

A Novel Oxygenative Carbon–Carbon Bond Cleavage Reaction by Irradiation of Alkylcobaloximes Having a Phenyl Group at the β -Position

Masashi Kijima,^{*1a} Hiroshi Yamashita,^{1b} Masatsune Kainosho,^{1b} and Takeo Sato^{1b}

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan, and Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan

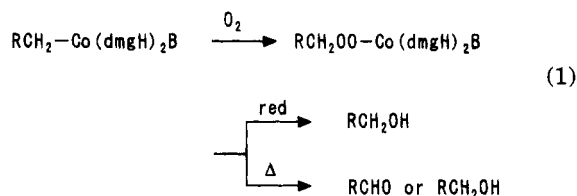
Received April 6, 1994 (Revised Manuscript Received August 30, 1994[®])

Upon irradiation in oxygen, alkylcobaloximes having a phenyl group at the β -position such as (2-phenylethyl)cobaloxime selectively gave carbonyl compounds due to oxygenative $\text{C}\alpha\text{--C}\beta$ bond cleavage through an (alkyldioxy)cobaloxime intermediate formed by the insertion of oxygen into the $\text{Co--C}\alpha$ bond. Another oxygen promoted the decomposition of (alkyldioxy)cobaloxime and was partially incorporated into the $\text{C}\alpha\text{--C}\beta$ cleaved products. Photoirradiation accelerated the $\text{C}\alpha\text{--C}\beta$ cleavage, whereas heating promoted the oxygenation at the α -position. Thermochemical investigation suggested that an *in situ* formation of an alkylperoxyl radical caused the $\text{C}\alpha\text{--C}\beta$ bond homolysis.

Bis(dimethylglyoximato)cobalt complexes, cobaloximes, have received much attention as a vitamin B₁₂ model² and as a synthetic reagent.³ The Co--C bond of alkylcobaloximes has been reported to be homolytically cleaved by irradiation with visible light in a manner similar to the activation of vitamin B₁₂ by apoenzyme.⁴ We have investigated the reactivity of photoactivated alkylcobaloximes with some organic and inorganic compounds.⁵

Reactions involving the fixation of O₂ are important not only for a biological system but also for some synthetic processes.⁶ Some reactions of alkylcobaloxime with molecular oxygen has been reported. When alkylcobaloximes are irradiated under O₂, O₂ is inserted into the Co--C bond, giving (alkyldioxy)cobaloxime,⁷ which are successively degraded to alcohols by reduction^{7c–e} or to carbonyl compounds or alcohols by heating (eq 1).^{7e–g}

In order to realize the oxygenative photolysis of alkylcobaloximes in a one-pot manner, benzyl(pyridine) cobaloxime **1a** was irradiated by a tungsten lamp (400 W rated) in chloroform at 35 °C for 48 h under O₂, giving PhCHO(65%) and PhCH₂OH (10%) due to the oxygenative decomposition of its benzyl ligand at the α -carbon.



This selective formation of the corresponding carbonyl compound by the one-pot reaction has been investigated elsewhere.⁸ On the other hand, in the case of the oxygenative photolysis of (2-phenylethyl)(pyridine)cobaloxime **1b**, the alkyl ligand was selectively converted to PhCHO (39%) with the loss of one carbon. It was found from our preliminary experiments that this oxygenative $\text{C}\alpha\text{--C}\beta$ cleavage reaction occurred only in the case of alkylcobaloximes having a phenyl group at the β -position.

In this study, we investigated a novel oxygenative carbon–carbon cleavage reaction of alkylcobaloximes having a β -phenyl group.

Results and Discussion

We prepared some new acyclic and cyclic alkylcobaloximes having a phenyl group at the β -position and their aerobic photolyses were carried out in chloroform using a tungsten lamp. After the reaction, organic products were separated and purified by silica gel column chromatography. Using this procedure, the unreacted cobaloxime was recovered, and the reacted one was partially eluted as chlorocobaloxime while the others remained in the silica gel. These isolated organic products and their yields are summarized in Table 1. Besides these isolated products, trace amounts of other oxygenated products and olefins can be detected by GC-MS in some cases. In order to realize this oxygenative $\text{C}\alpha\text{--C}\beta$ cleavage reaction, some control reactions were carried out using alkylcobaloximes (**1a,c**) and (alkyldioxy)cobaloximes (**2a,c**).

During the degradation of both **1a** and **1c**, the formation of (alkyldioxy)cobaloxime (**2a,c**) can be monitored by ¹H NMR spectroscopy (Figure 1). In both cases, the

[®] Abstract published in *Advance ACS Abstracts*, October 1, 1994.

