The Reaction of Bis(dimethylglyoximato)(pyridine)cobalt(I), Cobaloxime(I), with 2-(Allyloxy)ethyl Halides and the Photolysis of the Resulting Organo-cobaloximes[1)]

Masami Okabe and Masaru Tada*

Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 160

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The reactions of 2-(allyloxy)ethyl halides with cobaloxime(I) gave (tetrahydro-3-furanyl)methylcobaloximes *via* an electron transfer from cobaloxime(I) to the halides to give radical anions. The rupture of a halide ion to give an organic radical and the ring closure to give a (tetrahydro-3-furanyl)methyl radical are followed by the radical coupling between the organic radical and the cobaloxime(II). The structures of the organo-cobaloximes were determined by the analyses of the photolysis products under aerobic or anaerobic conditions.

The formation of organo-cobalt complexes by the reaction of cobalamin(I) or bis(dimethylglyoximato)-(pyridine)cobalt(I), hereafter cobaloxime(I) or $(Co^{I})^{-}$, with alkyl halides has been claimed to proceed by an S_N2 mechanism, an electron transfer mechanism, a four centered *syn*-substitution, and an S_Ni reaction with retention of configuration. The possibility of the last two mechanisms has been claimed as an interpretation of the reactions of 1-adamantyl bromide and 1-norbornyl bromide.[2)] The S_N2 mechanism has been proposed based on a kinetic study[3)] and the stereochemistry of products,[4)] and the electron transfer mechanism has been proposed by the indication of the radical intermediate.[5-7)]

In this paper we would like to report the experimental results supporting the electron transfer mechanism and the photolyses of the organo-cobaloximes which define the structures of the organo-cobaloximes. We used the cyclization of 2-(allyloxy)ethyl radical to (tetrahydro-3-furanyl)methyl radical as a probe of the radical intermediate (R·) formed by the rupture of halide ion (X^-) from the radical anion ($RX^{\cdot-}$) (Eq. 1).

$$(Co^{I})^- + RX \longrightarrow (Co^{II}) + RX^{\cdot-} \longrightarrow (Co^{II}) + R\cdot + X^- \longrightarrow (Co)R + X^- \quad (1)$$

Results

The Reaction of Cobaloxime(I) with Tosylates or Halides. 2-(Allyloxy)ethyl tosylates or 2-(allyloxy)ethyl halides were reacted with cobaloxime(I) in methanol under nitrogen; the results are summarized in Table 1. 2-(Allyloxy)ethyl tosylate (**1a**) gave a direct substitution product, 2-(allyloxy)ethylcobaloxime (**4a**) but 2-allyloxy-2-phenylethyl tosylate (**1b**) did not show any reactivity toward cobaloxime(I). The cobaloxime(I) anion reacted with 2-(allyloxy)ethyl bromide (**2a**) to give **4a** and (tetrahydro-3-furanyl)methylcobaloxime (**5a**). The reaction of cobaloxime(I) with 2-allyloxy-2-phenylethyl bromide (**2b**) and 2-allyloxy-2,2-diphenylethyl bromide (**2c**) gave (5-phenyltetrahydro-3-furanyl)methylcobaloxime (**5b**) and (5,5-diphenyltetrahydro-3-

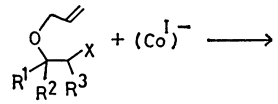
Table 1. Reaction of cobaloxime(I) anion, $(Co^{I})^-$, with tosylates and halides in methanol[a)]

Substrate	R^1	R^2	R^3	X	Product[b)] composition	Yield[c)] %
					4a : **5a**	
1a	H	H	H	OTs	100 : 0	47
2a	H	H	H	Br	71 : 29	60
3a	H	H	H	I	35 : 65	66
					4b : **5b**	
1b	Ph	H	H	OTs	— : —	0
2b	Ph	H	H	Br	0 : 100	38
3b	Ph	H	H	I	0 : 100	55
					4c : **5c**	
2c	Ph	Ph	H	Br	0 : 100	40
					4d : **5d**[d)]	
1d	H	$-(CH_2)_4-$		OTs	— : —	0
2d	H	$-(CH_2)_4-$		Br	0 : 100	55
3d	H	$-(CH_2)_4-$		I	0 : 100	51
					7 : **8**	
6	—	—	—		35 : 65	55

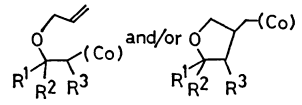
a) See the general procedure in the experimental section for reaction conditions. b) Determined by the amount of isolated organo-cobaloximes. c) (**4**+**5**) or (**7**+**8**). d) Consisting of two stereo-isomers.

furanyl)methylcobaloxime (**5c**), respectively. Similarly the cyclic halides, *trans*-2-(allyloxy)cyclohexyl bromide (**2d**) and iodide (**3d**), gave (7-oxabicyclo[4.3.0]non-9-yl)methylcobaloxime (**5d**) but no direct substitution product **4d**. The corresponding tosylate **1d** did not show any reactivity toward cobaloxime(I). 2,2-Diphenyl-2-(2-methyl-2-propenyloxy)ethyl bromide (**6**) gave both a non-cyclized organo-cobaloxime, 2,2-diphenyl-2-(2-methyl-2-propenyloxy)ethylcobaloxime (**7**), and a cyclized organo-cobaloxime, (5,5-diphenyl-3-methyltetrahydro-3-furanyl)methylcobaloxime (**8**).

