Reactions of alkylcobaloximes with oxygen under irradiation. Oxygenative conversions of the alkyl ligand

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Abstract

Alkylcobaloximes were irradiated under oxygen in chloroform, giving a carbonyl compound and an alcohol as main organic products. Chlorocobaloxime was isolated after the reaction in all cases. The reaction proceeds through a stable intermediate, (alkyldioxy)cobaloxime. The selectivity for the formation of oxygenated organic products was controlled by the nature of the alkyl ligand.
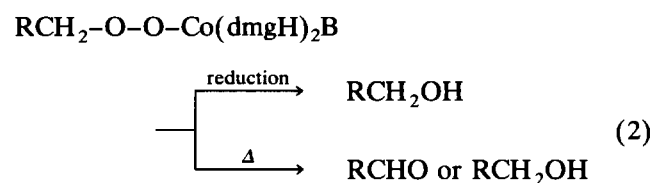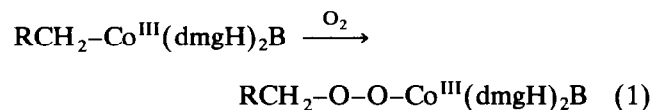
Key words: Cobalt; Irradiation; Peroxide; Radical; Dioxygen; Bond energy

1. Introduction

Alkylbis(dimethylglyoximato)cobalt(III), alkylcobaloxime 1, has received much attention [1] because it serves as a model of vitamin B_{12} and as a synthetic reagent. There has been some work on selective conversion of the alkyl ligand in alkylcobaloxime [2]. Understanding the reactivity of the cobalt–carbon bond of alkylcobaloxime when activated by an irradiation provides important information on the chemical reactivities of related organometallic compounds as well as vitamin B_{12}. Following this approach we have reported [3] some reactions of organocobaloximes with organic or inorganic compounds when irradiated with visible light.

Reactions involving fixation of oxygen are important not only for biological systems but also for synthetic processes [4]. The alkyl ligands of adenosylcobalamin and of related compounds have been reported [5] to be converted into the corresponding aldehydes by aerobic photolysis. Similar oxygenative decomposition of alkyl-

cobaloxime has been shown by Schrauzer [1]. Other work concerning the reaction of alkylcobaloxime and oxygen has been reported; for example, on irradiation of alkylcobaloxime under oxygen, oxygen is inserted into the Co–C bond, giving an (alkyldioxy)cobaloxime [6], and the latter is then degraded into a carbonyl compound or an alcohol by reduction or by heating [7] as shown in eqs. (1) and (2):

$$RCH_2-Co^{III}(dmgH)_2B \xrightarrow{O_2}$$

$$RCH_2-O-O-Co^{III}(dmgH)_2B \quad (1)$$

$RCH_2-O-O-Co(dmgH)_2B$

$$\left. \begin{array}{l} \xrightarrow{\text{reduction}} \ RCH_2OH \\ \\ \xrightarrow{\quad\Delta\quad} \ RCHO \ or \ RCH_2OH \end{array} \right\} \quad (2)$$

However, there have been very few reports [8] of the direct conversion of the alkyl ligand of alkylcobaloxime under oxygen.

We report an attempt at the oxygenative decomposition of alkylcobaloxime for synthetic purposes, with certain fundamental results on the direct conversion of

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alkyl ligand to oxygenated organic products in a one-pot process.

2. Experimental details

2.1. Measurements

NMR spectra were measured with a JEOL PMX 60si and a Varian XL-300 in $CDCl_3$ with Me_4Si as an internal standard. GC-MS were measured with a Perkin Elmer ITD system. Infrared spectra were recorded on a Hitachi 260-10 infrared spectrophotometer and a Perkin Elmer 1600 Series FT-IR. Elemental analyses were carried out with a Perkin Elmer model 240C elemental analyzer.

2.2. Materials

Alkylcobaloximes (1) were prepared according to Schrauzer [9]. (Alkyldioxy)cobaloximes (2) were prepared according to the reported method [6]. All cobaloximes were identified by NMR, IR, and elemental analyses. The solvents used in this study were purified by distillation before use. The other chemicals were of reagent grade.

2.3. General procedure

1 (2 mmol) and chloroform (30 ml) were placed in a 100 ml three-necked flask equipped with a gas inlet, a reflux condenser, and a gas outlet. The solution was irradiated with a tungsten lamp (400 W) for 3 h and oxygen was bubbled through. The solution was then reacted for 45 h under sealed O_2 conditions in a water bath (35°C). After the reaction, products were isolated by a silica gel column chromatography. Products were identified by NMR and GC-MS.

