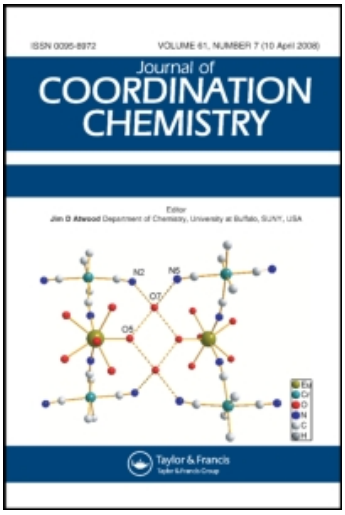

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HYDROPHOBIC VITAMIN B_{12}. VII.† RING-EXPANSION REACTIONS CATALYZED BY HYDROPHOBIC VITAMIN B_{12} IN OCTOPUS AZAPARACYCLOPHANE

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Ring-expansion reactions of alkyl ligands bound to heptapropyl cobyrinate at the axial site of the nuclear cobalt were found to be markedly favoured in the hydrophobic cavity of an octopus azaparacyclophane, relative to reactions in methanol and benzene, under anaerobic photolysis conditions at 20.0°C. Heptapropyl cobyrinate perchlorate catalyzed the same ring-expansion reactions, which convert 2-methyl-1,3-cyclopentanedione and 3-methyl-2-pyrrolidinone into 1,4-cyclohexanedione and 2-piperidinone, respectively, in the octopus cyclophane by utilizing vanadium trichloride as a co-catalyst under aerobic photolysis conditions.

Keywords: Paracyclophane, vitamin B_{12}, 1,2-migration, photolysis, ring expansion

INTRODUCTION

The vitamin B_{12} coenzyme is known to catalyze intramolecular 1,2-migration reactions in various apoproteins which provide specific microenvironments of a hydrophobic and water-deficient nature. In other words, such microenvironmental effects given by apoproteins seem to contribute not only to discrimination of substrate species but also to stabilization of reactive intermediates formed in the course of enzymic reactions.[1] However, studies of non-enzymic reactions have been exclusively related to clarification of the catalytic functions of the coenzyme, vitamin B_{12}, and relevant apoprotein models have received little treatment. We have been interested in the catalytic activity of vitamin B_{12} in hydrophobic microenvironments to simulate the catalytic function of the holoenzymes concerned. For this purpose, we have prepared hydrophobic vitamin B_{12} derivatives which have carboxylic ester groups in place of the peripheral amide functions of the naturally occurring vitamin B_{12},[2] so that the modified vitamin B_{12}'s are readily incorporated into apolar media, and have previously investigated various isomerization reactions, as mediated by those hydrophobic complexes, in single-compartment vesicles of peptide amphiphiles.[3–6] As a consequence, it became apparent that such artificial systems are capable of simulating the 1,2-migration of electron-withdrawing groups as typically catalyzed by methylmalonyl-CoA mutase and glutamate mutase due to both the repression of molecular motion and desolvation effects operating on the corresponding alkylated complexes, as exerted by the bilayer membranes. Furthermore, the

† Part 6 of this series is ref. 13.
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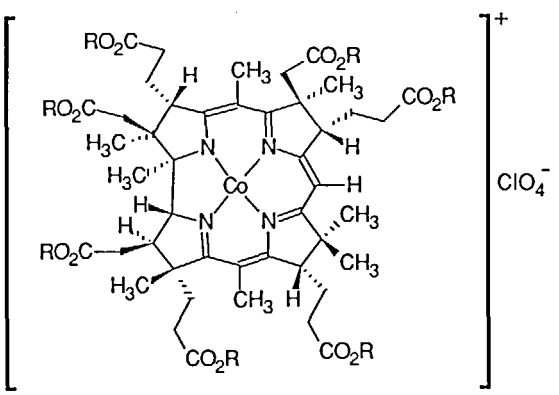
above artificial system was coupled with a substrate-activation process[7] provided by vanadium trichloride and atmospheric oxygen under irradiation with visible light to set up a true artificial holoenzyme system that shows turnover of the catalyst species. The resulting catalytic system was found to simulate the glutamate mutase reaction[8] and to carry out non-enzymic ring-expansion reactions.[9]

