = CH$_3$	Py	30		57	21
		Py-CCl$_4$ (1:1)	30		66	22
		Py	30	DTBN (0.1 equiv)	37	23
		Py	30	DTBN (0.5 equiv)	16	24
		Py	30	DTBN (1 equiv)	12	25
9, X = CH$_2$OH	**29**, X = CH$_2$OH	Py-CCl$_4$ (1:1)	60		53	26
 **10**	 **30**  **31**	Py	30		35 (**30**), 6 (**31**)	27
		Py	30	DTBN (0.1 equiv)	24 (**30**), 7 (**31**)	28
		Py	30	DTBN (0.5 equiv)	5 (**30**), 2 (**31**)	29
						
11, X = OH	**32**, X = OH	Py	60		32	30
12, X = OEt	**33**, X = OEt	Py	60		25	31
13, X = COOMe	**34**, X = COOMe	Py	180		36	32

Table I (*Continued*)

starting olefin	product	solvent	reaction time, min	additive	yield, %	run
 **14**	 **35**	Py	60		21 (trans), 11 (cis)	33
 **15**, X = H	 **36**, X = H	Py-CCl$_4$ (1:1)	60		49 (trans), 6 (cis)	34
16, X = COMe	**37**, X = COMe	Py	60		30 (trans), 15 (cis)	35
 **17**, X = H	 **38**, X = H	Py	30		30	36
		Py	30	DTBN (1 equiv)	10	37
		Py	30	LiCl (1 equiv)	37	38
		Py	30	LiCl (4 equiv)	47	39
18, X = Me	**39**, X = Me	Py	30		36	40
		Py	30	CuCl$_2$ (0.25 equiv)	69	41

[a] Unless otherwise stated, 0.025 M solution of olefin containing an equivalent molar amount of FeCl$_3$ was used. [b] Pyridine. [c] Tri-*tert*-butylphenol. [d] Benzene. [e] Without FeCl$_3$. [f] FeCl$_3$, 0.0025 M. [g] Di-*tert*-butyl nitroxide.

Chart I



dures. The experiment on **2** was carried out in detail, and it was found that only **40** (cis plus trans, 4%) and **41** (2%) (see Chart I) were identified as byproducts besides the main product **20** (57%). The byproducts are considered to be formed through radical initiation since their formation was quenched when the reaction was carried out in the presence of a radical scavenger, tri-*tert*-butylphenol (vide infra). When the irradiation was carried out in the absence of oxygen under conditions which were otherwise the same (under nitrogen), 16% of dichloride **40** was obtained as the sole identifiable product. The dark reaction in the presence of FeCl$_3$ and oxygen resulted in the recovery of the starting material.

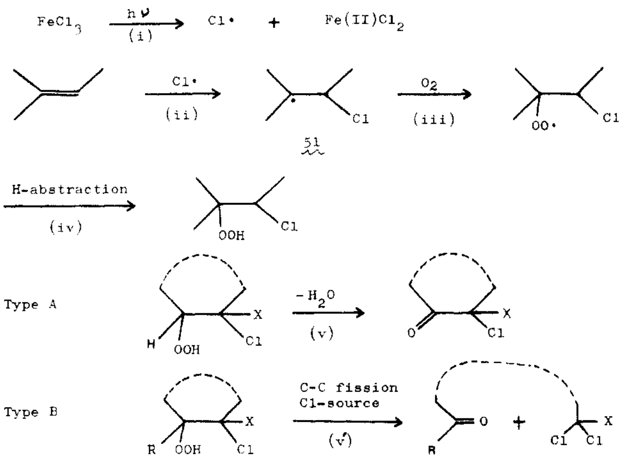
The other byproducts identified are as follows. A small amount of benzaldehyde was isolated as a byproduct from **7** (run 17). The reaction of **8** (run 21) gave a small amount of byproduct of unknown structure. It was confirmed that the byproduct was not **42** (Chart I), a regioisomer of **28**, by comparing it with an authentic sample. A 6% yield of dichloro compound **43** was isolated as a byproduct in the reaction of **11** (run 30). This dichloride was obtained in small amount as the sole product when **11** was irradiated under the FeCl$_3$ catalysis but in the absence of oxygen. A small amount of enone **44** was isolated in the reaction of **14** (run 33). However, no such carbonyl compounds were identified in cases of the other allyl alcohols **9**, **11**, or **15**. The reaction of **17** (run 39) gave a dichloro ketone, **45**, and a chlorohydrin, **46**, in 8% and 11% yields, respectively, as byproducts.

