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Hydrophobic Vitamin B_{12}. IV. Addition Reactions of Alcohols to Olefins as Catalyzed by Hydrophobic Vitamin B_{12} Derivatives[†]

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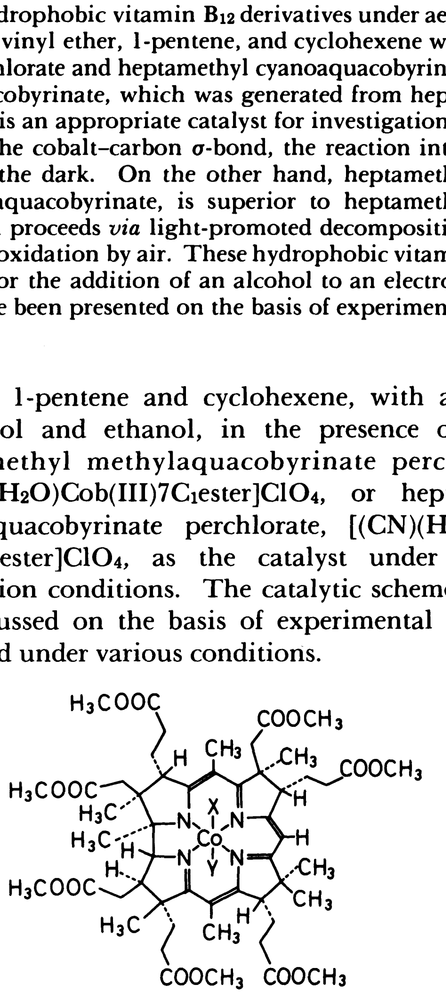
Addition reactions of alcohols to olefins were catalyzed by hydrophobic vitamin B_{12} derivatives under aerobic irradiation conditions at the room temperature range. Ethyl vinyl ether, 1-pentene, and cyclohexene were adopted as olefins, while heptamethyl methylaquacobyrinate perchlorate and heptamethyl cyanoaquacobyrinate perchlorate were used as the starting complexes. Heptamethyl cobyrinate, which was generated from heptamethyl methylaquacobyrinate perchlorate by aerobic photolysis, is an appropriate catalyst for investigation of the reaction mechanism because the alkylated complex having the cobalt-carbon σ-bond, the reaction intermediate, has a long lifetime sufficient for its identification in the dark. On the other hand, heptamethyl cyanocobyrinate, which was derived from heptamethyl cyanoaquacobyrinate, is superior to heptamethyl cobyrinate as the catalyst for the addition reaction. The reaction proceeds *via* light-promoted decomposition of the alkylated complex, and the catalyst is regenerated upon autoxidation by air. These hydrophobic vitamin B_{12} derivatives are particularly effective homogeneous catalysts for the addition of an alcohol to an electron-rich olefin. Plausible reaction schemes for the catalytic cycle have been presented on the basis of experimental findings.

Recently, reactions of olefins catalyzed by vitamin B_{12} and its model complexes have been studied rather extensively,[1)] but most of these studies deal with reduction of substrates as caused by the nucleophilic reactivity of the univalent cobalt species. On the other hand, the electrophilic reactivity of the tervalent cobalt species toward olefins has been scarcely examined. In this regard, Dolphin *et al.* reported that bromo(pyridine)cobaloxime and hydroxocobalamin undergo reaction with an electron-rich olefin such as ethyl vinyl ether in the presence of an alcohol to afford the corresponding alkylated complex, having the cobalt–carbon σ-bond, with the acetal moiety as the axial ligand under anaerobic conditions in the dark.[2)] Cobalamin and cobaloxime are not efficient catalysts for the reaction in the light of the following observations: (i) the reaction between the catalyst and ethyl vinyl ether proceeds extremely slowly; (ii) an electron-rich olefin such as ethyl vinyl ether undergoes reaction, while other ordinary olefins such as ethylene, 2-methyl-1-butene, 2-ethyl-1-butene, 3,3-dimethyl-1-butene, and ethyl acrylate are unreactive. In addition, cobalamin is soluble in water, methanol, and ethanol, which exercise large solvation effects, while apolar organic solvents can not be used as reaction media because of insolubility of the complex.

We have been dealing with hydrophobic vitamin B_{12} derivatives which have ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B_{12}.[3)] These modified cobalt complexes are readily soluble in a wide range of organic solvents and expected to be utilized as homogeneous catalysts in such media. In this regard, we have carried out in this work the reactions of an electron-rich olefin, ethyl vinyl ether, and ordinary olefins, 1-pentene and cyclohexene, with alcohols, methanol and ethanol, in the presence of either heptamethyl methylaquacobyrinate perchlorate, $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$, or heptamethyl cyanoaquacobyrinate perchlorate, $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$, as the catalyst under aerobic irradiation conditions. The catalytic schemes are to be discussed on the basis of experimental findings obtained under various conditions.



