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A Novel Rearrangement of Butenylcobaloximes. A Mechanism for Some Coenzyme B_{12} Catalyzed Rearrangements

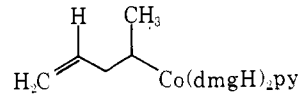
Sir:

Coenzyme B_{12} catalyzes a number of interesting rearrangements of organic molecules in biological systems,[1] two of which, the rearrangement of methylene glutarate to methylitaconate and the rearrangement of methylmalonyl- to succinyl-coenzyme A, can be represented by the general equation 1. Whilst there have been a number of indications that

(1)

i, X = CH_2; Y = CO·SCoA; Z = CO_2H

ii, X = O; Y = SCoA; Z = CO_2H



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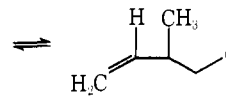

(2)

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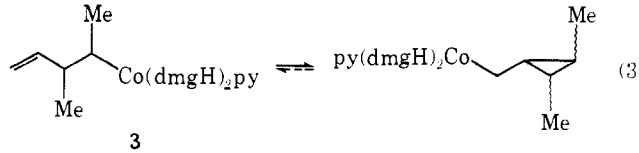
radical intermediates including cobalt(II) complexes[2] and organic radicals[3] may be involved, no really satisfactory explanation for the rearrangement of the organic fragment[4] and for the role of the cobalt(II) in these rearrangements has yet been proposed.

We have observed that freshly purified 1-methylbut-3-enylcobaloxime (**1**) and 2-methylbut-3-enylcobaloxime (**2**)[5] rearrange (4 M in $CDCl_3$ under N_2) to an equilibrium mixture containing **1** and **2**[6] in a ratio of ~1:10 (eq 2). The half-life[7] for the approach to equilibrium[8] from **1** or from **2** is ~100 min at 53 °C, but is very sensitive to the purity of the materials, the concentration, and other factors, as follows. (a) The half-life to equilibrium is increased 6-fold in the presence of 25 mol % di-*tert*-butylnitroxyl radical[9] *without detectable loss of organocobaloxime* in the period to complete equilibration. (b) The half-life is decreased 20- and 40-fold, respectively, in the presence of 1 and 2 mol % aquocobaloxime (**II**).[10] (c) The half-life is slightly increased in the presence of 100 mol % bromotrichloromethane, though there is considerable loss of organocobaloxime with concurrent formation of 1-methyl-2-(β,β,β-trichloromethyl)cyclopropane (**5**)[11] and bromocobaloxime(III) (**6**). (d) The half-life is increased ~8-fold when dichloromethane is used as solvent, and is longer still in dichloromethane–methanol mixtures. (e) With oxygen bubbling through the solution, equilbrium is attained with the loss of only ~30% of the total organocobaloxime.[13] (f) The half-life is increased in the presence of added pyridine. (g) The half-life is decreased in the presence of trifluoroacetic acid. With 250 mol % trifluoroacetic acid, equilibrium is attained within a few minutes at ambient temperature and without loss of organocobaloxime.

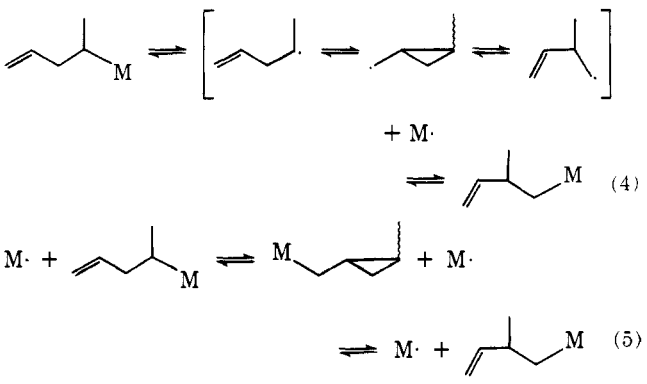
The above results clearly implicate cyclopropylcarbinyl intermediates and, indeed, 1,2-dimethylbut-3-enylcobaloxime (**3**) rearranges during purification to isomers of the corresponding 2,3-dimethylcyclopropylcarbinylcobaloxime (**4**)



(3)