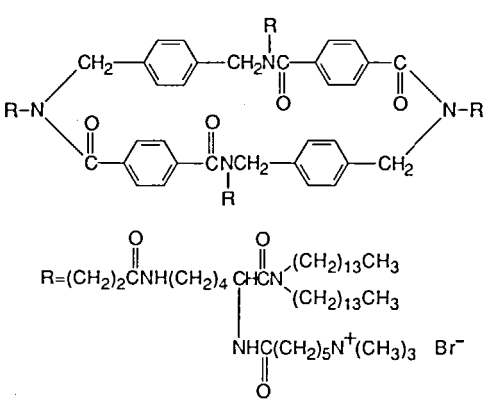
Recently, we have developed macrocyclic compounds which provide sizable intramolecular cavities, from the viewpoint of host-guest chemistry.[10] An octopus azaparacyclophane having eight hydrocarbon chains, APC[C_2Lys(C_5N^+)2C_{14}]$_4$, behaves as an effective cationic host over a wide pH range in aqueous media,[11] and incorporates a hydrophobic vitamin B_{12} derivative in a 1:1 molar ratio.[12] Carbon-skeleton rearrangement reactions of alkyl ligands bound to the hydrophobic vitamin B_{12}, as simulation of the methylmalonyl-CoA mutase reaction, were found to be markedly favoured in the hydrophobic cavity provided by the octopus cyclophane under anaerobic photolysis conditions at ordinary temperatures.[13]

In the light of the above accomplishments, we examined in the present work ring-expansion reactions catalyzed by a hydrophobic vitamin B_{12}, [Cob(II)7C_3ester]ClO_4, in the octopus cyclophane.



R = n-C_3H_7

[Cob(II)7C_3ester]ClO_4



APC[C_2Lys(C_5N^+)2C_{14}]$_4$

EXPERIMENTAL

General Analyses and Measurements

A Beckman Φ71 pH meter equipped with a Beckman 39505 combined electrode was used for pH measurements after calibration with a combination of appropriate standard aqueous buffers. Electronic absorption spectra were recorded with a Hitachi 340 or a Hitachi 220A spectrophotometer. GLC analyses were carried out with a Shimadzu GC-9A apparatus equipped with a Shimadzu C-R3A-FFC Chromatopac for data processing.

Materials

Heptapropyl cobyrinate perchlorate, [Cob(II)7C_3ester]ClO_4, and alkylated hydrophobic vitamin B_{12} derivatives were prepared with reference to methods reported previously,[3,8] A methanol solution (100 cm^3) containing heptapropyl cobyrinate perchlorate (300 mg, 2.2×10^{-4} mol) and 2-methyl-1,3-cyclopentanedione (50 mg, 4.5×10^{-4} mol) was mixed with 60 cm^3 of aqueous sodium carbonate buffer (0.02 mol dm^{-3}, pH 11.2), and 25 cm^3 of 15% (w/w) aqueous perchloric acid containing vanadium trichloride (50 mg, 3.2×10^{-4} mol) was added to the solution. The mixture was stirred vigorously for 5 min at room temperature, air was introduced into it for 2 min, and stirring was continued further for 1 h at the same temperature. The product was extracted with dichloromethane and purified by gel-filtration chromatography on a column of Sephadex LH-20 with methanol as an eluant to give a brownish solid (**1**), yield 101 mg (31%); λ_{max} (CH_2Cl_2) 268 (ε 2.21×10^4), 316 (2.36×10^4), 350sh (0.83×10^4), and 469 nm (1.10×10^4). Alkylated complex **2** was also prepared from heptapropyl cobyrinate perchlorate and 3-methyl-2-pyrrolidinone by the same procedure, yield 91 mg (28%); λ_{max} (CH_2Cl_2) 265 (ε 2.20×10^4), 315 (2.35×10^4), 350sh (0.84×10^4), and 465 nm (1.10×10^4).

The preparation of the octopus azaparacyclophane, APC[C_2Lys(C_5N^+)2C_{14}]$_4$, was described previously in detail.[11] 2-Methyl-1,3-cyclopentanedione, 3-methyl-2-pyrrolidinone, both purchased from Aldrich Chemical Co., Inc. (U.S.A.), 1,4-cyclohexanedione (Tokyo Kasei Kogyo Co., Ltd., Japan), and 2-piperidinone (Ishizu Seiyaku Co., Ltd., Japan) were distilled *in vacuo* before use, and confirmed to be sufficiently pure by GLC. Methanol and benzene were purified and dried just before use according to standard procedures.[14] Vanadium trichloride of reagent grade was obtained from Wako Pure Chemical Industries, Ltd., (Japan) and used without further purification.