(1) (a) University of Tsukuba. (b) Tokyo Metropolitan University.

(2) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97. Golding, B. T.; Sell, C. S.; Sellars, P. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 961.

Flor, H.; Pannhorst, W.; Retey, J. *Helv. Chim. Acta* **1978**, *61*, 1565.

(3) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343. Gupta, B. D.; Roy, S. *Tetrahedron Lett.* **1986**, *27*, 4905. Branchaud, B. P.; Meier, M. S.; Malekzadeh, M. N. *J. Org. Chem.* **1987**, *52*, 212.

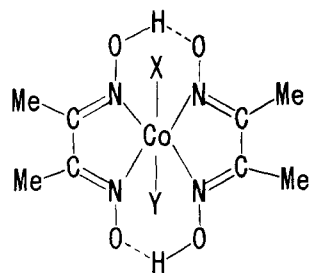
(4) Pratt, J. M.; Whitera, B. R. D. *J. Chem. Soc. A* **1971**, 252. Ramakrishna, D. N.; Symons, M. C. R. *J. Chem. Soc. Faraday Trans 1* **1984**, *80*, 423. Jensen, F. R.; Madan, V.; Buchandan, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 5285.

(5) Kijima, M.; Miyamori, K.; Sato, T. *J. Org. Chem.* **1987**, *52*, 706. *Ibid.* **1988**, *53*, 1719. *Ibid.* **1988**, *53*, 4147. Kijima, M.; Yamashita, H.; Sato, T. *J. Organomet. Chem.* **1992**, *426*, 399. Kijima, M.; Nakazato, K.; Sato, T. *Chem. Lett.* **1994**, 347.

(6) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315. Baldwin, J. M. *Prog. Biophys. Mol. Biol.* **1975**, *29*, 225. *Singlet Oxygen*; Wasserman, H. H.; Murray, R. W., Eds; Academic Press: New York, 1979. Drago, R. S.; Corden, B. B.; Barnes, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 2453. Otsuka, Y.; Ohno, M.; Ooi, T.; Inoue, S. *Nippon Kagaku Kaishi* **1985**, 387.

(7) (a) Gianotti, C.; Gaudemer, A.; Fontaine, C. *Tetrahedron Lett.* **1970**, 3209. (b) Merienne, C.; Gianotti, C.; Gaudemer, A. *J. Organomet. Chem.* **1973**, *54*, 281. (c) Jensen, F. R.; Kiskis, R. C. *J. Organomet. Chem.* **1973**, *49*, C46. (d) Sinozaki, H.; Tada, M. *Chem. Ind.* **1975**, 178. (e) Bied-Charreton, C.; Gaudemer, A. *J. Am. Chem. Soc.* **1976**, *98*, 3997. (f) Gupta, B. D.; Roy, S. *Inorg. Chim. Acta* **1985**, *108*, 261. (g) Gianotti, C.; Fontaine, C. *J. Organomet. Chem.* **1973**, *52*, C41.

(8) Kijima, M.; Yamashita, H.; Sato, T. *J. Organomet. Chem.* **1994**, *474*, 177.



Bis(dimethylglyoximate)cobalt Complexes

1: X= R	R groups:
Y= pyridine	a: PhCH ₂ -
	b: PhCH ₂ CH ₂ -
2: X= ROO	c: PhCH ₂ CH(CH ₃)-
Y= pyridine	d: PhCH(CH ₃)CH ₂ -
	e: PhCH ₂ CHCH ₂ CH ₂ Ph
	f:
	g:

initial formation of (alkyldioxy)cobaloxime and successive slow decrease according to the formation of oxygenative products suggest that (alkyldioxy)cobaloxime is a stable intermediate. From this comparison, O₂ similarly inserts into the Co–C α bond of **1a** and **1c** during the initial stage giving (alkyldioxy)cobaloxime **2**.

The fate of the α -carbon in **1c** was found to be CH₃-CHO. The time-dependent photolysis of **2c** shows the formation of CH₃CHO, and a comparable amount of CH₃-CHO to PhCHO is monitored at every time (Figure 1c). The CH₃CHO formation was also confirmed by trapping the vapor of photodegraded **2c** in an aqueous solution of 2,4-dinitrophenylhydrazine as acetaldehyde hydrazone. Furthermore, the result from the aerobic photolysis of **1e** (run 4) showed that the fate of the α -carbon is the corresponding aldehyde, PhCH₂CH₂CHO.