3 4

0002-7863/78/1500-3217$01.00/0

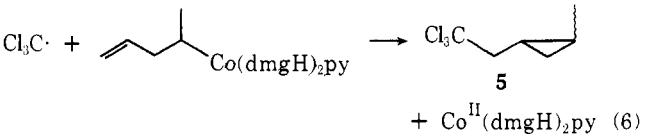


$M\cdot = Co^{II}(dmgH)_2py$

(eq 3). Such cyclopropylcarbinyl intermediates might be formed by a unimolecular mechanism[14] (shown in eq 4 as a process involving radical and cobalt(II) intermediates) or by a bimolecular mechanism (shown in eq 5 for a process involving homolytic displacement).

The three dissociative unimolecular processes can be ruled out: observations a and e above rule out the possibility of free organic radicals; observation e also rules out any cobaloxime(I)[15] formed in a carbonium ion mechanism; and observation g rules out any carbanion intermediates.

The bimolecular homolytic displacement mechanism is supported by the marked catalysis by small amounts of aquocobaloxime(II), and the formation of **5** and **6** in good yield when bromotrichloromethane is added to the solution is indicative of the presence of the required cobaloxime(II) and of trichloromethyl radicals formed by the chain reactions shown in eq 6 and 7. Reaction 6 is only one of a series of bimolecular



$$+ Co^{II}(dmgH)_2py \quad (6)$$

$$Co^{II}(dmgH)_2py + BrCCl_3 \longrightarrow BrCo^{III}(dmgH)_2py + Cl_3C\cdot \quad (7)$$

6

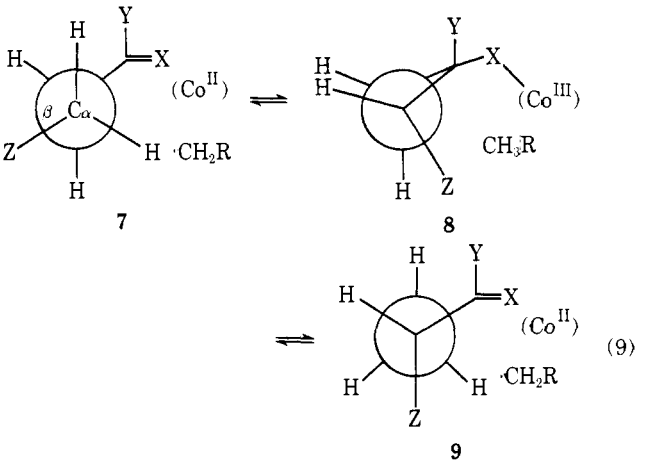
homolytic cyclizations of butenylcobaloximes induced by attack of electrophilic radicals at the δ carbon of the butenyl group and involving displacement of cobaloxime(II) species.[17] This, together with our studies on the displacement of cobaloxime(II) from alkyl-, benzyl-, and allylcobaloxime(III) complexes by other cobaloxime(II) species,[18,19] give adequate precedent for eq 5.

The other observations are also in accord with this bimolecular mechanism: the reduction in rate in the presence of bromotrichloromethane can be ascribed to some loss of cobaloxime(II) through the termination step 8;[20] the influence of solvent to the ease with which initiating radicals are formed at the reaction temperature;[21] the influence of pyridine to its ability to coordinate to the low concentration of cobaloxime(II), thereby reducing its electrophilic character; and the influence of trifluoroacetic acid to its ability to trap the pyridine, thereby reversing the latter process, and to weaken the carbon-cobalt bond by protonation of one or both dimethylglyoximato ligands of the butenylcobaloxime.[22]

In principle, reaction 5 can also take place with cobaloxime(III) as the attacking species, but this is unlikely in the present case, not only because of the low lability of the six-coordinate cobaloxime(III) complexes, but also because added chlorocobaloxime(III) and added electrophiles such as $Hg(OAc)_2$, which might be expected to induce the formation of some five-coordinate cobaloxime(III) species, have no accelerating effect on the reaction.

$$Cl_3C\cdot + Co^{II}(dmgH)_2py \rightarrow Cl_3C\text{-}Co(dmgH)_2py \quad (8)$$

