and 4.26 ppm (Figure 1a). The ^1H NMR spectrum of a sample of **1** prepared[6] using $^{15}NH_2{}^{15}NH_2$ (Figure 1b) confirms that these signals can be ascribed to protons attached to nitrogen atoms originally in the added hydrazine. Other features of the ^1H and ^{13}C NMR spectra[8] are consistent with a molecule with the formula $W(NPh)Me_3(NHNH_2)$ containing two types of methyl groups. Curiously, however, the ^{15}N NMR spectrum[9] of **1**-$^{15}N_2$ did *not* show two distinct ^{15}N signals expected for an imido-like sp^2-hybridized α-nitrogen atom and sp^3-hybridized β-nitrogen atom in an $NHNH_2$ ligand, but what appeared to be a doublet at ~57.0 ppm ($J_{NH} \approx 68$ Hz) overlapping with a triplet at ~54.9 ppm ($J_{NH} \approx 68$ Hz). Since no $NHNH_2{}^{1-}$ complex is known, we were compelled to determine the structure of **1**.[10]

Figure 2 shows **1** to be a dimer containing a μ-η^2,η^2-hydrazido^{2-} ligand and a μ-η^1,η^1-hydrazine ligand. Each metal has pseudooctahedral geometry; three methyl groups and the hydrazido^{2-} ligand occupy the four "equatorial" sites with the linear phenylimido groups trans to the hydrazine nitrogen atoms in the "axial" positions. Chemically the metal centers are equivalent and the molecule has noncrystallographic C_{2v} symmetry. No W-W bond is present since the W(1)-W(2) distance is long (3.731 (1) Å) and the dihedral angle between the $W(1)N_2$ and $W(2)N_2$ planes is large (~135°). This result is consistent with the complex containing W(6+) and $NHNH^{2-}$. The hydrazido^{2-} ligand is essentially symmetrically bound between W(1) and W(2) (W(1)-N(3) = 2.106 (12), W(1)-N(4) = 2.115 (11), W(2)-N(3) = 2.157 (11), W(2)-N(4) = 2.170 (12)Å) with an N-N distance of 1.391 (15) Å. The N(1)-N(2) distance of 1.434 (14) Å is close to that found in free hydrazine, the W(1)-N(1)-N(2)-W(2) linkage forms a zigzag arrangement, and W(1)-N(1) = 2.320 (11) and W(2)-N(2) = 2.353 (11) Å, all as one would expect for a bridging hydrazine ligand. Some other distances can be found in the figure, and a complete table of bond lengths and angles can be found in the supplementary material.

To our knowledge only one other type of related μ-η^2,η^2-N_2R_2 complex, $Fe_2(CO)_6(N_2R_2)$,[11] has been structurally elucidated. In $Fe_2(CO)_6(N_2Me_2)$ and $Fe_2(CO)_6(N_2C_{12}H_8)$ an Fe-Fe bond is present, the N-N bond lengths are 1.366 (8) and 1.399 (8) Å, respectively, and the dihedral angles between the FeN_2 planes are 91.1° and 89.5°, respectively.

Upon addition of 2 equiv of gaseous HCl to **1** in ether at -78 °C a pale yellow precipitate of $[W(NPh)Me_2Cl]_2(\mu$-$NH_2NH_2)(\mu$-NHNH) (**2**) forms in ~80% yield.[12] In the ^1H NMR spectrum of **2**[13] the methyl groups are inequivalent, the NHNH protons are equivalent, and there are two types of coupled NH_2NH_2 protons present (Figure 1c), all consistent with a chloride having replaced one of the exterior methyl groups on each metal to yield a molecule containing a C_2 axis that passes through the midpoint of the NHNH and NH_2NH_2 ligands. We suspect that neither the NHNH nor NH_2NH_2 ligand is protonated first, as an analogous reaction between **1** and DCl yields a product identical by ^1H NMR with that formed in the reaction between **1** and HCl.

