The g value of 1.979 and the $a\langle^{47}Ti/^{49}Ti\rangle$ value of 9.0 G are typical for Ti(III) species;[12] thus the reduction is formally attributed to a Ti(IV)/Ti(III) redox couple. Hyperfine couplings to two chemically equivalent phosphorus and a Rh nuclei of 2.8 and 1.8 G, respectively, were observed. Molecular orbital calculations on the related complexes **1** and **2** indicate that the LUMO is primarily Ti d_{z^2} in character (where the z axis is the Ti–Cu vector). If the situation is similar for **4**, then occupation of this orbital upon formation of **5** would account for the typical Ti(III) g and $a\langle^{47}Ti/^{49}Ti\rangle$ values. Furthermore, it suggests that the mechanism of coupling to Rh may involve a direct through-space interaction rather than a Fermi contact or through-bond process. Similar trans-annular interactions across four-membered rings have been postulated in Ti(III) dithiophosphinate complexes[12,45] and supported by extended Hückel MO calculations.[45] Single-crystal EPR experiments and MO calculations are underway to clarify the nature of the coupling mechanism in **5**.

Summary. The preparative route described herein demonstrates that use of a metalloligand such as **3** can provide a facile method for the synthesis of heterobimetallic complexes. The present report shows that such metalloligands can accommodate late metals in pseudo-square planar environments. Characterization of the reduced and oxidized forms of the Rh–Ti species **4** suggests the possibility of metal–metal interactions in these heterobimetallics. The reactivity and chemistry of these and related species are the subject of ongoing research and will be reported in due course.

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Registry No. **3**, 109863-51-6; **4**, 109863-53-8; **5**, 109863-54-9; **6**, 109863-55-0; Cp_2TiCl_2, 1271-19-8; $[(NBE)_2Rh]BF_4$, 36620-11-8; Cp_2Co, 1277-43-6; $HSCH_2CH_2CH_2Cl$, 17481-19-5; Ph_2PH, 829-85-6.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom parameters, and bond distances and angles associated with the cyclopentadienyl rings, the BF_4 anion, and the acetone of crystallization (9 pages); listings of $10|F_o|$ and $10|F_c|$ (21 pages). Ordering information is given on any current masthead page.

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Asymmetric Induction in the Nucleophilic Cyclopropane Ring Cleavage Reaction with Vitamin B_{12s}

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Vitamin B_{12s} reacts with cyclopropane derivatives having electron-withdrawing substituents such as acetyl, methoxycarbonyl, and cyano groups to give 3-substituted propyl–cobalt complexes. The alkylation with prochiral 1-acetyl-1-alkylcyclopropanes results in an asymmetric induction (ee 24–33%) at carbon 3 in the resulting alkyl ligands. Examination of the ^1H NMR spectra of the alkylation products indicates that (1) two prochiral methyl groups in 3,3-diacetylpropyl– and 3,3-bis(methoxycarbonyl)propyl–cobalt complexes are rendered diastereotopic by the presence of the chiral B_{12} and are observed to be spectroscopically nonequivalent and (2) enantiomeric methyl groups in 3-acetyl-3-alkylpropyl– and 3-acetyl-3-(methoxycarbonyl)propyl–cobalt complexes having an asymmetric center at carbon 3 are also rendered diastereotopic and spectroscopically distinguishable in a similar manner.

Introduction

An interest in vitamin B_{12} from the viewpoint of synthetic organic chemistry lies in its potentiality as a naturally occurring, chiral catalyst in asymmetric organic synthesis. Scheffold et al. have recently shown that vitamin B_{12} can be used as a catalyst for C–C bond formation processes.[1] Fischli et al. also found that B_{12} catalyzes enantioselective reduction of α,β-unsaturated carbonyl compounds.[2] Both catalytic reactions involve alkyl-cobalt complexes as the key intermediates. The most common procedure for preparing organometallic B_{12} derivatives utilizes the "supernucleophilicity" of the Co(I) species or B_{12s} toward alkylating agents such as alkyl halides and Michael olefins.[3] In order to achieve a high degree of enantioselectivity, the conformational flexibility of alkylating agent should be minimized at the transition state of alkylation. These considerations, coupled with our previous finding on the facile cyclopropane ring cleavage by anionic Rh(I) porphyrin complexes,[4] prompted us to investigate the hitherto unknown reaction of B_{12s} with cyclopropane derivatives.[5] We report here that cyclopropanes having electron-withdrawing groups readily react with B_{12s} to give 3-substituted propyl–cobalt complexes and that the alkylation with prochiral cyclopropane de-