Photolysis of Alkylated Complexes

A solution containing equimolar quantities of APC[C_2Lys(C_5N^+)2C_{14}]$_4$ and the alkylated complex (**1** or **2**) in dichloromethane (1 cm^3) was evaporated *in vacuo* to remove the solvent completely in the dark, and then 20 cm^3 of an aqueous phosphate–borate buffer (0.02 mol dm^{-3}; pH 9.2) was added to the residue to obtain the reaction sample with concentrations of the components at 5.0×10^{-5} mol dm^{-3}. The solution was deoxygenated with nitrogen, then irradiated with a 500 W tungsten lamp for 1 h at a distance of 30 cm and at 20.0°C. Complete decomposition of the

alkylated complex was confirmed by electronic spectroscopy (refer to Figure 1), and then the products were extracted with dichloromethane ($20\,cm^3 \times 3$). The dichloromethane extract was evaporated to dryness, and an appropriate amount of diethyl ether ($0.5\,cm^3$) was added to it. The products were identified by means of GLC, with coinjection of authentic samples into columns of Silicone DC-550 and Silicone SE-30. Quantitative analyses of the products were carried out by GLC on the basis of correlation lines established independently by using authentic samples. As for reactions in methanol or benzene, a reaction mixture was evaporated to dryness *in vacuo* before extraction with hexane. The hexane extract was evaporated to dryness and an appropriate amount of diethyl ether was added to it. The products were subjected to GLC analyses in a manner as stated above. Total yields listed in Tables I and II are less than 100% owing to losses during extraction. However, we confirmed that no other by-products were obtained.

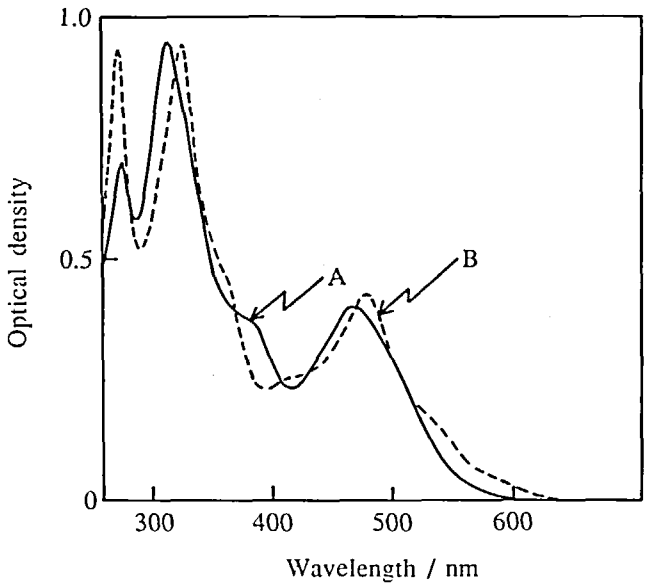


FIGURE 1 Electronic spectral change caused by anaerobic photolysis of **1** ($4.0 \times 10^{-5}\,mol\,dm^{-3}$) in dichloromethane at 20.0°C: A, before photolysis; B, after irradiation with a 500 W tungsten lamp for 1 h at a distance of 30 cm.

Catalytic Reaction

A dichloromethane solution ($5\,cm^3$) containing equimolar quantities of APC-$[C_2Lys(C_5N^+)2C_{14}]_4$ and $[Cob(II)7C_3ester]ClO_4$ (1.0×10^{-6} mol each) and the substrate, **1a** or **2a**, (6.0×10^{-5} mol) was evaporated *in vacuo* to remove the solvent completely, and then the residue was dissolved in aqueous sodium carbonate buffer ($0.02\,mol\,dm^{-3}$, pH 11.2; $20\,cm^3$). Aqueous 15% (w/w) perchloric acid ($5\,cm^3$) containing vanadium trichloride ($0.10\,mol\,dm^{-3}$) was added to the solution, and pH of the resulting solution was adjusted to 7.0 with 15% (w/w) aqueous sodium hydroxide. The reaction mixture was irradiated with a 500 W tungsten lamp at a distance of 30 cm along with air-bubbling at 20.0°C, and samples were taken out at

appropriate time intervals for product analysis by GLC, in a manner as described above. No oxygenation products were detected by GLC under the present experimental conditions.