$[W(NPh)Me_3]_2(\mu$-$NH_2NH_2)(\mu$-NHNH) can be dissolved in methanol and recovered unchanged upon removing the methanol in vacuo. Upon recovery of **1** from methanol-d_4, >90% of the protons in the NHNH ligand have been replaced by deuterium; virtually no deuterium is incorporated into the hydrazine ligand. When NEt_3 is added to a solution of **1** in methanol-d_4 no obvious change occurs and **1** can be recovered quantitatively by removing the methanol and triethylamine in vacuo. In this case, however, the recovered product is largely $[W(NPh)Me_3]_2(\mu$-$ND_2ND_2)(\mu$-NDND). It is also important to note that addition of excess NEt_3 to an ^1H NMR sample of **1** in acetone-d_6 causes the signal at 5.70 ppm to virtually disappear into the base line. Only small amounts of unidentifiable solids have been observed to precipitate from larger scale reaction mixtures under a variety of conditions, and removing all the solvent in vacuo yields **1** quantitatively. Among other things, we suspect that NEt_3 is deprotonating the NHNH ligand and are in the process of eludicating this and other reactions involving bases.

Acknowledgment. R.R.S. thanks the National Institutes of Health for support through Grant GM-31978. L.B. thanks the Sohio Corporation for a predoctoral fellowship during the 1983-1984 academic year. We thank S. J. Lippard for use of the diffractometer.

Supplementary Material Available: Tables of final atomic coordinates and thermal parameters and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

(6) Hydrazine-$^{15}N_2$ was prepared from hydrazine sulfate (99% ^{15}N) by a published method starting with 1.9 mmol (0.250 g) of $^{15}N_2H_4{\cdot}H_2SO_4$.[7]

(7) Audrieth, L. F.; Ogg, B. A. "The Chemistry of Hydrazine"; Wiley: New York, 1956; Chapter 3.

(8) ^1H NMR (CD_2Cl_2) δ 7.40-7.05 (m, 5, NC_6H_5), 4.12 (s, 1, NH), 3.63 (s, 2, NH_2), 0.72 (s, 6, CH_3), 0.57 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) δ 155 (s, C_{ipso}), 129, 125.6, 125.4 (d, J_{CH} = 180 Hz, C_o, C_m, C_p) 34.0 (q, J_{CH} = 122, J_{CW} = 60 Hz, CH_3), 18.5 (q, J_{CH} = 122, J_{CW} = 60 Hz, CH_3).

(9) The ^{15}N NMR spectrum was obtained at 9.04 MHz in CH_2Cl_2. The ^{15}N shift is relative to NH_3 (liquid). Aniline-^{15}N was employed as the external reference.

(10) **1**-0.5 toluene[5] crystallizes in the orthorhombic space group *Pbca* (No. 62) with a = 23.957 (3) Å, b = 15.329 (4) Å, c = 14.051 (2) Å, V = 5160.4 Å^3, and ρ_{calcd} = 1.95 g cm^{-3} for Z = 8. 2500 unique observed reflections ($I \geq 2\sigma(I)$) collected at 250 K on an Enraf-Nonius CAD4 diffractometer with Mo Kα (λ = 0.7107 Å) radiation to 2θ = 45° were used in the solution and refinement of the structure by conventional methods to a value of the discrepancy index R_1 = 0.043. No absorption correction applied. The disordered toluene molecule was found sandwiched between the phenyl ring of the two phenylimido ligands. The hydrogen atoms on the HNNH and H_2NNH_2 ligands were placed in positions in which interactions with other substituents were calculated to be minimized (assuming d_{NH} = 0.95 Å and N-N-H = 109.5°).

(11) (a) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2709. (b) Doedens, R. J. *Inorg. Chem.* **1970**, *9*, 429.

(12) Anal. Calcd for $WC_8H_{14}N_3Cl$: C, 25.86; H, 3.80; N, 11.31; Cl, 9.54. Found: C, 25.52; H, 5.54; N, 11.98; Cl, 10.25.