2.4. Experiments on the time-course of decomposition of cobaloximes

To a NMR tube (ϕ 5 mm) were added cobaloxime (0.05 mmol), $CDCl_3$ (0.5 ml), and dibenzyl ether (10 μl) and Me_4Si as internal standards. The reaction was carried out under irradiation (400 W) in a water bath (35°C) under aerobic conditions. Yields and the decomposition rates were determined from the integration ratio among criterion peaks; $\delta(CDCl_3)$ dibenzyl ether: 4.56(s, CH_2); **1a**: 2.88(s, CH_2), 1.93(s, dmgH CH_3); **1b**: 0.59(d, $PhCHCH_3$), 1.95(s, dmgH CH_3); **1d**: 1.65(t, $PhCH_2CH_2CH_2$), 2.08(s, dmgH CH_3); **1i**: 2.78(s, CH_2), 1.97(s, dmgH CH_3); **1j**: 3.03 and 3.14(d, CH_2), 1.61 and 1.66 (d, dmgH CH_3); **1k**: 2.92(s, CH_2), 1.93(s, dmgH CH_3); **2a**: 4.33(s, CH_2), 2.26(s, dmgH CH_3); **2b**: 1.25(d, $PhCHCH_3$), 2.15(s, dmgH, CH_3); **2d**: 3.36(t, $PhCH_2CH_2CH_2$), 2.28(s, dmgH CH_3); **2i**: 4.35(s, CH_2), 2.25(s, dmgH CH_3); **2j**: 4.40(s, CH_2), 1.91(s, dmgH CH_3), **2k**: 4.32(s, CH_2), 2.28(s, dmgH CH_3); **3**: 2.41 (s,

dmgH CH_3). Phenylthio(pyridine)cobaloxime: 2.00(s, dmgH CH_3), benzaldehyde: 10.0(s, CHO); benzyl alcohol: 4.67(s, CH_2); acetophenone: 2.63(s, CH_3); styrene: 5.15–5.85(sdd, $PhCH=CH_2$); 3-phenylpropanal: 9.83 (t, CHO).

The pseudo-first-order decomposition rate constants (k_d) of **1** and **2** were measured under conditions of excess concentration of $CDCl_3$ and constant concentration of O_2. All data were in close agreement with a first-order plot, $k_d t = \ln([C_0]/[C])$.

2.5. Estimation of bond dissociation energies

The dissociation energies of the C–H bond of alkoxyl radicals are estimated according to eqns. (3) and (4) [10]. Other bond dissociation energies were estimated according to eqns. (5)–(7). Here, mean values of D(RO–OR) (38 kcal/mol) and D(ROO–H) (90 kcal/mol) [10] were used in the calculation. Other thermodynamic values were adopted from reported [11] or calculated data [10]. The estimated bond-dissociation energies of some radicals were; $D(PhC(CH_3)$-$(O\cdot)$-$H) = 10$, $D(PhCH=CHCH(O\cdot)$-$H = 12$, $D(Ph$-$CH(O\cdot)$-$H = 13$, $D(PhCH_2CH_2CH(O\cdot)$-$H) = 17$, $D(CH_3CH_2CH_2CH_2CH(O\cdot)$-$H) = 17$, $D(PhCH_2O$-$O\cdot) = 34$, $D(PhCH(OO\cdot)$-$H) = 71$ kcal/mol.

$$D(RR'C(O\cdot)-H) = \Delta H_f^{\circ}(RR'C{=}O) + \Delta H_f^{\circ}(H)$$
$$- \Delta H_f^{\circ}(RR'CHO\cdot) \quad (3)$$

$$\Delta H_f^{\circ}(RR'CHO\cdot) = 1/2[\Delta H_f^{\circ}([RR'CHO]_2)$$
$$+ D(RO{-}OR)] \quad (4)$$

$$D(RR'CHO{-}O\cdot) = \Delta H_f^{\circ}(RR'CHO\cdot) + \Delta H_f^{\circ}(O)$$
$$- \Delta H_f^{\circ}(RR'CHOO\cdot) \quad (5)$$

$$D(RR'C(OO\cdot)-H)$$
$$= \Delta H_f^{\circ}(RR'C{=}O) + \Delta H_f^{\circ}(H)$$
$$+ \Delta H_f^{\circ}(O) - \Delta H_f^{\circ}(RR'CHOO\cdot) \quad (6)$$

$$\Delta H_f^{\circ}(RR'CHOO\cdot) = D(RR'CHOO{-}H) - \Delta H_f^{\circ}(H)$$
$$+ \Delta H_f^{\circ}(RR'CHOOH) \quad (7)$$

3. Results and discussion

Alkylcobaloximes (**1a–h**) were irradiated with a tungsten lamp (400 W) in chloroform under oxygen at 35°C for 48 h, and the results are in Table 1. Four products, *i.e.*, a carbonyl compound, an alcohol, an olefin, and a chlorocobaloxime were isolated after the reactions.