The nature of the solvent is of crucial importance for inducing the present reaction. The reaction proceeded well in pyridine or, most satisfactorily, in pyridine–CCl$_4$ or pyridine–benzene but not at all in other ordinary solvent systems containing no pyridine. In the solvent system of pyridine–CCl$_4$, 32–41% yield of the product (**22** plus **23**) was obtained even when only 0.1 equiv of FeCl$_3$ was used (runs 13 and 14). Evidently FeCl$_3$ functions catalytically in this solvent system, and CCl$_4$ serves as a chlorine source. A small amount of the product (**22** plus **23**) was obtained (9%) even in the absence of FeCl$_3$ (run 11), but the reaction in this case was complex, and the product was accompanied by several byproducts.

Good regioselectivity was observed with olefins having phenyl group or oxygen-containing substituents at the allylic position (**9**–**16**), and chlorine always added to that carbon of the double bond that is nearer to the substituent. This is an evident contrast to the case of 2-octene (**4**), in which both regioisomers, **22** and **23**, were obtained in about equal amounts.

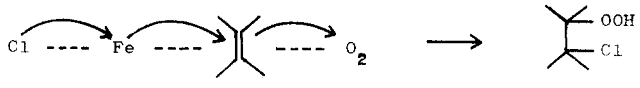
The stereoselectivity in cases of the substituted cyclic olefins **14**–**16** was poor, and each olefin gave a mixture of

Scheme I



X = H or alkyl

Scheme II



cis- and *trans*-α-chloro-β-hydroxy ketones in which the trans isomer was slightly predominant. The stereochemistry of each isomer was assigned in view of the coupling constant of the proton attached to the carbon bearing chlorine. The trans structure was assigned to an isomer exhibiting larger coupling constant (J = 10 Hz), while the cis structure was assigned to an isomer having a smaller coupling constant (J = 2 Hz).

The presence of high concentrations of radical scavenger did not exert any influence on the formation of the major products in the reactions of **2** and **4**, although it retarded the formation of the radical-initiated minor byproducts. Evidently this observation suggests that no unbound free-radical species are involved in the major reaction paths from these olefins. However, an evident effect of the radical scavenger was observed in cases of phenyl-substituted olefins **7**, **8**, and **10** and tri- and tetrasubstituted olefins **17** and **18**. As is evident from the results of runs 17–29, the yields of the main products from these olefins decreased in proportion to the amounts of the radical scavengers used.

Discussion

In our preliminary paper dealing with the present reaction,[1] we postulated a stepwise reaction scheme (Scheme I) involving (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. The hydroperoxides from mono- or disubstituted olefins are secondary, and they would give α-chloro ketones by dehydration (type A, step v), while the hydroperoxides from tri- or tetrasubstituted olefins are tertiary, and C–C bond cleavage would become the main reaction path (type B, step v′).

In analogy with the arguments presented earlier in the case of $UO_2(OAc)_2$-catalyzed photooxidation of olefin,[2] the mechanism involving the stepwise paths i–iv seems to be inconsistent with the following observations. (a) If the stepwise paths i–iv were operative, some products from the radical **51** should be obtained even when the irradiation was carried out in the absence of oxygen.[3] Actually, however, the irradiation of **2** or **11** in the presence of $FeCl_3$ but without oxygen resulted in the recovery of a major part of the starting material, along with a minor amount of the dichloride **40** or **43** (vide supra). Evidently molecular oxygen plays an important role in initiating the present reaction. (b) Although the radical scavengers inhibited the formation of the radical-initiated products, they exhibited no appreciable retarding effect on the major reaction pattern of olefins **2** and **4**. A more clear-cut observation is that the noncatalyzed photooxidation of **4**, which produced 9% of the products **22** and **23**, probably through the mechanism involving radical species as depicted in Scheme I, was completely quenched by the radical scavenger (run 12). (c) No bicyclic compound such as **52** (Chart I) was identified in the reaction product from **6**, although it is reported that the transannular reaction is the major reaction pattern in the radical-initiated reactions on **6**.[4]

In view of these observations and arguments raised in our earlier paper, we depicted the initial step of the present reaction as involving a photoinduced interligand electron transfer from the chlorine ligand to molecular oxygen through the metal ion and olefin molecule as shown in Scheme II (long-range electron transfer). Once the chlorine ligand is furnished with radical character through the electron transfer, it adds to the olefin, and successive (or probably simultaneous) coupling of the resulting radical with an oxygen anion radical followed by protonation completes the reaction to give the β-chloro hydroperoxide. All these processes are considered to occur consecutively within the coordination sphere of the iron ion, thus behaving as a nonradical reaction. The details concerning the long-range electron-transfer mechanism have been presented in our previous paper.[2] The hydroperoxides thus formed further decompose into α-chloro ketones or dichloro ketones by steps v or v′, respectively, as shown in Scheme I. The formation of the β-chloro hydroperoxides seems to correspond to the $UO_2(OAc)_2$-catalyzed photooxidation, which affords β-hydroxy hydroperoxides **47** as final products. Actually, we could isolate β-chloro hydroperoxides **48**–**50** as the primary products from the olefins **17**, **18**, and 2-methyl-2-butene, respectively, when the irradiated solutions were worked up under milder conditions (workup II, neutralizing the solvent pyridine followed by extraction). The hydroperoxides **48** and **49** gave chlorinated ketones **38** and **39**, respectively, under the conventional experimental conditions of workup I. However, the corresponding hydroperoxides were not identified in the type A reaction.