X=CN ,Y=CN : $(CN)_2Cob(III)7C_1ester$
X=CH$_3$,Y=H$_2$O : $[(CH_3)(H_2O)Cob(III)7C_1ester]^+$
X=CN ,Y=H$_2$O : $[(CN)(H_2O)Cob(III)7C_1ester]^+$
X=ROH,Y=ROH : $[(ROH)_2Cob(III)7C_1ester]^{2+}$
(R=alkyl and/or H)

Experimental

Materials. Cyanocobalamin was purchased from Nakarai Chemicals and used without further purification. Heptamethyl dicyanocobyrinate, $(CN)_2Cob(III)7C_1ester$, was derived from cyanocobalamin after the method of Werthemann *et al.*[4)] Preparation of heptamethyl cobyrinate perchlorate, $[Cob(II)7C_1ester]ClO_4$, has been described previously.[3a)] Ethyl vinyl ether, 1-pentene, cyclohexene, acrylonitrile, methanol, ethanol, and dichloromethane were purified and dried according to the standard procedures[5)] and confirmed to be sufficiently pure by GLC.

[†] Contribution No. 770 from this Department.

Heptamethyl Cyanoaquacobyrinate Perchlorate, [(CN)(H₂O)Cob(III)7C₁ester]ClO₄. $(CN)_2Cob(III)7C_1ester$ (50 mg, 4.6×10^{-5} mol) was dissolved in 40 mL of dichloromethane, and the resulting purple solution was treated with 25 mL of 30% aqueous perchloric acid at room temperature. The orange dichloromethane layer was separated from the acidic aqueous layer and washed with distilled water. After being dried over sodium sulfate, the orange layer was evaporated to dryness *in vacuo* at room temperature. The residue was reprecipitated from benzene upon addition of hexane to afford fine red crystals: yield 50 mg (92%); UV_{max} (C_6H_6) 325 (ε 1.79×10^4), 356 (2.75×10^4), 406 (0.79×10^4), 490 (1.15×10^4), and 520 nm (0.91×10^4); IR (KBr) 2150 ($C\equiv N$), 1730 (ester C=O), and 1100 and 620 cm^{-1} (ClO_4^-).

Found: C, 53.75; H, 6.40; N, 6.03. Calcd for $C_{53}H_{75}ClCoN_5O_{19}$: C, 53.92; H, 6.40; N, 5.93.

Heptamethyl Methylaquacobyrinate Perchlorate, [(CH₃)(H₂O)Cob(III)7C₁ester]ClO₄. $[Cob(II)7C_1ester]ClO_4$ (50 mg, 4.4×10^{-5} mol) was mixed with 600 mg of zinc powder dispersed in 30 mL of acetic acid, and the mixture was stirred for 10 min at room temperature under nitrogen atmosphere. All the following treatments were performed under subdued light. After the mixture turned dark green, it was stirred for 5 min upon addition of 1.0 g of methyl iodide. The residual zinc powder was removed by filtration, and 50 mL of 15%(w/w) aqueous sodium perchlorate was added to the filtrate. The reaction mixture was extracted with dichloromethane (50 mL×3), and the extract was washed with 5%(w/w) aqueous sodium hydrogencarbonate (50 mL) and distilled water (50 mL). After being dried over sodium sulfate, the yellow dichloromethane solution was evaporated to dryness *in vacuo* at room temperature. The residue was reprecipitated from benzene upon addition of hexane to afford brown powder: yield 43 mg (84%); UV_{max} (CH_2Cl_2) 264 (ε 2.14×10^4), 305 (2.36×10^4), 373 (0.85×10^4), and 457 nm (1.03×10^4); CD (CH_3OH) 260 ($\Delta\varepsilon$ −18.6), 323 (+13.7), 356 (−1.71), 378 (+1.38), 462 (−4.82), 508 (+2.87), and 550 nm (+1.69); IR (KBr) 1730 (ester C=O), and 1100 and 620 cm^{-1} (ClO_4^-); ^{1}H-NMR (CD_3OD, TMS) $\delta=-0.18$ (3H, s, CH_3-Co), 1.02, 1.14, 1.40, 1.45, 1.62, 1.80, 2.35, and 2.40 (24H, each s, CH_3), 3.65 (21H, m, CO_2CH_3), and 6.65 (1H, s, H at C-10).

Found: C, 54.49; H, 6.61; N, 4.96. Calcd for $C_{53}H_{78}ClCoN_4O_{19}$: C, 54.43; H, 6.72; N, 4.80.

Although both Coα- and Coβ-methyl isomers are generally expected to be formed, the methylated complex prepared by the present method is regarded as the Coβ-methyl isomer in the light of UV, CD, and ^{1}H-NMR data.[6]

Spectroscopic Measurements. Electronic absorption spectra were recorded on a Hitachi 340 or a Hitachi 220A spectrophotometer. ^{1}H-NMR spectra were taken on a Hitachi R-24B spectrometer. ESR spectra were obtained with a JEOL JES-ME-3 X-band spectrometer equipped with a 100-kHz field modulation unit; a standard MgO/Mn^{II} sample calibrated with a NMR magnetometer was employed for calibration of the magnetic field.