The ability of cobaloxime(II) to induce both ring closure and opening suggests a simple but novel mechanism for the related B_{12} catalyzed rearrangements of eq 1. Homolysis of the carbon-cobalt bond of the coenzyme is followed by the well-established abstraction of the appropriate hydrogen atom from C_α of the substrate **7**.[23] If this abstraction is assisted by attack of the cobalamin(II) fragment (B_{12r}) on the terminal unsaturated atom X, the resulting intermediate is a cyclopropylcarbinyl cobalamin (**8**) (or a related species where X = O). Transfer of a hydrogen atom from the adenosine fragment back to the intermediate at C_β with concurrent, prior, or subsequent loss of the cobalamin(II) fragment results in the ring opening of the cyclopropane ring and formation of the observed rearrangement product **9**.



$RCH_2(Co^{III})$ = coenzyme B_{12}

This mechanism requires retention of configuration in the hydrogen transfer, which is the observed stereochemistry in the methylmalonyl/succinyl system.[24,25] Moreover, the above mechanism provides a role for the cobalt fragment which could be particularly important if the prior loss of cobalt in the final stage of the rearrangement were to provide the driving force for the hydrogen transfer from the adenosine. At no stage is it necessary to postulate free organic radicals derived from the substrate.

Acknowledgment. We thank the Science Research Council and Imperial Chemical Industries Ltd., Plant Protection Division, for the award of a CASE studentship (to A.B.) and Dr. R. Huff for valuable discussions.

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(5) All compounds described here have been characterized by elemental

analysis and ^1H and ^{13}C NMR spectroscopy.
(6) The rearrangement was followed by observation of the methyl (doublet) proton resonances at δ 0.5 and 0.9 for **1** and **2**, respectively.
(7) We quote half-lives because, like a number of other reactions of organocobalt, -rhodium, and -iridium complexes which involve radical-chain displacements, the reactions proceed smoothly but show a characteristic dependence on the rate of initiation.
(8) We cannot rule out the presence of small quantities of methylcyclopropylcarbinylcobaloximes in the equilibrium mixture.
(9) Nitroxyl radicals broaden the ^1H NMR spectrum, but this is not sufficient to prevent observation of the rearrangement. The addition of diamagnetic traps such as nitrones has no effect on the rate.
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(11) The formation of 1-methyl-2-(β,β,β-trichloromethyl)cyclopropane has been the subject of an independent study.[12]
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(19) Bimolecular displacement of cobaloxime(II) from alkylcobaloxime(III) complexes by cobaloxime(II) reagents has been described in detail: D. Dodd, M. D. Johnson, and B. L. Lockman, *J. Am. Chem. Soc.*, **99**, 3664 (1977). Bimolecular displacement of cobaloxime(II) from allylcobaloxime(III) complexes by cobaloxime(II) reagents can be sufficiently fast as to be evident on the NMR time scale. This accounts, at least in part, for the dynamic character of allylcobaloximes: C. J. Cooksey, D. Dodd, B. D. Gupta, and M. D. Johnson, unpublished work; D. Dodd and M. D. Johnson, *J. Am. Chem. Soc.*, **96**, 2279 (1974).
(20) Trichloromethylcobaloxime is readily formed by the reaction between bromotrichloromethane and cobaloxime(II) by a two-step mechanism involving reactions 7 and 8.
(21) Any halogenomethyl radical from a chlorinated solvent can replace $Cl_3C\cdot$ in reaction 5, thereby causing the production of cobaloxime(II).
(22) Diprotonation of benzylcobaloxime leads to the formation of dibenzyl in good yield.
(23) In several rearrangements catalyzed by coenzyme B_{12}, it has been shown that the hydrogen atom from the substrate is transferred to the 5′ carbon of the adenosyl moiety; one of the three equivalent hydrogens of the 5′-methyl group is then transferred back to the substrate fragment.[1]
(24) M. Sprecher, M. J. Clark, and D. B. Sprinson, *Biochem. Biophys. Res. Commun.*, **15**, 581 (1964); *J. Biol. Chem.*, **241**, 872 (1966); J. Retey and F. Lynen, *Biochem. Biophys. Res. Commun.*, **16**, 358 (1964); J. Retey and B. Zagalak, *Angew. Chem.*, **85**, 721 (1973).
(25) Only one conformation of the substrate **7** is shown in reaction 9. Reaction of the other conformation would equally give retention of configuration.