Effect of Irradiation. The effect of irradiation on the aerobic photolysis of **1c** was investigated (Table 2). As the irradiation intensifies, the selectivity of the oxygenative α -C β cleavage reaction against the oxygenative decomposition at the α -carbon is enhanced. On the other hand, thermal decomposition of **1c** at 60 °C under O₂ for 24 h gave a 53% yield of the total oxygenated products and lowered the selectivity to 0.17. In other words, the oxygenative decomposition at the α -carbon of **1c** preferentially occurs during the thermal decomposition.

Effect of Oxygen. Next, the effect of oxygen on the decomposition of (alkyldioxy)cobaloximes (**2a,c**) was investigated. The aerobic photolysis of **2a** gave PhCHO in 55% yield, but the yield decreased to 12% under anaerobic conditions. Some control reactions of **2c** are summarized in Table 3. O₂ is found to assist the decomposition of both **2a** and **2c**. Such assistance is observed by the addition of PhSSPh instead of oxygen, and a significant amount of (phenylthio) cobaloxime was recovered after the reaction. Thus, O₂ and the radical trapping agent probably accelerate the decomposition of (alkyldioxy)cobaloxime to alkylperoxyl radical by S_{RN} or S_H and trap Co^{II}, preventing the reformation of **2**. The oxygenative C–C cleavage reaction preferentially occurred by the photolysis under oxygen (run 13).

Table 1. Oxygenative Photolysis of Alkylcobaloximes Having a 2-Phenylethyl-Type Ligand^a

run	cobaloxime	isolated products (%)
1	1b	PhCHO (39), PhCH ₂ CH ₂ OH (9)
2	1c	PhCHO (42), PhCH ₂ COCH ₃ (25), PhCH ₂ CH(OH)CH ₃ (9)
3	1d	PhCOCH ₃ (35)
4	1e	PhCHO (39), PhCH ₂ CH ₂ CHO (49), PhCH ₂ COCH ₂ CH ₂ Ph (12), PhCH=CHCH ₂ CH ₂ Ph (19)
5	1f	phthalaldehyde (17), indene (23)
6	1g	2-formylindene (17), 1,2-dihydronaphthalene (10), 1,4-dihydronaphthalene (3)

^a Conditions: [cobaloxime] = 67 mM, in CHCl₃, under O₂, at 35 °C, irradiation with a Pyrex-filtered tungsten lamp (400 W rated lamp) for 48 h.

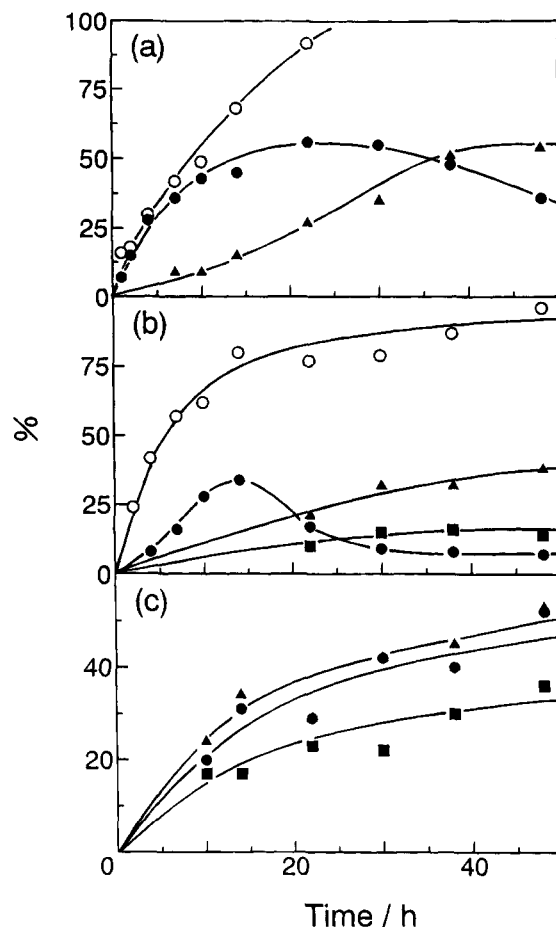


Figure 1. Time-course of the aerobic photolysis of **1a** (a) ○: conversion of **1a**, ●: yield of **2a**, ▲: yield of PhCHO; and **1c** (b) ○: conversion of **1c**, ●: yield of **2c**, ▲: yield of PhCHO, ■: yield of PhCH₂COCH₃; and time dependent formation of oxygenated products during the aerobic photolysis of **2c** (c) ●: yield of PhCHO, ▲: yield of CH₃CHO, ■: yield of PhCH₂COCH₃, measured with ¹H NMR spectroscopy in CDCl₃ at 35 °C.