Kinetic Measurements. Pseudo-first-order rate constants for the alkylation of heptamethyl cobyrinate, $[(ROH)_2Cob(III)7C_1ester]^{2+}$ (R=H and/or CH_3), with ethyl vinyl ether and methanol in dichloromethane were determined spectrophotometrically. A mixture of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ (5.0×10^{-5} mol dm^{-3}), ethyl vinyl ether, methanol, and dichloromethane was placed in a spectrophotometric cell of 1-cm path length which was thermostated at 21.5±0.1 °C. The solution was irradiated with a conventional 500-W tungsten lamp from a distance of 20 cm for 1 min. $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ was converted completely into $[(ROH)_2Cob(III)7C_1ester]^{2+}$ upon aerobic irradiation. Then, the complex thus formed was subjected to alkylation in the dark. Under the present experimental conditions, clear isosbestic points were observed in the course of alkylation along with absorbance decay of the 335-nm band which is characteristic of the dicationic cobalt complex. All the kinetic runs provided linear correlations for plots of $\ln(OD_t-OD_\infty)$ *vs.* time, where OD_t and OD_∞ stand for optical densities at time t and after completion of the reaction, respectively.

Catalytic Reactions. $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ was dissolved in a solution composed of ethyl vinyl ether and ethanol, and the mixture was placed in a Pyrex ampule (ϕ 20 mm). The reaction mixture was stirred and irradiated with a conventional 500-W tungsten lamp from a distance of 10 cm at 20±1 °C. As for the reaction carried out in the dark, the ampule was covered with aluminum foil. After an appropriate time interval, the reaction mixture was distilled *in vacuo* at room temperature and analyzed by means of GLC on a Shimadzu GC-4C apparatus with helium as a carrier gas. Identification of the reaction products was performed by coinjection of the distilled fraction with authentic samples into columns of Polyethylene Glycol 600, Silicone DC-550, and Silicone SE-30. A turnover number for the catalyst was calculated after correction for the blank reaction, if any, in the absence of the catalyst.

Results and Discussion

Reactions with [(CH₃)(H₂O)Cob(III)7C₁ester]ClO₄. When $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ dissolved in a solution of ethyl vinyl ether and methanol was irradiated with the visible light for a short period of time under aerobic conditions, the complex was transformed into $[(ROH)_2Cob(III)7C_1ester]^{2+}$ which shows absorption maxima at 335, 490, and 510 nm (Fig. 1).[7] Then, the mixture was allowed to stand in the dark to afford an alkylated complex having the cobalt–carbon bond, which shows absorption maxima at 303 and 464 nm (Fig. 2); clear isosbestic points being observed along the progress of the reaction. When the starting complex was replaced with another alkylated complex such as $[(C_2H_5)(H_2O)Cob(III)7C_1ester]ClO_4$ or $[((CH_3O)_2CHCH_2)(H_2O)Cob(III)7C_1ester]ClO_4$, the spectral changes identical with those shown in Figs. 1 and 2 were observed. Irradiation of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ with the visible light in methanol without ethyl vinyl ether under aerobic conditions resulted in the formation of $[(ROH)_2Cob(III)7C_1ester]^{2+}$, which was then converted into $[Cob(II)7C_1ester]^+$ in the dark, showing absorption maxima at 317 and 470 nm (Fig. 3). On the other hand, the anaerobic photolysis of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ in a solution of ethyl vinyl ether and methanol gave [Cob(II)-7C$_1$ester]$^+$ as shown in Fig. 4, and the alkylated complex was not detected in a short period of time while the solution was allowed to stand further in the dark.

The ^{1}H-NMR spectra for [(CH$_3$)(H$_2$O)Cob(III)-7C$_1$ester]ClO$_4$ and the alkylated complex, which was obtained under the conditions described above, are shown in Fig. 5. The spectrum for the latter does not show the proton signal at $\delta=-0.18$ attributable to the cobalt-bound methyl group and is consistent with the structural formula, [((C$_2$H$_5$O)(CH$_3$O)CHCH$_2$)(H$_2$O)-Cob(III)7C$_1$ester]$^+$.

In the light of the above observations, [(CH$_3$)(H$_2$O)-Cob(III)7C$_1$ester]ClO$_4$ is apparently converted into [(ROH)$_2$Cob(III)7C$_1$ester]$^{2+}$ by the aerobic photolysis, and the latter complex undergoes alkylation with

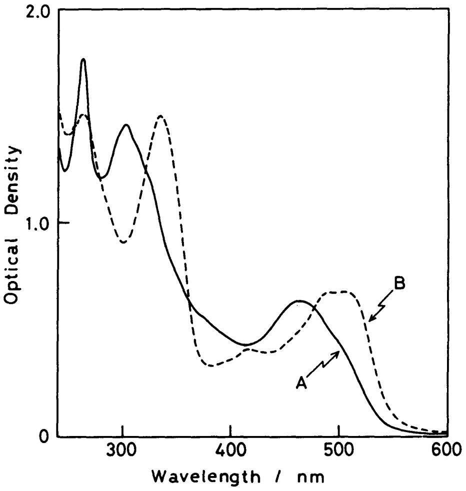


Fig. 1. Electronic spectra for the aerobic photolysis of [(CH$_3$)(H$_2$O)Cob(III)7C$_1$ester]ClO$_4$ in ethyl vinyl ether–methanol (1 : 1 v/v) at 21.5±0.1 °C: A, [(CH$_3$)-(H$_2$O)Cob(III)7C$_1$ester]ClO$_4$ (7.6×10^{-5} mol dm^{-3}) before photolysis; B, irradiation with a 500-W tungsten lamp from a distance of 30 cm for 5 min to afford [(ROH)$_2$Cob(III)7C$_1$ester]$^{2+}$.