The alkyl ligands in cobaloximes (**1a**, **1b**, **1e** and **1g**) are predominantly converted to carbonyl compounds. On the other hand, the alkyl ligands in cobaloximes (**1f**
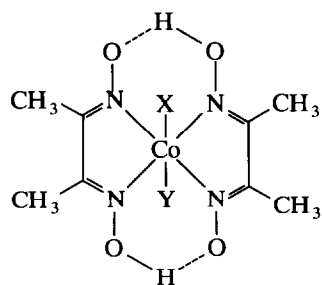
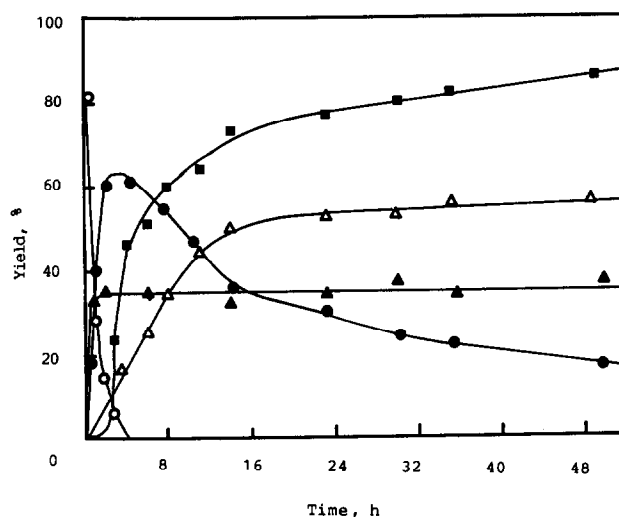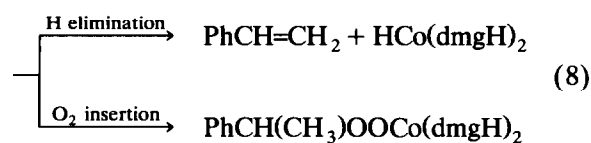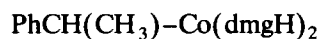|	X	Y
1a:	$PhCH_2$	pyridine
1b:	$PhCH(CH_3)$	pyridine
1c:	$PhCH_2CH_2$	pyridine
1d:	$PhCH_2CH_2CH_2$	pyridine
1e:	$PhCH=CHCH_2$	pyridine
1f:	$CH_3(CH_2)_4CH_2$	pyridine
1g:	$PhCH_2OCOCH(CH_3)$	pyridine
1h:	$PhCH_2OCOCH_2CH_2$	pyridine
1i:	$PhCH_2$	1-methylimidazole
1j:	$PhCH_2$	triphenylphosphine
1k:	$PhCH_2$	4-cyanopyridine
2a:	$PhCH_2OO$	pyridine
2b:	$PhCH(CH_3)OO$	pyridine
2d:	$PhCH_2CH_2CH_2OO$	pyridine

Fig. 1. Time course of the degradation of **1b** under irradiation: **1b**, ○; **2b**, ●; acetophenone, △; styrene, ▲; chlorocobaloxime, ■.

and **1h**) are selectively converted to alcohols. In the case of cobaloxime **1c**, the 2-phenylethyl ligand is specifically converted to benzaldehyde with a loss of a carbon [12].

Further investigations are carried out to understand the course of the reaction and the selectivities of product formation.