More important is to confirm the incorporation of an another oxygen into the product during the degradation of **2**. To confirm this oxygen effect, the photolysis of **2a** and **2c** under ¹⁸O₂ conditions were carried out. The former gives PhCHO, and its high-resolution ¹³C NMR spectrum shows one carbonyl carbon peak around 192.3 ppm. On the other hand, the latter gives PhCH₂COCH₃ and PhCHO, and their ¹³C NMR spectra show one peak around 206.4 ppm and two around 192.3 ppm (Figure 2), respectively. These results suggest that another

Table 2. Effect of Irradiation on the Aerobic Photolysis of 1c^a

run	light (W) ^b	products, %			selectivity: ^c C _α -C _β /C _α
		PhCHO	PhCH ₂ COCH ₃	PhCH ₂ CH(OH)CH ₃	
7	800	52	27	10	1.41
8	400	42	25	9	1.24
9	200	31	22	7	1.07
10	100	8	14	3	0.47
11	dark	trace	trace	0	-

^a Conditions: [1c] = 67 mM, in CHCl₃, under O₂, at 35 °C, irradiated with tungsten lamps, for 48 h. ^b Total rated wattage of tungsten lamps. ^c A ratio of the product yield by the oxygenative C-C cleavage reaction and the product yields by the oxygenation at α-carbon.

Table 3. Oxygen Dependence on the Decomposition of 2c^a

run	temp (°C)	irradiation ^b	O ₂ ^c	time (h)	main products(%)	
					PhCHO	PhCH ₂ COCH ₃
12	35	on	absence	48	5	12
13	35	on	presence	48	33	29
14	60	off	absence	24	0	34
15	60	off	presence	24	8	45

^a Conditions: [2c] = 40 mM in CHCl₃. ^b On: irradiation with a tungsten lamp (400 W rated); off: dark reaction. ^c Absence: under Ar; presence: under O₂.

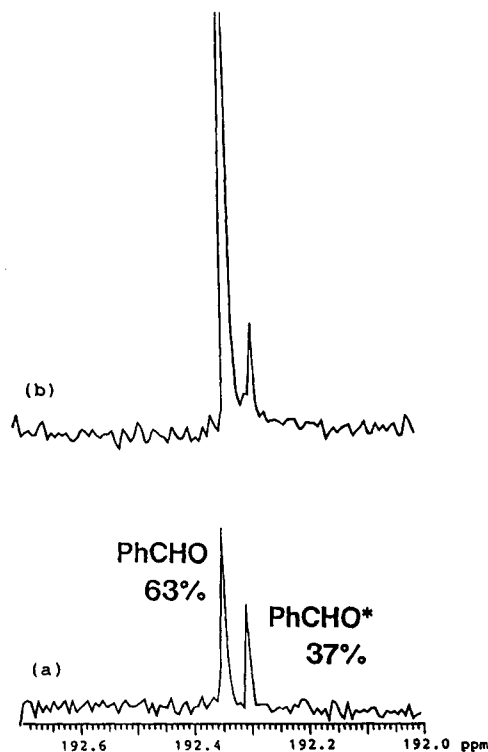
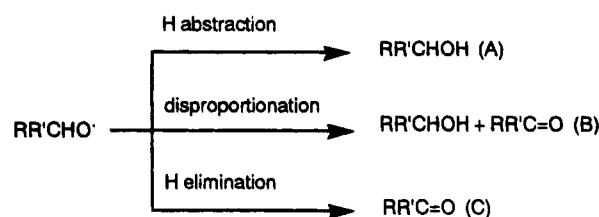


Figure 2. ¹³C NMR spectra of benzaldehyde formed by the photolysis of 2c under ¹⁸O₂. (a) Two carbonyl peaks due to -CHO and -CHO* were observed. (b) Authentic PhCHO was added.

oxygen does not incorporate into the oxygenative decomposition products at the α-carbon of 2a and 2c, but does into that formed by the C_α-C_β cleavage of 2c. However, no such incorporation was observed in the remaining products by oxygenative C_α-C_β cleavage such as CH₃-CHO (in the case of 2c) and PhCH₂CHO (in the case of 2e). From the intensities of the two carbonyl peaks of PhCHO, 37% ¹⁸O was estimated to be incorporated into PhCHO, which is comparable to the mass spectroscopy result (ratio between *m/z* = 105 and 107). Similarly, two

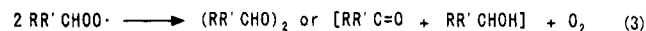
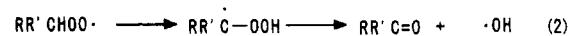
Scheme 1

¹³C NMR peaks of the carbonyl carbon around 192.3 ppm and three mass-parent peaks at 134, 136, and 138 are observed in phthalaldehyde produced by the photolysis of 2f under ¹⁸O₂. From this NMR spectrum, 38% ¹⁸O is estimated to be incorporated into phthalaldehyde.

