# Thermal and Photochemical Epimerization/Equilibration of Carbohydrate Cobaloximes

Gui-Xue Yu, David R. Tyler, and Bruce P. Branchaud*

*Department of Chemistry, University of Oregon, Eugene, Oregon 97403-1253*

*bbranch@oregon.uoregon.edu*

*Received August 1, 2000*

Epimeric carbohydrate alkyl cobaloximes **4**:**5**, **9**:**10**, and **12**:**13** can be equilibrated thermally or photochemically. In each case, one isomer is strongly favored: *exo*-3-deoxy-3-pyridyldimethylglyoximatocobalt-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **4** for the **4**:**5** epimer pair, *exo*-3-deoxy-3-pyridyldimethylglyoximatocobalt-5-*O*-carboxymethyl-1,2-*O*-isopropylidene-α-D-xylofuranose **9** for the **9**:**10** epimer pair, and equatorial 1-deoxy-1-pyridyldimethylglyoximatocobalt-2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranose **12** for the **12**:**13** epimer pair. These data indicate that there is a strong facial preference for the coupling of py(dmgH)$_2$Co$^\bullet$ radicals with alkyl R$^\bullet$ free radicals, with the preferred kinetic path leading to the more stable product.

## Introduction

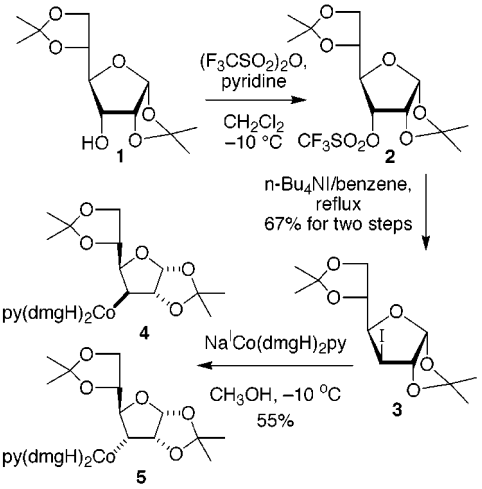
Reversible C−Co bond homolysis is a key feature of reactions catalyzed by coenzyme $B_{12}$-utilizing enzymes,[1] coenzyme $B_{12}$ model reactions,[2] and synthetic organic reactions using $B_{12}$ and $B_{12}$ model compounds.[3] In this paper we report studies of thermal and photochemical epimerizations of epimeric cobaloxime pairs **4**:**5**, **9**:**10**, and **12**:**13**.

## Results

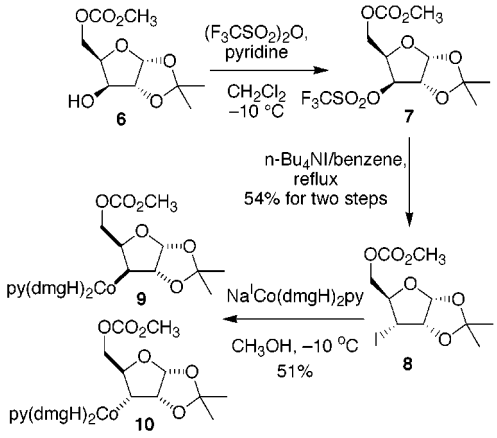
**Preparation of Carbohydrate Alkyl Cobaloximes.** Oxidative addition of NaCo$^{I}$(dmgH)$_2$py (dmgH = dimethylglyoxime monoanion) to 3-deoxy-3-iodo-1,2,5,6-di-*O*-isopropylidene-α-D-glucofuranose **3** (prepared as shown in Scheme 1) produced an inseparable mixture of epimers **4** and **5** in 55% isolated yield (**4**:**5** ratio = 62:38). Oxidative addition of NaCo$^{I}$(dmgH)$_2$py to 3-deoxy-3-iodo-5-*O*-carboxymethyl-1,2-*O*-isopropylidene-α-D-ribofuranoside **8** (prepared as shown in Scheme 2) produced an inseparable mixture of epimers **9** and **10** in 51% isolated yield (**9**:**10** ratio = 79:21 to 70:30). Oxidative addition of NaCo$^{I}$(dmgH)$_2$py to 1-deoxy-1-bromo-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide **11** produced an inseparable mixture of epimers **12** and **13** in 78% isolated yield (**12**:**13** ratio = 50:50).