In seeking by-products from bromide **2d**, 3-(allyloxy)cyclohexene (**9**), 9-methylene-7-oxabicyclo-[4.3.0]nonane (**10**), and another by-product, which was anticipated to be 9-methyl-7-oxabicyclo[4.3.0]-nonane (**11**) from NMR data, were obtained in 5, 3, and 1% yields, respectively. Similarly 4-methyl-2-phenyltetrahydrofuran (**12**) and 4-methylene-2-phenyltetrahydrofuran (**13**) were formed from bromide **2b**.



1a, **b**, and **d** (X=OTs)
2a, **b**, **c**, and **d** (X=Br)
3a, **b**, and **d** (X=I)

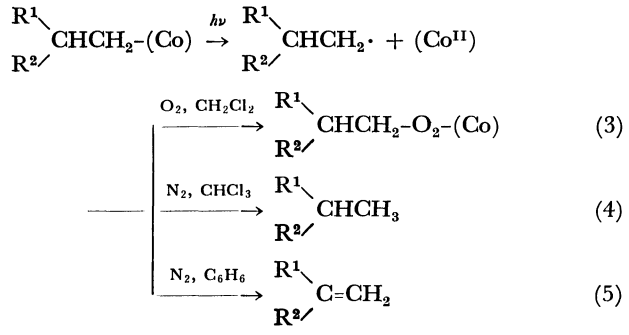


(2)

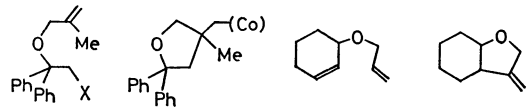
4a—d **5a—d**

a: $R^1=R^2=R^3=H$ **b**: $R^1=Ph$, $R^2=R^3=H$
c: $R^1=R^2=Ph$, $R^3=H$ **d**: $R^1=H$, $R^2+R^3=-(CH_2)_4-$

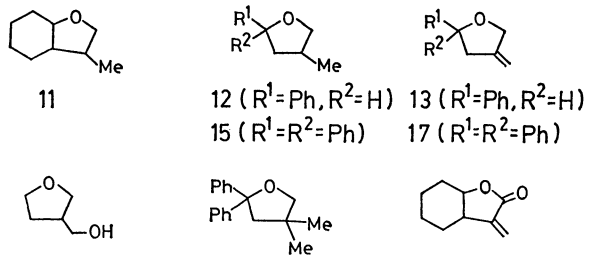
Photolyses of Organocobaloximes. The photolytic cleavage of the carbon-cobalt bond of an organocobaloxime gave an alkyl radical and cobaloxime(II) as primary products. Molecular oxygen inserts between the two radical species to give an alkyldioxycobaloxime under aerobic conditions (Eq. 3).[8] Under anaerobic conditions, however, the radical collapses into an olefin or a saturated compound depending upon the hydrogen-donating ability of the solvent used (Eqs. 4 and 5).[9,10]



The analyses of the photolysis products, therefore, can define the structures of the cyclized organocobaloximes. The aerobic photolysis of **5a** gave a peroxide and the $NaBH_4$-reduction of the peroxide gave 3-(hydroxymethyl)tetrahydrofuran (**14**), which was identical to the authentic sample.[11] Anaerobic photolyses of organocobaloximes **5b**, **5c**, and **8** in chloroform gave **12** (98%), 2,2-diphenyl-4-methyltetrahydrofuran (**15**) (78%), and 4,4-dimethyl-2,2-diphenyltetrahydrofuran (**16**) (70%), respectively. On the other hand, anaerobic photolyses of **5b** and **5c** in benzene gave **13** and 2,2-diphenyl-4-methylenetetrahydrofuran (**17**), respectively. The hydrogenolysis of **12** over Pd–C gave 2-methyl-4-phenyl-1-butanol which was identified with the authentic sample.[12] The structures of all other tetrahydrofuran derivatives were deduced unequivocally from elemental analyses and spectral data, especially from NMR spectra. Similarly the anaerobic photolysis of **5d** in benzene gave **10**, which became 9-methylene-7-oxabicyclo[4.3.0]nonan-8-one (**18**) by CrO_3-oxidation; **18** was identified by comparison with the authentic sample.[13]



6 (X=Br) 8 9 10
7 (X=(Co))



11 12 (R^1=Ph, R^2=H) 13 (R^1=Ph, R^2=H)
15 ($R^1=R^2$=Ph) 17 ($R^1=R^2$=Ph)

14 16 18

Discussion on Reaction Mechanism

In the reaction of cobaloxime(I) with halides, a carbenium ion intermediate has been excluded by the lack of a solvolysis product in methanol and also by the lack of a tetrahydropyran derivative which is expected to form *via* a more stable secondary cation.[14] A carbanion intermediate has been also excluded by the fact that the reaction in protic media, methanol or ethanol containing water, did not give a saturated product as a major one.