Thermochemical Investigations. These results were determined by thermochemical investigations. During the initial stage, O₂ is incorporated into the Co-C_α bond of 1, giving 2 under aerobic irradiation conditions. The homolysis of the Co-O bond of 2 gives RR'CHOO• which successively decomposes to RR'CHO• with the elimination of oxygen. The Co-O bond homolysis is supported by the isolation of chlorocobaloxime or (phenylthio)cobaloxime (stated in the paragraph about the effect of oxygen). The alkoxy radical formation is also supported by the isolation of alcohols (runs 1, 2, and 7-10).

A plausible reaction mechanism for the oxygenative C_α-C_β bond cleavage reaction can not be considered without the elucidation of the oxygenative decomposition at the α-carbon. Thus, at first, we focused on the oxygenative decomposition at the α-carbon.

There are some routes to give a carbonyl compound and an alcohol produced by the decomposition at the α-carbon of the alkylperoxy radical^{9,10} or hydrogen alkyl peroxide¹¹ (eqs 2-4). From thermochemical considerations, some bond dissociation energies can be calculated, *i.e.*, $D(\text{PhCH}_2\text{O}-\text{O}^\bullet) = 34$, $D(\text{PhCH}_2\text{CH}_2\text{O}-\text{O}^\bullet) = 57$, $D(\text{PhCH}_2\text{CH}(\text{CH}_3)\text{O}-\text{O}^\bullet) = 65$, $D(\text{PhCH}(\text{-H})\text{OO}^\bullet) = 71$, $D(\text{PhCH}_2\text{CH}(\text{-H})\text{OO}^\bullet) = 73$, $D(\text{PhCH}_2\text{C}(\text{-H})(\text{CH}_3)\text{OO}^\bullet) = 70$, $D(\text{PhCH}(\text{-H})\text{O}^\bullet) = 14$, $D(\text{PhCH}_2\text{CH}(\text{-H})\text{O}^\bullet) = 16$ and $D(\text{PhCH}_2\text{C}(\text{-H})(\text{CH}_3)\text{O}^\bullet) = 13$ kcal mol⁻¹. The bond dissociation energies of RR'C(-H)OO• are about 70 kcal mol⁻¹, which is higher than those of RR'CHO-O•. This suggests that the *in situ* alkoxy radical (RR'CHO•) or dialyl peroxide (RR'CHO)₂ formation (eq 3) preferentially occurs with the 1,3-H transfer (eq 2). Since the (RR'-



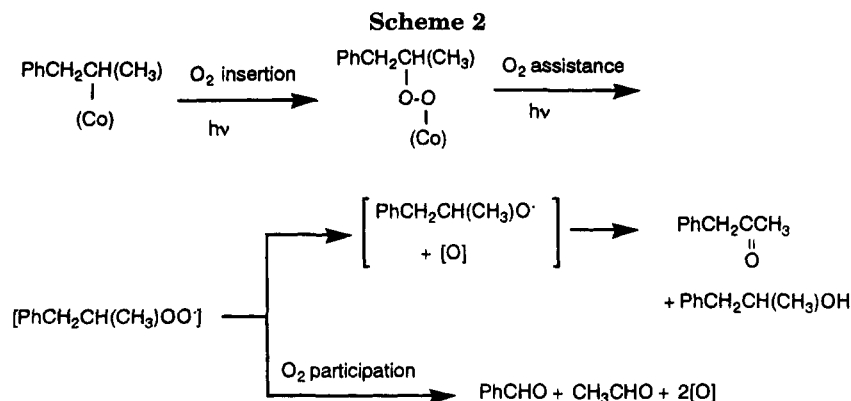
CHO)₂ is unstable (the mean value of $D(\text{RO}-\text{OR})$ ¹² is 38 kcal mol⁻¹), a rapid and successive decomposition occurs through RR'CHO•. The fate of RR'CHO• is summarized in Scheme 1. When the $D(\text{C}-\text{H})$ of RR'CHO• is high, RR'CHO• abstracts H from surrounding substrates giving RR'CHOH (path A) or the disproportionation occurs

(9) Fish, A. *Organic Peroxides: Rearrangement and Cyclization Reactions of Organic Peroxy Radicals*; Swern, D., Ed.; Wiley: New York, 1970; Vol. 1, p 141.

