Bromination and Mercuration of Bis-dimethlglyoximato(1-octenyl)-pyridinecobalt(III), 1-Octenyl Cobaloxime

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cis-1-Octenyl(pyridine)cobaloxime (I) and *trans*-1-octenyl(pyridine)cobaloxime (II) were prepared by the reaction of cobaloxime anion with *cis*- and *trans*-1-halooctene, respectively. Bromination of I and II in polar solvents gave preferentially *trans*-1-bromooctene. Bromination of I in carbon disulfide also gave preferentially *trans*-1-bromooctene, but bromination of II gave more *cis*-1-bromooctene. Mercuration of I and II with mercuric acetate in DMF gave preferentially 1-octenylmercury(II) compound with retention of configuration, but the mercuration in acetic acid gave *ca.* 1 : 2 mixture of *cis* and *trans*-1-octenylmercury(II) compound. Two mechanisms are proposed for these electrophilic displacement reactions; one involves the addition of electrophile as a first step, followed by the elimination of cobaloxime moiety, and the other involves the addition of bromonium or mercury(II) ion, followed by the elimination of cobaloxime moiety.

In recent years much attention has been paid to the electrophilic displacement of alkyl metal-complexes,[1] especially bis-dimethylglyoximato(alkyl)pyridinecobalt-(III).[2-5] Kinetic studies[6,7] and the stereochemical consequences of these reactions suggest that the nature of these reactions is a concerted S_E2 reaction with inversion of the configuration at the reaction center. Little is known about the electrophilic displacement of alkenyl cobalt-complex. Johnson and Meeks[8] recorded in a preliminary report that the halogenation of bis-dimethylglyoximato(styryl)pyridinecobalt(III) in acetic acid proceeded with retention of configuration to give β-halostyrene.

In this paper we wish to report the steric course of the electrophilic displacement, bromination, and mercuration of bis-dimethylglyoximato(*cis*-1-octenyl)pyridinecobalt(III) (I) and bis-dimethylglyoximato(*trans*-1-octenyl)pyridinecobalt(III) (II), for which the conventional name octenyl(pyridine)cobaloxime is used hereafter, and to discuss the reaction mechanism.

Experimental

Preparation of cis *and* trans-*1-Octenyl(pyridine)cobaloxime (I and II).* To the stirred mixture of *cis*-1-bromooctene (382 mg, 2 mmol) and dimeric pyridinecobaloxime,[9] $(Co(dmgH)_2py)_2$ (368 mg, 0.5 mmol) in 20 ml of ethanol containing sodium hydroxide (0.01 mol/l) was added under nitrogen 1.3 g of zinc powder in portions over the period of 3 days. The reaction mixture was filtered and the filtrate was condensed under reduced pressure. The condensate was passed through a column of Florisil (10 g) with dichloromethane to remove impurities. Evaporation of the solvent from the eluate gave essentially pure *cis*-1-octenyl(pyridine)-cobaloxime (I) in 35% yield. Recrystallization of I from acetonitrile gave pure cobaloxime.

The same procedure starting with *trans*-1-chlorooctene gave *trans*-1-octenyl(pyridine)cobaloxime (II) in the yield of 33%. I, mp 149—151 °C. Found: C, 52.47; H, 7.31; N, 14.87%. Calcd for $C_{21}H_{34}N_5O_4Co$: C, 52.61; H, 7.15; N, 14.61%. IR (KBr): 2940, 2855, 1598, 1439, 1230, 1080, and 725 cm^{-1}. NMR($CDCl_3$):[10] 8.75 (d, J=6.5, 2H), 7.80 (t, J=6.5, 1H), 7.40 (t, J=6.5, 2H), 5.80 (d, J=7, 1H), 4.96 (q, J=7, 1H), 2.08 (s, 12H), 1.0—1.4 (m, 10H), and 0.88 ppm (δ) (t, J=6, 3H).

II, mp 171—173 °C. Found: C, 52.32; H, 7.35; N, 14.90%. Calcd for $C_{21}H_{34}N_5O_4Co$: C, 52.61, H, 7.15; N, 14.61%. IR(KBr): 2940, 2860, 1600, 1560, 1442, 1225, 1082, and 945 cm^{-1}. NMR($CDCl_3$): 8.74 (d, J=6.5, 2H), 7.81 (t, J=6.6, 1H), 7.40 (t, J=6.6, 2H), 5.71 (d, J=14, 1H), 5.08 (quintet, J=14 and 7, 1H), 2.08 (s, 12H), 1.0—1.4 (m, 10H), and 0.82 ppm (δ) (t, J=6.5, 3H).