5-Hexenyl radical has a strong tendency to give cyclopentylmethyl radical irreversibly unless the radical center has an electron-attracting substituent.[15] The ring closure of 3-oxa-5-hexenyl radical, 2-(allyloxy)ethyl radical ($k=1.2\times10^6$ s^{-1}, 25 °C),[16] is faster than that of 5-hexenyl radical ($k=1.0\times10^5$ s^{-1}, 25 °C).[17] The oxa-system is, therefore, a better probe of a radical intermediate than the hydrocarbon system which is popular in radical chemistry.

Cobaloxime(I) anion and cobalamin(I) are strong nucleophiles in the reaction with methyl iodide and are called "supernucleophiles,"[18] but the bulky ligands in those cobalt complexes hinder the reaction with sterically bulky halides. Though we do not deny a normal S_N2 mechanism for simple halides such as methyl iodide, a four centered mechanism or a *syn*-displacement of halogen and bulky cobaloxime(I)[2]

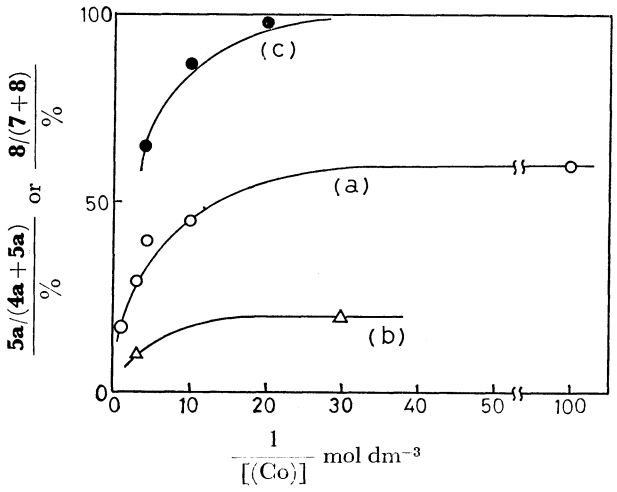


Fig. 1. Dependence of the formation of **5a** from **2a** (1.0×10^{-3} mol) and **8** from **6** (1.0×10^{-3} mol) on the concentration of cobaloxime [(Co)].
(a): Formation of **5a** in MeOH, (b): formation of **5a** in EtOH, (c): formation of **8** in MeOH.

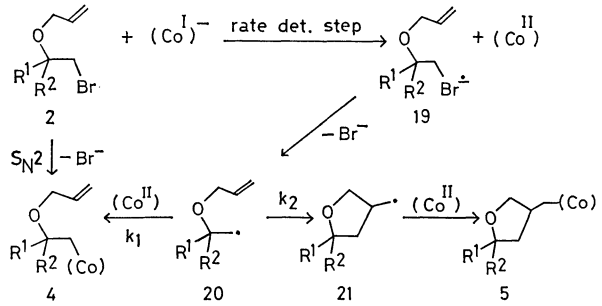
is hardly acceptable as the mechanism of the reactions of sterically hindered halides and cobaloxime(I). The present experimental results clearly show the intervention of a radical species which is evidenced by the formation of tetrahydrofuran derivatives. The formation of a radical from an organic halide is expected by the single electron transter from cobaloxime(I) to the organic halide followed by the rupture of a halide ion. The radical intermediate is further supported by the formation of **10**, **11**, **12**, and **13** as minor products. The electron transfer process should be sensitive to the polarity of the solvent, and indeed the reaction in ethanol produced less cyclized product **5a** from bromide **2a** than the reaction in methanol (see Fig. 1).

The formation of the non-cyclized organo-cobaloxime **7** from bromide **6** must be entirely due to the electron transfer mechanism, since the S_N2 mechanism must not be operative in the reactions of the β,β-disubstituted halides such as bromide **2c**. The substantial formation of the non-cyclized organo-cobaloxime **7**, therefore, must be due to the retardation of radical cyclization by the methyl substitution at the reaction center. The cyclization rate of 5-methyl-5-hexenyl radical to (1-methylcyclopentyl)methyl radical is *ca.* 1/50 to that of 5-hexenyl radical.[19] 2-(Allyloxy)ethyl halides (**2b**, **2c**, **2d**, **3b**, and **3d**) having the substituents at the β-position give only the cyclized organo-cobaloximes (**5b**, **5c**, and **5d**) due to the inhibition of the direct substitution. This steric hindrance must inhibit both S_N2 and the direct radical coupling process to give non-cyclized organo-cobaloximes.