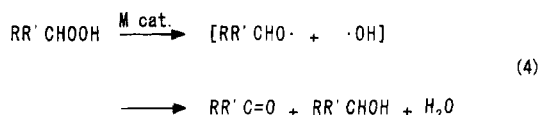
(10) Howard, J. A. *Free Radicals: Homogeneous Liquid-Phase Autooxidations*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, p 3.

(11) Sosnovsky, G.; Rawlinson, D. J. *Organic Peroxides: Metal Ion-Catalyzed Reactions of Symmetric Peroxides*; Swern, D., Ed.; Wiley: New York, Vol. 1, 1970; p 561.

(12) Benson, S. W.; Shaw, R. *Organic Peroxides: Thermochemistry of Organic Peroxides, Hydroperoxides, Polyoxides, and their Radicals*; Swern, D., Ed.; Wiley: New York, 1970; Vol. 1, p 105.



giving $RR'C=O$ and $RR'CHOH$ (path B). On the other hand, in the case of $RR'CHO\cdot$ having the weaker C–H bond, the H is abstracted by surrounding radical species giving $RR'C=O$ (path C). If $RR'CHOOH$ is formed during the reactions, it decomposes to $RR'CHO\cdot$ according to eq 4 or reproduces (alkyldioxy)cobaloxime by the reaction



with cobaloxime.¹³ In our previous examination, it has been revealed⁸ that $RR'CHO\cdot$ having a weak C–H bond around 10–14 kcal mol⁻¹ selectively gave $RR'C=O$, and those having a relatively strong one about 17 kcal mol⁻¹ preferentially gave $RR'CHOH$. Thus, **1a** and **1c** selectively produce the carbonyl compounds, and **1b** gives the alcohol.

In order to interpret the $C\alpha$ – $C\beta$ bond cleavage, further thermochemical considerations are carried out. A characteristic of the oxygenated alkanes having a phenyl group at the β -position is that the $C\alpha$ – $C\beta$ bond dissociation energies are low, $D(\text{PhCH}_2\text{--CH}_2\text{OO}\cdot) = 56$, $D(\text{PhCH}_2\text{--CH}(\text{CH}_3)\text{OO}\cdot) = 51$, $D(\text{PhCH}_2\text{--CH}_2\text{O}\cdot) = -1$, and $D(\text{PhCH}_2\text{--CH}(\text{CH}_3)\text{O}\cdot) = -7$ kcal mol⁻¹, in comparison with those of other compounds such as $D(\text{Ph--CH}_2\text{OO}\cdot) = 80$, $D(\text{PhCH}_2\text{CH}_2\text{--CH}_2\text{OO}\cdot) = 66$, $D(\text{Ph--CH}_2\text{O}\cdot) = 23$, and $D(\text{PhCH}_2\text{CH}_2\text{--CH}_2\text{O}\cdot) = 8$ kcal mol⁻¹. These data suggest that the homolysis of the $C\alpha$ – $C\beta$ bond of the alkylperoxy radical occurs in preference to the O–O cleavage. If the O–O cleavage occurred, the successive $C\alpha$ – $C\beta$ cleavage spontaneously occurred because of the extremely weak $C\alpha$ – $C\beta$ bond of the alkoxy radical. Thus, the photolysis of **1c** (Table 2) and **2c** gave the kinetically controlled products accompanying the $C\alpha$ – $C\beta$ cleavage, and the thermal decomposition of **1c** and **2c** (Table 3) gave thermodynamically controlled products by oxygenation at the α -carbon.

It must not be neglected that another oxygen is partially incorporated (37%) into the products accompanying this homolytic $C\alpha$ – $C\beta$ cleavage. It was found that PhCHO was produced with high selectivity with little formation of PhCH₂OH through the C–C cleavage route of **1b** or **1c** (runs 1 and 2). Thus, the formation of PhCHO is assumed to be due to a cyclic mechanism involving another oxygen during the cleavage in a solvent cage like an ozonide degradation mechanism rather than a simple decomposition of liberated PhCH₂OO \cdot produced by the

combination of PhCH₂ \cdot with O₂ after the homolysis of the C–C bond. The unexpected products such as phthalaldehyde (run 5) or 2-formylindene (run 6) are probably due to this complex mechanism. Further investigations concerning the reaction mechanism are under way.