**Epimerization of Carbohydrate Alkyl Cobaloximes.** Cobaloxime epimeric pairs **4**:**5** and **9**:**10** were each equilibrated by epimerization under thermal conditions. Cobaloxime epimeric pairs **4**:**5**, **9**:**10**, and **12**:**13** were each equilibrated by epimerization under photochemical conditions. All reactions were run in NMR tubes under an $N_2$ atmosphere in $N_2$-saturated $CDCl_3$. For all

**Scheme 1. Preparation of Cobaloximes 4 and 5**




**Scheme 2. Preparation of Cobaloximes 9 and 10**




(1) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994. (b) Schneider, Z.; Stroinski, A. *Comprehensive $B_{12}$: Chemistry, Biochemistry, Nutrition, Ecology, Medicine*; De Gruyter: Berlin, New York, 1987. (c) *$B_{12}$*; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. 1. Chemistry & Vol. 2. Biochemistry and Medicine.

(2) Finke, R. G. Coenzyme $B_{12}$−Based Chemical Precedent for Co−C Bond Homolysis and Other Key Elementary Steps. In *Vitamin $B_{12}$ and $B_{12}$ Proteins, Lectures Presented at the 4th European Symposium on Vitamin $B_{12}$ and $B_{12}$ Proteins*; Kraütler, B, Arigoni, D., Golding, B. T., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Chapter 25, pp 383−402. (b) Garr, C. D.; Finke, R. G. *Inorg. Chem.* **1996**, *35*, 5912−5922. (c) Garr, C. D.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 4414−4421.

(3) Branchaud, B. P.; Friestad, G. F. "Vitamin $B_{12}$," In *Encyclopedia of Reagents for Organic Synthesis*, Paquette, Leo A, Ed.; John Wiley & Sons: Chichester, West Sussex, 1995; pp. 5511−5514.

10.1021/jo005595v CCC: $20.00 
Published on Web 07/19/2001

**Scheme 3. Preparation of Cobaloximes 12 and 13**

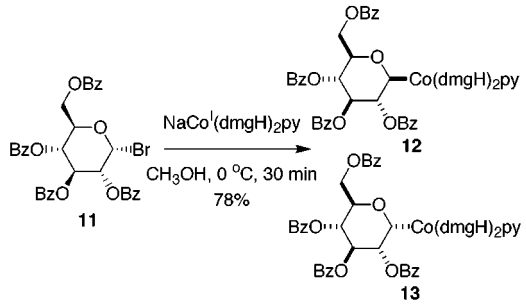



**Table 1. Data for Thermal Cobaloxime Isomerizations**

| time in minutes | **4**:**5** ratio[a] | time in minutes | **9**:**10** ratio[b] |
|---|---|---|---|
| 0 | 62:38 | 0 | 70:30 |
| 427 | 74:26 | 10 | 73:27 |
| 510 | 76:24 | 20 | 73:27 |
| 720 | 78:22 | 30 | 77:23 |
| 1300 | 87:13 | 40 | 77:23 |
| 1546 | 89:11 | 50 | 79:21 |
| 1811 | 90:10 | 60 | 81:19 |
| 2640 | 94:6 | 70 | 82:18 |
| 2910 | 96:4 | 80 | 83:17 |
| | | 95 | 84:16 |
| | | 110 | 84:16 |
| | | 130 | 87:13 |
| | | 150 | 88:12 |
| | | 170 | 90:10 |
| | | 190 | 91:9 |

[a] Thermal isomerization of 0.072 M **4**:**5** at 38 °C in $CDCl_3$. [b] Thermal isomerization of 0.100 M **9**:**10** at 78 °C in $CDCl_3$.