Bromination of 1-Octenyl(pyridine)cobaloximes (I and II). The solution of I or II (120 mg, 0.25 mmol) in one of the solvents (10 ml) was treated with one equivalent of bromine or NBS dissolved in 10 ml of the same solvent, and the mixture was stirred for 30 min at ambient temperature. After evaporation of most of the solvent, the products were dissolved in hexane. When DMF was used as the solvent, the reaction mixture was added to water and extracted with hexane. Passing of the hexane solution through the column of alumina (Merck activity II-III, 500 mg) gave the eluate containing 1-bromooctene. This eluate was subjected to GLC analysis (N_2, 5% Carbowax 20 M on Chromosorb W, 90 °C) for the determination of the product composition. Evaporation of the solvent of the eluate gave 1-bromooctenes in the yields listed in the tables. Assignment of the bromides to *cis* and *trans*-1-bromooctene was made by the comparison of GLC, IR, and NMR spectra of the products with those of the authentic samples. The reaction in carbon disulfide at a controlled temperature was carried out using a cooling bath (−50 °C) or by boiling the reaction mixture (46 °C). The effect of bromide ion on the product composition was determined by using a mixture of DMF and water (9 : 1) containing a certain amount of tetraethylammonium bromide.

Mercuration of 1-Octenyl(pyridine)cobaloximes (I and II). The solution of I or II (120 mg, 0.25 mmol) in DMF or acetic acid (5 ml) was treated with 1.2 equivalents of mercuric acetate and the mixture was stirred for 30 min at ambient temperature. The mixture was further stirred for 10 min after addition of 4 ml of saturated aqueous solution of sodium chloride and extracted with dichloromethane after further addition of water (20 ml). The extract was washed with water and then condensed at reduced pressure to remove any residual DMF. The crude product thus obtained was passed through a column of Florisil (1.2×15 cm) using dichloromethane, and evaporation of the solvent gave 1-octenylmercury(II) chloride (IVa and IVb) in the yields listed in Table 3. The product composition was determined by the relative intensities of the NMR signals of olefinic hydrogen of this product mixture in $CDCl_3$. Recrystallization of the product from hexane gave pure *cis* and *trans*-1-octenylmercury(II) chloride (IVa and IVb). The structures of IVa and IVb were deduced by transforming these organomercury(II) compounds into *cis* and *trans*-1-bromooctene with bromine in pyridine.

IVa, low melting solid. IR(KBr): 3005, 1598, 1460,

965, 950, and 690 cm^{-1}. NMR($CDCl_3$): 6.74 (double t, J=10 and 7, 1H), 6.03 (d, J=10, 1H), 2.28 (m, 2H), 1.2—1.6 (8H), and 0.91 ppm (δ) (t, J=6.5, 3H). IVb, mp 103—104 °C.[11] IR(KBr): 3005, 1600, 1462, 969, 952, and 717 cm^{-1}. NMR($CDCl_3$): 5.81 (m, 2H), 2.20 (m, 2H), 1.1—1.6 (8H), and 0.90 ppm (δ) (t, J=6.5, 3H).

Results and Discussion

cis-1-Octenyl(pyridine)cobaloxime and *trans*-1-octenyl(pyridine)cobaloxime (I and II) were prepared by the action of the cobaloxime anion on *cis*-1-bromooctene and *trans*-1-chlorooctene, respectively (Eqs. 1 and 2). The cobaloxime anion was usually prepared *in situ* from dimethylglyoxime, pyridine, cobalt(II) chloride, and sodium tetrahydroborate in methanol, but the yield (*ca.* 15%) of 1-octenyl(pyridine)cobaloxime was moderate by this method. We prepared the cobaloxime anion conveniently by the reduction of dimeric pyridinecobaloxime $(Co(dmgH)_2py)_2$[9] with zinc powder in ethanol containing sodium hydroxide (0.01 mol/l). The yields of 1-octenyl(pyridine)cobaloximes were always over 30%, though we did not maximize the yields.

The stereochemistry of 1-octenyl(pyridine)cobaloximes (I and II) can be easily assigned by examination of the coupling constants of the olefinic hydrogens, J=7 Hz for I and 14 Hz for II. The stereochemistry of 1-octenyl(pyridine)cobaloxime is the same as that of the starting halooctenes; this is in sharp contrast to the inversion of the configuration at the reaction center when the displacement of alkyl halide is carried out

$$n\text{-}C_6H_{13}\!\!\diagdown\!\!=\!\!\diagup\!\!X + [Co(dmgH)_2py]_2 \xrightarrow[NaOH/EtOH]{Zn} \underset{(I)}{n\text{-}C_6H_{13}\!\!\diagdown\!\!=\!\!\diagup\!\!Co(dmgH)_2py} \quad (1)$$