(13) ^1H NMR of $W_2(NPh)_2Me_4Cl_2(\mu$-η^2,η^2-$N_2H_2)(\mu$-η^1,η^1-$N_2H_4)$-(CD_3CN) δ 7.41-7.17 (m, 5, C_6H_5), 5.95 (s, 1 NH), 4.96 (d, $J_{H_AH_B}$ = 8 Hz, 1, NH_2), 4.56 (d, $J_{H_AH_B}$ = 8 Hz, 1, NH_2), 1.00 (s, 3, CH_3), 0.88 (s, 3, CH_3).

Cobalt-Carbon Bond Dissociation Energy of Coenzyme B_{12}

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According to the widely accepted mechanism of coenzyme B_{12} dependent rearrangements a principal role of the coenzyme is to undergo enzyme-induced cobalt-carbon bond homolysis, thereby generating a 5′-deoxyadenosyl radical (Ado·) which triggers the rearrangement of the substrate by abstracting a H atom from the latter.[1] Accordingly, a knowledge of the cobalt-carbon bond dissociation energy of coenzyme B_{12} (adenosylcobalamin, abbreviated Ado-B_{12}) and an understanding of the factors that may contribute to the weakening of this bond and to the enzyme-induced bond dissociation are central to a full appreciation of this distinctive coenzyme's role. Following our earlier development of procedures for the determination of transition metal-alkyl bond dissociation energies and their application to various coenzyme B_{12} model compounds,[2-4] we now report the determination of the cobalt-carbon bond dissociation energy of the coenzyme itself.

Our procedure is an adaptation of the kinetic approach that we developed and applied previously to determine the cobalt-carbon bond dissociation energies of various alkyl cobalt Schiff

(1) (a) Abeles, R. H. *Vitam. B_{12}, Proc. Eur.* Symp., *3rd* **1979**, 373. (b) Babior, B. M. *Vitam. B_{12}, Proc. Eur. Symp., 3rd* **1979**, 461. (c) Halpern, J. In "B_{12}"; Dolphin, D., Ed.; Wiley: New York, 1982; p 502 and references therein. (d) Halpern, J. *Pure Appl. Chem.* **1983**, *55*, 1059.

(2) (a) Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124. (b) Ng, F. T. T.; Rempel, G. L.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 621. (c) Ng, F. T. T.; Rempel, G. L.; Halpern, J. *Inorg. Chim. Acta* **1983**, *77*, L65.

(3) Tsou, T. T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 623.

(4) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.

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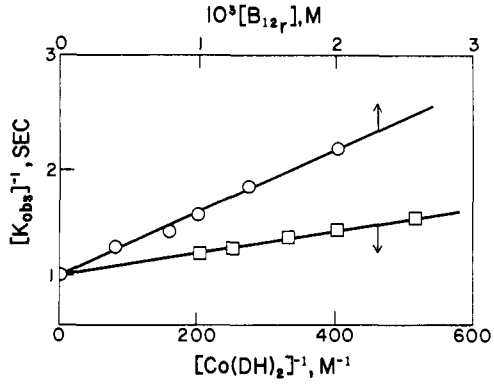

Figure 1. Plots of k_{obsd}^{-1} vs. $[B_{12r}]$ at 2.0×10^{-3} M $Co(DH)_2$ (○) and vs. $[Co(DH)_2]^{-1}$ at 1.0×10^{-3} M B_{12r} (□).

base compounds.[3] Successful application of this approach to coenzyme B_{12} required the identification of an appropriate, water-soluble, free radical trap that did not react with the coenzyme or influence the rate of cobalt–carbon bond dissociation. Bis(dimethylglyoximato)cobalt(II) [abbreviated $Co^{II}(DH)_2$], which previously was shown to combine rapidly with organic free radicals to form cobalt–carbon bonds that are considerably stronger than the corresponding cobalamin–carbon bonds, was found to be ideal for this purpose.[5]