**Table 2. Data for Photochemical Cobaloxime Isomerizations**

| time in minutes | **4**:**5** ratio[a] | **9**:**10** ratio[b] | **12**:**13** ratio[c] |
|---|---|---|---|
| 0 | 62:38 | 79:21 | 50:50 |
| 210 | 74:26 | 83:17 | 70:30 |
| 450 | 81:19 | 87:13 | 79:21 |
| 1050 | 90:10 | 90:10 | 100:0 |

[a] Photochemical isomerization of **4**:**5** at 15−20 °C in $CDCl_3$. [b] Photochemical isomerization of **9**:**10** at 15−20 °C in $CDCl_3$. [c] Photochemical isomerization of **12**:**13** at 15−20 °C in $CDCl_3$.

reactions $^1$H NMR data to determine isomer ratios were collected at the times indicated in Tables 1 and 2. All of the epimerizations reported here were clean: i.e., no significant decomposition was observed by $^1$H NMR. In a previously reported example of photochemical epimerization of a glucosyl cobaloxime, significant decomposition was observed along with epimerization after prolonged photolysis.[4] In each case one of the two epimers was much more thermodynamically stable than the other (**4** favored over **5**, **9** favored over **10**, **12** favored over **13**). A typical example is shown in Figure 1 for the photochemical epimerization/equilibration of **12** and **13**.

## Discussion

Thermal and photochemical epimerizations lead to primarily one epimer in each case. In thermal reactions the product distribution will be determined by the relative barriers for C−Co bond homolysis. In photochemical reactions, photoinduced bond homolysis should be equally facile for either epimer so that the product distribution will be determined by the relative kinetic

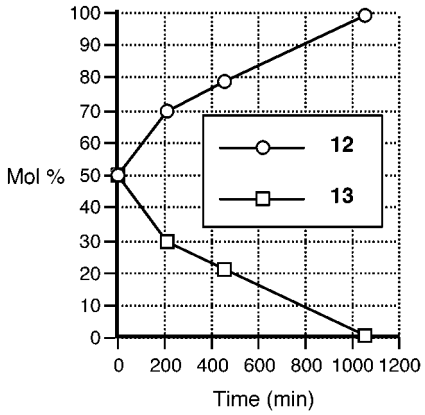



**Figure 1.** Plot of data for photochemical isomerization/equilibration of **12** and **13**.

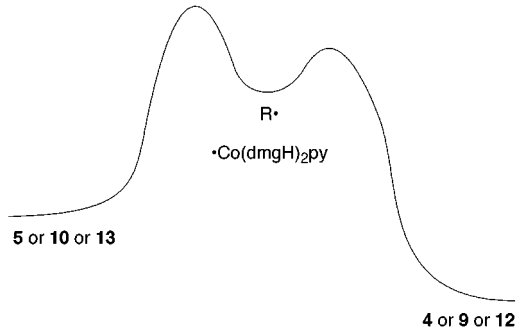



**Figure 2.** Qualitative energy profile that is consistent with the epimerization/equilibration data.

barriers to R$^\bullet$ + $^\bullet$Co(dmgH)$_2$py radical−radical combination. A qualitative energy profile consistent with the data is shown in Figure 2.

Most radical−radical combination reactions are very fast, nearly diffusion-controlled,[5] and would not be expected to exhibit much selectivity. In contrast, reactions of alkyl free radicals with cobaloxime radicals are significantly slower than diffusion-controlled—the rate constant for combination of $CH_3^\bullet$ + $^\bullet$Co(dmgH)$_2$py has been determined to be $5 \times 10^7$ $M^{-1}s^{-1}$ in one study and $8 \times 10^7$ $M^{-1}s^{-1}$ in another.[6] The R$^\bullet$ + $^\bullet$Co(dmgH)$_2$py reactions reported in this paper, with larger and more sterically congested radicals, should be even slower. Apparently, the alkyl free radicals derived from the epimeric cobaloxime pairs **4**:**5**, **9**:**10**, and **12**:**13** have significant steric effects on the rates for R$^\bullet$ + $^\bullet$Co(dmgH)$_2$py combinations on one face of the alkyl radicals versus the other face (exo versus endo for **4**:**5** and **9**:**10** or α versus β for **12**:**13**). The large, flat Co(dmgH)$_2$py ligand, with a cone angle of 180°, should produce large steric effects. Welker and co-workers have observed that the Co(dmgH)$_2$py group has a large steric effect in Diels−Alder reactions, shifting endo-selective reactions into exo-selective ones.[7] Our research on cobaloxime pi-cation chemistry has also

(4) Ghosez, A.; Gobel, T.; Giese, B. *Chem. Ber.* **1988**, *121*, 1807.

(5) For a review on radical−radical combination and disproportionation see: Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441.