TABLE I

Product analyses for photolysis of **1** and **1a** in various media at 20.0 ± 0.1°C[a].

Medium	Reactant	Yield/%	
		1a	**1b**
Methanol	**1**[b]	69	19
	1a[c]	76	9.0
Benzene	**1**[b]	57	28
	1a[c]	69	14
$APC[C_2Lys(C_5N^+)2C_{14}]_4$	**1**[d]	15	73
	1a[c]	71	15

[a] A 20 cm^3 sample was irradiated with a 500 W tungsten lamp for 1 h at a distance of 30 cm. [b] **1**, 5.0×10^{-5} mol dm^{-3}; under anaerobic conditions. [c] A 1.5×10^{-2} cm^3 sample of aqueous 15% (w/w) perchloric acid containing vanadium trichloride (0.1 mol dm^{-3}) was added to a solution of **1a** (5.0×10^{-5} mol dm^{-3}) dissolved in the respective medium; under aerobic conditions without [Cob(II)-7C_3ester]ClO_4. [d] $APC[C_2Lys(C_5N^+)2C_{14}]_4$ (5.0×10^{-5} mol dm^{-3}) in aqueous phosphate-borate buffer (0.05 mol dm^{-3}, pH 9.2); **1**, 5.0×10^{-5} mol dm^{-3}; under anaerobic conditions.

TABLE II

Product analyses for photolysis of **2** and **2a** in various media at 20.0 ± 0.1°C.[a]

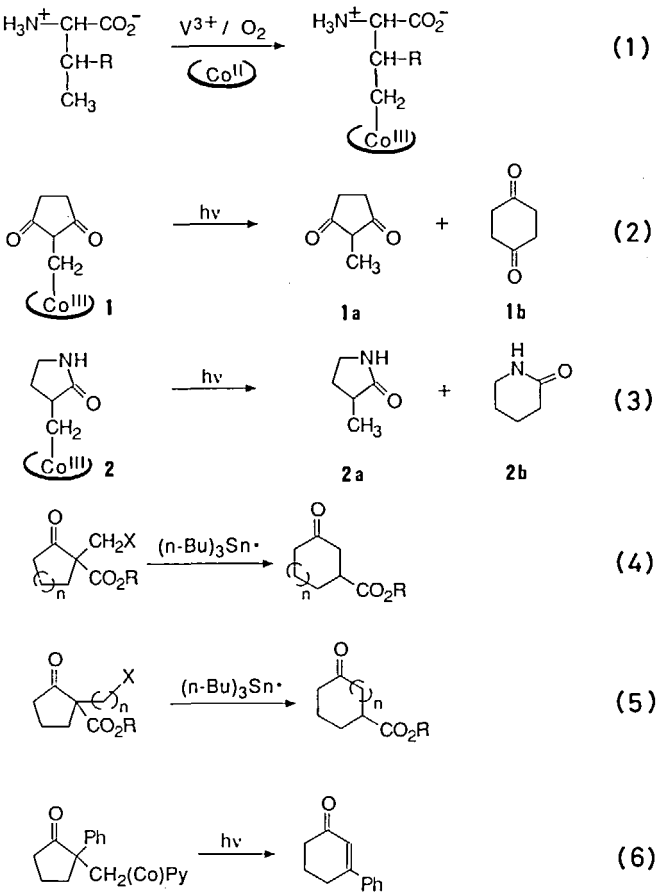
Medium	Reactant	Yield/%	
		2a	**2b**
Methanol	**2**[b]	83	3.0
	2a[c]	86	Trace
Benzene	**2**[b]	76	9.0
	2a[c]	83	2.0
$APC[C_2Lys(C_5N^+)2C_{14}]_4$	**2**[d]	61	26
	2a[c]	80	4.0