The tertiary hydroperoxides obtained from tri- or tetrasubstituted olefins were fairly stable when isolated, and no appreciable decomposition of **48** was observed even when they were refluxed in pyridine. Since workup I, which is usually carried out at a temperature below 40 °C, gives dichloro ketones as eventual products, it is evident that iron ions function as a catalyst for the transformation from the hydroperoxides to the dichloro ketones. Actually, the hydroperoxide **48** was decomposed into **38** smoothly by treating it with a mixture of $FeSO_4$ and $FeCl_3$ under acidic conditions. In view of the report[5] that Fe(II) ion reduces the hydroperoxide into a radical anion which then cleaves into alkoxy radical and hydroxyl anion, we pro-

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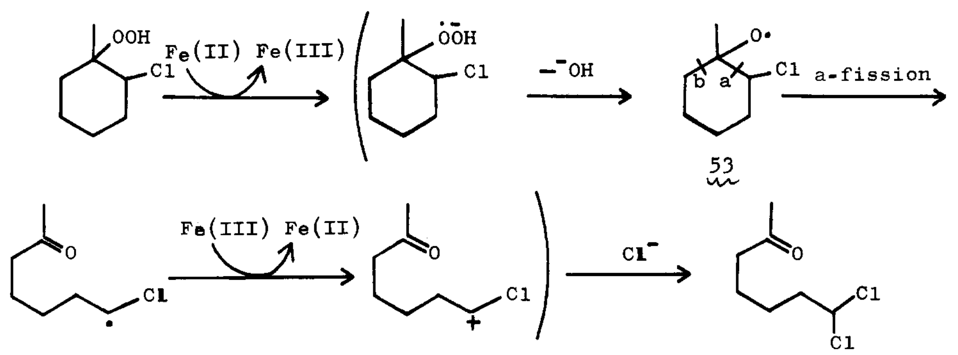
(3) Cf. F. Minisci and R. Galli, *Tetrahedron Lett.*, 3197 (1964).

(4) P. I. Abell, "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, 1973, p 102.

(5) G. Sosnovsky and D. J. Rawlinson, "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley-Interscience, New York, 1971, p 153.

Scheme III



posed the reaction paths from the hydroperoxides as shown in Scheme III. In support of this scheme, the yields of the products in the type B reaction increased when the irradiation was carried out in the presence of added chloride anion (runs 38 and 39). However, the paths involving radical species are also conceivable, because a sluggish but evident effect of the radical scavenger was observed in the type B reaction (run 37). The formation of the byproduct **45** could involve a C–C bond fission at b, instead of a in the intermediate **53** (Scheme III).

The present photooxidation proceeded well with olefins bearing substituents such as the hydroxyl, alkoxyl, acetoxyl, ethoxycarbonyl, or phenyl group. Furthermore, these substituents controlled the regioselectivity of the reaction, and induced the production of α-chloro ketones with the chlorine atom bonded to the carbon atom nearer to the substituent (except the case of **8**, vide infra). The selectivity could be rationalized in terms of the preliminary complexation of iron ion with the substituents. In our previous study,[6] we observed a stereoselectivity induced by an ester group in the $TiCl_4$-catalyzed photoreaction of ketones and ascribed the selectivity to the stereochemical control due to the coordination of the metal ion to the ester group.

When the phenyl group is on a position conjugating with the double bond, as in **8**, the resonance stabilization of the intermediate by the phenyl ring becomes important for the control of the regioselectivity, and **28** was obtained selectively. An evident retarding effect by the radical scavenger was observed with the phenyl-substituted olefins **7**, **8**, and **10**. One possible explanation for this might be obtained by assuming a development of some radical character during the reaction, due to the escape of the chlorine atom from the coordination sphere because of a quite large distance between the coordinating site on the phenyl ring and the reaction site on the double bond. However, no further experimental evidence has been obtained for this rationalization.

If the coordination of the iron ion on the substituent is important for the induction of the regioselectivity as described above, the stereochemistry of the reaction in the cyclic system (runs 33–35) should be controlled so as to give products in which chlorine and the substituent are cis.[7] Actually, however, the predominant products were trans isomers. We ascribed this seemingly contradictory result to the secondary epimerization of the primary cis product under the experimental conditions in view of the following results. First, as shown in the Table II, the ratio of trans to cis isomers of the product from **14** was found to increase as a function of the reaction time. Second, the isolated cis isomer of **35** gave a mixture of cis and transisomers when kept under the photooxidation conditions.