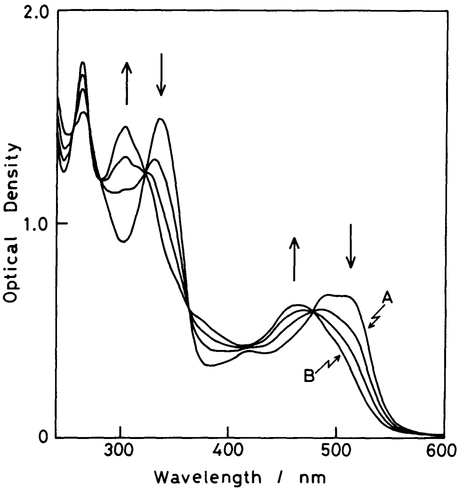


Fig. 2. Spectral change for formation of the cobalt–carbon bond derived from the aerobic photolysis product in the dark at 21.5±0.1 °C. Trends of spectral change with time are shown by arrows: A, the aerobic photolysis product, [(ROH)$_2$Cob(III)7C$_1$ester]$^{2+}$; B, the final product, [(C$_2$H$_5$O)(CH$_3$O)CHCH$_2$-Cob-(III)7C$_1$ester]$^+$. As for the amounts of reacting species, see Fig. 1.

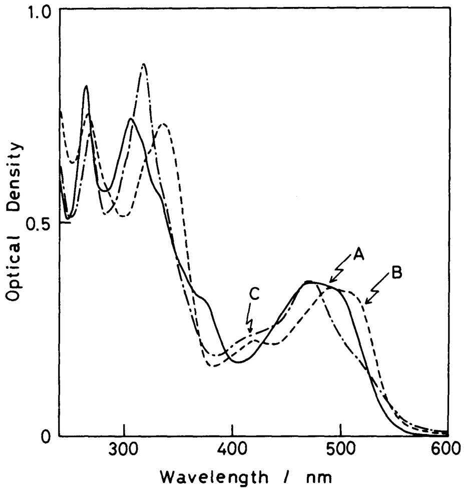


Fig. 3. Electronic spectra for the aerobic photolysis of [(CH$_3$)(H$_2$O)Cob(III)7C$_1$ester]ClO$_4$ in methanol at 21.5±0.1 °C: A, [(CH$_3$)(H$_2$O)Cob(III)7C$_1$ester]-ClO$_4$ (3.7×10^{-5} mol dm^{-3}) before photolysis; B, irradiated with a 500-W tungsten lamp from a distance of 30 cm for 5 min to afford [(ROH)$_2$Cob(III)7C$_1$-ester]$^{2+}$; C, on standing in the dark for 3 h after irradiation to afford [Cob(II)7C$_1$ester]$^+$.

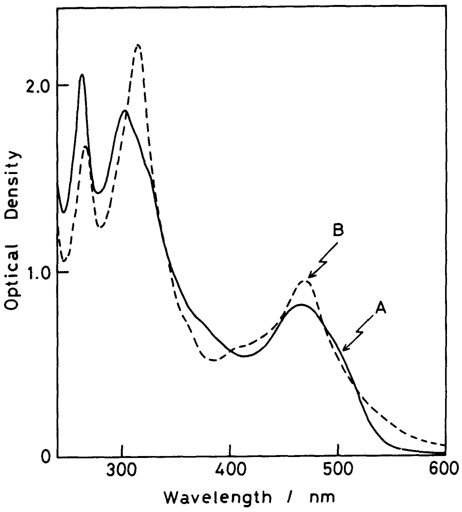


Fig. 4. Electronic spectra for the anaerobic photolysis of [(CH$_3$)(H$_2$O)Cob(III)7C$_1$ester]ClO$_4$ in ethyl vinyl ether–methanol (1 : 1 v/v) under argon atmosphere at 21.5±0.1 °C: A, [(CH$_3$)(H$_2$O)Cob(III)7C$_1$ester]-ClO$_4$ (8.66×10^{-5} mol dm^{-3}) before photolysis; B, irradiated with a 500-W tungsten lamp from a distance of 30 cm for 3 h to afford [Cob(II)7C$_1$ester]$^+$.