[a] A 20 cm^3 sample was irradiated with a 500 W tungsten lamp for 1 h at a distance of 30 cm. [b] **2**, 5.0×10^{-5} mol dm^{-3}; under anaerobic conditions. [c] A 1.5×10^{-2} cm^3 sample of aqueous 15% (w/w) perchloric acid containing vanadium trichloride (0.1 mol dm^{-3}) was added to a solution of **2a** (5.0×10^{-5} mol dm^{-3}) dissolved in the respective medium; under aerobic conditions without [Cob(II)-7C_3ester]ClO_4. [d] $APC[C_2Lys(C_5N^+)2C_{14}]_4$ (5.0×10^{-5} mol dm^{-3}) in aqueous phosphate-borate buffer (0.05 mol dm^{-3}, pH 9.2); **1**, 5.0×10^{-5} mol dm^{-3}; under anaerobic conditions.

RESULTS AND DISCUSSION

Carbon-skeleton rearrangement reactions as typically mediated by methylmalonyl-CoA mutase are known to be initiated by homolytic cleavage of the cobalt–carbon bond to form a 5′-deoxyadenosyl radical, which abstracts a hydrogen atom from a substrate to generate a substrate free radical.[1] The naturally occurring apoproteins,

which provide relevant reaction sites for vitamin B_{12}, are considered to play crucial roles in various isomerization reactions accompanied by carbon-skeleton rearrangements. We have been interested in the roles of such apoproteins and found previously that various carbon-skeleton rearrangement reactions, related to the methylmalonyl-CoA mutase reaction, are effectively mediated by the hydrophobic vitamin B_{12} in the octopus azaparacyclophane.[12,13,15] Our research interest is now focused on utilization of the artificial enzyme system for novel organic syntheses.



First, we prepared hydrophobic vitamin B_{12} derivatives bearing alkyl ligands, having five-membered rings, at one of the axial sites of the nuclear cobalt. There are various methods for preparation of hydrophobic vitamin B_{12} derivatives bearing various alkyl ligands.[7,16-19] Among them, a combination of molecular oxygen and vanadium(III) ions as oxidizing and reducing reagents, respectively, readily converts a methyl substituent, placed in substrate species, into the corresponding radical species which then undergoes coupling with a Co^{II} species as reported by Schrauzer and his associates (equation (*1*)).[7] We adopted their method in this work, and prepared two different alkylated complexes, **1** and **2**. The reactions shown by equations (*2*) and (*3*) were carried out by utilizing $APC[C_2Lys(C_5N^+)2C_{14}]_4$ in

aqueous phosphate–borate buffer at 20.0°C under anaerobic irradiation with visible light in a manner as described previously,[13] and the products, 2-methyl-1,3-cyclopentanedione (**1a**), 1,4-cyclohexanedione (**1b**), 3-methyl-2-pyrrolidinone (**2a**), and 2-piperidinone (**2b**), were analyzed by GLC. The product analyses for the reactions in various media are summarized in Tables I and II. These analytical results indicate that the conversions of the five-membered ring compounds into the corresponding six-membered ones take place much more favourably in the octopus cyclophane, relative to those in methanol and benzene. This finding means that the alkylated hydrophobic vitamin B_{12}'s are readily incorporated into the hydrophobic internal cavity of the octopus cyclophane, and the ring expansion is much enhanced under such microenvironmental conditions, in a manner as described previously.[13] The yields of the ring-expansion products are much low in the absence of the hydrophobic vitamin B_{12} regardless of the medium conditions as shown in Tables I and II. Thus, the hydrophobic vitamin B_{12} is undoubtedly the essential mediator for promotion of the ring-expansion reactions. Ring-expansion reactions shown by equations (*4*) and (*5*) were reported to proceed *via* free radical mechanism.[20,21] However, those reactions require much severe conditions, relative to the present reactions, and some experimental manipulation to avoid undesired side reactions. Photolysis reactions of 1-substituted 2-oxocyclopentylmethylcobaloximes were examined previously, and the corresponding six-membered cyclic olefins were obtained as shown by equation (*6*).[22] However, such cyclic olefins were not detected in the present study.