The thermal decomposition of coenzyme B_{12}, which proceeds at conveniently measurable rates in aqueous solution at temperatures above 80 °C, was found to be inhibited by added cob(II)alamin (vitamin B_{12r}, abbreviated B_{12r}) and accelerated by added $Co^{II}(DH)_2$. With both B_{12r} and $Co^{II}(DH)_2$ in (constant) excess, the decomposition exhibited pseudo-first-order kinetics according to the scheme of eq 1–3, and the corresponding rate

$$\text{Ado-B}_{12} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Ado}\cdot + \text{B}_{12r} \quad (1)$$

$$\text{Ado}\cdot + \text{Co}^{II}(\text{DH})_2 \xrightarrow{k_2} \text{Ado–Co(DH)}_2 \quad (2)$$

$$\text{Ado-B}_{12} + \text{Co}^{II}(\text{DH})_2 \rightarrow \text{B}_{12r} + \text{Ado–Co(DH)}_2 \quad (3)$$

law, eq 4 which rearranges to eq 5.[6-8]

$$\frac{-\text{d ln [Ado-B}_{12}]}{dt} = k_{obsd} = \frac{k_1 k_2 [\text{Co}^{II}(\text{DH})_2]}{k_{-1}[\text{B}_{12r}] + k_2[\text{Co}^{II}(\text{DH})_2]} \quad (4)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{k_{-1}[\text{B}_{12r}]}{k_1 k_2 [\text{Co}^{II}(\text{DH})_2]} \quad (5)$$

In accord with eq 5, kinetic measurements at 100 °C, encompassing the concentration ranges 4.0×10^{-4} to 2.0×10^{-3} M B_{12r} and 2.0×10^{-3} to 5.0×10^{-3} M $Co(DH)_2$ yielded excellent linear plots of k_{obsd}^{-1} vs. $[B_{12r}]$ and k_{obsd}^{-1} vs. $[Co^{II}(DH)_2]^{-1}$ depicted in Figure 1.[9] The slopes and interecepts of these plots yielded $k_1 = (1.00 \pm 0.04) \times 10^{-4}$ s^{-1} and $k_{-1}/k_2 = 1.07 \pm 0.02$ at 100 °C. Measurements over the temperature range 84–103 °C yielded the following values of k_1 (s^{-1}): 1.98×10^{-5} (84.0 °C), 3.05×10^{-5} (88.8 °C), 5.93×10^{-5} (95.0 °C), 1.00×10^{-4} (100.0 °C), 1.31×10^{-4} (103.0 °C), corresponding to $\Delta H_1^{\ddagger} = 26.3 \pm 0.6$ kcal/mol and $\Delta S_1^{\ddagger} = -6 \pm 2$ cal/(mol K).

Coenzyme B_{12} is known to undergo a reversible dissociation of the pendant axial 5,6-dimethylbenzimidazole ligand and thus to exist in solution as an equilibrium mixture of the "base-on" and "base-off" forms.[10] In view of the much higher thermal stability of the "base-off" form[11] its contribution to the dissociation reaction (eq 1) may be neglected and the measured values of k_1 must be corrected to reflect only the contribution of the reactive "base-on" form, i.e., $(k_1)_{corr} = k_1$ ($[\text{Ado-B}_{12}]_{total}/[\text{Ado-B}_{12}]_{base\ on}$). The thermodynamic parameters of the base-on ⇌ base-off equilibrium were determined from spectrophotometric measurements of the equilibrium quotient over the temperature range 15–55 °C to be $\Delta H° = 4.5 \pm 0.3$ kcal/mol and $\Delta S° = +12$ cal/(mol K).[12] Using these values we obtain $(\Delta H_1^{\ddagger})_{corr} = 28.6 \pm 1$ kcal/mol and $(\Delta S_1^{\ddagger})_{corr} = +2 \pm 3$ cal/(mol K). The correction is sufficiently small so as not to constitute a serious source of error.

The cobalt–carbon bond dissociation energy of Ado-B_{12} (D_{Co-Ado}) can be deduced from the kinetic measurement through the relation, $D_{Co-Ado} = (\Delta H_1^{\ddagger})_{corr} - (\Delta H_{-1}^{\ddagger})$. Several prior studies[3,5,13,14] have revealed that the recombinations of various radicals with a variety of cobalt(II) complexes including B_{12r} proceed at rates that are close to diffusion controlled, a conclusion supported for the present case by the direct demonstration that the cage recombination of Ado· and B_{12r} occurs with a rate constant (1.39×10^9 s^{-1}) that is competitive with cage escape.[14] Utilizing this assumption, $\Delta H_{-1}^{\ddagger}$ can be estimated to be ca. 2 kcal/mol, and, thus, the cobalt–carbon bond dissociation energy of coenzyme B_{12} (D_{Co-Ado}) is determined to be 26 ± 2 kcal/mol. (The absence of significant discrimination between the recombination rates of Ado· with B_{12r} and with $Co(DH)_2$ ($k_{-1}/k_2 = 1.07$) also is consistent with these processes being diffusion controlled.)