$$n\text{-}C_6H_{13}\!\!\diagdown\!\!=\!\!\diagdown\!\!X + [Co(dmgH)_2py]_2 \xrightarrow[NaOH/EtOH]{Zn} \underset{(II)}{n\text{-}C_6H_{13}\!\!\diagdown\!\!=\!\!\diagdown\!\!Co(dmgH)_2py} \quad (2)$$

with cobaloxime anion.[1] These facts suggest that the formation of alkenyl cobaloxime results from the addition of cobaloxime anion to 1-haloalkene and the elimination of halide anion. This process usually proceeds with retention of configuration,[12,13] whereas the reaction of alkyl halide with cobaloxime anion takes S_N2 process with inversion of configuration.[14]

The reaction of bromine with *cis*- and *trans*-1-octenyl(pyridine)cobaloxime (I and II) was carried out in polar solvents such as acetic acid, pyridine, DMF, and methanol; the bromine was consumed smoothly at ambient temperature (*ca.* 20 °C). The reaction gave only *cis* and *trans*-1-bromooctene (IIIa and IIIb); the results are shown in Table 1. The yields listed in the table were obtained from the isolated bromides; the yields analyzed by GLC gave much better figures. The relative ratio of the two isomeric bromides of the isolated products was essentially the same as the ratio of the crude products, and we did not maximize the isolated yields. The results summarized in Table 1 show that the bromination of *cis*-cobaloxime I in polar solvents proceeds almost completely with inversion of the configuration, whereas *trans*-cobaloxime II takes a different steric course, retention.

$$\left.\begin{array}{l} n\text{-}C_6H_{13}\!\!\diagdown\!\!=\!\!\diagup\!\!Co(dmgH)_2py \\ \quad (I) \\ n\text{-}C_6H_{13}\!\!\diagdown\!\!=\!\!\diagdown\!\!Co(dmgH)_2py \\ \quad (II) \end{array}\right\} \xrightarrow{Br_2} \left.\begin{array}{l} n\text{-}C_6H_{13}\!\!\diagdown\!\!=\!\!\diagup\!\!Br \\ \quad (IIIa) \\ + \\ n\text{-}C_6H_{13}\!\!\diagdown\!\!=\!\!\diagdown\!\!Br \\ \quad (IIIb) \end{array}\right. \quad (3)$$

The bromination of *cis* and *trans*-1-octenyl(pyridine)-cobaloxime (I and II) in carbon disulfide gave the results shown in Table 2. *cis*-Cobaloxime I gave preferentially *trans*-1-bromooctene (IIIb) with inversion, and *trans*-1-octenyl(pyridine)cobaloxime (II) gave more *cis*-1-bromooctene IIIa again with predominant inversion. The temperature effect on the product composition is opposite for I and II; a lowering of temperature induces more retention with I and more inversion with II. The stereoselectivity of the reaction in carbon disulfide is worse than in polar solvents, even at the lower temperatures. The low stereoselectivity in the bromination of 1-octenyl(pyridine)cobaloximes in carbon disulfide suggests the possibility of the intrusion of a radical mechanism. Bromination of the cobaloximes in the presence of 2,4,6-tri-*t*-butylphenol (2 equivalents), however, changed the isomeric ratio of the products by less than 5%. In the case of *trans*-cobaloxime II, addition of 2,4,6-tri-*t*-butylphenol gave products with more *cis*-bromide IIIa (64%) than its *trans*-isomer IIIb (36%). The preferential formation of thermo-

Table 1. Stereochemical compositions of 1-bromooctene

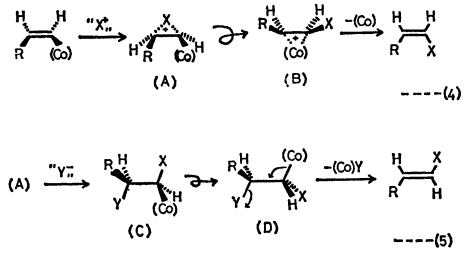
Starting material	Solvent	Yield[a] (%)	IIIa[b] (%)	IIIb[b] (%)
I	Methanol	67	2	98
	Pyridine	73	5	95
	Acetic acid	67	8	92
II	Methanol	68	10	90
	DMF	58	8	92

a) Isolated yield; some part of the products was lost on evaporation of the solvents. b) Calculated from the ratio of the peak area in GLC analysis.