ethyl vinyl ether and methanol in the dark. Pseudo-first-order rate constants for the alkylation in various solutions were evaluated on the basis of spectral change typically shown in Fig. 2 and summarized in Table 1. The alkylation rate was found to increase as the concentration of ethyl vinyl ether was increased on one hand and to be reduced as the quantity of methanol was increased on the other. This result indicates that the reaction rate is controlled by the complex formation (*vide infra*) between ethyl vinyl ether and $[(ROH)_2Cob(III)7C_1ester]^{2+}$, which is enhanced as the solvent polarity is reduced: solvent polarity parmeters ($E_T(30)$) methanol, 55.5; dichloromethane, 41.1; ethyl vinyl ether, 35.1 kcal mol^{-1}.[8)]

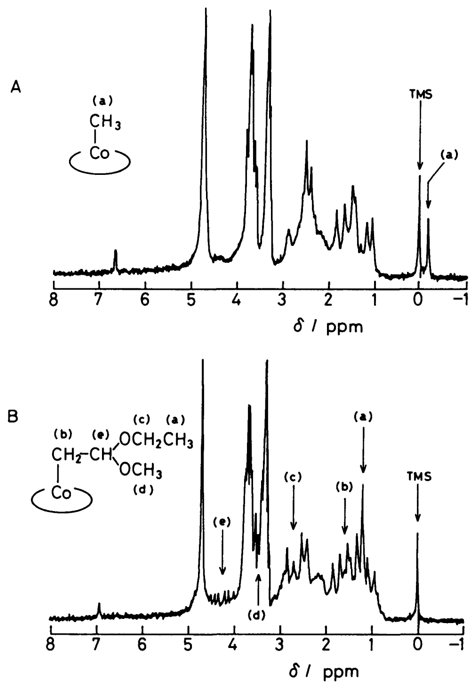


Fig. 5. ^1H-NMR (60 MHz) spectra of alkylated hydrophobic vitamin B_{12}'s in CD_3OD: A, $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$; B, $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ (20 mg) in ethyl vinyl ether–methanol (1 : 1 v/v, 10 mL) being irradiated with a 500-W tungsten lamp from a distance of 30 cm for 3 h, allowed to stand in the dark for 24 h, and evaporated to dryness *in vacuo*.

Table 1. Pseudo-first-order rate constants for alkylation of hydrophobic vitamin B_{12}[a)] at 21.5±0.1 °C under aerobic conditions in the dark

Entry	Medium (mL)			$k_{obsd}\times 10^5/s^{-1}$	k_{rel}[c)]
	CH_3OH	EVE[b)]	CH_2Cl_2		
1	0.75	0.50	1.75	3.41	1.00
2	0.75	0.60	1.65	5.49	1.61
3	0.75	0.70	1.55	7.17	2.10
4	0.75	0.75	1.50	7.85	2.30
5	0.75	0.80	1.45	9.10	2.67
6	0.75	0.90	1.35	12.6	3.70
7	0.75	1.00	1.25	15.5	4.55
8	0.50	0.75	1.75	9.08	2.66
9	1.00	0.75	1.25	2.88	0.84
10	1.50	1.50	0	9.35	2.74
11	1.00	2.00	0	17.1	5.01
12	0.75	2.25	0	24.9	7.30

a) $[(ROH)_2Cob(III)7C_1ester]^{2+}$ ($R=H$ and/or CH_3), 5.0×10^{-5} mol dm^{-3}. b) Ethyl vinyl ether. c) Relative rate; k_{obsd} for entry 1 as a reference.

Reactions with $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$. When $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ dissolved in a solution of ethyl vinyl ether and methanol was irradiated with the visible light under aerobic conditions and subsequently allowed to stand in the dark, the electronic spectrum did not undergo significant change; different from the spectral behavior of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ under comparable conditions. This does not mean, however, that the reaction does not take place. $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ shows no ESR signal in a solution of ethyl vinyl ether and methanol before irradiation (Fig. 6A), but characteristic signals due to the Co^{II} species[3a)] were detected upon irradiation with the visible light under anaerobic conditions (Fig. 6B).

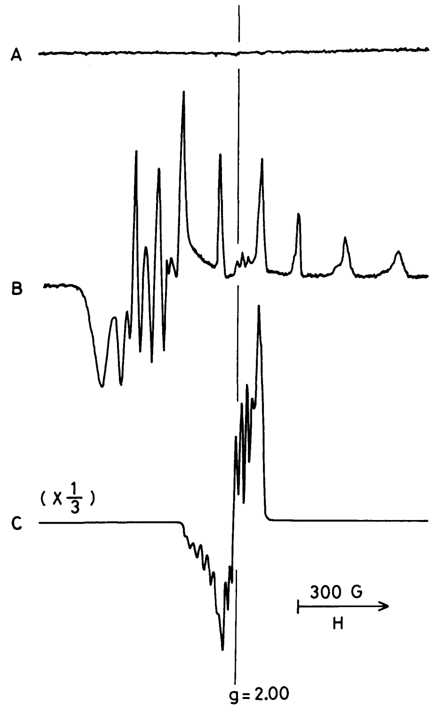


Fig. 6. ESR spectra for the following samples at 77 K: A, $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ (2.7×10^{-3} mol dm^{-3}) in ethyl vinyl ether–methanol (3 : 1 v/v) in the dark under anaerobic conditions; B, sample A being irradiated with a 300-W tungsten lamp from a distance of 20 cm for 2 h at room temperature under anaerobic conditions; C, sample B being exposed to the open air.