(6) Endicott, J. F.; Ferraudi, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 243. (b) Lerner, D. A.; Bonneau, R.; Giannotti, C. *J. Photochem.* **1979**, *11*, 73.

(7) Richardson, B. M., Welker, M. E. *J. Org. Chem.* **1997**, *62*, 1299−1304. (b) Chapman, J. J.: Welker, M. E. *Organometallics* **1997**, 7477−755. (c) Adams, T. A.; Welker, M. E.; Day, C. S. *J. Org. Chem.* **1998**, *63*, 3683−3686.

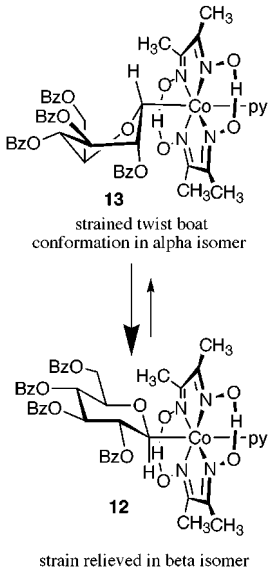
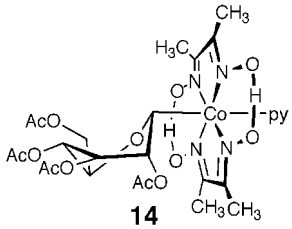



**Figure 3.** Structures of **12** and **13**, illustrating the "supersteric" effect of the cobaloxime ligand.

revealed a large "supersteric" effect for the $Co(dmgH)_2py$ group.[8]




Giese and co-workers have previously noted that the bulky cobaloxime group causes **14** to adopt a twist boat conformation to allow the bulky cobaloxime group to become pseudoequatorial. As shown in Figure 3, **12** should be favored over **13** since **12** has an equatorial cobaloxime group and a more stable chair conformation whereas **13** has the less stable twist boat. It is not hard to imagine that some of the significant steric effects in **12** and **13** will be expressed in the transition states for $R^{\bullet} + {}^{\bullet}Co(dmgH)_2py$ combination reactions to form **12** and **13**.

Similar arguments can be made for **4**:**5** and **9**:**10**. Figure 4 illustrates this for the **9**:**10** isomerzations, which should have a large difference in steric effects for less stable endo **10** and more stable exo **9**.

Some of the radical reactions that are used in organic synthesis can be very stereoselective.[9] In those reactions the stereoselectivity is obtained by the reaction of a radical with a nonradical, for example in the addition of a radical to an alkene. The present case is unusual in that stereoselectivity is seen for a radical−radical reaction.

## Experimental Section

**General.** All organic and inorganic reagents were purchased from commercial suppliers and were used as received. Carbohydrate starting materials 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**), 5-*O*-Carbomethoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**6**) and 1-deoxy-1-bromo-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**11**) were purchased from commercial suppliers and were used as received. All solvents were used as received with the exception of anhydrous tetrahydrofuran (THF), which was purified by distillation from sodium benzophenone ketyl radical under anaerobic $N_2$. Gravity silica gel chromatography was performed with 60−200 mesh silica gel. Analytical TLC was performed on aluminum-backed silica gel plates. $^1H$ NMR and $^{13}C$ NMR spectra were obtained at 300 and 75 MHz, respectively. IR spectra were measured with an FT-IR instrument. High-resolution mass spectra (HRMS) were done with the peak match method. Electron impact ionization (EI) was performed at 70 eV, and fast atom bombardment (FAB) was performed with Xe atoms at 8 kV and 1 mA with 3-nitrobenzyl alcohol (3NBA) matrix. Elemental analyses were performed by Desert Analytics, Tucson, AZ 85717.