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(4) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Chem. Soc., Chem. Commun.* **1975**, 572.

(5) For nucleophilic ring-opening reactions of epoxides, see: (a) ref 3b. (b) Dixon, R. M.; Golding, B. T.; Howarth, O. W.; Murphy, J. L. *J. Chem. Soc., Chem. Commun.* **1983**, 243.

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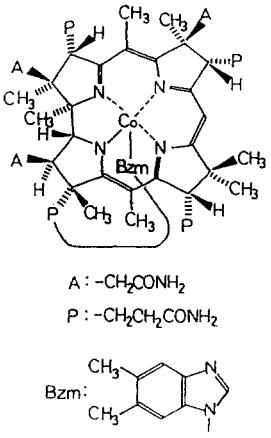


Figure 1. Basic structure of vitamin B_{12}.

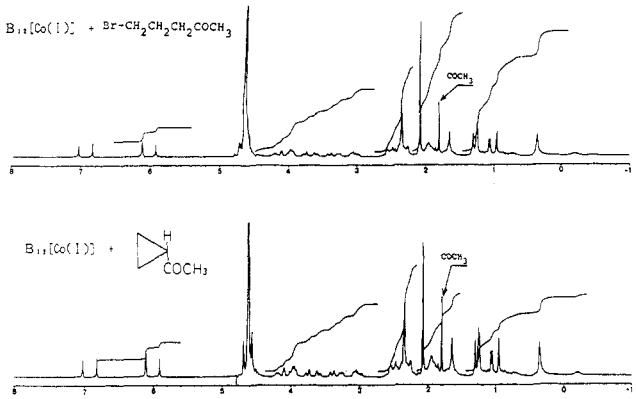


Figure 2. ^1H NMR spectra (270 MHz) of **2a** for ^2H_2O solutions at 25 °C: top, **2a** obtained according to eq 2; bottom, **2a** obtained according to eq 1.

rivatives results in an asymmetric induction in the alkyl ligands derived therefrom. The basic chiral corrin structure of B_{12} is shown in Figure 1.

Results and Discussion

Alkylation of B_{12s} with Cyclopropanes. The reaction of a cyclopropane derivative (1) having acetyl, methoxycarbonyl, or cyano group with B_{12s} prepared by reducing cyanocobalamin with Zn in 15% aqueous NH_4Cl took place readily and gave 3-mono- or 3,3-disubstituted propyl–cobalt complexes (**2**, eq 1), which were purified by the standard procedure[6] based on phenol extraction, chromatography on cellulose CM-52, and recrystallization from water–acetone. Yields (%): **2a** (93), **2b** (69), **2c** (61), **2d** (72), **2e** (60), **2f** (64), **2g** (70), **2h** (57), **2i** (85), and **2j** (72). A spiro compound (**1k**) gave the corresponding cyclopropane ring cleavage product **2k** in 78% yield. The competitive alkylation of B_{12s} using an equimolar mixture of **1a** and **1d**, **1a** and **1c**, or **1c** and **1d** gave the product ratio **2a**:**2d** = ~0:~100, **2a**:**2c** = ~0:~100, or **2d**:**2c** = ~0:~100, respectively. These and similar experiments indicated the relative reactivities in the order **1c** ≫ **1d**, ≫ **1a**, **1f–j** ≫ **1b**, and methyl cyclopropanecarboxylate was practically unreactive. Also unreactive were dimethyl esters of cyclobutane- and cyclopentane-1,1-dicarboxylic acids. The organometallic B_{12} derivatives were identified by comparison of their ^1H NMR, UV–visible, and IR spectra with those of authentic samples obtained by the reactions of B_{12s} with the corresponding open-chain halides **3** (eq 2). An example is illustrated in Figure 2, which shows the identical ^1H NMR spectra of the 4-oxopentyl–cobalt