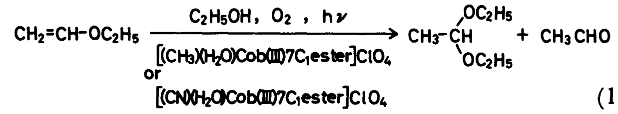
Since such an ESR spectral change caused by the irradiation was insignificant for the cyanoaqua complex dissolved in diethyl ether and methanol under anaerobic conditions, a photosensitive alkylated complex was undoubtedly produced by the reaction of the complex with ethyl vinyl ether and methanol. Immediately after the reaction system was exposed to the open air, the ESR signals characteristic of the Co^{II} species were replaced with the ones due to the superoxo complex $Co^{III}-O_2^{\cdot-}$, the unpaired spin density being largely localized at the coordinated $O_2^{\cdot-}$ group,[9] as shown in Fig. 6C. Since the superoxo complex was eventually converted into the original cyano complex[10] under irradiation conditions as confirmed by ESR and electronic spectroscopy, the Co^{II} species generated by the photolysis was readily oxidized to afford the Co^{III} species *via* formation of the superoxo complex under aerobic conditions.

The axial ligation constant (K) for $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ with ethyl vinyl ether in dichloromethane was evaluated according to the method described previously;[3a] $\log K = -2$. Even though the ligation constant was not evaluated because of its much smaller value in a polar medium used in the present reaction, such complex formation must take place so that the olefin is activated prior to the attack by methanol.

It is now clear that the alkylated complex is produced as the reaction intermediate in the course of the reaction with $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ as the starting catalyst in a manner as observed for the reaction with $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ (*vide supra*). In the light of the observation by electronic spectroscopy, the alkylated complex derived from $[(CN)(ROH)Cob(III)7C_1ester]ClO_4$ is decomposed by the trans effect provided by the axial cyano ligand much more readily than the one derived from $[(ROH)_2Cob(III)7C_1ester]^{2+}$.

When ethyl vinyl ether was used as an olefin, any oxygenation product was not detected by GLC. However, small amounts of cyclohexene oxide and 2-cyclohexen-1-ol (the total quantity, *ca.* 10 mole% of an amount of the alcohol adduct of cyclohexene produced) were obtained under the conditions described below by the reaction of cyclohexene with the superoxo complex. This result provides another evidence for the formation of the superoxo complex.

Catalytic Reactions and Turnover Behavior. The addition of an alcohol to ethyl vinyl ether took place by the catalysis of either $[(ROH)_2Cob(III)7C_1ester]^{2+}$ or $[(CN)(ROH)Cob(III)7C_1ester]^{+}$ under aerobic irradiation conditions. Acetaldehyde ethyl methyl acetal and acetaldehyde diethyl acetal were the major products when methanol and ethanol were used, respectively. When a mixture of ethyl vinyl ether (1.9 g, 2.6×10^{-2} mol), ethanol (0.39 g, 8.6×10^{-3} mol), and $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ (3.0 mg, 2.6×10^{-6} mol) was irradiated aerobically at 20±1 °C for 50 h with a 500-W tungsten lamp from a distance of 30 cm, acetaldehyde diethyl acetal was obtained in a yield, 10±2 times as much as the molar quantity of the hydrophobic vitamin B_{12} (refer to Eq. 1). In the course of the reaction, both alkylated and alkyl-free complexes, $[((C_2H_5O)_2CHCH_2)(ROH)Cob(III)7C_1ester]^{+}$ and $[(ROH)_2Cob(III)7C_1ester]^{2+}$, respectively, were observed by means of electronic spectroscopy.



$$CH_2{=}CH{-}OC_2H_5 \xrightarrow[\substack{[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4 \\ \text{or} \\ [(CN)(H_2O)Cob(III)7C_1ester]ClO_4}]{C_2H_5OH,\ O_2,\ h\nu} CH_3{-}CH(OC_2H_5)_2 + CH_3CHO \qquad (1)$$

In the case that $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ was used in place of the methylaqua complex otherwise under the same conditions, acetaldehyde diethyl acetal was obtained in a yield, 60±10 times as much as the molar quantity of the catalyst. This result indicates that the cyano complex is superior to the cyano-free complex as the catalyst for addition of an alcohol to the olefin. Time courses for the formation of acetaldehyde diethyl acetal as catalyzed by the former complex at 20±1 °C under aerobic conditions are shown in Fig. 7. The formation of the acetal was detected to a minor extent in the dark because the alkylated complex is thermally de-