TABLE 1. Photolysis of alkylcobaloxime under oxygen [a]

Entry	Cobaloxime	Organic products (yield, %)
1	**1a**	$PhCHO(65)$, $PhCH_2OH(10)$
2	**1b**	$PhCOCH_3(60)$, $PhCH=CH_2(12)$
3	**1c**	$PhCHO(36)$, $PhCH_2CH_2OH(9)$
4	**1d**	$PhCH_2CH_2CHO(19)$, $PhCH_2CH_2CH_2OH(10)$
5	**1e**	$PhCH=CHCHO(97)$
6	**1f**	$CH_3(CH_2)_4CH_2OH(10)$
7	**1g**	$PhCH_2OCOCOCH_3(53)$, $PhCH_2OCOCH(OH)CH_3(18)$
8	**1h**	$PhCH_2OCOCH_2CH_2OH(15)$, $PhCH_2OCOCH=CH_2(15)$

[a] Conditions: [1] = 67 mM, in $CHCl_3$, under O_2, at 35°C, for 48 h, irradiation by a tungsten lamp (400 W).

3.1. Time-dependent photolysis of alkylcobaloxime (1b)

The time-course of the photolysis of 1-phenyl-ethyl(pyridine)cobaloxime (**1b**) under oxygen was monitored by ^1H NMR spectroscopy and is shown in Fig. 1. Products other than **1b**, (1-phenylethyldioxy)cobaloxime (**2b**), acetophenone and styrene were not detected.

1b is rapidly consumed during a few hours. In contrast, rapid formation of (alkyldioxy)cobaloxime (**2b**) is observed, and its moderate decomposition occurs afterwards. As **2b** decomposes, production of acetophenone increases. This strongly suggests that the oxygenated organic product arises from the decomposition of **2b**.

Styrene is produced in the initial stage of this reaction. Later, its yield does not increase. Formation of styrene can be explained by elimination of a β-hydrogen [13] from **1b** rather than from β-scission of hydroperoxyalkyl radical suggested by Schrauzer et al. [14]. Elimination of β-hydrogen from **1b** competes with the insertion of oxygen into the $Co-C_\alpha$ bond of **1b** in these reaction conditions (eqn. (8)). This side reaction can be minimized under low temperature conditions [15*].

$$PhCH(CH_3)-Co(dmgH)_2$$

$$\begin{array}{l} \xrightarrow{\text{H elimination}} PhCH=CH_2 + HCo(dmgH)_2 \\ \\ \xrightarrow{\text{O}_2 \text{ insertion}} PhCH(CH_3)OOCo(dmgH)_2 \end{array} \quad (8)$$
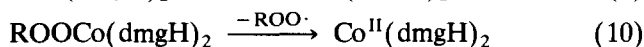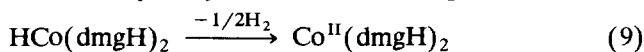
*Reference number with asterisk indicates a note in the list of references.

TABLE 2. Rate constants in the decomposition of alkylcobaloxime 1 and (alkyldioxy)cobaloxime 2 [a]

Entry	Cobaloxime	$k_d\ (\times 10^{-6}),\ s^{-1}$
9	1a	9.7
10	1b	96.2
11	1d	2.3
12	1i	11.0
13	1j	9.1
14	1k	12.4
15	2a	2.1
16	2b	1.9
17	2d	2.8
18	2a [b]	3.3
19	2a [c]	1.0

[a] Conditions: [cobaloxime] = 100 mM, in $CDCl_3$, at 35°C, under aerobic conditions, irradiation by a tungsten lamp (400 W). [b] Addition of diphenyl disulfide. [c] Under dark conditions.

Chlorocobaloxime is produced gradually as the reaction proceeds. This can be explained by reaction of chloroform with a divalent cobaloxime [16] produced by the rapid β-hydrogen elimination of 1b at the initial stage (eqns. (8) and (9)) and by the gradual decomposition of (alkyldioxy)cobaloxime (2b) (eqn. (10)).

$$HCo(dmgH)_2 \xrightarrow{-1/2H_2} Co^{II}(dmgH)_2 \qquad (9)$$

$$ROOCo(dmgH)_2 \xrightarrow{-ROO\cdot} Co^{II}(dmgH)_2 \qquad (10)$$

3.2. Rates of decomposition of alkylcobaloximes and (alkyldioxy)cobaloximes

The rates of decomposition (k_d) of alkylcobaloximes and (alkyldioxy)cobaloximes were estimated from data of time-course experiments monitored by ^1H NMR spectroscopy, and are summarized in Table 2.

