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Reaction of Organocobaloxime with Thiol under Irradiation

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The reactivity of photoactivated organocobaloxime was investigated by the reaction of thiol. Alkyl(pyridine)cobaloxime and ethyl mercaptoacetate were irradiated with a tungsten lamp under anaerobic conditions in an organic solvent to give ethyl alkylthioacetate, diethyl 2,2′-dithioacetate, and ethoxycarbonylmethylthiocobaloxime. Mechanistic investigations were carried out to determine the reaction course. Sulfide was assumed to be produced via a homolytic substitution between alkylcobaloxime and disulfide formed during the reaction. Disulfide was formed from thiol catalytically in the presence of cobaloxime under anaerobic conditions. Homolytic methyl-transfer scarcely occurred from methylcobaloxime into thiol.

Bis(dimethylglyoximato)cobalt complexes, cobaloximes, have been paid much attention as a vitamin B_{12} model.[1] Under irradiation, the Co–C bond of alkylcobalamin and related model complexes have been reported[2] to cleave homolytically with regards to an active state of the cobalamin by apoenzyme. Methylcobalamin has been known to participate in methionine synthesis.[3] Whether the methyl-transfer from methylcobalamin to homocysteine occurs via a homolytic or ionic reaction has been discussed.[3] Schrauzer et al. have reported[4] that the methyl group does not transfer into homocysteine via a homolytic reaction but via an ionic reaction in an aqueous media by using methylcobaloxime as a methylcobalamin model. Recently, we have suggested[5] the possibility of an alkyl-transfer reaction of alkylcobaloxime into thiol via a homolytic reaction in a nonaqueous media. The reactivities under hydrophobic conditions frequently offer some important information concerning the enzymic active-center in the hydrophobic core. In addition, little is known about the reactions of cobalamins and their model compounds with sulfur compounds under hydrophobic conditions, although they seem to play an important part in biological systems. This paper deals with the reactions of organocobaloximes with thiol in organic solvents under visible-light irradiation.

Results and Discussion

Homolytic Alkyl Group Transfer Reaction of Photoactivated Organocobaloxime into Thiol. Benzylbis(dimethylglyoximato)pyridinecobalt(III), benzylcobaloxime, **1a** (1.5 mmol) and ethyl mercaptoacetate **2** (1 mmol) were dissolved in 15 mL of CH_2Cl_2, which were irradiated with tungsten lamp (400 W) for 24 h at 35 °C under an argon atmosphere. Three products, ethyl(benzylthio)acetate **3a**, and diethyl 2,2′-dithioacetate **4a**, and ethoxycarbonylmethylthiocobaloxime **5a**, were isolated as indicated in Eq. 1.

$$\underset{\mathbf{2}}{HSCH_2CO_2Et} \xrightarrow[h\nu]{PhCH_2Co(DH)_2py\ \ \mathbf{1a}} \underset{\mathbf{3a}\ (52\%)}{PhCH_2SCH_2CO_2Et} + \underset{\mathbf{4a}\ (15\%)}{(SCH_2CO_2Et)_2} + \underset{\mathbf{5a}\ (30\%)}{EtOCOCH_2SCo(DH)_2py} \quad (1)$$

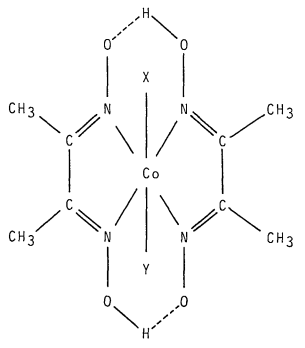
The solvent effect of this reaction is examined (Table 1). Sulfide **3a** was obtained in good yield in all solvents. The highest yield of **3a** was obtained when the reaction was carried out in dichloromethane (Entry 2). Dichloromethane has been found to be superior to other solvents regarding its efficiency in the benzyl-transfer reaction and in the recovery of cobaloxime as alkylthiocobaloxime **5a**.