2-(Allyloxy)ethyl tosylate (**1a**) gave only the direct substitution product **4a**. This result suggests the lack of a radical intermediate in the reaction of **1a**. The tosylates (**1b** and **1d**) which have substituents at 2-position did not react with cobaloxime(I) due to the steric inhibition. Compared to a halogen, a tosyl group is a hard leaving group and the S_N2 reaction with the soft and bulky nucleophile, cobaloxime(I), is sluggish even in the case of tosylate **1a**. The reaction is slowered by the steric hindrance in the case of tosylates **1b** and **1d**, and no organo-cobaloxime is obtained.

The reaction scheme is summarized below (Scheme 1). The proportion of **4** and **5** from the radical intermediate **20** can be expressed by $[\mathbf{4}]/[\mathbf{5}]=k_1[(Co^{II})]/k_2$ and depends on the concentration of the (Co^{II}) intermediate. By carrying out the reaction in diluted state, we can decrease [(Co^{II})] and retard the formation of **4**, as shown in Fig. 1. Similarly, the formation of **8** from bromide **6** increases and overcomes completely the formation of **7** in diluted state. The radical coupling between the less hindered redical **20a** and (Co^{II}) is substantial but the radicals (**20b**, **20c**, and **20d**) having bulky substituents, from **2b**, **2c**, **2d**, **3b**, and **3d**, lack its reactivity to (Co^{II}) and only cyclized organo-cobaloximes (**5b**, **5c**, and **5d**) were obtained. The reaction of cobaloxime(I) with less hindered bromides may take an S_N2 process competitively with an electron transfer process. In high dilution state (total cobaloxime: 1.0×10^{-2} mol dm^{-3}), the non-cyclized organo-cobaloxime **4a** (40% from **2a**) must be formed by S_N2 mechanism, since the formation of **4a** by radical coupling is negligible under these reaction conditions (see Fig. 1). The variation in product ratio **4**/**5** from **1a**, **2a**, and **3a** indicates that the initial step (**2a** or **3a**→**19**) is a rate determining step, since iodide **3a** gives more cyclyzed product **5a** than bromide **2a**. The reaction of **2a** in polar methanol gives more cyclyzed product **5a**, formed by electron transfer mechanism, than in less polar ethanol.

In conclusion the reaction of cobaloxime(I) with organic halides takes place *via* an electron transfer mechanism as the most important one and the reaction with less hindered tosylates proceeds by an S_N2 mechanism.



Scheme 1.

Experimental

Syntheses of 2-(Allyloxy)ethyl Tosylates. 2-(Allyloxy)ethyl Tosylate (1a): 2-(Allyloxy)ethyl tosylate was prepared by Bergman's method.[16] Tosylation of 2-(allyloxy)ethanol was carried out in a conventional manner with tosyl chloride in pyridine overnight at 0 °C and the purification by chromatography on silica gel gave tosylate **1a**, oil. NMR (CCl_4): δ 2.43 (s, 3H), 3.53 (t, 2H, J=5 Hz), 3.81—3.95 (m, 2H), 4.02 (t, 2H, J=5 Hz), 4.99—5.27 (m, 2H), 5.52—5.98 (m, 1H), 7.23 (d, 2H, J=8 Hz), and 7.68 (d, 2H, J=8 Hz).

*2-Allyloxy-2-phenylethyl Tosylate (**1b**)*: Phenyloxirane (11.63 g, 0.097 mol) was added dropwise to a mixture of 70 cm^3 of allyl alcohol and 0.13 cm^3 of concd sulfuric acid during 5 min. The mixture was stirred for 30 min at room temperature and refluxed for 1 h. After being cooled, the mixture was treated with 0.2 g of sodium hydroxide and excess allyl alcohol was removed under reduced pressure. Ethereal solution of the residue was washed with water (50 $cm^3 \times 2$) and dried over sodium sulfate. Distillation of the product after removal of the ether gave 2-allyloxy-2-phenylethanol (65%), bp 114—115 °C/627.0 Pa. Tosylation of the alcohol in the same manner as in the case of **1a** gave tosylate **1b**,[20] oil. NMR(CCl_4): δ 2.40 (s, 3H), 3.71—3.86 (m, 2H), 3.87—4.00 (m, 2H), 4.46 (t, 1H, J=6 Hz), 4.92—5.20 (m, 2H), 5.48—5.85 (m, 1H), 7.05—7.21 (m, 7H), and 7.54 (d, 2H, J=8 Hz).

*2-(Allyloxy)cyclohexyl Tosylate (**1d**)*: 2-(Allyloxy)cyclohexanol was prepared by the acid catalyzed addition of allyl alcohol to 1,2-epoxycyclohexane in the manner mentioned above, bp 93 °C/1067 Pa.[21] Tosylation of the alcohol in the same manner as in the case of **1a** gave tosylate **1d** (70%), oil. NMR (CCl_4): δ 1.10—2.20 (m, 8H), 2.46 (s, 3H), 3.15—3.41 (m, 1H), 3.82—3.94 (m, 2H), 4.39 (double triplet, 1H, J=4 and 7 Hz, $W_{1/2}$=19 Hz), 5.02—5.30 (m, 2H), 5.56—6.00 (m, 1H), 7.45 (d, 2H, J=8 Hz), and 7.96 (d, 2H, J=8 Hz). The tosylate **1d** was transformed by a simple substitution into 2-allyloxy-1-iodocyclohexane (**3d**) whose structural evidence will be described later, in the section for **3d**.

