Table I. Variation of ORD Intensity with Temperature (methanol solution)[a]

Compound	Temp (°C)	λ_{max}, nm	Relative rotation[b]
Ib	−15.0	254	1.00 ± 0.02
	+14.5		0.84
	+45.0		0.75
Ic	−15.0	261	1.00
	+15.0		0.88
	+45.0		0.76
Id	−14.0	258	1.00
	+14.0		0.86
	+45.0		0.64
Ie	−15.0	255	1.00
	+15.0		0.93
	+45.0		0.85
X	−15.0	263	1.00
	+14.8		0.94
	+45.0		0.91

[a] No appreciable changes in λ_{max} were observed upon change in temperature. [b] Corrected for expansion.

Table II. Variation of the Methyl Proton Resonances of 2,2'-Dimethyl-6,6'-dinitrobiphenyl (Ib) with Temperature

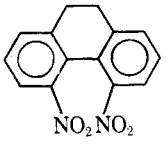
Temp (°C)[a]	Solvent	(Hz)[b]
55	Chlorobenzene	27.0 ± 0.1
41		28.2
34		28.3
28	Methylene chloride	23.7
2		24.5
−35		25.7
−48		26.0

[a] Calibrated from ethylene glycol and methanol resonances. [b] Downfield from the methyl resonance of internal toluene.

net conversion to a species of opposite rotation upon heating.

The proton nmr of Ib, provides some further confirmation of this explanation. The chemical shifts of the methyl protons of Ib (measured versus internal toluene) vary slightly with temperature as would be expected for an increase in IIb/IIIb with increasing temperature (see Table II).

The temperature dependence of the ORD spectra of 4,5-dinitro,9,10-dihydrophenanthrene[7] (X) was measured for comparison. Due to its dimethylene bridge, the 90° barrier VIII should not be accessible, effectively preventing equilibration of conformations analogous to II and III. As the data of Table I indicate, the temperature dependence of the rotation of X is significantly less than for Ib–c.



X

If optically active biphenyls have a single minimum between $\phi = 0$ and 180° the observed temperature dependence might be attributed to population of excited torsional vibrational modes about the C_1–C_1 bond. The observed decrease in rotation for Ib–e upon such a small increase in temperature would probably require extensive population of excited modes that were so anharmonic as to change the sign of the net rotation for these molecules but not for X. Upon consideration of the ORD and NMR evidence we feel the most likely conclusion to be that, even those biphenyls with fairly bulky groups on the ortho positions exist in pairs of disastereomeric conformations for each enantiomer in solution. These conformations are analogous to those reported for biphenyl, itself, in the gas phase.

Table III. Specific Rotation (methanol, 45°) at Peaks and Troughs[a]

Compound	Specific rotation (wavelength in nm)
Ib[b]	+13,000 (254), +3200 (280),[c] −880 (303), +590 (322), −2900 (~400)
Ic[b]	+450 (261), 300 (297),[c] −150 (370)
Id[b]	+670 (258), +10 (304), +66 (325), −130 (380)
Ie[b]	−4100 (255), −470 (304), −740 (316), +280 (364), −280 (445)
X	−18,000 (263), −7900 (285), −11,000 (300), +5000 (~350), −250 (445)

[a] The samples used were not necessarily optically pure. These values are nevertheless included upon the suggestion of a referee. [b] Specific rotation for these compounds under other conditions can be found in ref 5b. [c] Indicates shoulder.

Some useful analogies to the present work are provided by a recent study of 2,2-dithienyl which concluded that this molecule exists in two equilibrating conformations, reported to be the planar s-cis and s-trans,[8] the correlation of specific rotation with conformation in methyl 2-deoxy-α-L- and 3-deoxy-β-L-*erythro*-pentopyranosides,[9] and the correlation of rotation with temperature for di-5-(2'-deoxyuridilyl) disulfides.[10]

The biphenyls (Ib–e) were all prepared by published procedures.[11] The 2,2'-dinitrodiphenic acid was resolved with α-methylbenzylamine and 2,2'-dimethyl,-6,6'-dinitrobiphenyl was prepared from the resolved acid. Satisfactory spectra and elemental analyses were obtained for all compounds.