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Effect of Anion Type on Rate of Facilitated Transport of Cations across Liquid Membranes via Neutral Macrocyclic Carriers

Sir:

Transport of cations across a hydrophobic organic layer (liquid membrane) which separates two water phases has attracted recent interest.[1] The carrier is usually a synthetic or naturally derived cyclic multidentate ligand. When such uncharged carrier ligands are employed, the complexed cation carries its anionic counterion(s) with it through the organic phase.[2,3] The nature of the anion should thus be a factor in determining the rate of cation transport.[4] We show here that the rate of transport of a given cation through such a membrane can be varied by several orders of magnitude simply by altering the anion present in the original salt solution.

Two crown ethers, dibenzo-18-crown-6 and *tert*-butylbenzo-15-crown-5, were used as membrane carriers inasmuch as the cation-binding properties of 18-crown-6 and 15-crown-5 ligands and their derivatives have been studied more extensively than those of other synthetic macrocycles.[5,6] The liquid membrane system used was adapted from the work of Kobuke et al.[7] and is similar in principle to the Schulman Bridge used by Cussler[4] and Smid[2] and their co-workers. A chloroform layer containing 7.0×10^{-4} M carrier sits at the bottom of a deep evaporating dish and is stirred by a magnetic stirrer driven at 200 rpm. Atop this layer are two water phases separated by a glass cylinder. The inner phase (transfer surface area = 36.3 cm^2, volume = 42 mL) is a concentrated salt solution serving as the cation source and the outer phase (transfer surface area = 76.8 cm^2, volume = 168 mL) is a receiving solution for transferred salt. Vessels were covered and maintained at 25 ± 0.5 °C in a thermostated room. Experimental runs were conducted over a two-day time period during which 2-mL samples were withdrawn at intervals from the receiving water phase. These samples were analyzed for cation concentration on a Perkin-Elmer Model 603 atomic absorption spectrophotometer.

Salts of four cations, Li^+, Na^+, K^+, and Ba^{2+}, were used in this study, the latter three of which are known to bind to dibenzo-18-crown-6 in both water and methanol.[5] Reaction has also been reported in these solvents between Na^+ and K^+ and benzo-15-crown-5.[5] Molar concentrations of the salt solutions used are listed in Table I. At least three separate units were employed in the determination of cation transport rate for each salt-macrocycle combination. One of these contained a blank membrane having no macrocycle carrier, while the other two or more which contained carrier served to produce the results listed in Table I. In no case was there any detectable movement

Table I. Rate of Transfer of Various Salts through a Chloroform Membrane Containing 7×10^{-4} M Dibenzo-18-crown-6 or *tert*-Butylbenzo-15-crown-5

Salt		Transfer rates,[a] (mol/h) × 10^7	
Type	Concn, mol/L	Dibenzo-18-crown-6[b]	*tert*-Butylbenzo-15-crown-5[c]
LiCl	1.0	0	0
LiBr	1.0	0	0
LiI	1.0	0.33	0
NaCl	1.0	0.31	0
NaBr	1.0	1.6	0
NaI	1.0	15	0
KF	1.0	0.85	
KCl	1.0	6.1	0.17
KBr	1.0	88	1.8
KI	1.0	620	36
KI	0.50	370	
KI	0.10	34	
KI	0.010	0.46	
KNO_3	1.0	250	1.9
KOH	1.0	2.1	
$KClO_4$	0.10	123	2.0
K acetate	1.0	1.4	
K benzoate	1.0	110	
K picrate	0.0020	510	2.1
K_3PO_4	1.0	<1	
K_2HPO_4	1.0	<1	
KH_2PO_4	1.0	290	1.3
KBF_4	0.020	3.1	0
KPF_6	0.020	66	0.78
$BaCl_2$	1.0	<1	
$BaBr_2$	1.0	<1	
BaI_2	1.0	280	

[a] Each value is the average of two or more independent determinations. The experimental values deviate from the reported values by an average of ±10%. [b] 2,3,11,12-Dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene. [c] 2,3-(4′-*tert*-butyl)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene.

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