The consumption of 1 is due to the insertion of oxygen into the $Co-C_\alpha$ bond and the elimination of β-hydrogen in certain cases (entries 2 and 8). Remarkable differences among three cobaloximes (1a, 1b and 1d) in decomposition rates are observed (Table 2, entries 9–11, $k_{1b} > k_{1a} > k_{1d}$). A similar tendency has been observed [17] in the study of the kinetics of insertion of molecular oxygen into the Co–C bond of alkylcobaloximes. Rates of decomposition of alkylcobaloximes are related to the Co–C bond dissociation energies of alkylcobaloximes. That is to say, the weaker the Co–C bond, the faster the reaction with oxygen. These energies will be ranked 1b < 1a < 1d by comparison with the C–H bond dissociation energies of the corresponding hydrocarbons [18*].

When the pyridine ligand in 1a is replaced by other base ligands, the decomposition rates change little (entries 12–14; compare 1a, entry 9). Although basicity of the base ligand has been reported to affect the energy of dissociation of the C–Co bond of alkylcobaloximes [13], no remarkable effect is observed. In addition, base

ligands with a low basicity such as triphenylphosphine are liberated after the reaction.

The consumption of 2 is due to the production of organic oxygenated products. Contrary to the decomposition of alkylcobaloxime with O_2, the decomposition rates of three (alkyldioxy)cobaloximes (2a–2d) are effectively identical (entries 15–17). The rates of decomposition of 2 are not affected by the alkyl moiety at its fifth ligand. The results suggest that the degradation of 2 was due to homolysis at the Co–O bond or at the O–O bond rather than at the O–C bond. The decomposition rates of 2 are slower than those of alkylcobaloximes which have a benzylic ligand (compare the results given as entries 9, 10 with entries 15, 16).

3.3. Effect of solvent

Photodegradations of benzylcobaloxime 1a (10 mM) were carried out under oxygen for 48 h in four organic solvents (chloroform, toluene, ethanol and benzene). In all cases, benzaldehyde was a main organic product (yields: 37%, 21%, 13% and 8% respectively). Chloroform was the most effective solvent of benzylcobaloxime. Furthermore, the highest selectivity for formation of benzaldehyde and the highest conversion of benzyl ligand to oxygenated products were observed with chloroform as solvent. One reason why chloroform solvent shows the highest reactivity is that the reactive cobaloxime is changed into a stable chlorocobaloxime after the reaction.

3.4. Effect of irradiation

When the reactions are carried out in the dark, 1a does not decompose with O_2 under the conditions shown in Table 2. On the other hand, the decomposition rate of 2a is markedly retarded under dark conditions (Table 2, entry 19). Visible light is necessary for the insertion of oxygen into the $Co-C\alpha$ bond of 1 and it accelerates the decomposition of 2.

3.5. Effects of oxygen on the decomposition of (alkyldioxy)cobaloxime

To investigate the effects of oxygen on the decomposition of 2, some control experiments were carried out (Table 3).

On irradiation at 35°C, the decomposition of 2a is retarded under anaerobic conditions (entry 20) by comparison with the result under oxygen (entry 21). In addition, the reaction is accelerated by addition of diphenyl disulfide (Table 2, entry 18), and a considerable amount of (phenylthio)cobaloxime is obtained after the reaction. It is already known [7] that (alkyldioxy)cobaloximes are thermally unstable, so the effect of oxygen on thermal decomposition was examined; the yield of benzaldehyde was higher under oxygen (entry 23) than the yield under anaerobic condi-

TABLE 3. Effects of oxygen on the decomposition of (benzyl-dioxy)cobaloxime 2a [a]

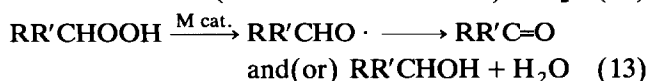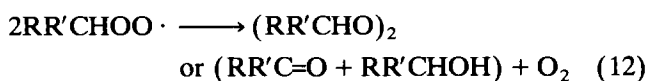| Entry	Temp (°C)	Irrad. [b]	Oxygen	Time (h)	Yield [c] (%)
20	35	on	absence	48	12
21	35	on	presence	48	55
22	60	off	absence	24	57
23	60	off	presence	24	85

[a] Conditions: [2a] = 40 mM in $CHCl_3$. [b] Irradiation with a tungsten lamp (400 W); on = irradiation conditions, off = dark conditions. [c] Yield of benzaldehyde.

tions (entry 22). The homolysis of the Co–O bond of (alkyldioxy)cobaloxime is therefore accelerated by the S_{RN} or S_H reaction of some radical species such as paramagnetic oxygen or the phenylthio radical.