In conclusion, the reaction course of the aerobic photolysis of **1c** involving both the α -oxygenation and the oxygenative cleavage of $C\alpha$ – $C\beta$ bond is summarized in Scheme 2. On irradiation of visible light, O₂ inserts into the Co–C α bond of alkylcobaloxime **1c**, giving (alkyldioxy)cobaloxime **2c**. The stable **2c** is degraded to an alkylperoxy radical under aerobic irradiation. The α -oxygenated products are formed by the decomposition of the alkylperoxy radical through the alkoxy radical accompanying its O–O bond homolysis. The selectivity of α -oxygenated products between the carbonyl compound and the alcohol is controlled by the $C\alpha$ –H bond dissociation energy of the alkoxy radical. On the other hand, the oxygenated products due to the $C\alpha$ – $C\beta$ bond cleavage are directly formed by the decomposition of the alkylperoxy radical accompanying its $C\alpha$ – $C\beta$ bond homolysis, which involves another oxygen.

Experimental Section

Materials. Alkylcobaloximes **1** were prepared according to the procedure of Schrauzer.¹⁴ (Alkyldioxy)cobaloximes **2** were prepared according to the reported method.^{7a,b} All cobaloximes were identified by NMR, IR, and elemental analysis. The elemental analysis data are the following **1c**: Anal. Calcd for C₂₂H₃₀OCoN₅O₄: C, 54.21; H, 6.20; N, 14.37. Found: C, 54.41; H, 6.21; N, 14.33. **1d**: Anal. Calcd for C₂₂H₃₀CoN₅O₄: C, 54.21; H, 6.20; N, 14.37. Found: C, 54.60; H, 6.24; N, 14.67. **1e**: Anal. Calcd for C₂₉H₃₆CoN₅O₄: C, 60.31; H, 6.28; N, 12.13. Found: C, 60.70; H, 6.41; N, 12.29. **1f**: Anal. Calcd for C₂₂H₂₈CoN₅O₄: C, 54.43; H, 5.81; N, 14.43. Found: C, 54.21; H, 5.90; N, 14.42. **2b**: Anal. Calcd for C₂₁H₂₈CoN₅O₆: C, 49.91; H, 5.58; N, 13.86. Found: C, 49.90; H, 5.41; N, 13.56. The solvents used in this study were purified by distillation before use. The other chemicals were of reagent grade.

Aerobic Photolyses of Alkylcobaloximes. The alkylcobaloximes **1** had an absorption band at 440 nm (sh, $\epsilon = 10\,500$ M⁻¹ cm⁻¹). The solution of alkylcobaloxime **1** (2 mmol) dissolved in CHCl₃ (30 mL) in a three-necked flask was irradiated with a Pyrex-filtered tungsten lamp (400 W rated) at a distance of 20 cm for 4 h by bubbling with oxygen and reacted further for 45 h under sealed O₂ conditions in a water bath controlled at 35 °C. After the reaction, products were isolated by silica gel column chromatography with an eluent of CH₂Cl₂. Products were identified by NMR, IR, and GC-MS by comparison with those of authentic samples. Color temperature and luminous intensity of the 200 W lamp were about 3000 K and 290 cd, respectively.

(13) Giannotti, C.; Fontaine, C.; Chiaroni, A.; Riche, C. *J. Organomet. Chem.* **1976**, *113*, 57.

(14) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.

Time-Course Experiments on the Decomposition of 1.

To an NMR tube were added **1** (0.05 mmol), CDCl_3 (0.5 mL), and benzyl ether (10 μL) with Me_4Si as the internal standard. The reaction was carried out under aerobic irradiation conditions. Yields of products were determined from the integration ratio among the criterion peaks: ^1H NMR δ (CDCl_3) dibenzyl ether: 4.56 (s, CH_2); **1a**: 2.88 (s, CH_2), 1.93 (s, dmgh); **2a**: 4.33 (s, CH_2), 2.26 (s, dmgh); **1c**: 0.31 (d, CH_3), 2.17 (d, dmgh); **2c**: 0.82 (d, CH_3), 2.30 (d, dmgh); benzaldehyde: 10.1 (s, CHO); phenylacetone: 2.15 (s, CH_3), 3.71 (s, CH_2); acetaldehyde: 2.20 (d, CH_3), 9.80 (q, CHO); here, dmgh denotes dimethylglyoximate.