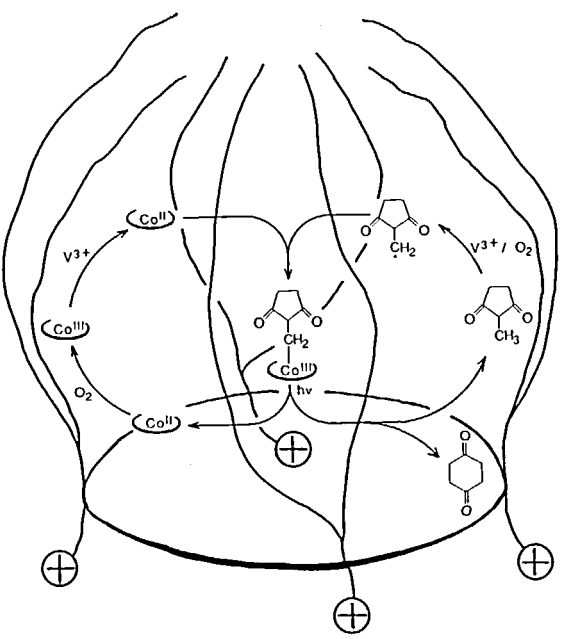


FIGURE 2 Schematic representation of catalytic ring-expansion reaction in the octopus cyclophane.

In the second place, a novel substrate-activation process, composed of molecular oxygen and vanadium trichloride, was coupled with the above mediator system, composed of [Cob(II)7C_3ester]ClO_4 and APC[C_2Lys(C_5N^+)2C_{14}]$_4$, to carry out the

catalytic conversion of the five-membered ring ketons into the corresponding six-membered ones. In the light of the above results, the reaction must proceed according to the following sequence along with turnover of the catalyst species in the presence of a large excess of vanadium trichloride under aerobic irradiation with visible light as illustrated in Figure 2: the substrate (**1a** or **2a**) is activated by vanadium(III) ions and molecular oxygen, and the alkylated complex (**1** or **2**) thus formed as the intermediate undergoes photolysis to afford the original substrate (**1a** or **2a**) and the ring-expansion product (**1b** or **2b**); **1a** or **2a** is re-cycled as the substrate. Vanadium trichloride acts not only as an activator for molecular oxygen but also as a reductant for the hydrophobic vitamin B_{12}, retaining the complex in the reactive Co^{II} state. The substrates, **1a** and **2a**, were converted efficiently into the corresponding ring-expansion products, **1b** and **2b**, respectively, in the presence of [Cob(II)7C_3ester]ClO_4 and the octopus cyclophane as shown in Figures 3 and 4, respectively (refer to equations (*7*) and (*8*), respectively). Judging from the time courses of the reactions shown in these figures, the reactions apparently proceed catalytically, and the substrates are expected to be completely converted into the corresponding ring-expansion products after a sufficient period of reaction time. On the other hand, only a small amount of **1b** or **2b** was detected without the hydrophobic vitamin B_{12} under otherwise identical conditions.