*Syntheses of 2-(Allyloxy)ethyl Halides. 2-(Allyloxy)ethyl Bromide (**2a**)*: Bromide **2a** was prepared from tosylate **1a** (0.69 g) by the displacement of the tosyl group with a bromide ion. The displacement was carried out by the active magnesium bromide, prepared *in situ* from 1.92 g (1.2×10^{-2} mol) of 1,2-dibromoethane and 0.244 g (1.0×10^{-2} mol) of magnesium in 15 cm^3 of ether.[22] After stirring overnight at room temperature, the reaction mixture was diluted with water and extracted with ether. The ethereal extract gave 0.267 g (60%) of bromide **2a** on distillation. **2a**, bp 85—95 °C/13400 Pa.[23] NMR(CCl_4): δ 3.34 (t, 2H, J=6 Hz), 3.63 (t, 2H, J=6 Hz), 3.86—4.00 (m, 2H), 5.02—5.30 (m, 2H), and 5.59—6.01 (m, 1H).

*2-Allyloxy-2-phenylethyl Bromide (**2b**)*: A solution of 13.2 g (5.0×10^{-2} mol) of 1,2-dibromo-1-phenylethane and 5 cm^3 of pyridine in 200 cm^3 of allyl alcohol was refluxed for 4 h. After removal of excess allyl alcohol under reduced pressure and addition of water (100 cm^3), the mixture was extracted by ether–benzene (1:1). Chromatography of the extract on silica gel gave the starting dibromide and 2.6 g (21%) of bromide **2b**, bp 78 °C/20.00 Pa.[23] NMR (CCl_4): δ 3.23—3.60 (m, 2H), 3.70—4.08 (m, 2H), 4.99 (dd, 1H, J=6 and 8 Hz), 5.04—5.35 (m, 2H), 5.65—6.05 (m, 1H), and 7.30 (s, 5H).

*2-Allyloxy-2,2-diphenylethyl Bromide (**2c**)*: A solution of 1.60 g (1.0×10^{-2} mol) of bromine in 10 cm^3 of methanol-free dichloromethane was added to a cooled (−5 °C) solution of 1.80 g (1.0×10^{-2} mol) of 1,1-diphenylethylene in 20 cm^3 of methanol-free dichloromethane. After stirring for 30 min at 0 °C, the solvent was removed under reduced pressure at 0 °C and 15 cm^3 of allyl alcohol was added to the residue. To the cooled mixture (−5 °C) was added 0.66 g of potassium hydroxide and the reaction mixture was stirred for 1 h at 0 °C and for an additional hour at room temperature. Dichloromethane was added to the mixture and the solution was washed with water and dried over calcium chloride. Removal of the solvent gave the crude product and recrystallization from methanol gave 1.70 g (55%) of bromide **2c**, mp 66—67 °C; Found: C, 64.30; H, 5.42%. Calcd for $C_{17}H_{17}BrO$: C, 64.37; H, 5.40%. NMR (CCl_4): δ 3.59—3.71 (m, 2H), 4.00 (s, 2H), 4.90—5.32 (m, 2H), 5.56—5.94 (m, 1H), and 6.98—7.30 (m, 10H).

*2-(2-Methyl-2-propenyloxy)-2,2-diphenylethyl Bromide (**6**)*: The same procedure for the preparation of bromide **2c** was employed by using 2-methyl-2-propen-1-ol instead of allyl alcohol. **6**, oil. NMR (CCl_4): δ 1.77 (s, 3H), 3.67 (s, 2H), 4.23 (s, 2H), 4.90 (br. s, 1H), 5.13 (br. s, 1H), and 7.24—7.53 (m, 10H).

The bromide **6** was treated with an excess amount of tributylstannane to give a mixture of 1-(2-methyl-2-propenyloxy)-1,1-diphenylethane and 4,4-dimethyl-2,2-diphenyltetrahydrofuran (**16**) (described later) in 1:3 ratio. The structure of the former compound, and therefore the structure of **6**, was evidenced by an unequivocal synthesis from 2-methyl-2-propenyl chloride and sodium 1,1-diphenylethoxide in THF. 1-(2-Methyl-2-propenyloxy)-1,1-diphenylethane, oil. IR (CCl_4): 1662, 901, and 700 cm^{-1}; NMR (CCl_4): δ 1.72 (s, 3H), 1.85 (s, 3H), 3.59 (br. s, 2H), 4.78 (br. s, 1H), 5.01 (br. s, 1H), and 7.06—7.40 (m, 10H).

*2-Allyloxy-1-bromocyclohexane (**2d**)*: The same procedure for the preparation of bromide **2a** was employed by using 2-(allyloxy)cyclohexyl tosylate (**1d**) instead of tosylate **1a**. **2d**, bp 100—105 °C/1600 Pa.[24] NMR (CCl_4): δ 1.16—2.44 (m, 8H), 3.41 (double triplet, 1H, J=4 and 7 Hz, $W_{1/2}$=18 Hz), 3.90—4.17 (m, 3H), 5.03—5.40 (m, 2H), and 5.70—6.12 (m, 1H).