Table II. Trans-cis ratio of the product 35 as a function of the reaction time of 14

reaction time, h	yield, % trans	cis	trans/cis
$^1/_4$	10	6	1.6
$^1/_2$	15	8	1.8
1	21	11	1.9
2	22	9	2.4

We tentatively presented a reaction scheme involving long-range electron transfer (Scheme II) for the present photooxidation. Although we have no experimental evidence for the nature of the actual light-absorbing species, $FeCl_3$ modified by olefin coordination and solvation would be the most probable candidate. Since the photoinduced formation of a charge-transfer complex between the olefin and an oxygen molecule has been well-known, we believe it is quite acceptable to speculate a reaction intermediate comprising four species. The effect of pyridine can be speculated as replacement of the water molecule on the iron ion, facilitation of the coordination of olefin molecule, and subsequent photoinduced electron transfer.

Whatever the reaction mechanism may be, the most important idea should be that the metal ion fills the role of a mediator to combine several species together, which would otherwise not react with each other. This has also been a remarkable outcome observed in the $TiCl_4$-catalyzed photocoupling of ketones with alcohols.[8]

Experimental Section

General Procedures. The instrumentation was the same as has been described previously.[9] Preparative GLC analyses were carried out on a 2.5 m × 6 mm stainless column packed with Silicone SE 30 or Carbowax 20 M on silanized Chromosorb W. Preparative TLC was carried out on a silica gel plate by using benzene or $CHCl_3$ as a developing solvent. The irradiation was carried out on a solution of olefin (10 mL, 0.025 M), containing an appropriate amount of the additives as specified in Table I, in Pyrex test tubes for 30–180 min while oxygen gas was bubbled through. A high-pressure mercury vapor lamp [Ushio UM 452 (450 W)] was used as a light source. The irradiated solution was conventionally worked up in the following way (workup I). The solvent was removed in vacuo, and the reaction products were extracted with CCl_4 or CH_2Cl_2 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 cases where the isolation of the chloro hydroperoxides was desired, the pyridine

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(6) T. Sato, H. Kaneko, and S. Yamaguchi, *J. Org. Chem.*, **45**, 3778 (1980).

(7) J. H.-H. Chan and B. Rickborn, *J. Am. Chem. Soc.*, **90**, 6406 (1968).

(8) Reference 6 and references citered therein.

(9) T. Sato, K. Tamura, K. Maruyama, O. Ogawa, and T. Imamura, *J. Chem. Soc., Perkin Trans. 1*, 779 (1976).

solution after the irradiation was neutralized with 4 M HCl and shaken with $CHCl_3$ or CH_2Cl_2. The extract was dried (Na_2SO_4), and the solvent was removed in vacuo (workup II). Unless otherwise stated, workup I was adopted.

Unless otherwise stated, all the spectroscopic data were determined on a sample collected on preparative GLC or TLC, a CCl_4 solution being used for the NMR and IR spectral determinations.

Materials. The materials described below were synthesized according to the reported methods: 1-ethoxy-2-butene (**12**),[10] 4,4-dimethyl-2-cyclohexenol (**14**),[11] 2-cyclooctenol (**15**),[12] 2-cyclooctenyl acetate (**16**),[12] 1-methylcyclohexene (**17**),[13] di-*tert*-butyl nitroxide.[14] Other materials were obtained commercially. For the larger scale experiment, 1,2-dimethylcyclohexene was prepared from 2-methylcyclohexanone in a manner similar to that for the preparation of 1-methylcyclohexene. This product contained 2,3-dimethylcyclohexene (26%) as a contaminant.

Photooxidation of Cyclohexene (1). The product was almost pure 2-chlorocyclohexanone (**19**). The IR[15] and NMR[16] spectra of the purified sample (GLC) were identical with those reported.

Photooxidation of Cyclooctene (2). The crude material was subjected to GLC to give 2-chlorocyclooctanone (**20**), *trans*- and *cis*-dichlorocyclooctanes (**40**), and epoxycyclooctane (**41**). For **20**: mass spectrum, *m/e* (relative intensity) 160 (M, with isotope peak of chlorine at M + 2, 34), 125, 117, 116, 98 (base peak), 55, 42; IR ν_{max} 2925, 2860, 1720, 1470, 1450, 1330, 1090, 845, 742, 675 cm^{-1}; NMR δ 1.1–2.1 (8 H, m), 2.1–2.5 (3 H, m), 2.7–3.0 (1 H, m), 4.14 (1 H, t, J = 7 Hz). For *trans*-**40**: mass spectrum, *m/e* 144 (M - HCl), 109, 82 (base peak), 67; IR ν_{max} 2925, 2860, 1470, 1445, 1245, 1020, 735 cm^{-1}; NMR δ 1.3–2.5 (12 H, m), 4.2–4.3 (2 H, m). The NMR and IR spectra were identical with those of the authentic sample prepared by chlorination of **2** in pyridine. For *cis*-**40**: IR ν_{max} 2925, 2860, 1480, 1445, 1260, 1035, 775, 735 cm^{-1}; NMR δ 1.3–2.5 (12 H, m), 4.1–4.6 (2 H, m). For **41** the IR[17] and NMR[18] spectra were identical with those reported.