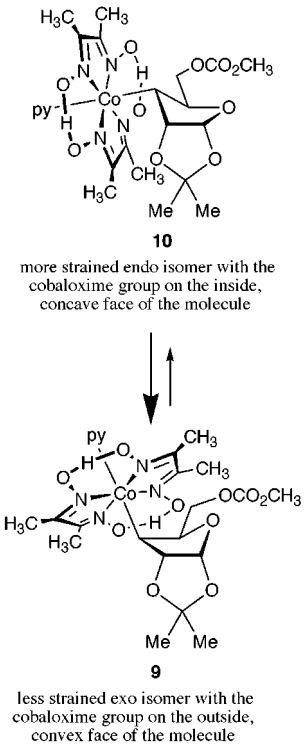



**Figure 4.** Structures of **9** and **10**, illustrating the "supersteric" effect of the cobaloxime ligand.

**Preparation of 3-*O*-Trifluoromethanesulfonyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranoside (2).** A 500 mL three-neck-round-bottom flask was equipped with a 1.5 in magnetic stir bar and two 50 mL addition funnels. Pyridine (1.34 g, $1.70 \times 10^{-2}$ mol) and 100 mL of $CH_2Cl_2$ were added. The solution was cooled to −10 °C (ice-acetone bath). Triflic anhydride, $(CF_3SO_2)_2O$, (2.70 mL, 4.16 g, $1.54 \times 10^{-2}$ mol), dissolved in 20 mL of $CH_2Cl_2$, was added from one addition funnel over a period of 20 min. A thick white suspension was formed and shaking of the reaction vessel by hand was necessary. After the addition of triflic anhydride, the reaction mixture was allowed to stir 15 more min, then 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose **1** (2.00 g, $7.68 \times 10^{-3}$ mol) dissolved in 20 mL of $CH_2Cl_2$ was added dropwise via the other addition funnel over a period of 30 min. The reaction mixture was then stirred for 2 h. The slurry was poured into 200 mL ice-$H_2O$ mixture. The organic layer was separated and the aqueous portion was extracted twice with $CH_2Cl_2$ (100 mL × 2). The combined organic portions were dried over anhydrous $Na_2SO_4$ and the solvent was removed by rotary evaporation. Due to the instability of sugar triflate intermediate **2**, the thick colorless liquid obtained above was used for the next reaction immediately.

(8) Nishikubo, Y.; Branchaud, B. P. *J. Am. Chem. Soc.* **1999**, *121*, 10924−10927.

(9) Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*; VCH Publishers: New York, 1996.

**Preparation of 3-Deoxy-3-iodo-1,2,5,6-di-*O*-isopropylidene-α-D-glucofuranose (3).** A solution of triflate **2** was dissolved in 100 mL anhydrous benzene was placed in a 500 mL round-bottom flask equipped with a 1.5 in magnetic stir bar and a water cooling condenser. The solution was deoxygenated for 10 min by bubbling $N_2$ through it, then *n*-$Bu_4NI$ (5.68 g, $1.54 \times 10^{-2}$ mol) was added. This solution was refluxed for 6 h then the solvent was removed by rotary evaporation. The light brown solid residue was extracted with hot hexanes (100 mL × 3), the extracts were combined then the combined extract was filtered through a fritted glass funnel. Removal of the organic solvent afforded an almost colorless thick liquid. After high vacuum removal of residual solvents, pure **3**, a known compound,[10] was obtained in a 67% overall yield (1.91 g, $5.16 \times 10^{-3}$ mol) from **1**. $^1$H NMR ($CDCl_3$) $\delta$ 1.30−1.50 (4 singlets, 12 H,), 3.26 (m, 1 H), 4.08 (m, 3 H), 4.44 (d, 1 H), 5.05 (d, 1 H), 5.96 (d, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 25.10, 26.35, 26.54, 26.96, 34.08, 67.42, 79.10, 79.67, 88.36, 104.85, 109.59, 112.64.