Gupta et al. [7] have suggested the involvement of an alkylperoxyl radical during the decomposition of (alkyldioxy)cobaloxime. Giannotti et al. [19] have confirmed that irradiation accelerates homolysis of the thermal O–O bond of alkyldioxycobaloxime, by observing the spin adduct of 3,4-dihydro-2,2-dimethyl-2H-pyrrole 1-oxide and alkoxyl radical. In this case, the fate of reactive cobaloxime is to form not hydroxocobaloxime but chlorocobaloxime. Moreover, the formation of (phenylthio)cobaloxime (entry 15) supports the hypothesis of the homolysis of the Co–O bond of 2.

We conclude that the Co–O bond of 2 is homolytically cleaved, at first, to form an alkylperoxyl radical. There are three plausible routes by which the alkylperoxyl radical could decompose to a carbonyl compound; (1) self-decomposition after isomerization of the alkylperoxyl radical by a 1 : 3-transfer of H from C to O [20] (eqn. (11)), (2) a self-decomposition in a cyclic mechanism [21] (eqn. (12)), and (3) a metal-catalyzed decomposition of an alkyl hydroperoxide formed by an abstraction of H from a solvent [22] (eqn. (13)). Presence of an alkoxyl radical during the decomposition is appropriate, since considerable amounts of alcohols are formed after the reaction (entries 1, 3, 4, 6–8). In addition, the formation of the alkoxyl radical has an advantage in converting the alkylperoxyl radical into the carbonyl compound, as indicated by comparison between RR′C(O ·)–H and RR′C(OO ·)–H of C–H bond dissociation energies (see Experimental details). Further investigations of the reaction mechanism are under way.

$$RR'CHOO \cdot \longrightarrow RR'\overset{\cdot}{C}OOH \longrightarrow RR'C=O + \cdot OH \quad (11)$$

$$2RR'CHOO \cdot \longrightarrow (RR'CHO)_2$$
$$\text{or } (RR'C=O + RR'CHOH) + O_2 \quad (12)$$

$$RR'CHOOH \xrightarrow{M \text{ cat.}} RR'CHO \cdot \longrightarrow RR'C=O$$
$$\text{and(or) } RR'CHOH + H_2O \quad (13)$$

3.6. Product selectivity

The selectivity of formation of organic products from the carbonyl compound and the alcohol can be explained by the stability of the alkoxyl radical (RR′CHO ·). An order of C–H bond dissociation energies (D_{C-H}) in alkoxyl radicals is calculated as $RCH(O \cdot)–H > PhCH(O \cdot)–H > PhC(CH_3)(O \cdot)–H$. When the D_{C-H} of an alkoxyl radical (RR′CHO ·) is low, the hydrogen of the alkoxyl radical is immediately abstracted by a radical such as the divalent cobaloxime in a solvent cage, giving the carbonyl compound (RR′C=O), or a disproportionation of the alkoxyl radical occurs, giving the carbonyl compound and the alcohol (RR′CHOH). Thus, unstable alkoxyl radicals generated from 1a, 1b, 1e and 1g are selectively converted to the corresponding carbonyl compounds. On the other hand, the more stable alkoxyl radicals generated from 1d, 1f and 1h whose D_{C-H} are higher than the former, can abstract hydrogen from surrounding solvent to yield the corresponding alcohols.

4. Conclusions

The one-pot oxygenative decompositions of alkylcobaloximes in chloroform under irradiation demonstrate the direct conversion of alkyl ligands to corresponding carbonyl compounds or alcohols. The reaction proceeds via a stable (alkyldioxy)cobaloxime. Irradiation was not only necessary for the insertion of O_2 to the C–Co bond of alkylcobaloxime but is also effective for the decomposition of (alkyldioxy)cobaloxime. The rates of insertion of O_2 into alkylcobaloximes were influenced by the stability of the C–Co bond, whereas the decomposition rates of (alkyldioxy)cobaloximes were scarcely influenced by their alkyl moieties. The course of decomposition of (alkyldioxy)cobaloxime was proposed as the first stage of O–Co bond homolysis and the successive autodecomposition of the O–O bond as homolysis of the alkylperoxyl radical. The product selectivity was explained in terms of stability of the alkoxyl radical.

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18 Similar calculations to those described in Experimental details were carried out; $D(PhCH(CH_3)-H) = 85$ kcal/mol, $D(PhCH_2-H) = 88$ kcal/mol, and $D(PhCH_2CH_2CH_2-H) = 100$ kcal/mol. These results coincided well with the reported data [11].

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