Similarly, a benzyl-transfer reaction occurs when **1a** is treated with other thiols, such as benzenethiol, α-toluenethiol, and 2-mercaptoethanol. The yields of

Table 1. Solvent Effect of the Benzyl-Transfer Reaction[a]

Entry	Solvent	Yield[b]/%			Conversion of **1a**/%	Selectivity	
		3a	**4a**	**5a**		A[c]	B[d]
1	Benzene	54	36	34	58	0.93	0.59
2	Dichloromethane	61	47	58	66	0.92	0.88
3	Tetrahydrofuran	56	34	47	73	0.76	0.64
4	Methanol	52	30	26	58	0.89	0.45

a) Conditions: **1a**=0.5 mmol, **2**=1 mmol in solvent (15 mL), at 35 °C for 24 h, irradiation with tungsten lamp (400 W), under Ar. b) Yields were calculated on the basis of **1a**. c) Selectivity for **3a** (yield of **3a**/conversion of **1a**). d) Selectivity for **5a** (yield of **5a**/conversion of **1a**).



Cobaloxime

py= pyridine

N-MeIm= N-methylimidazole

PPh_3= triphenylphosphine

1a:	X= $PhCH_2$	Y=	py
1b:	= CH_3	=	py
1c:	= $CH_3(CH_2)_4CH_2$	=	py
1d:	= $EtOCOCH_2CH_2$	=	py
1e:	= $PhCH_2CH_2$	=	py
1f:	= PhCH=CH	=	py
1g:	= $PhCH=CHCH_2$	=	py
1h:	= cyclo-C_6H_{11}	=	py
1i:	= $CH_3CH(CN)$	=	py
1j:	= $PhCH_2$	=	N-MeIm
1k:	= $PhCH_2$	=	PPh_3
5a:	= $EtOCOCH_2S$	=	py
5b:	= PhS	=	py
6 :	= Cl	=	py

the corresponding benzyl sulfides and disulfides were: benzyl phenyl sulfide (51%), diphenyl disulfide (43%), dibenzyl sulfide (38%), dibenzyl disulfide (49%), 2-(benzylthio)ethanol (34%), and 2,2′-dithiodiethanol (18%). These results suggest that the benzyl group tends to transfer into a more acidic thiol.

Several organocobaloximes (**1a—i**) reacted with two equivalents of **2** under irradiation. The results are summarized in Table 2. The yields were calculated on the basis of **1**.

Cobaloximes bonded to the primary alkyl group (Entries 5—8) or the vinyl group (Entry 9) scarcely afforded sulfides **3**. However, a benzyl group (Entry 10), an allyl group (Entry 11), or a secondary carbon (Entries 12,13) attached to cobaloximes can be efficiently transferred into thiol. Considerable amounts of disulfides **4** were obtained in these cases. Organo ligands were converted into **3**, alkanes by hydrogen abstraction, olefins by β-hydrogen elimination, and some undetermined products. The Co–C bond dissociation energy of a cobalt complex bonded to a primary carbon ligand has been reported[6] to be higher than that of a cobalt complex bonded to a secondary carbon ligand (about 5—10 kcal mol^{-1}). It is well known that secondary carbon radicals are more stable than primary carbon radicals due to an I-effect, and that benzyl radicals and allyl radicals are relatively stable due to an M-effect. The different reactivities in the reactions of these cobaloximes **1** with thiol **2** are presumed to be due to the Co–C bond dissociation energy or the different reactivities of the carbon radicals.

Table 2. Reaction of Photoactivated Organocobaloximes **1** and Ethyl Mercaptoacetate **2**[a]

Entry	Cobaloxime 1	Yield[b]/% 3	4	5	Conversion of 1/%
5	**1b**	Trace	189	1	75
6	**1c**	0	185	15	54
7	**1d**	0	92	25	26
8	**1e**	0	122	28	53
9	**1f**	0	170	28	76
10	**1a**	56	78	39	56
11	**1g**	27	162	9	99
12	**1h**	5	107	60	81
13	**1i**	22	69	17	80

a) Conditions: **1**=1 mmol, **2**=2 mmol, in CH_2Cl_2 (15 mL), at 35 °C, for 24 h, irradiation with tungsten lamp (400 W), under Ar. b) Yields were calculated on the basis of **1**.

Benzylcobaloxime-coordinated *N*-methyl imidazole **1j** was treated with ethyl mercaptoacetate **2** under the same conditions as given in Table 2 to give sulfide **3a** in 38% yield and disulfide **4a** in 51% yield. Benzylcobaloxime coordinated with triphenylphosphine **1k** gave **3a** in 24% and **4a** in 45%, respectively. After all, the pyridine coordinated cobaloxime **1a** showed the highest reactivity regarding the benzyl-transfer reaction. The basicities of the axial-ligand has been reported[7] to affect the Co–C bond dissociation energy; that is, the pK_a value of the base ligand is correlated with the Co–C bond dissociation energy. However, benzylcobaloxime **1k** of which Co–C bond dissociation energy[8] is expected to be the lowest among three cobaloximes, showed a lower reactivity than **1a**. In the case of the reaction of **1k** with **2**, a large amount of triphenylphosphine was recovered after the reaction. During the reaction, a week base ligand might be exchanged with thiol **2**,[9] which is responsible for the low reactivity of **1k**.