**Preparation of 3-Deoxy-3-pyridyldimethylglyoximatocobalt-1,2:5,6-di- *O*-isopropylidene-α-D-glucofuranose (4) and 3-deoxy-3-pyridyldimethylglyoximatocobalt-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (5).** A suspension of bis(dimethylglyoximato)(pyridine)(chloride)cobalt ($ClCo^{III}$-$(dmgH)_2py$[11] (2.93 g, $7.30 \times 10^{-3}$ mol) in 100 mL methanol was placed in a 500 mL round-bottom flask equipped with a rubber septum and a 1.5 in stir bar. The suspension was deoxygenated by bubbling Ar through it for 20 min at −10 °C (ice−acetone) followed by the addition of $NaBH_4$ (0.560 g, $1.46 \times 10^{-2}$ mol). A dark green solution was generated instantly. A deoxygenated solution of **3** (1.35 g, $3.65 \times 10^{-3}$ mol) in 10 mL THF was added via a cannula. The reaction solution was stirred under $N_2$ and allowed to warm to ambient temperature over 1 h. The product was isolated by anaerobic extraction using deoxygenated $N_2$-saturated solvents. Further purification was accomplished by gravity silica gel (60−200 mesh) column chromatography using deoxygenated $N_2$-saturated ethyl acetate. An inseparable mixture of epimers **4** and **5** was obtained in 55% yield (1.23 g, $2.01 \times 10^{-3}$ mol) as an orange solid. The $^1$H NMR showed that the two epimers were present a ratio of approximately 3S (exo) **4**: 3R (endo) **5** = 65:35. $^1$H NMR ($CDCl_3$) for the major 3S (exo) isomer **4** $\delta$ 0.87 (m, 1 H), 1.21−1.44 (group of s, 12 H), 2.06−2.18 (group of s, 12 H), 3.41 (t, 1 H), 3.61 (t, 1 H), 4.22 (d, 1 H), 4.49 (m, 1 H), 4.61 (t, 1 H), 5.42 (d, 1 H), 7.30 (m, 2 H), 7.71 (m, 1 H), 8.54 (m, 2 H), 18.30 (broad s, 2 H); $^1$H NMR ($CDCl_3$) for the minor 3R (endo) isomer **5** $\delta$ 1.21−1.44 (group of s, 12 H), 2.06−2.18 (group of s, 12 H), 3.02 (m, 1 H), 4.03 (m, 1 H), 4.15 (m, 2 H), 4.34 (m, 1 H), 4.84 (d, 1 H), 5.20 (d, 1 H), 7.30 (m, 2 H), 7.71 (m, 1 H), 8.54 (m, 2 H), 18.30 (broad s, 2 H); $^{13}$C NMR ($CDCl_3$) for the epimeric mixture $\delta$ 12.19, 12.28, 12.44, 25.52, 25.55, 26.21, 26.53, 26.69, 26.96, 27.54, 41.20 (broad, C−Co), 60.34, 62.70, 63.35, 69.67, 73.05, 76.47, 80.91, 85.39, 85.99, 86.95, 101.63, 103.97, 108.44, 108.73, 109.34, 110.54, 125.16, 125.26, 137.61, 137.80, 149.39, 149.50, 150.97, 151.03, 151.79, 151.87 (Due to the chirality of the C center to which Co is attached, the dmgH ligand methyl carbons are no longer equivalent, but some peaks were superimposed). A sample which was purified by silica gel column chromatography and eluted with deoxygenated $N_2$-saturated ethyl acetate showed a satisfactory elemental analysis: mp. 70−78 °C (dec). Anal. Calcd for $C_{25}H_{38}N_5O_9Co$: C, 49.10; H, 6.26; N, 11.45. Found: C, 48.82; H, 6.09, N, 11.27.

**Preparation of 3-Deoxy-3-iodo-5-*O*-carboxymethyl-1,2-*O*-isopropylidene-α-D-ribofuranoside (8).** Using a similar procedure for the preparation of **2** pyridine (2.68 mL, 2.62 g, $3.56 \times 10^{-2}$ mol) in 200 mL $CH_2Cl_2$, triflic anhydride (5.40 mL, 8.32 g, $3.22 \times 10^{-2}$ mol) in 20 mL $CH_2Cl_2$, and 5-*O*-carbomethoxy-1,2-*O*-isopropylidene-α-D-xylofuranose **6** (4.00 g, $1.61 \times 10^{-2}$ mol) in 20 mL $CH_2Cl_2$ were reacted in a 500 mL round-bottom flask at −10 °C (ice-acetone bath) for 2 h. The reaction mixture was poured into 200 mL ice−water which was subsequently separated and the aqueous portion was extracted with $CH_2Cl_2$ (150 mL × 2). The combined organic portions were dried over anhydrous $Na_2SO_4$ and the solvent was removed by rotary evaporation. The resultant triflate **7**, a colorless oil, was converted to the corresponding iodide compound **8** directly by refluxing with *n*-$Bu_4NI$ (1.90 g, $3.22 \times 10^{-2}$ mol) in 200 mL deoxygenated benzene for 7 h. After removal of the benzene by rotary evaporation, the residue was extracted with hot hexanes (150 mL × 3). The extracts were combined then the combined extract was filtered through a fritted glass funnel then the solvent was then removed by rotary evaporation to afford a light brown solid. Recrystallization from ethyl acetate and hexane afforded pure **8** as white needles in 54% overall yield (3.10 g, $8.70 \times 10^{-3}$ mol) from **6**. $^1$H NMR ($CDCl_3$) $\delta$ 1.38 (s, 3 H), 1.56 (s, 3 H), 3.81 (s, 3 H), 3.88 (m, 1 H), 2.27−4.36 (m, 2 H), 4.57−4.66 (m, 2 H), 5.85 (d, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.50, 26.39, 26.46, 55.04, 64.12, 80.56, 80.72, 103.46, 111.74, 155.27. A sample which was recrystallized twice from hexane showed a satisfactory elemental analysis: mp 106−106.5 °C. Anal. Calcd for $C_{10}H_{15}IO_6$: C, 33.54; H, 4.22; I, 35.44. Found: C, 33.77; H, 4.17; N, 35.99.

