(**14**);[15] protoadamantane (**3**)[5,16] was the second. From the relative proportions of isomers in the rearrangement of *exo*-**8**, it is possible to derive relative rate constants for each step.[17] On the basis of three separate isomerizations, rate constants relative to **3** → **1** are 0.6 for *exo*-**8** → **14** and 0.05 for **14** → **3**.

These results are consistent with the proposed pathway deduced on the basis of the molecular mechanics calculations. The darkened lines and arrows in Figure 1 represent our predictions of the most favorable pathways leading from each tricyclodecane to adamantane (**1**). We are testing these predictions experimentally in conjunction with ^{13}C labeling techniques and are employing this approach for the elucidation of other polycyclic rearrangement mechanisms.

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(15) Prepared from 2,6-trimethylenenorbornan-2-ol (ref 14) by treatment with PBr_3, followed by reduction with $LiAlH_4$ (*m/e* 136).
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Reactions of Vinyl Ethers with Cobalamins and Cobaloximes

Sir:

Vinyl ethers were recently claimed[1] to react with Co(III) derivatives of vitamin B_{12}, *i.e.*, hydroxocobalamin, and with cobaloximes such as bromo(pyridine)cobaloxime, to yield organocobalt compounds according to eq 1. Reaction eq 1 was assumed to

$$[Co^{III}] + CH_2{=}CHOR \longrightarrow \underset{\mathbf{1}}{[Co](CH_2{=}CHOR)} \xrightarrow{OR^-} \underset{\mathbf{2}}{[Co]CH_2CH(OR)_2} \quad (1)$$

proceed *via* a π complex, **1**, of the vinyl ether with the Co(III) starting materials, whose subsequent reaction with alkoxide ion was proposed to yield acetals of the corresponding formylmethylcobalt complexes **2**. A reaction of the type written in eq 1 would represent an intriguing new pathway for the synthesis of organocobalt compounds in protic media, and parallels were drawn to certain coenzyme B_{12} dependent enzymatic reactions, *i.e.*, dioldehydrase. Unfortunately, all our attempts to reproduce reaction **1** have been unsuccessful. We also failed to detect the formation of π complexes of the Co(III) complexes with vinyl ethers (R = *e.g.*, C_2H_5, eq 1). Although complexes of this type have been postulated as reactive intermediates in the solvolysis of 2-acetoxyethylcobaloximes,[2] their direct formation according to eq 1 could not be demonstrated neither by us nor by Dolphin and Silverman, using various spectroscopic and synthetic techniques. The existence of π complexes such as **1** would seem doubtful in view of the inability of the Co(III) ion to form sufficiently stable d_π–p_π bonds with organic π-electron systems. The $CH_2{=}CH$ moiety in vinyl ethers could also not be regarded as sufficiently strongly σ bonding to coordinate with the Co(III) ion in corrins or cobaloximes. Although the reaction of hydroxocobalamin with 2-hydroxyethyl vinyl ether or ethyl vinyl ether was claimed to produce mixtures of formylmethylcobalamin with the corresponding acetals of formylmethylcobalamin quantitatively,[3,4] this could not be reproduced under a variety of conditions. Upon addition of ethoxide ion or of NaOH, to a mixture of these vinyl ethers and hydroxocobalamin in ethanol or ethanol–water, only a slow formation of a Co(II)–corrin was observed which also occurred in the absence of vinyl ethers. The formation of reduced corrins from hydroxocobalamin in alkali is well known.[5] We also failed to obtain the corresponding organocobaloxime derivative by allowing bromo(pyridine)cobaloxime to react with ethyl vinyl ether in the presence of ethanol, CH_2Cl_2, and varying amounts of triethylamine; the only product isolated was pyridinecobaloxime(II).[6,7] These results demonstrate that the Co(III) starting materials cannot even be maintained in this oxidation state under the reaction conditions.

In subsequent experiments we also examined the reaction of vinyl ethers with vitamin B_{12r}, vitamin B_{12s}, and with hydridocobalamin.[8] Only the latter, generated from hydroxocobalamin by reduction with Zn in glacial acetic acid, underwent reaction, however, affording a mixture of ethylene and ethane. Initially,

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(2) (a) B. T. Golding, H. L. Holland, U. Horn, and S. Sakrikar, *Angew. Chem., Int. Ed. Engl.*, **9**, 959 (1970); (b) R. B. Silverman, D. Dolphin, and B. M. Babior, *J. Amer. Chem. Soc.*, **94**, 4028 (1972).
(3) Formylmethylcobalamin, the corresponding cobaloximes, and their acetals were synthesized by the authors of ref 1, as well as by us,[4] utilizing conventional reductive alkylation techniques. The reported properties of the cobalamin derivatives are in slight disagreement, however. Silverman and Dolphin claim that the acetals of formylmethylcobalamin undergo simple hydrolysis to yield formylmethylcobalamin on protonation. In contrast, we observed that the acetals decompose on protonation with Co–C bond cleavage. We found no evidence for the intermediate formation of formylmethylcobalamin, which, if formed, should have been readily detectable in view of its stability in neutral and weakly acidic aqueous media.
(4) G. N. Schrauzer, W. J. Michaely, and R. J. Holland, *J. Amer. Chem. Soc.*, **95**, 2024 (1973).
(5) (a) R. Bonnett, J. R. Cannon, A. W. Johnson, and A. R. Todd, *J. Chem. Soc.*, 1158 (1957); (b) J. M. Pratt, *ibid.*, 5154 (1964); (c) R. H. Yamada, T. Kato, S. Shimizu, and S. Fukui, *Biochim. Biophys. Acta*, **117**, 13 (1966).
(6) The reducing agent in this system is apparently generated from secondary reactions between triethylamine, ethanol, and CH_2Cl_2. The reactions in this system are very complicated, and evidence for the intermediate appearance of the cobaloxime(I) nucleophile has been obtained. The latter may in turn react with the CH_2Cl_2 present to yield chloromethyl(pyridine)cobaloxime, which is known to be unstable under basic conditions.
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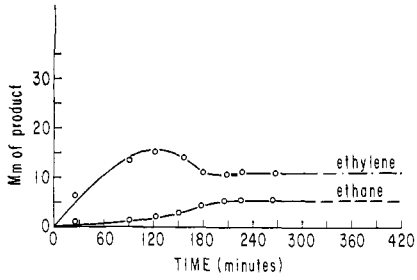