Degradation of (Alkyldioxy)cobaloxime 2. A Pyrex Schlenk tube was charged with 5 mL of CHCl_3 , which was degassed and replaced with argon gas using a freeze-pump-thaw method. **2** (0.2 mmol) was rapidly added to the frozen CHCl_3 under an argon atmosphere, and the deaeration was repeated. The reaction vessel was operated in an appropriate manner, such as the photolysis using a tungsten lamp or the thermal degradation under aerobic or anaerobic conditions. Products yields were determined by GLC using *m*-xylene as an internal standard after removing cobaloximes by column chromatography. The $^{18}\text{O}_2$ incorporation experiment was similarly carried out under an $^{18}\text{O}_2$ (>99%) atmosphere after the reaction vessel was deaerated.

Estimation of Bond Dissociation Energies. The O–O, C–H, and C–C bond dissociation energies of $\text{PhCH}_2\text{CH}_2\text{OO}^\bullet$ and $\text{PhCH}_2\text{CH}_2\text{O}^\bullet$ were estimated according to the thermochemical eqs 5–9. Those of other radicals were similarly

$$D(\text{PhCH}_2\text{CH}_2\text{O}-\text{O}^\bullet) = \Delta H_f^\circ(\text{PhCH}_2\text{CH}_2\text{O}^\bullet) + \Delta H_f^\circ(\text{O}) - \Delta H_f^\circ(\text{PhCH}_2\text{CH}_2\text{OO}^\bullet) \quad (5)$$

$$D(\text{PhCH}_2\text{CH}(\text{H})\text{OO}^\bullet) = \Delta H_f^\circ(\text{PhCH}_2\text{CHO}) + \Delta H_f^\circ(\text{H}) + \Delta H_f^\circ(\text{O}) - \Delta H_f^\circ(\text{PhCH}_2\text{CH}_2\text{OO}^\bullet) \quad (6)$$

$$D(\text{PhCH}_2-\text{CH}_2\text{OO}^\bullet) = \Delta H_f^\circ(\text{PhCH}_2^\bullet) + \Delta H_f^\circ(\text{CH}_2\text{O}) + \Delta H_f^\circ(\text{O}) - \Delta H_f^\circ(\text{PhCH}_2\text{CH}_2\text{OO}^\bullet) \quad (7)$$

$$D(\text{PhCH}_2\text{CH}(\text{H})\text{O}^\bullet) = \Delta H_f^\circ(\text{PhCH}_2\text{CHO}) + \Delta H_f^\circ(\text{H}) - \Delta H_f^\circ(\text{PhCH}_2\text{CH}_2\text{O}^\bullet) \quad (8)$$

$$D(\text{PhCH}_2-\text{CH}_2\text{O}^\bullet) = \Delta H_f^\circ(\text{PhCH}_2^\bullet) + \Delta H_f^\circ(\text{CH}_2\text{O}) - \Delta H_f^\circ(\text{PhCH}_2\text{CH}_2\text{O}^\bullet) \quad (9)$$

estimated. In these calculations, reported data^{12,15} and calculated data¹⁶ were used.

Acknowledgment. We would like to thank Dr. Y. Miyake, Tokyo Metropolitan University, for her expert technical help with the NMR measurements and Professor K. Nishiyama, Tokai University, for his kind discussions.

(15) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC: Tokyo, 1992; Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

(16) For the estimation of ΔH_f° values of some radicals, a mean value¹² of $D(\text{RO}-\text{OR})$ (38 kcal mol⁻¹) and $D(\text{ROO}-\text{H})$ (90 kcal mol⁻¹) were adopted in the calculations. The calculated ΔH_f° 's are; $\Delta H_f^\circ(\text{PhCH}_2\text{OO}^\bullet) = 32.5$, $\Delta H_f^\circ(\text{PhCH}_2\text{O}^\bullet) = 29.9$, $\Delta H_f^\circ(\text{PhCH}_2\text{CH}_2\text{OO}^\bullet) = 25.7$, $\Delta H_f^\circ(\text{PhCH}_2\text{CH}_2\text{O}^\bullet) = 23.15$, $\Delta H_f^\circ(\text{PhCH}_2\text{CH}(\text{CH}_3)\text{OO}^\bullet) = 17$, $\Delta H_f^\circ(\text{PhCH}_2\text{CH}(\text{CH}_3)\text{O}^\bullet) = 14.6$, $\Delta H_f^\circ(\text{PhCH}_2\text{CHO}) = -12.6$, and $\Delta H_f^\circ(\text{PhCH}_2\text{C}(=\text{O})\text{CH}_3) = -24.4$ kcal mol⁻¹.