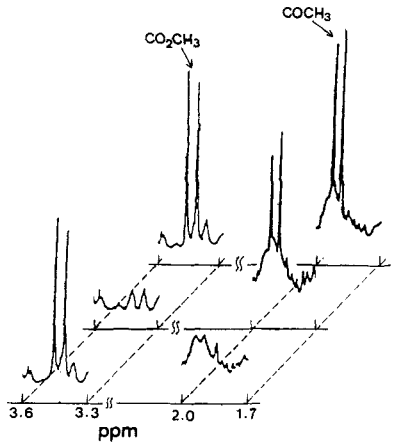
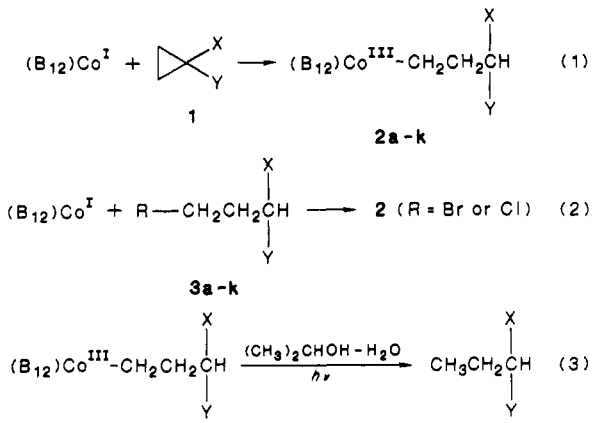


Figure 3. ^1H NMR spectra (3.3–3.6 and 1.7–2.0 ppm regions) of **2e** for ^2H_2O solutions at 25 °C: top, **2e** obtained according to eq 1; middle, **2e** having deuteriated methoxycarbonyl moiety; bottom, **2e** having deuteriated acetyl moiety.

derivative **2a** obtained either from acetylcyclopropane according to eq 1 or from 1-bromo-4-oxopentane according to eq 2. A singlet at δ 1.80 can be readily assigned to the acetyl methyl protons by comparing the spectrum with that of methylcobalamin.[7] The exclusive C_1–C_2 bond cleavage of cyclopropane ring was further confirmed by converting the alkyl ligands of **2d** and **2j** to dimethyl ethylmalonate and 3-benzylpentan-2-one, respectively, upon anaerobic photolysis in 2-propanol-water (9:1) (eq 3).



a, X = $COCH_3$, Y = H; **b**, X = CN, Y = H; **c**, X = Y = $COCH_3$; **d**, X = Y = CO_2CH_3; **e**, X = $COCH_3$, Y = CO_2CH_3; **f**, X = $COCH_3$, Y = CH_2CH_3; **g**, X = $COCH_3$, Y = $(CH_2)_2CH_3$; **h**, X = $COCH_3$, Y = $(CH_2)_5CH_3$; **i**, X = $COCH_3$, Y = $CH_2CH(CH_3)_2$; **j**, X = $COCH_3$, Y = $CH_2C_6H_5$; **k**, X,Y = $-CO(CH_2)_3-$

The present reaction can be readily interpreted in terms of nucleophilic cyclopropane ring cleavage by B_{12s}. There is ample precedent for such processes using other nucleophiles.[4,8-11] From a synthetic point of view, the present reaction provides a new general route to alkyl–cobalt complexes of B_{12} having a substituted three-carbon unit just as the nucleophilic addition of B_{12s} to Michael olefins leads to alkyl–cobalt complexes having a two-carbon unit.