Catalytic Disulfide Formation. In the reaction of organocobaloxime **1** with thiols, significant amounts of disulfides were obtained in every case, in addition to the sulfides due to the organo-ligand transfer reaction (Table 2). The disulfide formation might proceed catalytically, since the phenylthiocobaloxime has been reported[10] to catalyze the photochemical hydrogen evolution and diphenyl disulfide formation from benzenethiol. To make sure of the catalytic reactivity of cobaloxime, thiols were irradiated in the presence of cobaloxime under anaerobic condition. The results are summarized in Table 3.

Thiols were converted into disulfides in all cases, and cobaloxime worked as an effective catalyst. By prolonging the reaction time the reaction came to completion (Entry 15). Phenylthiocobaloxime **5b** showed the highest reactivity. The different reactivities among the cobaloximes (**1a**, **5b**, **6**) are due to a facility to form a Co(II) complex through a homolytic cleavage of the Co-ligand bond or through the formation of alkylthiocobaloxime **5a** by a nucleophilic substitution of thiol **2**.

The effect of irradiation was investigated by some control experiments (Table 4). Since both cobaloximes and related complexes have been reported[11] as being good catalysts for the oxidation of thiol to disulfide by oxygen, the effect of oxygen was also investigated.

Table 3. Cobaloxime-Catalyzed Disulfide Formation from Thiols under Irradiation[a]

Entry	Thiol	Cobaloxime	Time / h	Disulfide[b] / %	Turnover number of catalyst
14	**2**	**1a**	15	48	24
15	**2**	**1a**	48	100	50
16	$HOCH_2CH_2SH$	**1a**	15	47	23.5
17	$PhCH_2SH$	**1a**	15	33	16.5
18	PhSH	**1a**	15	52	26
19	**2**	**5b**	15	60	30
20	**2**	**6**	15	30	15

a) Conditions: thiol=1 mmol, cobaloxime=0.02 mmol, in CH_2Cl_2 (2 mL), at 35 °C, under Ar, irradiation with tungsten lamp (400 W). b) Yields were calculated on the basis of **1**.

Table 4. Control Experiments on Disulfide Formation from Thiol Catalyzed by Cobaloxime[a]

Entry	**1a**	Light	Atmosphere	Disulfide[b] / %
21	Presence	On	O_2	56
22	Presence	On	Ar	48
23	Presence	Dark	O_2	11
24	Presence	Dark	Ar	33
25	Absence	On	O_2	0
26	Absence	On	Ar	0

a) Conditions: **1a**=0.02 mmol, **2**=1 mmol, in CH_2Cl_2 (2 mL), at 35 °C, for 15 h, irradiation with tungsten lamp (400 W). b) Yields were calculated on the basis of **2**.

The presence of cobaloxime **1a** was necessary in order to make the reaction proceed (Entries 21—24). Visible-light irradiation promoted disulfide formation (Entries 21,22). Contrary to the promotion of disufide formation by oxygen under irradiation conditions (Entries 21,22), oxygen inhibited the reaction under dark conditions (Entries 23,24). Under an oxygen atmosphere, benzylcobaloxime has been reported[12] to insert oxygen into the Co–C bond to give benzyldioxycobaloxime, which degradated smoothly at 35 °C only under irradiation.[13] The different reactivity between **1a** and benzyldioxycobaloxime regarding the ligand-exchange reaction by thiol is presumed to reflect the result.

Mechanistic Investigation of the Reaction of Benzylcobaloxime with Thiol. The effects of the reaction time and the temperature on the homolytic benzyl-transfer reaction into thiol were investigated (Table 5). Irradiation was neccesary to transfer the benzyl group of **1a** into thiol **2** (Enteries 27, 29, 30). On the other hand, a considerable amount of disulfide **4a** was formed under dark conditions at 35 °C (Entry 28), and even at a lower temperature (Entry 31). The yield of sulfide **3a** could be increased by prolonging the reaction time, but the yield of disulfide **4a** decreased reversely (Entries 27, 29). Under dark reactions (Entries 28, 31), only a trace amount of alkylthiocobaloxime **5a** was detected, in spite of the formation of a large amount of disulfide **4a**.