**Preparation of 3-Deoxy-3-pyridyldimethylglyoximatocobalt-5-*O*-carboxymethyl-1,2-*O*-isopropylidene-α-D-xylofuranose (9) and 3-Deoxy-3-pyridyldimethylglyoximatocobalt-5-*O*-carboxymethyl-1,2-*O*-isopropylidene-α-D-ribofuranose (10).** In a 500 mL round-bottom flask equipped with a magnetic stir bar, a suspension of $ClCo^{III}(dmgH)_2py$ (3.32 g, $8.26 \times 10^{-3}$ mol) in 100 mL methanol at −10 °C was deoxygenated by bubbling $N_2$ through for 20 min, followed by the addition of $NaBH_4$ (0.63 g, $1.65 \times 10^2$ mol). A dark green solution was generated instantly. A deoxygenated solution of **8** (1.48 g, $4.13 \times 10^{-3}$ mol) in 10 mL THF was added via a cannula. This solution was stirred under $N_2$ and allowed to warm to ambient temperature over 1 h. Anaerobic extraction afforded an inseparable mixture of epimers **9** and **10** as a nearly pure orange solid ($^1$H NMR). Further purification was accomplished by silica gel column chromatography using deoxygenated $N_2$-saturated ethyl acetate. The mixture of compounds **9** and **10** was isolated as an orange solid in 51% yield (1.26 g, $2.11 \times 10^{-3}$ mol). The $^1$H NMR showed that the two epimers were present a ratio of approximately 3S (exo) **9**: 3R (endo) **10** = 79:21. Another run of this preparation provided a **9**:**10** ratio of 70:30. $^1$H NMR ($CDCl_3$) $\delta$: 1.25−1.44 (group of singlets, 6 H), 1.73 (m, 1 H), 2.09−2.18 (group of singlets, 12 H), 3.74−3.76 (two s, 3 H), 4.09−4.89 (m, 4 H), 5.31−5.42 (two d, 1 H), 7.32 (m, 2 H), 7.73 (m, 1 H), 8.53 (m, 2 H), 18.15−18.24 (two broad s, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 12.07, 12.16, 12.39, 12.45, 26.53, 26.71, 26.89, 27.56, 54.34, 68.71, 80.75, 83.10, 85.18, 85.27, 87.79, 101.09, 104.19, 110.34, 125.22, 137.75, 149.52, 149.41, 151.19, 152.42, 155.65 (Due to the concentration difference of two epimers, some carbon peaks are not recorded here). A sample which was purified by silica gel chromatography twice showed a satisfactory elemental analysis: mp 187−190 °C (dec). Anal. Calcd for $C_{23}H_{34}N_5O_{10}Co$: C, 46.08; H, 5.72; N,11.68. Found: C, 45.95; H, 5.80; N, 11.37.