^1H NMR Spectra of Alkyl–Cobalt Complexes. The ^1H NMR spectra of **2c** and **2d** showed a pair of singlets of equal intensities for the methyl protons in $COCH_3$ or

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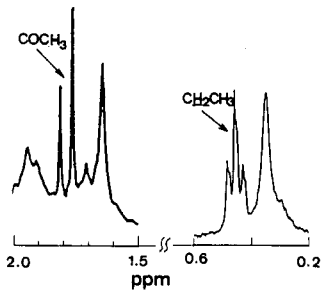


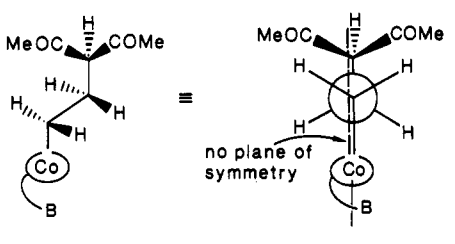
Figure 4. ^1H NMR spectrum (1.5–2.0 and 0.2–0.6 ppm regions) of **2f** obtained according to eq 1 for ^2H_2O solution at 25 °C.

Table I. ^1H NMR Data for Methyl Protons in Alkyl–Cobalt Complexes[a]

compd	chem shift, ppm	rel intensity of methyl resonances in compds prepared according to eq 1	rel intensity of methyl resonances in compds prepared according to eq 2
2a	1.80[b]		
2c	1.86, 1.89[b]	1:1	1:1
2d	3.44, 3.48[c]	1:1	1:1
2e	1.89, 1.93[b]	~1:1	1:1
	3.42, 3.47[c]		
2f	1.81, 1.76[b]	1:1.6	1:1
	0.45, 0.46[c]		
2g	1.81, 1.77[b]	1:1.6	1:1
2h	1.81, 1.78[b]	1:1.6	1:1
2i	1.78, 1.81[b]	1:1.7	1:1
2j	1.99, 1.84[b]	1:2.0	1:1

[a] Spectra were taken at 270 MHz for ^2H_2O solutions at 25 °C, H^2HO (δ 4.63) being used as an internal reference. [b] $COCH_3$. [c] CO_2CH_3 or CH_2CH_3.

CO_2CH_3 groups, as expected since they are diastereotopic. The corresponding resonances for **2e** are shown in Figure 3, which also includes the spectra of **2e** having deuteriated acetyl or deuteriated methoxycarbonyl moiety. Compounds **2f–j** gave a similar splitting of the acetyl methyl signals as shown in Figure 4 for **2f** as obtained according to eq 1. These observations reflect the chiral-recognition ability of B_{12},[12] indicating that (1) two prochiral methyl groups in the alkyl ligands of **2c** and **2d** are rendered diastereotopic by the presence of the chiral B_{12} and are observed to be spectroscopically nonequivalent (referring to the projection shown in **4**) and (2) enantiomeric methyl



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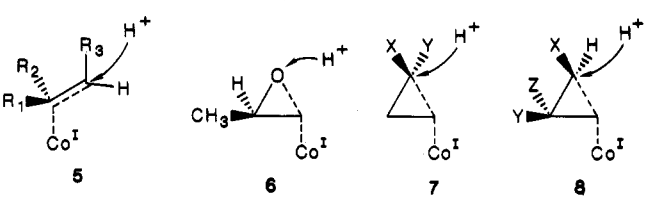
groups in the alkyl ligands of **2e** and **2f–j** having an asymmetric center at carbon 3 are also rendered diastereotopic and spectroscopically distinguishable in a similar manner. In Table I are shown the ^1H NMR data for methyl proton resonances.