In order to establish the reaction course, the reactivity of three products (**3a**, **4a**, and **5a**) were investigated. Sulfide **3a** did not react with an equimolar amount of thiol **2**, disulfide **4a**, or benzylcobaloxime **1a** under the condtions described in Table 5. Disulfide **4a** reacted with 1.5 equivalent of benzylcobaloxime **1a** for 24 hours to give sulfide **3a** (110%) and alkylthiocobaloxime **5a** (90%) (Eq. 2); such homolytic displacement has been reported previously.[14] The higher yield of **3a** than 100% is presumed to be due to the reaction of excess **1a** with **5a** produced during the reaction. Alkylthiocobaloxime **5a** was found to be spontaneously decomposed into disulfide **4a** by irradiation or by heat; the time-dependent decomposition of **5a** is shown in Fig. 1. No superior activation effect of **5a** upon irradiation was observed. Alkylthiocobaloxime **5a** and equimolar benzylcobaloxime **1a** were irradiated for 24 hours to give sulfide **3a** in 14% yield, which was ascribed to a homolytic

Table 5. Reaction of Photoactivated Benzylcobaloxime **1a** and Ethyl Mercaptoacetate **2**[a]

Entry	Temp/°C	Time/h	Yield[b] / %			Conversion of **2** / %
			3a	**4a**	**5a**	
27	35[d]	24	52	15	30	100
28[c]	35[d]	24	6	81	Trace	87
29	35[d]	48	61	6	33	100
30	−20[e]	24	55	18	25	100
31[c]	−20[e]	24	0	76	Trace	76

a) Conditions: benzylcobaloxime **1a**, 1.5 mmol; ethyl mercaptoacetate **2**, 1.0 mmol; CH_2Cl_2, 15 mL; irradiation with tungsten lamp (400 W), under Ar. b) Yields were calculated on the basis of **2**. c) Dark reaction. d) Set in a incubator. e) Set in a cooled-EtOH bath.

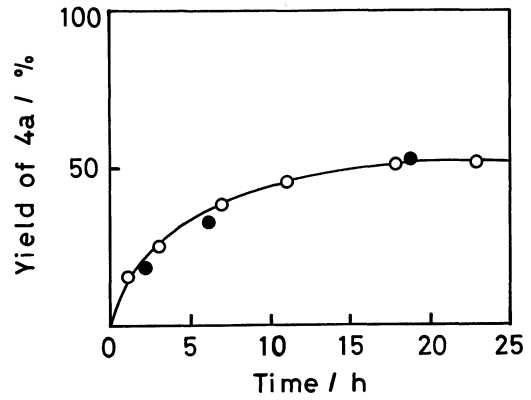


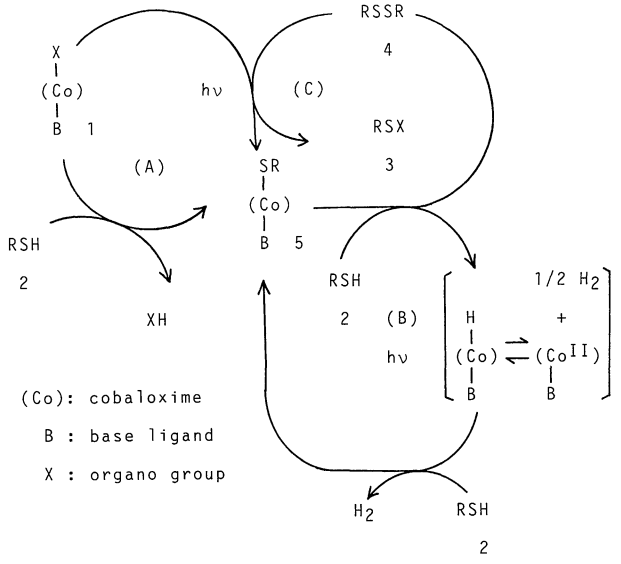
Fig. 1. Time-dependent decomposition of alkylthiocobaloxime **5a** under an argon atmosphere at 35°C. ○: Under irradiation with tungsten lamp (400 W), ●: under dark.