A preparative TLC of the crude material afforded **20** in a pure state in 40% yield.

Photooxidation of 1-Octene (3). The product was almost pure 1-chloro-2-octanone (**21**), accompanied by a trace amount of aldehyde of unknown structure. For **21** (GLC): mass spectrum, *m/e* (relative intensity) 162 (M, with isotope peak of chlorine at M + 2, 36), 113, 105, 92, 85, 77, 57, 55, 43; IR ν_{max} 2920, 2850, 1717, 1455, 1400, 1060, 760 cm^{-1}; NMR δ 0.93 (3 H, br t), 1.2–1.8 (8 H, br), 2.64 (2 H, t, J = 6.9 Hz), 4.00 (2 H, s).

Photooxidation of 2-Octene (4). The product was a mixture of 2-chloro-3-octanone (**22**) and 3-chloro-2-octanone (**23**). The separation of each component was effected on TLC. The ratio of each component was determined from the integrated areas of NMR signals of methyl protons, δ 1.61 for **22** and δ 2.15 for **23**. For **22**: mass spectrum (with **23**) *m/e* (relative intensity) 162 (M, with isotope peak of chlorine at M + 2, 40), 99 (base peak), 92, 71, 55, 43; IR ν_{max} 2950, 2920, 2860, 1715, 1465, 1350, 1240 cm^{-1}; NMR δ 0.75–1.80 (10 H, m), 1.50 (3 H, d, J = 7 Hz), 2.52 (1 H, q, J = 7 Hz), 4.08 (1 H, q, J = 7 Hz). For **23**: IR ν_{max} 2950, 2860, 1720, 1474, 1362 cm^{-1}; NMR δ 0.78–2.01 (11 H, m), 2.20 (3 H, s), 3.90 (1 H, t, J = 7 Hz).

Photooxidation of 1,3-Cyclooctadiene (5). The product was mainly a mixture of 8-chloro-2-cyclooctenone (**24**) and 4-chloro-2-cyclooctenone (**25**). The ratio of each component was determined by use of the NMR signal of the proton on the carbon carrying chlorine at δ 4.55 for **24** and δ 4.78–4.89 for **25**. TLC afforded pure **25**, while the complete isolation of **24** from **25** was not accomplished. Hence the spectra of **24** were obtained by subtracting the signals of **25** from the whole spectra. For **24**: IR ν_{max} 3000, 2920, 2850, 1670, 1610, 1455, 1250, 1160, 780 cm^{-1}; NMR δ 1.40–2.72 (8 H, br), 4.55 (1 H, dd, J = 5 and 9 Hz), 5.92 and 6.07 (2 H, AB q, J = 13 Hz, upper and lower field signals further split into triplets with J = 2 and 6 Hz, respectively). For **25**: IR ν_{max} 2930, 2850, 1660, 1450, 1387, 1170, 820, 800 cm^{-1}; NMR δ 1.5–2.7 (8 H, m), 4.78–4.89 (1 H, m), 5.65 and 6.03 (2 H, AB q, J = 12 Hz, lower field signals further split into doublets with J = 5 Hz).

Anal. Calcd for $C_8H_{11}ClO$: C, 60.57; H, 6.99. Found: C, 61.29; H, 7.23.

Photooxidation of 1,5-Cyclooctadiene (6). The product was almost pure 8-chloro-4-cyclooctenone (**26**), which was purified on a GLC: IR ν_{max} 3010, 2940, 2860, 2715, 1460, 1035, 880, 730 cm^{-1}; NMR δ 1.8–3.2 (8 H, m), 4.30 (1 H, br t, J = 5 Hz), 5.5–5.8 (2 H, m).

Anal. Calcd for $C_8H_{11}ClO$: C, 60.57; H, 6.99. Found: C, 60.94; H, 7.25.

Photooxidation of *trans*-Stilbene (7). The product was purified on a TLC to give 2-chloro-1,2-diphenylethanone (**27**), *cis*- and *trans*-stilbene, and benzaldehyde. The IR[19] and NMR[20] spectra of **27** were identical with those reported.