*2-(Allyloxy)ethyl Iodide (**3a**)*: A mixture of 5.12 g (2.0×10^{-2} mol) of **1a** and 15.0 g (1.0×10^{-1} mol) of sodium iodide in 80 cm^3 of acetone was refluxed for 24 h. After cooling, 100 cm^3 of ether was added to the mixture and the resulting salts were filtered off. The filtrate was concentrated and dissolved in 100 cm^3 of ether. The ethereal solution was washed with aqueous sodium thiosulfate and dried over sodium sulfate. Distillation of the residue gave 2.78 g (65%) of iodide **3a**, bp 84 °C/4533 Pa.[17] NMR (CCl_4): δ 3.08 (t, 2H, J=7 Hz), 3.52 (t, 2H, J=7 Hz), 3.77—3.98 (m, 2H), 4.90—5.22 (m, 2H), and 5.48—5.90 (m, 1H).

*2-Allyloxy-2-phenylethyl Iodide (**3b**)*: The tosyl group of **1b** was replaced by iodide by a similar procedure for the preparation of **2a** from **1a**, but active magnesium iodide was prepared from magnesium and iodine in ether.[22] The product was worked up as in the case of bromide **2a** but additional washing by aqueous sodium thiosulfate. Distillation gave iodide **3b** (27%), bp 110 °C/86.66 Pa. NMR (CCl_4): δ 3.17—3.35 (m, 2H), 3.65—4.07 (m, 2H), 4.40 (dd, 1H, J=6 and 8 Hz), 5.02—5.35 (m, 2H), 5.65—6.07 (m, 1H), and 7.30 (s, 5H). The iodide **3b** was transformed into its quarternary salt, 2-allyloxy-2-phenylethylpyridinium iodide.[20]

*2-Allyloxy-1-iodocyclohexane (**3d**)*: The same procedure for the preparation of iodide **3b** gave iodide **3d** (53%), bp 82 °C/120.0 Pa. NMR(CCl_4): δ 1.15—2.50(m, 8H), 3.41(double triplet, 1H, J=4 and 7 Hz, $W_{1/2}$=19 Hz), 3.92—4.30 (m, 3H), 5.02—5.41(m, 2H), and 5.70—6.15(m, 1H). The iodide **3d** was treated with potassium *t*-butoxide in THF to give 3-(allyloxy)cyclohexene (**9**), which was synthesized unequivocally from 3-bromocyclohexene and sodium allylate in THF. **9**, bp *ca.* 60 °C/2780 Pa. NMR(CCl_4): δ 1.45—2.70(m, 6H), 3.74—3.92(m, 1H), 3.93—4.11(m, 2H), 5.04—5.40(m, 2H), and 5.65—6.15(m, 3H).

Reaction of Cobaloxime(I) with 2-(Allyloxy)ethyl Tosylates or 2-(Allyloxy)ethyl Halides. General Procedure: To a mixture of 0.238 g (1.0×10^{-3} mol) of cobalt(II) chloride hexahydrate and 0.233 g (2.0×10^{-3} mol) of dimethylglyoxime in 3 cm^3 of methanol was added 0.2 cm^3 of 10 mol dm^{-3}

aq sodium hydroxide (2.0×10^{-3} mol) and 0.1 cm^3 (1.2×10^{-3} mol) of pyridine. The mixture was stirred under nitrogen for 15 min at 0 °C and treated with 0.1 cm^3 (1.0×10^{-3} mol) of 10 mol dm^{-3} aq sodium hydroxide and 0.046 g (1.25×10^{-3} mol) of sodium borohydride. After stirring for 5 min the resulting methanol solution of cobaloxime (I)[25] (1.0×10^{-3} mol) was treated with one of the 2-(allyloxy)-ethyl tosylates or halides (1.0×10^{-3} mol) and the reaction mixture was stirred under nitrogen for 4—6 h at room temperature. The mixture was extracted with benzene (10 $cm^3\times4$) after addition of 40 cm^3 of water and the extract was washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The residue was placed on Florisil column and elution with chloroform–ethyl acetate (1:1) gave orange eluate. Evaporation of the solvent gave organo-cobaloximes in the yields listed in Table 1. All the organo-cobaloximes have strong absorptions at *ca.* 1600, 1500—1560, *ca.* 1235, 1100—880 cm^{-1} (several bands) and the absorptions due to the alkyl ligands are weak. IR data therefore are omitted from the spectral data in the following description of this section.

4a, Mp 175 °C(decomp); Found: C, 47.17; H, 6.10; N, 15.55%. Calcd for $C_{18}H_{28}N_5O_5Co$: C, 47.68; H, 6.23; N, 15.45%. NMR($CDCl_3$): δ 1.58 (t, 2H, J=8 Hz), 2.07(s, 12H), 3.10(t, 2H, J=8 Hz), 3.74—3.86(m, 2H), 4.90—5.22(m, 2H), 5.58—6.00(m, 1H), 7.10—7.27(m, 2H), 7.49—7.70(m, 1H), and 8.40—8.50(m, 2H).