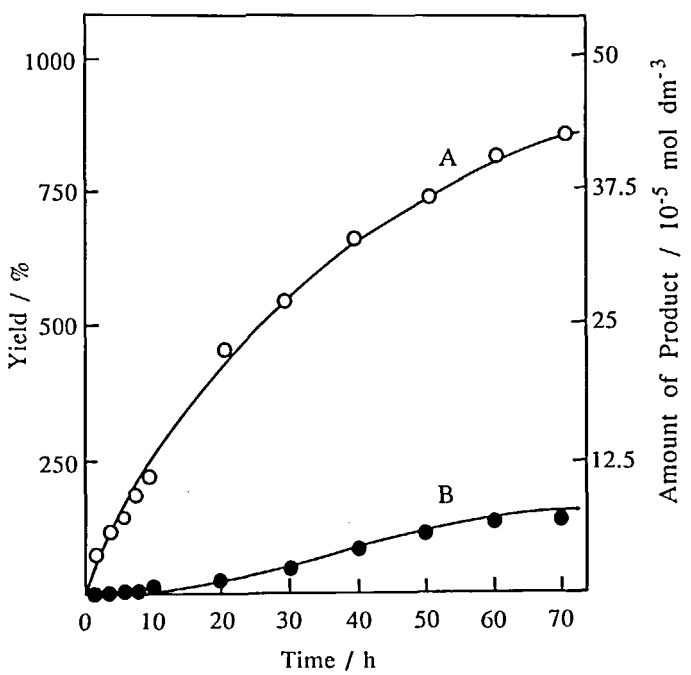


FIGURE 3 Conversion of 2-methyl-1,3-cyclopentanedione into 1,4-cyclohexanedione in the octopus cyclophane under aerobic irradiation conditions at pH 7.0 and 20.0 ± 0.1°C: APC[C_2Lys(C_5N^+)2C_{14}]$_4$, 5.0×10^{-5} mol dm^{-3}; 2-methyl-1,3-cyclopentanedione, 3.0×10^{-3} mol dm^{-3}; vanadium trichloride, 0.1 mol dm^{-3}. A, [Cob(II)7C_3ester]ClO_4 added (5.0×10^{-5} mol dm^{-3}); B, without [Cob(II)7C_3ester]-ClO_4.

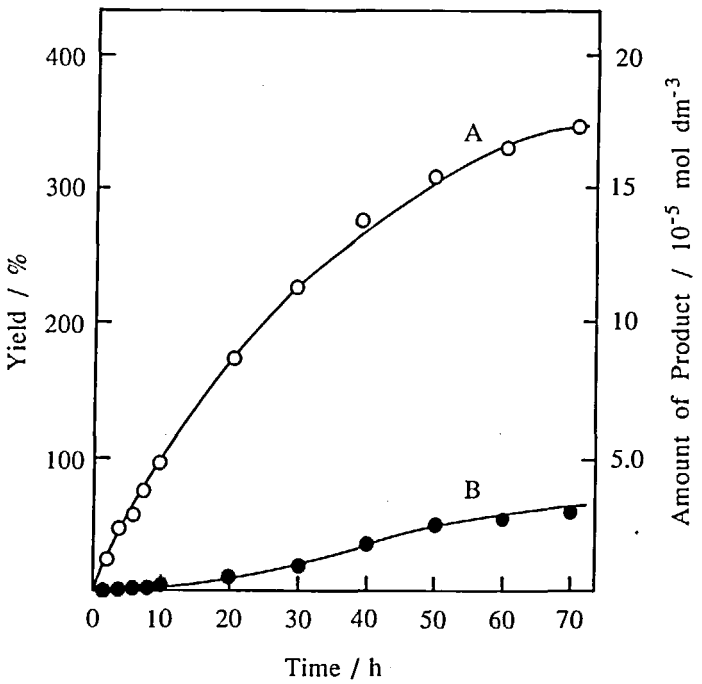
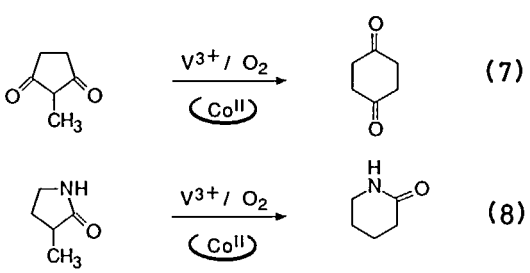


FIGURE 4 Conversion of 3-methyl-2-pyrrolidinone into 2-piperidinone in the octopus cyclophane under aerobic irradiation conditions at pH 7.0 and 20.0 ± 0.1°C: APC[C_2Lys(C_5N^+)2C_{14}]$_4$, 5.0×10^{-5} mol dm^{-3}; 3-methyl-2-pyrrolidinone, 3.0×10^{-3} mol dm^{-3}; vanadium trichloride, 0.1 mol dm^{-3}. A, [Cob(II)7C_3ester]ClO_4 added (5.0×10^{-5} mol dm^{-3}); B, without [Cob(II)7C_3ester]ClO_4.



In conclusion, the octopus azaparacyclophane is effective as an apoenzyme model for functional simulation of vitamin B_{12}-dependent enzymes. The non-enzymic 1,2-migration of the electron-withdrawing groups, as observed in the present ring-expansion reactions, must arise from both repression of molecular motion and desolvation effects operating on the alkylated complexes placed in the cyclophane, as clarified previously.[13] The nuclear bivalent cobalt of the hydrophobic vitamin B_{12} promotes the carbon-skeleton rearrangement *via* formation of a tight pair with the radical intermediate.[13] A combination of vanadium(III) ions and molecular oxygen is quite effective for activation of substrate species without utilizing activated substrates such as halogenated ones, and for regeneration of the active Co^{II} species so that the real catalytic cycle is performed.

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