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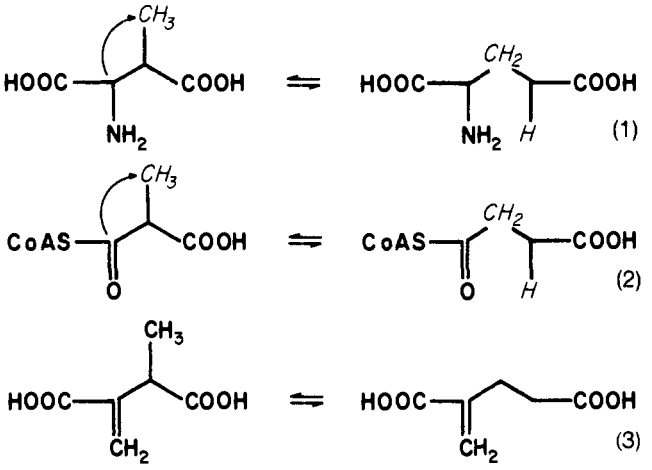
The Mechanism of Action of Vitamin B_{12}

Sir:

Vitamin B_{12}, in the form of its coenzyme, is an obligatory cofactor in ten, known enzyme-catalyzed rearrangement reactions.[1] Of the ten, three are carbon-skeleton rearrangement reactions. They are the reversible interconversions β-methylasparate ⇄ glutamate[2] (eq 1), methylmalonyl-CoA ⇄ succinyl-CoA[3] (eq 2), and β-methylitaconate ⇄ α-methyleneglutarate[4] (eq 3).



The outstanding feature of these reactions is the reversible conversion of an apparently unactivated methyl group into a methylene group, followed by incorporation of the latter into the backbone chain of the product (eq 1-3). These reactions hold special fascination because there have been no analogous transformations in organic chemistry and, thus, no suitable nonenzymatic model reactions. The difficulty in founding a secure chemical theory for these rearrangements is compounded by the absence of experimental knowledge of any reactive intermediates in the reactions. The only acceptable substrates for the enzymes which govern the rearrangements are those shown in eq 1-3.[5]

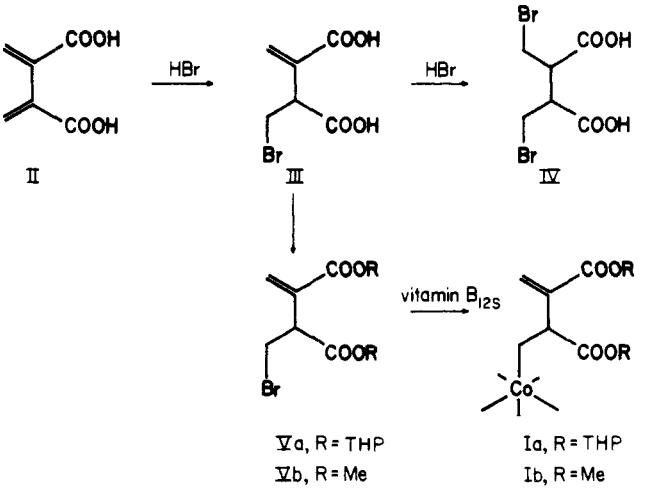
The course of the rearrangements follows from carbon-labeling experiments which dictate that in the β-methylaspartate rearrangement (eq 1) the glycyl fragment migrates to the methyl carbon as shown in eq 1 (arrow),[6] and in the methylmalonyl-CoA rearrangement (eq 2) the carbonyl-SCoA fragment migrates to methyl as shown in eq 2 (arrow).[7] Carbon-labeling has also been used to show that the methylmalonyl-CoA rearrangement (eq 2) is intramolecular.[8]

Formally, the hydrogen migration is intramolecular, as shown in eq 1 and 2 (italics). In fact, the transfer of hydrogen is intermolecular and is mediated by the 5′-methylene of the deoxyadenosine of the coenzyme.[9] This finding has been shown to apply to all the members of the coenzyme B_{12} series, including each of the three carbon-skeleton rearrangements of eq 1-3.[10,11]

As a result of the hydrogen-labeling experiments, one knows of the crucial role played by the deoxyadenosine in removing hydrogen from the substrate at an early stage in the reaction sequence then returning hydrogen to the substrate at a later stage.[9-11] By contrast, the requirements for the carbon-skeleton rearrangement, which occurs in the interim, are almost totally undefined.