Photooxidation of β-Methylstyrene (8). The product was a mixture of 2-chloro-1-phenyl-1-propanone (**28**) and an unknown compound, which were separated on a TLC. For **28**: IR ν_{max} 3050, 2980, 2930, 1683, 1515, 1445, 1345, 1255, 1200, 1028, 955, 715, 680 cm^{-1}; NMR δ 1.65 (3 H, d, J = 6 Hz), 5.07 (1 H, q, J = 6 Hz), 7.25–7.65 (3 H, m), 7.73–8.10 (2 H, m).

Anal. Calcd for C_9H_9ClO: C, 64.11; H, 5.38. Found: C, 64.11; H, 5.36.

Photooxidation of 3-Phenyl-2-propen-1-ol (9). The product was almost pure 2-chloro-3-hydroxy-1-phenyl-1-propanone (**29**). The product (TLC) was identical with an authentic sample prepared by the known method:[21] IR ν_{max} 3600–3100, 1685, 1595, 1450, 1260, 1150 cm^{-1}; NMR δ 3.80 and 4.05 (2 H, AB q, J = 10 Hz, upper and lower field signals further split into doublets with J = 5 and 7 Hz, respectively), 4.78 (1 H, br s), 5.05 (1 H, dd, J = 5 and 7 Hz), 7.0–7.6 (3 H, m), 7.8–8.0 (2 H, m).

Photooxidation of 1-Phenyl-2-butene (10). The product was a mixture of 3-chloro-4-phenyl-2-butanone (**30**) and 3-chloro-1-phenyl-2-butanone (**31**). TLC afforded **31** in a pure state, while the complete isolation of **30** from **31** was not effected. The compound **31** was identical with the authentic sample prepared by the known method.[22] The spectroscopic data for **30** were obtained by subtracting those of **31** from the spectra of the mixture. For **30**: IR ν_{max} 3040, 3000, 2900, 1710, 1595, 1480, 1345, 1140, 1065, 1020, 920 cm^{-1}; NMR δ 2.13 (3 H, s), 2.91 and 3.22 (2 H, AB q, J = 14 Hz, upper and lower field signals further split into doublets with J = 8 and 6 Hz, respectively), 4.20 (1 H, dd, J = 6 and 8 Hz), 6.87–7.23 (5 H, m). For **31**: IR ν_{max} 3050, 3020, 2975, 2930, 1717, 1673, 1595, 1498, 1450, 1377, 1060, 1030 cm^{-1}; NMR δ 1.47 (3 H, d, J = 7 Hz), 3.78 (2 H, AB q, J = 14 and 16 Hz), 4.20 (1 H, q, J = 7 Hz), 6.75–7.35 (5 H, br).

Photooxidation of 2-Buten-1-ol (11). The product was mainly 3-chloro-4-hydroxy-2-butanone (**32**) accompanied by 2,3-dichloro-1-butanol (**43**) (5:1), and these were separated by GLC into pure components. Both were identified by comparison with the respective authentic samples prepared by known methods. For **32**:[21] mass spectrum, *m/e* 92 (M – CH_2O), 87, 79 (base peak), 62, 43; IR ν_{max} 3600–3100, 2925, 2870, 1715, 1632, 1360, 1160, 1075, 1040 cm^{-1}; NMR δ 2.45 (3 H, s), 3.13 (1 H, br s), 4.05 (2 H, dd, J = 4 and 10 Hz), 4.35 (1 H, t, J = 10 Hz). For **43**[23]: IR ν_{max} 3600–3100, 2990, 1455, 1385, 1075 cm^{-1}; NMR δ 1.68 (3 H, d, J = 7 Hz), 1.85 (1 H, br s), 3.1–3.3 (1 H, m), 3.95 (3 H, m).

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Photooxidation of 1-Ethoxy-2-butene (12). The product was almost pure 3-chloro-4-ethoxy-2-butanone (**33**) by GLC: IR ν_{max} 2970, 2925, 2870, 1720, 1380, 1360, 1120 cm^{-1}; NMR δ 1.15 (3 H, t, J = 8 Hz), 2.25 (3 H, s), 3.47 (2 H, q, J = 8 Hz), 3.70 (2 H, dd, J = 3 and 5 Hz), 4.10 (1 H, t, J = 5 Hz).

Photooxidation of Methyl 3-Pentenoate (13). The product was almost pure methyl 3-chloro-4-oxopentanoate (**34**) by GLC: mass spectrum, m/e (relative intensity) 164 (M, with isotope peak of chlorine at M + 2, 35), 133, 122, 113, 97, 87, 59, 55, 43 (base peak); IR ν_{max} 3000, 2960, 2850, 1740, 1720, 1440, 1360, 1160, 1000 cm^{-1}; NMR δ 2.28 (3 H, s), 2.65 and 3.00 (2 H, AB q, J = 17 Hz, upper and lower field signals further split into doublets with J = 7 and 9 Hz, respectively), 3.57 (3 H, s), 4.43 (1 H, dd, J = 7 and 9 Hz).