Table 2. Dependence of the stereoselectivity of bromination in CS_2 on reaction temperature

Starting material	Reaction temperature	Yield[a] (%)	IIIa[b] (%)	IIIb[b] (%)
I	46 °C	80	11	89
	20 °C	72	13	87
	−50 °C	80	17	83
	20 °C[c]		14	86
II	46 °C	80	56	44
	20 °C	67	59	41
	−50 °C	65	72	28
	20 °C[c]		64	36

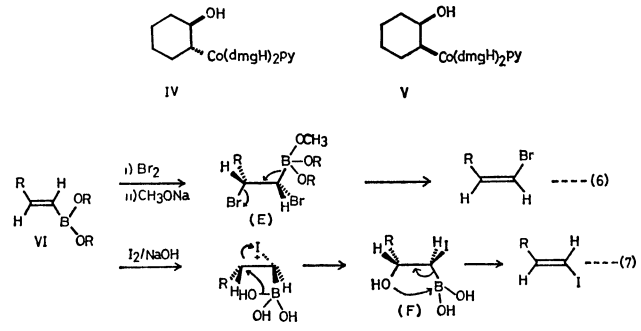
a) Isolated yield; some part of the products was lost on evaporation of the solvent. b) Calculated from the ratio of the peak area in GLC analysis. c) Carried out in the presence of 2 equivalents of 2,4,6-tri-*t*-butylphenol.

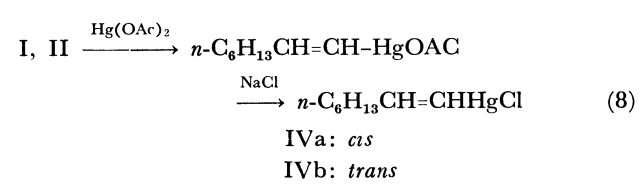


dynamically unstable *cis*-bromide IIIa from *trans*-cobaloxime II and the slight effect on the product composition from the radical inhibitor, 2,4,6-tri-*t*-butylphenol, exclude the possibility that the bromination of I and IIb is a radical process. The minor temperature effect on the product composition can be understood by considering a slight thermal isomerization of IIIa to IIIb under reaction conditions. Vinyl-type organocobaloxime is more stable than the corresponding alkyl cobaloxime; inparticular the former resists photodecomposition and photo-oxygenation under the conditions in which the latter decomposes with extreme easiness, giving alkyl radical as an intermediate. This feature is one of the reasons for eliminating a radical process for the bromination of cobaloxime I and II. A concerted S_E2 reaction also does not seem reasonable since the S_E2 reaction of alkyl cobaloxime has been settled to proceed with inversion of configuration due to the steric hindrance of the front side by dimethylglyoximato-ligand.[1] Bromination in the present study, nevertheless, proceeds with preferential retention under some conditions. These discussions imply a π-participated mechanism, as is generally believed to be responsible for the halogenation of vinyl-type organometallic compounds vinyl borane,[15] vinyl silicone,[16] and vinyl mercury(II) compound.[17] We prefer, therefore, the π-participated mechanisms depicted in Eq. 4 for the bromination with retention and in Eq. 5 for the bromination with inversion. There is large steric repulsion between the alkyl group and dimethylglyoximato-ligand in the intermediate (A) and also between alkyl and bromide in the intermediate (B). The bromination of *cis*-1-octenyl(pyridine)cobaloxime (I) *via* the route depicted in Eq. 4 must be disadvantageous for this reason. In the case of *trans*-1-octenyl(pyridine)-cobaloxime (II), the lack of severe steric repulsion in the intermediates of the types of (A) and (B) drives the reaction, as in Eq. 4, almost completely in non-polar solvents and appreciably in carbon disulfide. The reaction of *trans*-cobaloxime II in carbon disulfide, however, proceeds still preferentially with inversion, especially at the lower temperature. This means that the bridged carbonium ions (A) and (B) from *trans*-cobaloxime II are not sufficiently stabilized in polar solvents and an addition-elimination mechanism (Eq. 5) is still the favorable one. This concept is supported by the effect of temperature on the product composition—the lowering of temperature induces more inversion. In the latter mechanism (Eq. 5), we preclude the *cis*-elimination of halo-cobaloxime (CoY) from the intermediate (C) by the following reasons. Organo-(pyridine)cobaloxime has a central cobalt(III) ion whose coordination number is saturated by six ligand sites to take the nominal electronic structure of an inert gas. In support of this concept, notice that *trans*-2-hydroxycyclohexyl(pyridine)cobaloxime (IV) enters the elimination reaction with extreme easiness, giving cyclohexene, whereas its *cis* isomer V does not eliminate the cobaloxime residue easily.[1] These features are nicely illustrated by the halogen displacement of vinyl boronate (VI), in which *trans*-elimination takes place from the intermediate (E) in the presence of sodium methoxide (Eq. 6)[18] and *cis*-elimination takes place from the intermediate (F) in the presence of a weaker base (Eq. 7).[19] In these examples the intermediate (E) has the boron with saturated coordination number, whereas the intermediate (F) has the boron with unsaturated coordination number.