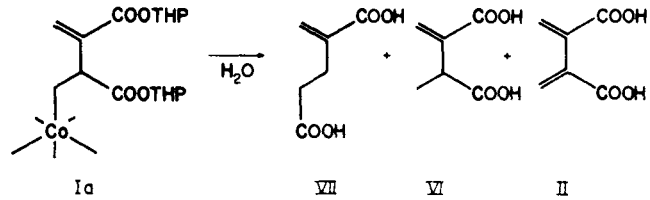
It appeared possible that this void might be filled by further synthetic exploration.

Accordingly, the derivatives I of vitamin B_{12}, in which the methyl carbon of methylitaconic acid is attached to cobalt, have been synthesized. Although many carbon-cobalt bonded derivatives of vitamin B_{12} have been prepared, these (Ia, Ib) are the first in which one of the substrates of the carbon-skeleton rearrangements of eq 1-3 has been attached to cobalt.[13] The synthesis of Ia and Ib was carried out as follows. Butadiene-2,3-dicarboxylic acid[14] (II) was treated in dioxane with 1.15 equiv of 32% HBr in acetic acid. The product was exclusively the monobromide III: mp 118-120°; NMR (acetone-d_6) three-proton aliphatic multiplet at τ 6.2, one-proton vinyl singlet at τ 4.0, and one-proton vinyl singlet at τ 3.6. Use of larger amounts of HBr leads to increasing amounts of the corresponding dibromide IV: mp 175-177°; NMR (acetone-d_6) two-proton multiplet at τ 6.7 and four-proton doublet (J = 5.2 Hz) at τ 7.4. The monobromide was esterified with dihydropyran in benzene and with methanol and HCl yielding the bis(tetrahydropyranyl) ester Va and the dimethyl ester Vb, respectively. The former is a relatively sensitive compound and should be stored at 0°. Both esters Va and Vb reacted smoothly with vitamin B_{12s} yielding the alkyl cobalamins Ia and Ib, respectively.[15] The dimethyl ester Ib is stable in the absence of light and can be purified in the same manner as other carbon-cobalt bonded derivatives of vitamin B_{12}.[12] By contrast, the bis(tetrahydropyranyl) ester Ia is quite sensitive. It cannot be purified by extraction with phenol[16] but is best simply precipitated from the aqueous reaction mixture with acetone. The resulting red solid is then washed repeatedly with acetone.[17]



When an aqueous solution of the bis(tetrahydropyranyl) ester cobalamin Ia is exposed to light (Westinghouse 275-W sunlamp) for 48-60 hr or allowed to stand *in the dark* for 168-200 hr, both reactions being conducted under an atmosphere of nitrogen, the slow formation of hydroxocobalamin is observed (development of the characteristic band at 352 mμ in the ultraviolet spectrum) in aliquots removed from the reaction mixture at 24-hr intervals. When the reaction was complete, it was made acid with 10% HCl, it was then extracted continuously overnight with ether. An NMR spectrum of the ether concentrate revealed the presence of three products derived from the organic ligand, β-methylitaconic acid[19] (VI), butadiene-2,3-dicarboxylic acid[14] (II), and α-methyleneglutaric acid[20] (VII), in the approximate ratio 1:2:1.[21]

The three products, II, VI, and VII, were separated from one another by chromatography on silica gel (elution with 20-25% ethyl acetate in hexane). The yields of *pure, re-*



crystallized products follow: α-methyleneglutaric acid (VII), 15%; methylitaconic acid (VI), 7%; and butadiene-2,3-dicarboxylic acid (II), 3.5%.[22,23,26]