The value of the Co–Ado bond dissociation energy determined in these studies is in the range of Co–C bond dissociation energies recently determined for a variety of related organocobalt compounds including Schiff base and dimethylglyoxime compounds.[2-4,15] The Co–C bonds in all these compounds are relatively weak (with bond dissociation energies ranging from 18 to 30 kcal/mol) consistent with the biochemical role of coenzyme B_{12} as a facile free radical source.[1] Considerable further weakening of the Co–Ado bond would be required to accommodate the rates reported for certain coenzyme B_{12} promoted reactions ($\sim 10^2$ for methylmalonyl-CoA mutase).[16] In view of marked sensitivity of Co-C bond dissociation energies[2-4] (and bond lengths)[17] in

(5) (a) Halpern, J.; Phelan, P. *J. Am. Chem. Soc.* **1972**, *94*, 1881. (b) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171 and references therein.

(6) The reaction was followed spectrophotometrically by monitoring the formation of B_{12r} at 650 nm where the absorbances of Ado-B_{12}, $Co(DH)_2$, and Ado–$Co(DH)_2$ are negligible. The formation of B_{12r} was quantitative. The formation of Ado–$Co(DH)_2$ was confirmed (NMR) but was difficult to quantitate since (as demonstrated in separate control experiments) this compound decomposes under our reaction conditions at rates ($t_{0.5} \sim 1$ h at 100 °C) comparable to those of its formation. In the case of the closely related reaction of neopentyl-B_{12} with $Co(DH)_2$, which exhibits similar kinetics and which yields the *stable* product neopentyl-$Co(DH)_2$, the *quantitative* formation of the latter was established. (N. Feilchenfeld, S.-H. Kim, and J. Halpern, unpublished results.) The kinetic measurements were made in acetate-buffered solutions (pH 4.3) since, at the reaction temperatures, $Co(DH)_2$ is unstable at higher pHs due to base-induced decomposition.[7]

(7) Simandi, L. I.; Nemeth, S.; Bodo-Zahonyi, E. *Inorg. Chim. Acta* **1980**, *45*, L143 and references therein.

(8) It is of interest that no 8,5′-cyclic adenosine (Hogenkamp, H. P. C. *J. Biol. Chem.* **1963**, *238*, 477), the principal product of photolysis or thermolysis of coenzyme B_{12} in aqueous solution in the absence of $Co(DH)_2$ (or other efficient radical traps), was formed under the conditions of our reactions ($\gtrsim 10^{-3}$ M $Co(DH)_2$). Assuming the trapping of Ado· by $Co(DH)_2$ to be diffusion controlled ($k \sim 10^9$ M^{-1} s^{-1}) this implies an *upper limit* of ca. 10^5 s^{-1} for the rate constant of the cyclization of Ado· at ca. 100 °C.

(9) The dependence of k_{obsd} on $[B_{12r}]$ and $[Co(DH)_2]$ was examined in detail at 100 °C (Figure 1). At the other temperatures only the values of k_1 were measured directly from the kinetics of the reaction of Ado-B_{12} with $Co(DH)_2$ in the presence of a limiting excess of the latter ($(1-6) \times 10^{-3}$ M) and with no added B_{12r}.

(10) (a) Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2267. (b) Brown, K. L.; Nuss, D. M.; Montejano, Y. D.; Jacobsen, D. W. *Inorg. Chem.* **1984**, *23*, 1463.

(11) (a) Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2274. (b) Schrauzer, G. N.; Grate, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 541.