5a, Mp 185 °C(decomp); Found: C, 47.36; H, 6.23; N, 15.52%. Calcd for $C_{18}H_{28}N_5O_5Co$: C, 47.68; H, 6.23; N, 15.45%. NMR($CDCl_3$): δ 1.20—2.00(m, 5H), 2.11(s, 12H), 2.90—3.10(m, 1H), 3.46—3.73(m, 3H), 7.15—7.31(m, 2H), 7.54—7.73(m, 1H), and 8.42—8.53(m, 2H).

5b, Mp 175 °C(decomp); Found: C, 54.18; H, 6.07; N, 13.59%. Calcd for $C_{24}H_{32}N_5O_5Co$: C, 54.44; H, 6.09; N, 13.23%. NMR($CDCl_3$): δ 1.55—2.20(m, 5H), 2.01(s, 6H), 2.08(s, 6H), 3.18—3.36(m, 1H), 3.95—4.13(m, 1H), 4.86(t, 1H, J=7 Hz), 7.18—7.40(m, 7H), 7.60—7.80(m, 1H), and 8.43—8.60(m, 2H).

5c, Mp 205 °C(decomp); Found: C, 59.14; H, 6.02; N, 11.63%. Calcd for $C_{30}H_{36}N_5O_5Co$: C, 59.50; H, 5.99; N, 11.56%. NMR($CDCl_3$): δ 1.40—1.72(m, 3H), 1.90—2.12(m, 1H), 1.93(s, 6H), 2.00(s, 6H), 2.77(dd, 1H, J=6 and 11 Hz), 3.40(t, 1H, J=7 Hz), 3.97(t, 1H, J=7 Hz), 7.00—7.37(m, 12H), 7.47—7.66(m, 1H), and 8.39—8.51(m, 2H).

Organo-cobaloxime **7** decomposed quickly on Florisil to give 1,1-diphenylethylene and could not be isolated in pure form. This is a common property for 2-alkoxy-2,2-diphenylethylcobaloxime. The NMR data of **7** were read from those of the mixture of **7** and **8**. **7**, NMR($CDCl_3$): δ 1.75 (s, 3H), 1.85(s, 12H), 2.61(s, 2H), 3.50(s, 2H), 4.95(br. s, 1H), 5.32(br. s, 1H), 7.00—7.56(m, 12H), 7.60—7.88 (m, 1H), and 8.55—8.70(m, 2H).

8, Mp 180 °C(decomp); Found: C, 59.94; H, 6.16; N, 11.33%. Calcd for $C_{31}H_{38}N_5O_5Co$: C, 60.09; H, 6.18; N, 11.30%. NMR($CDCl_3$): δ 0.82(s, 3H), 1.75(s, 2H), 2.07(s, 12H), 2.47(s, 2H), 3.50(d, 1H, J=8 Hz), 3.58(d, 1H, J=8 Hz), 7.10—7.56(m, 12H), 7.63—7.85(m, 1H), and 8.58—8.70(m, 2H).

5d, Mp 175 °C(decomp); Found: C, 52.02; H, 6.91; N, 13.84%. Calcd for $C_{22}H_{34}N_5O_5Co$: C, 52.07; H, 6.75; N, 13.80%. NMR($CDCl_3$): δ 1.14—1.95(m, 12H), 2.15(s, 12H), 3.04—3.32(m, 1H), 3.70—4.15(m, 2H), 7.35—7.52 (m, 2H), 7.75—7.96(m, 1H), and 8.66—8.78 (m, 2H).

General Procedure of the Photolyses of Organo-cobaloximes under Anaerobic Conditions. *Photolyses in Chloroform*: An appropriate amount of an organo-cobaloxime (0.1—2.0 g) was dissolved in chloroform (20—100 cm^3) and the dissolved oxygen was purged by bubbling nitrogen from a syringe needle. The solution was irradiated with two circle-type fluorescent lamps (30 W×2) until the starting organo-cobaloxime disappeared (5—12 h). The concentrate of the reaction mixture was subjected to a Florisil chromatography and a 3-methyltetrahydrofuran derivative was isolated from colorless chloroform eluate in a high yield (see text). In the case of 9-methyl-7-oxabicyclo[4.3.0]nonane (**11**), Kugel-Rohr distillation (100—200 °C/13322 Pa) yielded **11**, which consists of two isomers with different configurations of the methyl group, in a poor yield (8%) due to the volatility.

11, Oil. NMR(CCl_4): δ 0.93 and 1.00(d, total 3H, J=7 Hz), 1.13—2.12(m, 10H), 3.13—3.49(m, 1H), and 3.70—4.26(m, 2H). One component of **11** was identified with the hydrogenation product of **10**.