The significance of this experiment lies in the isolation of α-methyleneglutaric acid (VII). *This is the first instance in which a derivative of a bona fide substrate molecule has been induced to undergo the carbon-skeleton rearrangement in association with vitamin B_{12} and in the absence of any enzyme.* The conditions under which the reaction was carried out, in the dark, under anaerobic conditions and at ambient temperature, make it highly probable that this is a direct reflection of the mode of action of vitamin B_{12} when it is bound to the enzyme. It is especially significant that the rearrangement occurs in the absence of enzyme. This signals a much stronger role for the coenzyme than has hitherto been imagined possible.[1g] That the rearrangement occurs starting from a cobalt–carbon bonded precursor demonstrates the value of the hypothesis which has been advanced for the intermediate formation of the cobalt–carbon substrate bond and the exchange reaction leading thereto.[24]

This discovery opens the way to detailed exploration of the mechanism of the rearrangement reaction, unencumbered by the enzyme. Indeed, the enzyme may ultimately be relegated to the secondary roles of substrate guidance and rate enhancement. It remains to be seen whether the important stereospecificity associated with most of the rearrangements lies in the province of the enzyme or that of the coenzyme.

Stripped of the enzyme in its role as *deus ex machina*, the mechanism of the rearrangement reaction appears, as one possibility, to be that of the reversible interconversion of allylcarbinyl isomers. One might speculate on the possible further intermediacy of the cyclopropane isomer in this reaction. The unique advantage of the present work is that both these and many other hypotheses can now be explored experimentally, whereas previously, they could not be tested at all.[4] Since both organometallic derivatives and carbonium ions allow the interconversion of allylcarbinyl isomers,[25] we prefer, at this time, to reserve judgement on the charge states of cobalt and carbon in the rearrangement. Indeed, the advantage of cobalt may lie in its ready assumption of any one of three valence states, thus to accommodate the diverse substrates of the several enzyme reactions dependent on coenzyme B_{12}.[27]

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(15) Vitamin B_{12s} was prepared by sodium borohydride reduction of hydroxocobalamin.[12]

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(17) The properties of the alkyl cobalamins Ia and Ib follow. The dimethyl ester Ib showed λ_{max}^{water} (ε): 333 (10,600), 375 (9400), 525 mμ (7500). On 0.1-mm Cellulose F plates (E. Merck), relative to cyanocobalamin as 1.0, the dimethyl ester Ib showed R_{CN} (solvent system): 1.38 (2-butanol, water, 25% ammonium hydroxide, 50:36:14), 1.47 (1-butanol, ethanol, water; 50:15:35), and 1.48 (1-butanol, 2-propanol, water; 37:26:37).[18] In keeping with its sensitivity toward decomposition, we have been unable, as yet, to obtain well-defined and well-resolved chromatograms of the bis(tetrahydropyranyl) ester Ia. The intensity of absorption of Ia was estimated by allowing it to decompose with light to hydroxocobalamin, then comparing the relative intensities of the absorptions. Thus, the spectrum of Ia shows λ_{max}^{water} (ε): 525 (7280), 438 (4480, sh), 372 (9120, sh), 337 (12,150), 312 mμ (12,660); and λ_{min} 410 mμ (3820). In acid solution the diester Ia showed $\lambda_{max}^{(0.1\ N\ HCl)}$ (ε): 460 (6400), 375 (4500, sh), 352 (7400), 316 (12,400), 306 mμ (13,500); and λ_{min} 410 mμ (3200). When the acid solution was made basic with KOH, the spectrum returned nearly to that of the original alkyl cobalamin Ia with λ_{max} (ε): 510 mμ (5400) but with a new peak at 352 mμ (9400) signaling the rise of hydroxocobalamin.

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(21) Whereas the ratio of α-methyleneglutarate (VII) to the other two products was reasonably constant in a number of experiments, the ratio of butadiene-2,3-dicarboxylic acid (II) to methylitaconic acid (VI) varied from 1:2 to 2:1 over several experiments. The reason for this variation is not known.

(22) Cf. J. N. Lowe and L. L. Ingraham, *J. Am. Chem. Soc.*, **93**, 3801 (1971).