displacement between **1a** and **4a** produced by a self-decomposition of **5a**, rather than a homolytic displacement between cobaloximes **1a** and **5a**.

$$\underset{\mathbf{1a}}{PhCH_2Co(DH)_2py} + \underset{\mathbf{4a}}{(SCH_2CO_2Et)_2} \xrightarrow{h\nu} \underset{\mathbf{3a}}{PhCH_2SCH_2CO_2Et} + \underset{\mathbf{5a}}{EtOCOCH_2SCo(DH)_2py} \quad (2)$$

A mechanistic investigation of the catalytic formation of disulfide **4a** was carried out. Althgough disulfide can be formed by the self-decomposition of alkylthiocobaloxime **5a**, the slow conversion rate and slight effectiveness of irradiation (Fig. 1) are opposed to the facts of efficient catalytic formation of disulfide (Table 3) and stimulation of the catalytic cycle by irradiation (Table 4). Thus, thiol might react with **5a** nucleophilically to give disulfide and hydridocobaloxime in analogy with an exchange reaction between thiol and disulfide.[15] Hydridocobaloxime is in equilibrium with hydrogen and a divalent cobaloxime, which is reported[16] to react with thiol to give alkylthiocobaloxime. This reaction cycle is presumed to be stimulated by irradiation.

Whether sulfide **3** was produced by a direct displacement of **1a** with thiol **2** or a displacement of **1a** with disulfide **4** formed during the reaction was investigated. A sufficient amount of disulfide **4a** was present at least during the reaction, due to catalytic disulfide formation (Tables 2, 3, and 5 (Entries 28, 31)). A bimolecular homolytic displacement of **1a** with **4a** occurs quantitatively (Eq. 2). The results given in Table 5 (Entries 27, 29), i. e., the consumption of disulfide **4a** and the supply of alkylthiocobaloxime **5a**, according to an increase in the sulfide yield, can be well explained by assuming a homolytic substitution between **1a** and **4a**. In addition, a bimolecular homolytic displacement of organocobaloximes usually occurs with a substrate having a weak bond such as



Scheme 1.

$BrCCl_3$, PhSSPh, RSO_2Cl etc.[17] It is concluded that sulfide **3a** is produced by a homolytic substitution of **1a** and **4a**.

Further, the initiation step of this reaction was investigated. A slight amount of toluene was detected from the reaction mixture by GC-MS. Similarly, slight amounts of alkanes were also detected in the case of a reaction of **1e** or **1g** with **2** (Table 2, Entries 8 and 11). The formation of toluene suggests that hydrogen abstraction from thiol by a benzyl radical generated by the irradiation of **1a** or nucleophilic substitution of **1a** by thiol. Disulfide **4a** and a trace amount of alkylthiocobaloxime **5a** were formed under dark condition at −20°C (Table 5, Entry 31). It appears more likely that **5a** is produced by the nucleophilic substitution of thiol. In addition, it is hard to abstract the hydrogen from thiol by a benzyl radical, since the S–H bond dissociation energy is relatively high (about 90 kcal mol^{-1}).[18]

From these results, the reaction course is assumed to be as represented in Scheme 1. Initially, alkylcobaloxime **1** reacts with thiol **2** to give a slight amount of alkylthiocobaloxime **5** by nucleophilic substitution by thiol (path A). Cobaloxime **5** works as an efficient catalyst for the formation of disulfide **4** (path B), successively. Disulfide **4**, formed by the path B, reacts with cobaloxime **1** to give the final product, sulfide **3**, and a alkylthiocobaloxime **5** (path C). The reformation of alkylthiocobaloxime **5** accerelates the reaction (path B and C) as a result of an increase in the concentration of catalyst **5**.

In conclusion, a ligand-transfer reaction of organocobaloxime **1** into alkanethiol occurs in case of cobaloximes coordinated a benzyl group, an allyl group, and a secondary carbon as an organo-ligand. While the primary alkyl ligands of cobaloximes (**1b**—**e**) scarcely transfer into ethyl 2-mercaptoacetate under

the conditions used in this study, cobaloximes coordinated with a primary alkyl ligand are expected to transfer the alkyl ligand into more acidic thiols, such as benzenethiol. Actually, the alkyl group of 5-hexenyl(pyridine)cobaloxime has been reported[19] to be trapped by diphenyl disulfide under irradiation.