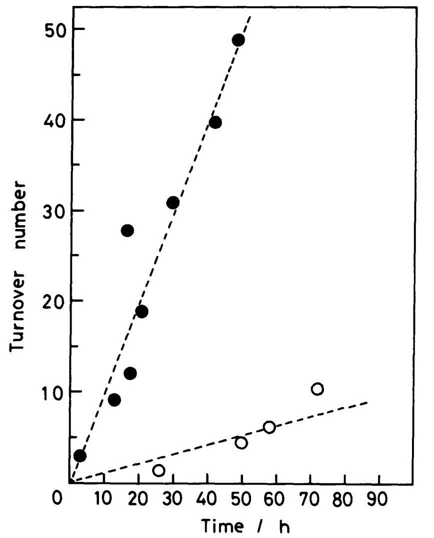
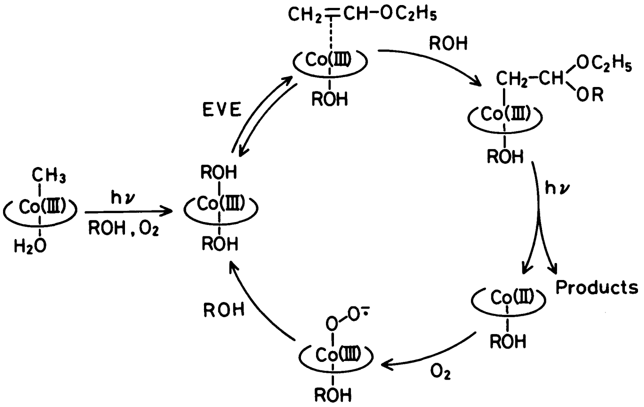


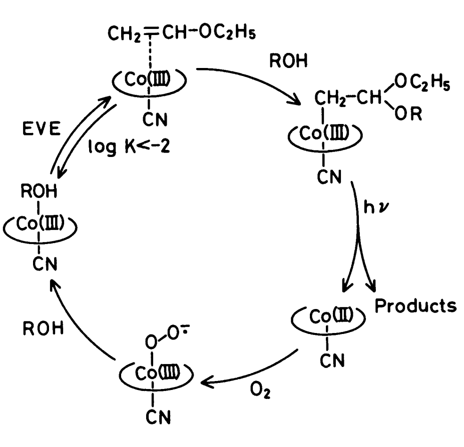
Fig. 7. Time courses for formation of acetaldehyde diethyl acetal as catalyzed by $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ under aerobic conditions at 20±1 °C. Composition of the initial reaction mixture: $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$, 6.0 mg ($5.1\times10^{-6}$ mol); ethyl vinyl ether, 2.5 mL (1.9 g, 2.6×10^{-2} mol); ethanol, 0.50 mL (0.39 g, 8.6×10^{-3} mol). Turnover numbers for $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ were calculated after correction for the blank reaction in the absence of the catalyst: ●, irradiated with a 500-W tungsten lamp from a distance of 10 cm; ○, in the dark.

composed by the trans effect originated from the axial cyano ligand. The acetal products, obtained by the reactions with C_2D_5OD and C_2H_5OD as alcohol components, were identified by NMR spectroscopy. A mixture of $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ (10 mg, 8.5×10^{-6} mol), ethyl vinyl ether (2.25 g, 3.1×10^{-2} mol), and a deuterated ethanol (C_2H_5OD or C_2D_5OD, 0.48 g) was irradiated for 200 h, and the products were recovered in a manner as described in the experimental section. The major products were $CH_2DCH(OC_2H_5)(OC_2D_5)$ and $CH_3CH(OC_2H_5)_2$ when C_2D_5OD and C_2H_5OD were used, respectively; splitting patterns of the CH signal at $\delta=4.7$ being a triplet and a quartet, respectively. This clearly indicates that the hydrogen atom is abstracted from the ethyl group of ethanol.

Judging from the spectral measurements and the product analyses, the catalytic reactions with the use of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ and $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ plausibly proceed *via* reaction cycles shown in Schemes 1 and 2, respectively. When the former complex is used as the starting one for example, the complex is first converted into the methyl-free complex by the aerobic photolysis. Ethyl vinyl ether, which is activated upon complex formation with the methyl-free complex in the second place, is subjected to the nucleophilic attack of an alcohol to afford an alkylated complex as the intermediate. The alkylated complex is then decomposed by the visible light to give the Co^{II} species and an acetal. $[(ROH)_2Cob(III)7C_1ester]^{2+}$ is regenerated by autoxidation of the Co^{II} species *via* formation of the superoxo-Co^{III} complex under aerobic conditions (see Scheme 1). It needs to be noted that the present reaction sequence is apparently similar to that of the coenzyme B_{12}-dependent enzymatic reaction, in which an alkylated complex is repeatedly produced and a product is obtained upon homolytic cleavage of the cobalt–carbon bond.[11]

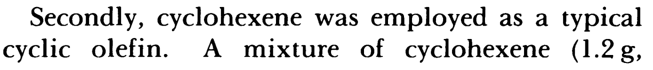


Scheme 1.



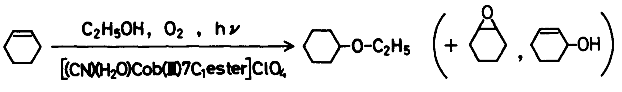
Scheme 2.