(23) The product yields are calculated on the basis of the amount of hydroxocobalamin used in the reaction, since the conversion to alkyl cobalamin appears to be quantitative. The per cent yields quoted in the text were taken from an experiment in which 1.639 g of hydroxocobalamin was used, where the theoretical yield of product derived from the organic ligand would be 0.177 g. The first product to be eluted in the second chromatography was α-methyleneglutaric acid (VII) which, after two recrystallizations (ether–$CHCl_3$ and $CHCl_3$–CCl_4), weighed 0.026 g and had mp 126–128° (Fisher-Johns hot stage) and 130–132° (capillary), reported[20] mp 130–132°. The second product to be eluted was methylitaconic acid (VI) which, after one recrystallization (ether–$CHCl_3$) weighed 0.012 g and had mp 150–151°, reported[19] mp 150–152°. The final product to be eluted was butadiene-2,3-dicarboxylic acid (II) which, after one recrystallization (Et_2O–$CHCl_3$–Me_2CO), weighed 0.006 g and had mp 182–185°, reported[14] mp 185–187°. The spectral properties (ir and NMR) of the above products were in excellent agreement with those of authentic samples of these substances.

(24) Numerous authors have considered the intermediacy of organocorrin intermediates to be likely in these rearrangements. See ref 1g, 1h, 11, and 13. See also R. B. Silverman, D. Dolphin, and B. M. Babior, *J. Am. Chem. Soc.*, **94**, 4030 (1972), and R. H. Abeles, "Proceedings of the Robert A. Welch Conferences on Chemical Research, XV, Bio-Organic Chemistry and Mechanism, W. O. Milligan, Ed., Houston, Texas, 1972, p 113, together with the remarks of R. Breslow, pp 119 and 120, at that meeting.

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(26) A control reaction in which the bis(tetrahydropyranyl) bromomethylitaconate (Va) was allowed to react in the absence of hydroxocobalamin ($NaBH_4$ in water followed by quenching with acetone, sunlamp illumina-

tion, and extraction with ether following acidification with HCl) yielded no detectable rearrangement product, α-methyleneglutaric acid (VII). The same result, negative with respect to rearrangement product VII, was obtained when the entire reaction sequence was carried out with Va and cobalt(II) nitrate in place of hydroxocobalamin.

(27) Note Added in Proof. We have found that the reaction reported above (Ia → VII + VI + II) is quite sensitive to temperature. The best yields of rearranged product, α-methyleneglutaric acid (VII), are obtained when the temperature of the reaction is maintained at 20°C or slightly below.

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Medium Effects on the Hexacyanocobaltate(III) Photoaquation. Evidence for the Occurrence of Cage Recombination in Ligand Photosubstitution Reactions

Sir:

The cage effect[1] may be expected to affect virtually every type of dissociative photochemical reaction in solution, provided that the geminate products are reactive enough to recombine appreciably during the very short lifetime of the solvent cage. The occurrence of cage recombination has been extensively documented and studied in the photochemical homolysis of many organic and simple inorganic molecules.[2] In spite of a long standing mechanistic proposal[3] which included cage recombination, the importance of such processes in the photochemistry of coordination compounds has only very recently been experimentally demonstrated. In fact, efficient radical cage recombination has been shown to occur in a number of homolytic photoreactions of coordination compounds, namely, in the redox decomposition of cobalt(III) complexes.[4,5] For the other most important class of photoreactions of coordination compounds, namely, ligand photosubstitution, the possibility of cage recombination has never been considered. As a matter of fact, ligand photosubstitution involves heterolytic metal–ligand bond splitting, and the geminate products of such a process are not highly reactive radical species. However, the presence of a vacant coordination site at the metal could easily entail a reactivity high enough to allow recombination prior to the cage breakdown. Thus, the importance of cage recombination in ligand photosubstitution is up to now a matter for speculation awaiting appropriate experimental testing. An experimental study of the solvent dependence of a typical ligand photosubstitution reaction[6] is reported in this communication which provides evidence for the occurrence of cage recombination in this type of photoreaction.