12,[26] Oil. NMR(CCl_4): δ 1.05(d, 3H, J=7 Hz), 1.89 (t, 2H, J=7 Hz), 2.16—2.50(m, 1H), 3.32(t, 1H, J=8 Hz), 4.05(t, 1H, J=8 Hz), 4.86(t, 1H, J=7 Hz), and 7.15 (s, 5H). **12** was hydrogenolyzed over Pd–C in ethanol and the product was identified by comparison with the authentic sample of 2-methyl-4-phenyl-1-butanol.[12]

15, Mp 49 °C; Found: C, 85.65; H, 7.68%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%. IR(CCl_4): 1025 and 695 cm^{-1}; NMR(CCl_4): δ 1.00(d, 3H, J=6 Hz), 2.00(t, 1H, J=11 Hz), 2.10—2.53(m, 1H), 2.75(dd, 1H, J=6 and 11 Hz), 4.04(t, 1H, J=8 Hz), 4.42(t, 1H, J=8 Hz), and 6.85—7.40(m, 10H).

16, Mp 44.5 °C; Found: C, 85.78; H, 8.07%. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%. IR(CCl_4): 1062 and 703 cm^{-1}; NMR(CCl_4): δ 1.00(s, 6H), 2.44(s, 2H), 3.55(s, 2H), and 6.96—7.42(m, 10H).

Photolyses in Benzene: An appropriate amount of an organo-cobaloxime (30—50 mg) in benzene (20 cm^3) was irradiated in the same manner as in the case of the photolyses in chloroform. The same work-up gave the products **10**, **13**, and **17** from **5d**, **5b**, and **5c**, respectively.

10, Oil. IR(CCl_4): 1670, 1050, 1030, and 885 cm^{-1}; NMR(CCl_4): δ 1.10—2.00(m, 8H), 2.26—2.60(m, 1H), 3.83—4.01(m, 1H), 4.25(d, 1H, J=14 Hz), 4.45(d, 1H, J=14 Hz), and 4.83—5.01(m, 2H). **10** was oxidized by chromic trioxide in dichloromethane containing pyridine to give *cis*-9-methylene-7-oxabicyclo[4.3.0]nonan-8-one (**18**).[13]

13, Oil. MS: (*m/e*) 160(M^+); IR(CCl_4): 1054, 883, and 695 cm^{-1}; NMR(CCl_4): δ 2.24(dd, 1H, J=7 and 16 Hz), 2.85(dd, 1H, J=6 and 16 Hz), 4.23(d, 1H, J=13 Hz), 4.42(d, 1H, J=13 Hz), 4.71—5.00(m, 3H), and 7.23 (m, 5H). Hydrogenolysis of **13** over Pd–C in ethanol gave 2-methyl-4-phenyl-1-butanol which was identified by comparison with the authentic sample.[12]

17, Mp 51—51.5 °C; Found: C, 86.21; H, 6.80%. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83%. MS: (*m/e*) 236(M^+); IR(CCl_4): 1670, 1046, 883, and 698 cm^{-1}; NMR(CCl_4): δ 3.10—3.20(m, 2H), 4.27—4.36(m, 2H), 4.72—4.80(m, 1H), 4.85—4.96(m, 1H), and 7.00—7.40(m, 10H).

*Photolysis of Organo-cobaloxime **5a** under Aerobic Conditions.* A solution of 4.70 g (1.0×10^{-2} mol) of **5a** in 600 cm^3 of dichloromethane was irradiated for 7 h in the same manner for the photolysis under anaerobic conditions, but the solution was bubbled with air during the irradiation. The concentrate of the reaction mixture was chromatographed on Florisil. The first orange band (chloroform–ethyl acetate, 1:1) contained the starting organo-cobaloxime (70%) and the second brown band (chloroform–ethyl acetate–methanol, 2:2:1) yielded the oxygenated product, (tetrahydro-3-furanyl)methyl cobaloximato peroxide, in 20% yield; NMR ($CDCl_3$): δ 1.20—2.20(m, 3H), 2.30(s, 12H), 3.20—3.50

(m, 3H), 3.53—3.79(m, 3H), 7.14—7.30(m, 2H), 7.59—7.78(m, 1H), and 8.31—8.42(m, 2H). The peroxide (0.960 g, 2.0×10^{-3} mol) in 40 cm^3 of methanol was reduced by sodium borohydride (92 mg, 2.5×10^{-3} mol) in the presence of 0.3 cm^3 of 10 mol dm^{-3} aq sodium hydroxide. After the mixture was stirred overnight, the methanol was evaporated and the residue was extracted with ether (10 $cm^3\times4$). The combined extracts were passed through a short column of silica gel. Kugel-Rohr distillation of the eluate with dichloromethane gave 106 mg (52%) of (tetrahydro-3-furanyl)-methanol (**14**), bp 120—140 °C (bath temperature)/2666 Pa. NMR(CCl_4): δ 1.38—1.74(m, 1H), 1.75—2.16(m, 1H), 2.20—2.51(m, 1H), 2.77(br. s, 1H), and 3.30—3.95(m, 6H). 3,5-Dinitrobenzoate of **14**, mp 80.5—81.0 °C.[11]

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