Asymmetric Induction at Carbon 3. The diastereomer ratios in alkyl–cobalt complexes can be evaluated from the relative intensities of the diastereotopic methyl signals and are summarized in Table I for **2e–j** as obtained by the method of eq 1 using prochiral cyclopropane derivatives and by the method of eq 2 using racemic alkyl halides. Inspection of Table I reveals that the nucleophilic substitution reactions (eq 2) show no optical selectivity irrespective of the substrates used. A similar situation applies also to **2e** as obtained by the present cyclopropane ring cleavage reaction (eq 1). However, when this reaction is applied to a cyclopropane having substituents of different electronic nature (**1f–j**), two diastereomeric alkyl–cobalt complexes are formed with 24–33% ee optical induction at carbon 3 of the alkyl ligand and the bulkier alkyl substituents on cyclopropane ring seem to lead to higher optical selectivities. The failure of the substitution processes (eq 2) to show optical selectivity may be due to the flexible nature of the transition state of this reaction using open-chain halides.

The present reaction (eq 1) provides the first example of asymmetric alkylations of B_{12s} with prochiral alkylating agents. The diastereoselection is comparable with that in the B_{12}-catalyzed reduction of unsaturated substrates in which diastereomeric alkyl–cobalt complexes are proposed as intermediates.[2c] Golding et al. have found a much higher optical selectivity in the enantiomer-selective alkylation of B_{12s} with racemic epoxypropane giving rise to a diastereomer ratio of 3:1.[5b] These and the present reactions may be related, but a difference lies in the position of asymmetric center and the timing of its generation. In the reduction of unsaturated substrates, an asymmetric center at C-1 is generated during the face-selective attack of B_{12s} on a double bond (referring to the transition-state structure represented in **5**). In the ring cleavage of epoxypropane, the asymmetric center at C-2 is intact during the reaction (**6**). In the present reaction, an asymmetric center at C-3 is generated that subsequently undergoes protonation (**7**). For this reaction, therefore, the timing



5 **6** **7** **8**

of protonation at C-3 relative to the initial attack of B_{12s} on C-1 is essentially important for the mechanism of asymmetric induction. For the practical purposes of enhancing optical selectivity, use of cyclopropanes having an asymmetric center at C-2 as substrates (**8**) would be an interesting extention of this study. Further work is now under way along these lines.

Experimental Section

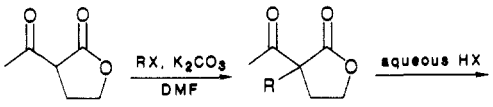
General Analyses. ^1H NMR spectra were taken on a JEOL JNM-GX 270 or JNM-PMX 60 spectrometer. IR spectra were obtained on a Hitachi 260-10 spectrophotometer. Electronic spectra were recorded on a Hitachi spectrophotometer. Gas chromatographic analyses were made with a Shimadzu GC-4C gas chromatograph using helium as a carrier gas. Identification of the reaction products were performed by coinjection with authentic samples on columns of poly(ethylene glycol) 20M and silicone DC QF-1.

Cyclopropanes (1) and Alkyl Halides (3). Acetyl- (**1a**) and cyanocyclopropane (**1b**) were commercial products. 1,1-Bis(methoxycarbonyl)cyclopropane (**1d**) was prepared by the alkylation–cyclopropanation of dimethyl malonate with 1,2-dibromoethane in the presence of K_2CO_3 in DMF:[13] yield 28%, bp 38–40 °C (1 mmHg). In essentially the same way were obtained 1,1-diacetylcyclopropane (**1c**) and 1-acetyl-1-(methoxycarbonyl)cyclopropane (**1e**) by using acetylacetone and methyl

(12) For the ^1H NMR characterization mainly of corrin proton resonances of diastereoisomeric alkylcobalamins, see ref 5b.