A considerable amount of mechanistic information is already available on the photoaquation of the hexacyanocobaltate(III) ion. Reaction 1

$$Co(CN)_6^{3-} + H_2O \xrightarrow{h\nu} Co(CN)_5H_2O^{2-} + CN^- \qquad (1)$$

is known to occur very cleanly in aqueous solution with quantum yield 0.31, independent of pH, CN^- concentration, and wavelength of excitation in the whole ligand field region.[7] The first excited singlet $^1T_{1g}$ is populated with unit efficiency either by direct light absorption or by internal conversion from the upper $^1T_{2g}$ one. The reactive state is the lowest triplet $^3T_{1g}$ which aquates with almost unit efficiency and is populated from the lowest singlet by a moderately efficient ($\Phi_{ISC} \approx 0.4$) intersystem crossing process.[8] As to the chemical mechanism of the photoaquation reaction, there is little doubt that this process, which occurs thermally via dissociative activation,[9] must be an essentially dissociative one (D or I_d in Langford and Gray's nomenclature).[9] Experimental studies on the photosubstitution reactions of several acidopentacyanocobaltates have confirmed this prediction.[10,11]

Table I. Solvent Effects on the Hexacyanocobaltate(III) Photoaquation

Solvent	%[a]	ε[b]	η[c]	Φ[d]
Water	–	78	1.0	0.31
Methanol–water	60	54	1.7	0.27
Glycerol–water	20	73	2.0	0.24
Ethanol–water	60	50	2.6	0.25
Glycerol–water	40	67	4.7	0.17
Ethylene glycol–water	60	57	5.3	0.14
Glycerol–water	60	60	14.7	0.10

[a] Volume per cent of the alcoholic solvent. [b] Bulk dielectric constant of the solvent mixtures.[13] [c] Bulk viscosity of the solvent mixture.[14] [d] Photoaquation quantum yields; experimental conditions as in ref 12.

We have now studied the photoaquation $Co(CN)_6^{3-}$ in a variety of water–alcohol solvent mixtures. The spectra of both $Co(CN)_6^{3-}$ and $Co(CN)_5H_2O^{2-}$ were appreciably the same in all the solvent systems used and no qualitative changes in photochemical behavior were observed when changing the solvent with respect to pure water. In all of the solvent systems used, the extent of thermal back-anation was absolutely negligible in the time scale of the experiments. The quantum yield values[12] for reaction 1 in the various solvent systems used are collected in Table I.

Inspection of the table reveals a pronounced variation of the photoaquation quantum yields with the solvent composition. One may notice that the quantum yield values are not simply related to the amount of water in the solvent mixture. Furthermore, the nature of the alcoholic solvent, and in particular its hydrogen bonding ability, which might affect the excited state lifetime of cyanide complexes,[15] seems to be of negligible importance in determining the observed trend. As far as the bulk physical properties of the solvent mixtures are concerned, Table I shows that the quantum yields correlate remarkably well with the solvent viscosity, exhibiting a continuous decrease as the solvent viscosity is increased (Figure 1). On the other hand, no such regular correlation has been found for any other relevant physical property of the solvent (see, for example, the dielectric constant values which have been included in Table I for the sake of comparison).

These observations are strongly indicative of a cage recombination mechanism for the photoaquation of $Co(CN)_6^{3-}$. The following simplified mechanism can be formulated in order to account for the observations:

$$Co(CN)_6^{3-} \xrightarrow{h\nu} {}^*Co(CN)_6^{3-} \qquad (2)$$

$${}^*Co(CN)_6^{3-} \rightarrow Co(CN)_6^{3-} \qquad (3)$$

$${}^*Co(CN)_6^{3-} \rightarrow [Co(CN)_5^{2-}\cdot CN^-]_{cage} \qquad (4)$$

$$[Co(CN)_5^{2-}\cdot CN^-]_{cage} \rightarrow Co(CN)_6^{3-} \qquad (5)$$

$$[Co(CN)_5^{2-}\cdot CN^-]_{cage} \xrightarrow{H_2O} Co(CN)_5H_2O^{2-} + CN^- \qquad (6)$$

According to such a mechanism, the observed photoaquation quantum yield is given by

$$\Phi = \frac{k_4}{(k_3 + k_4)} \frac{k_6}{(k_6 + k_5)} = \Phi' \frac{k_6}{(k_6 + k_5)} \qquad (7)$$

where Φ' is the primary quantum yield of bond cleavage. While a dependence of Φ' on the solvent composition cannot be definitely ruled out, the experimental results seem to indicate that the major source of the observed medium effects is the competition between processes 5 and 6. The rate constant for diffusive cage escape, k_6, is expected to decrease