Next we examined the effect of the anion on the steric course of the reaction. Succinimide anion is considered to be a poor nucleophile, as exemplified in the oxybromination of olefin by *N*-bromosuccinimide in water or alcohol.[20] The use of *N*-bromosuccinimide as a bromonium ion source forces the reaction to take the route shown in Eq. 4, and the reaction proceeded more stereospecifically with retention of configuration, I : 72% retention and II : 71% retention in carbon disulfide. It is of special interest that the stereoselectivity was reversed, more retention, when *N*-bromosuccinimide was used. On the same ground, the existence of more bromide ions in the reaction system may induce more inversion as a result of the enhanced probability of giving the intermediate (C). Actually addition of tetraethylammonium bromide upon bromination of II with bromine in DMF caused more inversion—IIIa(*cis*)/IIIb(*trans*)=8/92, 14/86, and 29/71 when 0, 1.9, and 7.7 equivalents, respectively, of tetraethylammonium bromide was added.

The reaction of *cis*- and *trans*-1-octenyl(pyridine)-cobaloxime (I and II) with mercuric acetate followed by the treatment with sodium chloride was less stereospecific and gave *cis* and *trans*-1-octenylmercury(II) chloride (Eq. 8), as summarized in Table 3.





I, II $\xrightarrow{Hg(OAc)_2}$ n-C_6H_{13}CH=CH-HgOAC $\xrightarrow{NaCl}$ n-C_6H_{13}CH=CHHgCl (8)

IVa: *cis*

IVb: *trans*

1-Octenylmercury(II) chloride thus formed was identified by transformation of these mercury-compounds

TABLE 3. ISOMERIC COMPOSITION OF 1-OCTENYLMERCURY(II) CHLORIDE FROM 1-OCTENYL(PYRIDINE)COBALOXIME

Starting material	Solvent	Yield[a] (%)	IVa[b] (%)	IVb[b] (%)
I	DMF	80	74	24
	Acetic acid	93	35	65
II	DMF	50	37	63
	Acetic acid	70	31	69

a) Isolated yield. b) Determined by the relative intensity of the NMR signals of olefinic hydrogen.

into *cis* and *trans*-1-bromooctene (IIIa and IIIb) by treatment with bromine in pyridine. In DMF, mercuration of I and II gave more products with retention. The low stereospecificity is not due to the isomerization of the starting *cis* and *trans*-cobaloxime (I and II), since mercuration of the cobaloxime with less than one equivalent of mercuric acetate recovered the starting cobaloxime in intact form. The reaction of *cis*-cobaloxime I in acetic acid, however, gave predominantly *trans*-1-octenylmercury(II) chloride (IVb). One of the possible courses is an addition-elimination mechanism due to the nucleophilic nature of acetic acid to give the intermediate of type (C) (Y=OAc) in Eq. 5, since the intermediate (A) and (B) are rather unstable due to the steric repulsion between alkyl and mercury (II) ion. A radical mechanism resulting from the initial electron transfer from the cobaloxime to mercury (II) ion (Eq. 9)[21] may be a mechanistic candidate, but the preferential formation of thermodynamically unstable *cis*-1-octenylmercury(II) chloride (IVa) from *cis* cobaloxime in DMF can be a justification for precluding the radical mechanism. Thus the mercuration of 1-octenyl(pyridine)cobaloxime (I and II) in polar solvents such as acetic acid and DMF can be considered to take both paths depicted in Eq. 4 and 5 competitively.

$$C_6H_{13}CH{=}CH\text{-}Co(dmgH)_2py + Hg^{2+} \longrightarrow [C_6H_{13}CH{=}CH\text{-}Co(dmgH)_2py]^+ + Hg^+ \xrightarrow{-Co(dmgH)_2py^+} C_6H_{13}CH{=}CH\cdot + Hg^+ \longrightarrow C_6H_{13}CH{=}CHHg^+ \quad (9)$$

In conclusion, the electrophilic substitution of 1-octenyl(pyridine)cobaloxime takes two competitive reaction paths—a stepwise mechanism involving bridged carbonium ions (Eq. 4) and a mechanism involving addition-elimination (Eq. 5). The relative importance of the two mechanisms depends on the stereochemistry of the starting 1-octenyl(pyridine)cobaloxime, the nature of the electrophilic reagent, and the solvent system of the reaction.

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