Photooxidation of 4,4-Dimethyl-2-cyclohexen-1-ol (14). The product was mainly a mixture of *cis*- and *trans*-6-chloro-2,2-dimethyl-5-hydroxycyclohexanone (**35**), accompanied by a small amount of 4,4-dimethyl-2-cyclohexen-1-one (**44**). Purification by GLC resulted in partial crystallization, and the mixture was separated into CCl$_4$-soluble and insoluble parts. The CCl$_4$-insoluble crystalline material was *cis*-**35**. The CCl$_4$-soluble fraction was mainly *trans*-**35** contaminated with a small amount of the cis isomer. The spectroscopic data of the trans isomer were obtained by subtracting those of the cis isomer from the spectra of the mixture. For *cis*-**35**: IR ν_{max} 3600–3200, 2925, 1720, 1450, 1355, 1220, 1070 cm^{-1}; NMR (CDCl$_3$) δ 1.10 (3 H, s), 1.20 (3 H, s), 1.3–2.2 (4 H, m), 4.28 (1 H, m), 4.80 (1 H, d, J = 3 Hz). For *trans*-**35**: IR, identical with the cis isomer; NMR δ 1.10 (3 H, s), 1.20 (3 H, s), 1.3–2.2 (4 H, m), 3.58 (1 H, dt, J = 5 and 10 Hz), 4.50 (1 H, d, J = 10 Hz). The assignment of the signals was confirmed by the decoupling technique.

Photooxidation of 2-Cycloocten-1-ol (15). The product was a mixture of *cis*- and *trans*-2-chloro-3-hydroxycyclooctanone (**36**). Fractionation was not achieved by TLC or GLC, and the spectroscopic data were obtained on the mixture. The ratio of cis and trans isomers was determined from the integrated area of NMR signals of the protons on the carbon carrying chlorine at δ 4.10 for the trans isomer and δ 4.47 for the cis isomer. For **36**: IR ν_{max} 3600–3100, 2925, 2855, 1715, 1060 cm^{-1}; NMR δ 1.2–2.1 (8 H, m), 2.3–2.6 (2 H, m), 3.10 (1 H, br s), 3.73 (td, J = 5 and 10 Hz, for trans), 4.10 (d, J = 10 Hz, for trans), 4.47 (d, J = 3 Hz, for cis). The mixture of cis and trans isomers of **36** (42 mg) was oxidized with pyridinium chlorochromate (323 mg) in methylene dichloride (2 mL) to afford 2-chloro-1,3-cyclooctanedione as single product, thus establishing the structure of **36**. 2-Chloro-1,3-cyclooctanedione (GLC): IR ν_{max} 2920, 2850, 1700, 1445, 1330, 1230, 1205, 1120, 1040 cm^{-1}; NMR δ 1.35–2.00 (6 H, m), 2.2–2.6 (2 H, m), 2.6–2.9 (2 H, m), 4.65 (1 H, s).

Photooxidation of 2-Cyclooctenyl Acetate (16). The product was mainly a mixture of *cis*- and *trans*-2-chloro-3-acetoxycyclooctanones (**37**). GLC separated each component in its pure state. For *cis*-**37**: IR ν_{max} 2920, 2850, 1740, 1720, 1230, 1035 cm^{-1}; NMR δ 1.1–2.1 (8 H, m), 2.05 (3 H, s), 2.55–2.75 (2 H, m), 4.70 (1 H, d, J = 3 Hz), 5.45–5.65 (1 H, m). For *trans*-**37**: IR ν_{max} 2920, 2850, 1740, 1715, 1230, 1135 cm^{-1}; NMR δ 1.1–2.1 (8 H, m), 2.05 (3 H, s), 2.2–2.5 (1 H, m), 2.7–3.1 (1 H, m), 4.05 (1 H, d, J = 11 Hz), 5.18 (1 H, td, J = 6 and 11 Hz).

Photooxidation of 1-Methylcyclohexene (17). The product was mainly 7,7-dichloro-2-heptanone (**38**), accompanied by 3,7-dichloro-2-heptanone (**45**) and 2-chloro-1-methylcyclohexanol (**46**). Each component was isolated in its pure state by TLC. For **38**: mass spectrum, (with **45**), m/e (relative intensity) 182 (M, with isotope peaks of chlorine at M + 2, 66, and M + 4, 16), 167, 146, 131, 111, 103, 67, 58, 43 (base peak); IR ν_{max} 2990, 2940, 2860, 1710, 1408, 1363, 1230, 1173, 740 cm^{-1}; NMR δ 1.30–1.71 (4 H, m), 2.00 (3 H, s), 2.01–2.47 (4 H, m), 5.64 (1 H, t, J = 6 Hz). Anal. Calcd for $C_7H_{12}Cl_2O$: C, 45.92; H, 6.61. Found: C, 45.96; H, 6.70.