**Preparation of 1-Deoxy-1-pyridyldimethylglyoximatocobalt-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose (12) and 1-Deoxy-1-pyridyldimethylglyoximatocobalt-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (13).** In a 250 mL round-bottom flask, a suspension of $CoCl_2 \cdot 6H_2O$ (0.180 g, $7.60 \times 10^{-4}$ mol) and $dmgH_2$ (0.176 g, $1.42 \times 10^{-3}$ mol) in 50 mL methanol at 0 °C was deoxygenated by bubbling $N_2$ through for 10 min followed by the addition of NaOH (0.0568 g, $1.42 \times 10^{-3}$ mol) and pyridine (61.0 microliters, $7.60 \times 10^{-4}$ mol). A brown solution was formed which was deoxygenated for 10 more min. To this brown solution, $NaBH_4$ (0.0580 g, $1.42 \times 10^{-3}$ mol) was added. A dark green solution was formed instantly. 1-deoxy-1-bromo-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide **11** (0.250 g, $3.79 \times 10^{-4}$ mol), dissolved in 5 mL THF, was then added to the reaction system via a cannula. The reaction mixture changed to a brown suspension rapidly. After stirring for 1 h, TLC showed that no starting material was left. The reaction mixture was then adsorbed onto ∼2 g silica gel (60−

(10) Binkly, R. W.; Ambrose, M. G.; Hehemann, D. G. *J. Org. Chem.* **1980**, *45*, 4387.

(11) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.

200 mesh) and dried by rotary evaporation. Purification was accomplished by gravity silica gel column chromatography using deoxygenated $N_2$-saturated ethyl acetate. The orange band was collected in a $N_2$ filled flask. Removal of the solvent by rotary evaporation afforded **12** and **13** as a mixture of epimers in 78% yield (0.280 g, $2.96 \times 10^{-4}$ mol) as an orange solid. The epimeric ratio is approximately 1:1. $^1$H NMR ($CDCl_3$) (reported as total for both **12** and **13**; for example 24 H for glyoxime methyls at 2.05−2.15 with 12 for **12** and 12 for **13**) $\delta$ 2.05−2.15 (singlets, 24 H), 3.78 (m, 1 H), 3.95 (m, 1 H), 4.30 (m, 3 H), 4.55 (m, 2 H), 5.01−5.22 (m, 3 H), 5.45−5.69 (m, 4 H), 7.10−8.90 (m, 50 H), 18.20 (broad s, 4 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 12.09, 12.18, 12.24, 63.26, 63.84, 70.11, 70.17, 70.51, 72.63, 73.70, 73.83, 75.39, 77.72, 125.00, 125.07, 127.98, 128.21, 128.33, 128.49, 129.72, 129.92 129.98, 130.51, 132.26, 132.62, 132.73, 132.84, 133.01, 133.25, 137.56, 137.61, 149.67, 149.74, 150.21, 150.29, 151.11, 164.82, 164.95, 165.27, 165.36, 165.60, 166.08, 166.21, 166.27 (some carbon peaks were superimposed). A sample which was purified by silica gel column chromatography using deoxygenated $N_2$-saturated ethyl acetate showed a satisfactory elemental analysis: mp 144−150 °C (dec). Anal. Calcd for $C_{47}H_{46}N_5O_{13}Co$: C, 59.56; H, 4.89; N, 7.39. Found C, 59.21; H, 4.87; N, 7.10.

**General Information on Photolysis and Thermolysis Reactions.** All reactions were performed in NMR tubes fitted with rubber septa. Reaction solutions were deoxygenated by bubbling Ar through the solution (about 1 mL/min) via long needles. The reaction solutions were under positive Ar pressure via a needle throughout the course of the reactions. The argon was deoxygenated by passage through a heated column of BASF catalyst R3-11 in the black (reduced) form, then it was dried through a column of 3 Å molecular sieves.

**Photolysis Reactions.** The light source used was a 300 W incandescent floodlamp (300 W light bulb). The lamp was mounted in a ceramic socket and positioned 2 in. from a 1400 mL beaker of water. The water bath was stirred with a magnetic stir bar and was cooled with a circulating bath, maintained at 15−20 °C, circulating water through a coil of copper tubing immersed in the beaker. The lamp and the beaker were wrapped in aluminum foil and a stream of air was directed over the light bulb to cool it. Reactions were removed from the apparatus and monitored periodically by $^1$H NMR.

**Thermolysis Reactions.** Samples were prepared in NMR tubes as described above. Thermal isomerization of **4**:**5** was performed using a constant-temperature bath set at 38 °C. Thermal isomerization of **9**:**10** was carried in a 300 MHz NMR at 78 °C.

**Acknowledgment.** We acknowledge the financial assistance of the Alfred P. Sloan Foundation and the National Science Foundation.

JO005595V