From a biological perspective, the methyl-transfer reaction from methylcobalamin to homocysteine in a homolytic manner is concluded to occur hardly from the results of our cobaloxime model reactions. An indirect methyl-transfer reaction, i.e., homolytic substitution between methylcobalamin and homocystine, has only a slight possibility to occur, except an activation of cobalamin or thiol by a specific enzymic environment. Again, the radical mechanism would be eliminated according to the results of our cobalamin model study under hydrophobic conditions, together with Schrauzer's results[4] for an aqueous media.

Experimental

General. ^{1}H NMR spectra were measured with a JEOL PMX 60-si and a Varian XL-300 NMR spectrometer in $CDCl_3$ with Me_4Si as an internal standard. GC-MS were measured with Perkin Elmer ITD system.

Materials. Cobaloxime (**1** and **6**) were prepared by the procedure of Schrauzer.[20] Alkylthiocobaloxime **5** was also prepared according to the reported method.[4] The solvents used in this study were purified as usual. The other chemicals used in this study were of reagent grade.

The ^{1}H NMR ($CDCl_3$) data of main compounds used in this study; **1a**: δ=2.0 (s, 12H, $C\underline{H}_3$), 2.9 (s, 2H, $PhC\underline{H}_2$), 7.0 (m, 5H, Ph), 7.4 (m, 2H, Py), 7.7 (m, 1H, Py), 8.6 (m, 2H, Py); **2**: δ=1.4 (t, 3H, $C\underline{H}_3CH_2$), 2.1 (t, 1H, SH), 3.3 (d, 2H, $HSC\underline{H}_2$), 4.3 (q, 2H, $CH_3C\underline{H}_2$); **3a**: δ=1.3 (t, 3H, $C\underline{H}_3CH_2$), 3.1 (s, 2H, $PhC\underline{H}_2$), 3.9 (s, SCH_2), 4.3 (q, 2H, $CH_3C\underline{H}_2$), 7.4 (s, 5H, Ph); **4a**: δ=1.3 (t, 6H, $C\underline{H}_3CH_2$), 3.6 (s, 4H, SCH_2), 4.3 (q, 4H, $CH_3C\underline{H}_2$); **5a**: δ=1.2 (t, 3H, $C\underline{H}_3CH_2$), 2.3 (s, 12H, CH_3), 2.4 (s, 2H, SCH_2), 4.0 (q, 2 H, $CH_3C\underline{H}_2$), 7.3 (m, 2H, py), 7.7 (m, 1H, py), 8.3 (m, 2H, py).

The Reaction of Benzyl(pyridine)cobaloxime (1a) with Ethyl Mercaptoacetate (2) under Irradiation. Benzylcobaloxime **1a** (0.689 g, 1.5 mmol), ethyl mercaptoacetate (109 μL, 1 mmol), and 15 mL of CH_2Cl_2 were put into a Schlenk tube, which was deoxygenated and replaced with argon gas by a freeze-pump-thaw technique. The reaction vessel was irradiated by two tungsten lamps (200 W×2) at a distance of 20 cm from reaction vessel with stirring for 24 hours at 35 °C. After the reaction, the solvent was evaporated to give a reaction mixture which was analyzed by ^{1}H NMR to determine the product yields and conversion. The yields were determined from the peak ratio of **1a**: δ=2.0 (s, 12H, CH_3), δ=2.9 (s, 2H, CH_2), **5a**: δ=2.3 (s, 14H, CH_3 and CH_2S), **3a**: δ=3.1 (s, 2H ,$PhC\underline{H}_2$), δ=3.9 (s, 2H, CH_2S), **2**: δ=3.3 (t, 3H, CH_3), and **4a**: δ=3.6 (s, 2H, CH_2). Organic products and cobaloximes were isolated by silica-gel column chromatography with an eluent of CH_2Cl_2 and acetone. The isolated yields coincided with the NMR yields. The yields and conversions in other experiments were obtained by a similar manner described here.

Disulfide Formation from Thiol in the Presence of Cobaloxime under Anaerobic Conditions. Benzylcobaloxime **1a** (9 mg, 0.02 mmol), ethyl 2-mercaptoacetate **2** (109 μL, 1 mmol), and CH_2Cl_2 (2 mL) were put into a Schlenk tube; the mixture was then degassed and replaced with argon by a freeze-pump-thaw method. The reaction was carried out under irradiation by two tungsten lamps (200 W×2) at a distance of 20 cm from the reaction vessel for 15 hours at 35 °C.

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