(13) White, D. A. *Synth. Commun.* **1977**, *7*, 559.

acetoacetate, respectively. **1c**: yield 47%; bp 44–46 °C (5 mmHg). **1e**: yield, 66%; bp 40–42 °C (1 mmHg). 1-Chloro-3,3-bis(methoxycarbonyl)propane (**3d**) and 1-chloro-3-acetyl-3-(methoxycarbonyl)propane (**3e**) were prepared by the ring opening of **1d** and **1e**, respectively. Thus, into a mixture of **1d** (12.9 g), NaCl (11.4 g), and methanol (10 g) was added concentrated sulfuric acid (12.9 g) at 0–5 °C. The mixture was stirred at that temperature for 30 min and at 25–30 °C for 6 h and then poured on water. The organic layer was separated and the aqueous layer extracted with dichloromethane after neutralization with $NaHCO_3$. The combined organic extracts were dried, and the solvent was removed. The residue was distilled to give **3d**. **3d**: yield 10%; bp 76 °C (1 mmHg). **3e**: yield 41%; bp 78–80 °C (3 mmHg). 1-Acetyl-1-ethyl- (**1f**), 1-acetyl-1-propyl- (**1g**), 1-acetyl-1-hexyl- (**1h**), 1-acetyl-1-isobutyl- (**1i**), and 1-acetyl-1-benzylcyclopropane (**1j**) and their alkyl halide counterparts (**3f–j**) were obtained by following the general procedure for the preparation of acetylcyclopropane[14] with an additional alkylation step (eq 4). The preparation of **1f** and **3f** is described as a typical example. A mixture of α-acetyl-γ-butyrolactone (commercial product, 20 g), ethyl bromide (17 g), K_2CO_3 (22.1 g), and DMF (80 mL) was stirred at room temperature for 2 days. The solvent was removed in vacuo, and water (100 mL) was added to the residue. The mixture was acidified with 1M HCl and extracted with ether (50 mL × 3). After usual workup was obtained α-acetyl-α-ethyl-γ-butyrolactone (**9f**) by distillation: yield 19 g (79%); bp 77–80 °C (3 mmHg). A mixture of **9f** (13.2 g) and aqueous HBr (47%, 18.5 mL) was stirred at 40–50 °C for 3 h. Water (50 mL) was added, and the mixture was extracted with chloroform (50 mL × 3). Workup and distillation gave 1-bromo-3-acetylpentane (**3f**): yield 8 g (50%); bp 52–54 °C (3 mmHg). To a solution of NaOH (2.1 g) in water (5 mL) was added **3f** (5 g) in a period of 30 min. The mixture was stirred at 70–80 °C for 3 h, acidified with aqueous HCl, and extracted with ether (50 mL × 3). Workup and distillation afforded 1-acetyl-1-ethylcyclopropane (**1f**): yield 1.4 g (48%); bp 60–61 °C (35 mmHg). Yields (%) and boiling points (°C) (*p* (mmHg)) for other compounds are as follows **9g**, 68 and 83–85 (3); **3g** (R = Cl), 72 and 44–46 (3); **1g**, 59 and 61–62 (15); **9h**, 62 and 120–123 (3); **3h** (R = Cl), 70 and 90–92 (5); **1h**, 82 and 124–126 (5); **9i**, 22 and 95–98 (5); **3i** (R = Cl), 64 and 57–60 (5); **1i**, 78 and 74–77 (15); **9j**, not distilled; **3j** (R = Cl), 59 and 104 (3); **1j**, 55 and 151–154 (15). Spiro[2.4]heptan-4-one (**1k**), bp 30 °C (5 mmHg), was obtained similarly by treating with aqueous NaOH of 2-(2-bromoethyl)cyclohexanone (**3k**, R = Br), bp 68–70 °C (5 mmHg), which in turn was prepared in 43% yield by the alkylation of 2-(ethoxycarbonyl)cyclohexanone with 1,2-dibromoethane followed by hydrolytic decarboxylation.



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(4)

(14) *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. 4, pp 597–600.