For **45**: IR ν_{max} 2950, 2870, 1720, 1432, 1360, 1237, 1165, 750 cm^{-1}; NMR δ 1.40–2.03 (6 H, m), 1.96 (3 H, s), 3.45 (2 H, t, J = 6 Hz), 4.04 (1 H, dd, J = 6 and 8 Hz). For **46**: IR (neat) ν_{max} 3400, 2940, 2870, 1450, 1380, 1337, 1145, 1120, 975, 930, 760 cm^{-1}; NMR δ 1.27 (3 H, s), 1.2–2.3 (8 H, m), 2.10 (1 H, br s), 3.92 (1 H, dd, J = 4 and 10 Hz).

When the photolysate was processed according to workup II followed by vacuum distillation, the hydroperoxide **48** was obtained in a pure state: bp 47–51 °C (0.25 mmHg); IR ν_{max} 3340, 2920, 2860, 1625, 1435, 1370, 1140, 965, 850, 735 cm^{-1}; NMR δ 1.23 (3 H, s), 1.3–2.5 (9 H, m), 4.31 (1 H, dd, J = 3 and 7 Hz).

Anal. Calcd for $C_7H_{13}ClO_2$: C, 51.07; H, 7.96. Found: C, 51.01; H, 8.26.

Photooxidation of 1,2-Dimethylcyclohexene (18). The product was almost pure 7,7-dichloro-2-octanone (**39**): mass spectrum, m/e (relative intensity) 196 (M, with isotope peaks of chlorine at M + 2, 68, and M + 4, 13), 160, 145, 125, 102 (base peak), 89, 81, 76, 71, 67, 58, 43; IR ν_{max} 2980, 2950, 2870, 1715, 1370, 1165, 695 cm^{-1}; NMR δ 1.50–1.80 (4 H, m), 2.08 (3 H, s), 2.20 (3 H, s), 2.13–2.30 (2 H, br), 2.3–2.6 (2 H, m).

When the photolysate was processed according to workup II, the hydroperoxide **49** was obtained in almost pure state. Vacuum distillation gave a pure sample: bp 55–56 °C (0.2 mmHg); IR ν_{max} 3400, 2980, 2925, 2860, 1445, 1370, 1173, 1040, 935, 865, 823 cm^{-1}; NMR δ 1.37 (3 H, s), 1.51 (3 H, s), 1.3–2.2 (8 H, m), 7.88 (1 H, br s).

Photooxidation of 2-Methyl-2-butene. The work-up II of the photolysate gave 2-chloro-1,1-dimethylpropyl hydroperoxide (**50**). Bp 33-35 °C (0.7 mmHg). IR ν_{max} 3300, 2970, 2930, 1590, 1440, 1363, 1140, 1054, 1000, 835, 740, 660, cm^{-1}; NMR δ 1.19 (3 H, s), 1.32 (3H, s), 1.45 (3 H, d, J = 7 Hz), 4.31 (1 H, q, J = 7 Hz) 8.30 (1 H, b).

Registry No. 1, 110-83-8; **2**, 931-88-4; **3**, 111-66-0; **4**, 111-67-1; **5**, 1700-10-3; **6**, 111-78-4; **7**, 103-30-0; **8**, 637-50-3; **9**, 1504-54-7; **10**, 1560-06-1; **11**, 6117-91-5; **12**, 18409-00-2; **13**, 818-58-6; **14**, 5020-09-7; **15**, 3212-75-7; **16**, 31059-36-6; **17**, 591-49-1; **18**, 1674-10-8; **19**, 822-87-7; **20**, 4828-34-6; **21**, 63988-10-3; **22**, 66241-39-2; **23**, 24251-77-2; **24**, 66241-41-6; **25**, 66241-42-7; **26**, 75896-24-1; **27**, 447-31-4; **28**, 6084-17-9; **29**, 55056-02-5; **30**, 20849-77-8; **31**, 24767-67-7; **32**, 66241-40-5; **33**, 6986-47-6; **34**, 75896-25-2; **35** (cis isomer), 75896-26-3; **35** (trans isomer), 75896-27-4; **36** (cis isomer), 75896-28-5; **36** (trans isomer), 75896-29-6; **37** (cis isomer), 75908-23-5; **37** (trans isomer), 75896-30-9; **38**, 66241-43-8; **39**, 66241-45-0; **40** (cis isomer), 16250-67-2; **40** (trans isomer), 22828-42-8; 41, 286-62-4; **43**, 4089-67-2; **44**, 1073-13-8; **45**, 66241-44-9; **46**, 75908-24-6; **48**, 75908-25-7; **49**, 18649-67-7; **50**, 75896-31-0; 2-chloro-1,3-cyclooctanedione, 75896-32-1; 2-methyl-2-butene, 513-35-9.