(12) These values refer to the pH (4.3) of the kinetic measurements where there is significant contribution from the protonated base-off form. At pH 7.6 the corresponding values were determined to be $\Delta H° = 7.2$ kcal/mol and $\Delta S° = 17.9$ cal/(mol K). These fall within the range of the literature values of the corresponding thermodynamic parameters which range from 3.5 to 8.6 kcal/mol for $\Delta H°$ and from 4.9 to 17 cal/(mol K) for $\Delta S°$.[10]

(13) (a) Endicott, J. F.; Ferraudi, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 243. (b) Mak, C. Y.; Endicott, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 123. (c) Elroi, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1978**, *100*, 5540.

(14) Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 4000.

(15) Finke, R. G.; Smith, B. L.; Mayer, B. J.; Molinero, A. A. *Inorg. Chem.* **1983**, *22*, 3677.

(16) (a) Kellermeyer, R. W.; Allen, S. H. G.; Stjernholm, R.; Wood, H. G. *J. Biol. Chem.* **1964**, *239*, 2562. (b) Overath, P.; Stadtman, E. R.; Kellerman, G. M.; Lynen, F. *Biochem. Z.* **1962**, *336*, 77. (c) Canata, J. J.; Focesi, A.; Mazumker, R.; Warner, R. C.; Ochoa, S. *J. Biol. Chem.* **1965**, *240*, 3249.

related organocobalt compounds to steric influences, a likely mechanism for such bond weakening is a steric interaction with the 5′-deoxyadenosyl group resulting from an enzyme-induced "upward" conformational distortion of the corrin ring in the enzyme-bound coenzyme.

Acknowledgment. Support of this research through grants from the National Institutes of Health (AM-13339) and the National Science Foundation (CHE82-17950) is gratefully acknowledged. The NMR facilities were supported in part through the University of Chicago Cancer Center Grant NIH CA-14599.

(17) Summers, M. F.; Toscano, P. J.; Bresciani-Pahor, N.; Nardin, G.; Randaccio, L.; Marzilli, L. G. *J. Am. Chem. Soc.* **1983**, *105*, 6259 and references therein.

(18) **Note Added in Proof**: Subsequent to submission of this communication, Finke and Hay[19] reported a related study of the thermolysis of coenzyme B_{12} in *ethylene glycol* with 2,2,6,6-tetramethylpiperidinyl-1-oxy (Tempo) as a radical trap. Although the full kinetics for trapping of the 5′-deoxyadenosyl radical, in competition with its recombination with B_{12r}, were not observed, the limiting kinetics yielded a significantly higher values (34.5 kcal/mol) for $(\Delta H^{\ddagger})_{corr}$ and a correspondingly higher value of 32 kcal/mol for the Co–C bond dissociation energy. The reason for this ca. 6 kcal/mol discrepancy, which may be solvent related, is unclear. We thank Prof. Finke for informing us of these results and for helpful comments.

(19) Finke, R. G.; Hay, B. P. *Inorg. Chem.* **1984**, *23*, 3041.

Free Radical Rearrangement Involving the 1,2-Migration of a Thioester Group. Model for the Coenzyme B_{12} Dependent Methylmalonyl-CoA Mutase Reaction

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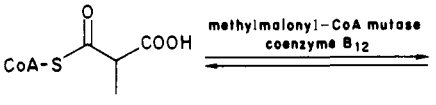
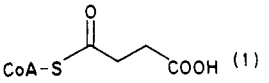
Notwithstanding extensive investigation and discussion, the mechanisms of the remarkable reactions promoted by coenzyme B_{12}, exemplified by the methylmalonyl-CoA (**1**) to succinyl-CoA (**2**) rearrangement (eq 1), continue to be unresolved and controversial.[1]



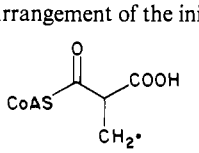
1



(1)