Alkylation of B_{12s}.[6] Into a solution of B_{12s} prepared by reducing cyanocobalamin (100–500 mg) with Zn dust (pretreated with 1–10% HCl, 1–2 g) in 15% aqueous NH_4Cl (30 mL) was added a cyclopropane substrate (10–30 equiv) under nitrogen in the dark. The mixture was stirred for 0.5–3 h (depending on the reactivity of substrate) at room temperature and extracted with phenol–dichloromethane (1:1, 20–30 mL). The organic layer was separated, and to it was added dichloromethane (200–300 mL). The cobalamins were extracted with water. The water was removed at <40 °C in vacuo (1 mmHg). The residue was chromatographed on a column of cellulose CM-52 (pretreated with deionized water, 2 × 30 cm) with water as eluant. The main organocobalamin fraction that followed the unreacted cyanocobalamin band was collected. Water was removed as above, and the residue was recrystallized from acetone–water (10:1) to give an alkyl–cobalt complex, which was identified by comparison of its UV–visible, IR, and ^1H NMR spectra (270 MHz) with those of the authentic specimen obtained by the reaction of B_{12s} with the corresponding open-chain halide as the substrate (eq 2) in otherwise the same way as above. Amounts of cyanocobalamin and products (yields) according to the method of eq 1 are as follows: 100 mg, **2a** (101 mg, 93%); 78 mg, **2b** (30 mg, 37%); 500 mg, **2c** (416 mg, 61%); 100 mg, **2d** (81 mg, 72%); 100 mg, **2e** (67 mg, 60%); 161 mg, **2f** (110 mg, 64%); 138 mg, **2g** (103 mg, 70%); 117 mg, **2h** (73 mg, 57%); 128 mg, **2i** (117 mg, 85%); 110 mg, **2j** (88 mg, 72%); 134 mg, **2k** (109 mg, 78%). Amounts of cyanocobalamin and products (yields) according to the method of eq 2 are as follows: 100 mg, **2a** (59 mg, 55%); 123 mg, **2b** (114 mg, 90%); 100 mg, **2d** (38 mg, 34%); 130 mg, **2e** (111 mg, 78%); 139 mg, **2f** (68 mg, 48%); 108 mg, **2g** (96 mg, 83%); 138 mg, **2h** (103 mg, 67%); 130 mg, **2i** (117 mg, 84%); 105 mg, **2j** (86 mg, 74%); 149 mg, **2k** (127 mg, 80%).

Competitive Reactions. The alkylation of B_{12s} prepared from cyanocobalamin (50 mg) with an equimolar mixture of two cyclopropanes (both in 100 equiv) was carried out, and the organocobalamin(s) were isolated as above but without the recrystallization procedure. The product ratios were determined from the ^1H NMR spectra.

Photolysis. A well nitrogen-purged solution of **2d** (122 mg) in 2-propanol–water (9:1, 50 mL) was irradiated with 100-W high-pressure Hg lamp for 6 h. The organic product was extracted with ether, purified by means of preparative gas chromatography, and identified as dimethyl ethylmalonate (37%) on the basis of gas chromatography and ^1H NMR spectrum. The photolysis of **2j** was carried out with a 500-W Xenon lamp (>500 nm) and gave 3-benzylpentan-2-one which was identified as above.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Projects (No. 61470092) from the Ministry of Education, Science, and Culture of Japan.

Registry No. **1a**, 765-43-5; **1b**, 5500-21-0; **1c**, 695-70-5; **1d**, 6914-71-2; **1e**, 38806-09-6; **1f**, 16278-12-9; **1g**, 109765-85-7; **1h**, 109765-86-8; **1i**, 109765-87-9; **1j**, 109765-88-0; **1k**, 5771-32-4; **2a**, 109786-36-9; **2b**, 89414-81-3; **2c**, 109786-37-0; **2d**, 109786-38-1; **2e**, 109786-39-2; **2f**, 109786-41-6; **2h**, 109786-42-7; **2i**, 109786-43-8; **2j**, 109786-44-9; **2k**, 109786-45-0; **3f**, 66760-26-7; **9f**, 31770-00-0; vitamin B_{12s}, 18534-66-2; vitamin B_{12}, 68-19-9; dimethyl malonate, 108-59-8; 1,2-dibromoethane, 106-93-4; α-acetyl-γ-butyrolactone, 517-23-7; ethyul bromide, 74-96-4.