In order to make further clarification on the catalytic performance of the hydrophobic vitamin B_{12}, other olefins were also used in place of ethyl vinyl ether. Firstly, 1-pentene was used as a typical straight-chain olefin. The methyl-free Co^{III} complex, generated by the aerobic photolysis of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ in 1-pentene and methanol, was transformed into the corresponding alkylated complex in the dark along with the spectral change similar to that shown in Fig. 2. However, the alkylation rate is extremely slow (*ca.* 1/50 of the rate with ethyl vinyl ether), while the alkylated complex is quite photo-labile and readily decomposed even under room light. When a mixture of 1-pentene (0.96 g, 1.4×10^{-2} mol), ethanol (1.2 g, 2.6×10^{-2} mol), and $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ (3.9 mg, 3.3×10^{-6} mol) was irradiated at 20±1 °C for 150 h with a 500-W tungsten lamp from a distance of 10 cm under aerobic conditions, ethyl pentyl ether and ethyl 1-methylbutyl ether were obtained in the following yields; 15±5 and *ca.* 2 times, respectively, as much as the molar quantity of the hydrophobic vitamin B_{12} (refer to Eq. 2). Meanwhile, the reaction with $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ in place of the cyanoaqua complex otherwise under the same conditions afforded the former and latter ethers in the following respective yields; 3±1 and *ca.* 0.5 times as much as the molar quantity of the catalyst.



$$CH_2{=}CH{-}C_3H_7 \xrightarrow[\substack{[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4 \\ \text{or} \\ [(CN)(H_2O)Cob(III)7C_1ester]ClO_4}]{C_2H_5OH,\ O_2\ ,\ h\nu} C_2H_5{-}O{-}C_5H_{11} + CH_3{-}CH\begin{smallmatrix} C_3H_7 \\ OC_2H_5 \end{smallmatrix} \tag{2}$$

Secondly, cyclohexene was employed as a typical cyclic olefin. A mixture of cyclohexene (1.2 g, 1.5×10^{-2} mol), ethanol (1.2 g, 2.6×10^{-2} mol), and $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ (9.7 mg, 8.2×10^{-6} mol) was irradiated at 20±1 °C for 150 h with a 500-W tungsten lamp from a distance of 10 cm under aerobic conditions, and cyclohexyl ethyl ether was obtained in a yield, 2±1 times as much as the molar quantity of the catalyst (refer to Eq. 3). The



(3)

extremely low reactivity of cyclohexene may be partly attributed to a significant steric hindrance between the olefin and the catalyst against the formation of the corresponding complex.

Thirdly, acrylonitrile was used as a typical electron-deficient olefin. $[(ROH)_2Cob(III)7C_1ester]^{2+}$ was slowly converted into $[Cob(II)7C_1ester]^+$ in acrylonitrile and methanol under aerobic conditions in the dark without forming the corresponding alkylated complex. When a mixture of acrylonitrile (2.0 g, 3.8×10^{-2} mol), ethanol (0.39 g, 8.6×10^{-3} mol), and $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ (10 mg, 8.5×10^{-6} mol) was aerobically irradiated for 100 h under conditions identical with those described above, any ethanol adduct (*e.g.*, 3-ethoxypropionitrile or 2-ethoxypropionitrile) was not detected by GLC.

In conclusion, it became apparent that the hydrophobic vitamin B_{12} catalyzes the nucleophilic attack of an alcohol on an olefin under mild conditions, aerobic irradiation with the visible light at the room temperature range. As for the substrate selectivity, an electron-rich olefin is more reactive with the present catalysts than ordinary olefins. $[(ROH)_2Cob(III)7C_1ester]^{2+}$ is an appropriate catalyst for investigation of the reaction mechanism because the alkylated intermediate complex has a long lifetime enough for its identification in the dark. On the other hand, $[(CN)(ROH)Cob(III)7C_1ester]^+$ is superior to the cyano-free Co^{III} complex as the catalyst for the addition reaction due to the trans effect exercised by the axial cyano ligand for the cleavage of the cobalt–carbon bond.

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7) Either $[(CH_3OH)(H_2O)Cob(III)7C_1ester]^{2+}$ or $[(CH_3OH)_2Cob(III)7C_1ester]^{2+}$ is likely produced under irradiation conditions in the presence of a large excess of methanol. Since these complexes were not isolated for identification, we can not specify the structure at present.

8) The $E_T(30)$ value for ethyl vinyl ether was evaluated by electronic spectroscopy with dicyano(8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinato)cobalt(III) as a probe. See: Y. Murakami, Y. Aoyama, and S. Nakanishi, *Inorg. Nucl. Chem. Lett.,* **12**, 809 (1976). As for $E_T(30)$, see: C. Reichardt, "Solvent Effects in Organic Chemistry," Verlag Chemie, Weinheim (1979).

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10) $[(CN)(H_2O)Cob(III)7C_1ester]^+$ is most likely converted into $[(CN)(ROH)Cob(III)7C_1ester]^+$ (R=alkyl) in the presence of a large excess of an alcohol after the initial reaction cycle without showing any significant change in spectral behavior.

11) B. T. Golding, "B_{12}," ed by D. Dolphin, John Wiley, New York (1982), Vol. 1, Chap. 15.