Figure 1. Production of ethylene and ethane from the reaction of hydridocobalamin with 100 mM of ethyl vinyl ether in acetic acid in the absence of reducing agent.

only ethylene is produced; ethane appears after prolonged reaction times (Figure 1). Hydridocobalamin is expected to react with the vinyl ether to yield 2-ethoxyethylcobalamin as the initial product. The latter is unstable in acidic media, decomposing with Co–C bond cleavage and formation of ethylene according to eq 2.[9,10] The ethane is a secondary product of the

$$\begin{matrix} H \\ | \\ [Co] \end{matrix} + CH_2{=}CHOC_2H_5 \longrightarrow \begin{matrix} CH_2CH_2OC_2H_5 \\ | \\ [Co] \end{matrix} \xrightarrow{H^+} [Co^{III}] + C_2H_4 + C_2H_5OH \quad (2)$$

reaction[8] of ethylene with hydridocobalamin, affording ethylcobalamin, which in turn undergoes reductive Co–C bond cleavage in the presence of excess reducing agent. Quantitative conversions of ethyl vinyl ether into mixtures of C_2H_4 and C_2H_6 were observed in the reactions of hydridocobalamin in the presence of excess reducing agent (Zn dust in acetic acid). In summary, our findings do not confirm the claim that Co(III) derivatives of corrins and cobaloximes react with vinyl ethers according to eq 1. The reaction for this reason also cannot be regarded as a model of dioldehydrase action. On the other hand, the demonstrated reaction of hydridocobalamin with ethyl vinyl ether takes a course in agreement with known reactions of hydridocobalamin with olefinic substrates, and of 2-alkoxyethylcorrin derivatives.[11]

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Tetrameric Phosphinecopper(I) Halides. X-Ray Crystallographic Evidence for a "Cubane" Structure for the Cu_4Cl_4 Core of $(PPh_3CuCl)_4$ and a "Step" Structure for the Cu_4Br_4 Core in Crystalline $(PPh_3CuBr)_4 \cdot 2CHCl_3$

Sir:

Our recent structural analyses of $(PPh_3CuH)_6$ (in which distances between adjacent copper atoms range from 2.494 (6) to 2.674 (5) Å)[1] and $(PPh_3Ir)_2Cu_4(C{\equiv}CPh)_8$ (Cu···Cu = 2.663 (6)–2.829 (6) Å),[2] coupled with a consideration of copper–copper distances within other copper cluster complexes[3–7] (in at least some of which *bonding* Cu···Cu interactions are believed to be present), have led us to be suspicious of the widely quoted value of 2.60 Å for the *nonbonding* Cu···Cu separation in $(AsEt_3CuI)_4$, a molecule with a "cubane" skeleton.[8] This distance is, indeed, likely to be of low accuracy because (1) the structural analysis was performed in the 1930's, (2) a very limited data set was used, (3) least-squares refinement of atomic parameters was not, at that time, possible, and (4) the copper atoms (Z = 29) are not the major contributors to the intensities of scattered X-rays, since Z(I) = 53 and Z(As) = 33.

We have now completed X-ray diffraction studies on the related tetramers $(PPh_3CuCl)_4$ and $(PPh_3CuBr)_4 \cdot 2CHCl_3$. As outlined below, $(PPh_3CuCl)_4$ has the expected[8,9] "cubane" structure (and *long* Cu···Cu distances). Unexpectedly, the Cu_4Br_4 core in crystalline $(PPh_3CuBr)_4 \cdot 2CHCl_3$ *does not* define a cube, but has an entirely different configuration, which we term a "step" structure.

Details of the crystallographic results are as follows. The species $(PPh_3CuCl)_4$ crystallizes in the centrosymmetric orthorhombic space group *Pbcn* (No. 60; D_{2h}^{14}) with a = 17.468 (2), b = 20.519 (3), c = 18.215 (2) Å, and Z = 4. X-Ray diffraction data were collected with a Picker FACS-1 diffractometer using Mo Kα radiation and a θ–2θ scan technique; the structure was solved *via* Patterson, Fourier, and least-squares refinement methods. All atoms, including hydrogens, have been located, the final discrepancy indices being R_F = 8.7% and R_{wF} = 4.8% for the 3067 independent reflections representing data complete to 2θ = 40° (or R_F = 3.8% and R_{wF} = 4.0% for the 1818 reflections for which $I > 3\sigma(I)$). The molecule has crystallographically required C_2 (2) symmetry with the four copper and four chlorine atoms defining a distorted cube (see Figure 1).

The twelve edges of the cube are defined by Cu–Cl bonds. The six crystallographically independent values vary appreciably, with Cu(1)–Cl(1) = 2.497 (2), Cu(1)–Cl(2) = 2.409 (2), Cu(1)–Cl(2′) = 2.434 (2), Cu(2)–Cl(1) = 2.363 (2), Cu(2)–Cl(2) = 2.457 (2), and Cu(2)–Cl(1′) = 2.505 (2) Å. Copper–copper distances are, again, rather irregular, but all are greater than 3.1

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