2

It is widely accepted[1,2] that the rearrangement is *initiated* by the enzyme-induced homolytic dissociation of the cobalt–carbon bond of coenzyme B_{12} to form a 5′-deoxyadenosyl radical, which abstracts an H atom from the substrate to generate a substrate free radical, i.e., **3**. However, there is little evidence or agreement concerning the nature of the rearrangement step itself. Possible mechansims that have been proposed include, in addition to rearrangement of the initial radical itself (i.e., **3** → **4**), rearrangement of the corresponding carbanion or carbonium ion, formed by reduction or oxidation of the initial radical, or of an organocobalt derivative (**5**) formed by combination of the initial radical with the coenzyme-derived vitamin B_{12r}.[1]



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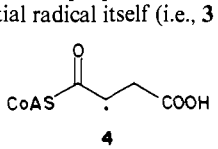

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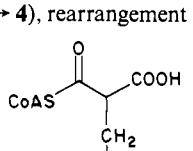

5

Several attempts have been reported[3–8] to probe the mechanisms of coenzyme B_{12} promoted rearrangements by preparing model substrate–cobalt adducts analogous to **5** [where (Co) = cobalamin or a related cobalt complex] and decomposing these under various conditions (thermal, photolytic, reductive, etc.). In some cases workup of the decomposed solutions yielded some rearranged products (e.g., analogous of **2**).[5,6] However, it was not possible to draw convincing conclusions about the rearrangement mechanisms which were variously interpreted as proceeding through free radicals, carbanions, or organometallic intermediates.[3–8] Direct studies on various functionalized free radicals have revealed a few examples of $\beta \rightarrow \alpha$ migrations of acyl groups[8] but not, hitherto, of an ester or thio ester group.[3c,8c,9,10] We now report unequivocal evidence of such a 1,2-migration of a thio ester group in a model free radical related to **3** and measurements of the kinetics of this rearrangement.

Our procedure parallels that previously used by Walling[12] to study the rearrangement of the 5-hexenyl radical. The model radical **7**, which also has been invoked in several earlier attempts to model the methylmalonyl-CoA rearrangement,[5,6] was generated from the corresponding bromide **6**[13] by reduction with *n*-Bu_3SnH,[14] and the competition between direct trapping with *n*-Bu_3SnH (k_t) to yield **8** and rearrangement (k_r), followed by trapping to yield **10** in accord with eq 1, was monitored as a function of the initial *n*-Bu_3SnH concentration. Only the direct trapping product **8** and that resulting from 1,2-migration of the thioester group (**10**) were obtained, together in essentially quantiative yield (GC, based on reacted **6**). No other products, notably that resulting from migration of the ester group (**11**), were detected.

(1) For comprehensive reviews, see: (a) "B_{12}"; Dolphin, D., Ed.; Wiley: New York, 1982. (b) *Vitam. B_{12}, Proc. Eur. Symp., 3rd* **1979**.

(2) (a) Abeles, R. H., ref 1b, p 373. (b) Babior, B. M., ref 1b, p 461. (c) Halpern, J., ref 1a, Vol. 1, p 502.

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(10) Prior attempts to observe 1,2-migration of a thio ester group include studies by Aeberhard et al.[11] on the photolysis and thermolysis of the perester $(CH_3)_3CO_3CCH_2CH(COOEt)(COSEt)$, a potential precursor of the $\cdot CH_2CH(COOEt)(COSEt)$ radical. No rearranged product resulting from thio ester migration was observed when the perester was photolyzed in hexane at room temperature. Thermolysis in cumene at 140 °C yielded only a trace (ca. 0.1%) of the rearranged thiosuccinate ester, $EtS(CO)CH_2CH_2COOEt$.

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(13) Starting materials and products prepared as in ref 5a.

(14) Typical conditions: 0.001–0.005 M *n*-Bu_3SnH;[15] 10–50% excess **6**; benzene;[16] 60–113 °C.

(15) The initial *n*-Bu_3SnH concentration range was limited by the low yields of rearranged product **10** at higher *n*-Bu_3SnH concentrations and by the difficulty of product isolation at lower concentrations. For the concentration range used the results were consistent and reproducible.

(16) Toluene proved unacceptable as a solvent since H abstraction from the solvent ($7 + C_6H_5CH_3 \rightarrow 8 + C_6H_5CH_2\cdot$) turned out to be a significant side reaction compared with the relatively slow rearrangement **7** → **9**.

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