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Facile α/β Diastereomerism in Organocobalt Corrins. Access to Minor Isomers of Alkylcobalt Corrinoids by Anaerobic Photolysis

In recent publications[1-3] we have demonstrated the generality of the phenomenon of facile α/β diastereomerism during the synthesis of organocobalt corrinoids. Thus, reductive alkylation of $(H_2O)_2Cbi$,[4] or of factor B,[5] with alkyl halides in the presence of zinc reductants leads to mixtures of the diastereomeric α- and β-RCbi's, the ratio of which varies widely depending on the nature of R.[2] For CH_3Cbi, the β diastereomer predominates by 96:4 and no α diastereomer could be detected for CH_3CH_2Cbi. In contrast, for $NCCH_2Cbi$ and CF_3CH_2Cbi, the α diastereomer predominates by 73:27 and 87:13, respectively, and only very small amounts ($\leq 7\%$) of the β diastereomers of CF_3Cbi and CF_2HCbi are obtained.[8] While it was originally thought that these products were under thermodynamic control,[3] recent work on the thermal interconversion of diastereomers suggests that this is not the case, at least for most RCbi's.[9] While we do not yet understand the basis for the preference of the various alkyl ligands for the α or β position during reductive alkylation, in the majority of cases only one diastereomer is readily accessible for further study. Separation and purification of the minor isomer is usually tedious and provides a very small amount of material, and in some cases, only one diastereomer can be obtained. We now report a simple method of generating the minor isomers of alkylcobalt corrinoids in reasonable yields by anaerobic photolysis.

Under anaerobic conditions in pH 7.0 phosphate-buffered aqueous solution, both α- and β-CH_3Cbi underwent a facile, photoinduced isomerization to give a mixture of the diastereomers under illumination with a 3-V lamp (powered by a dc transformer) at a distance of 38 cm, with a negligible amount (<5%) of dealkylation (Figure 1). No additional products were detectable at any time during the irradiation. The rate of reaction starting from each diastereomer obeyed first-order kinetics, although the α diastereomer was considerably more reactive (Table I and Figure 1). Under stronger illumination (e.g. room light), the reaction was over in a few seconds.[10] The final reaction mixture contained 26% α-CH_3Cbi and 74% β-CH_3Cbi and remained at this composition even under prolonged illumination. This is in stark contrast to the distribution of products obtained by reductive alkylation (4% α-CH_3Cbi)[2] and to the apparent equilibrium distribution of diastereomers (7% α-CH_3Cbi).[9] The latter suggests that irradiation leads to a photostationary state, with a distinctly nonthermodynamic distribution of products, a well-known phenomenon in both organic[11,12] and inorganic[15,16] photochemistry.

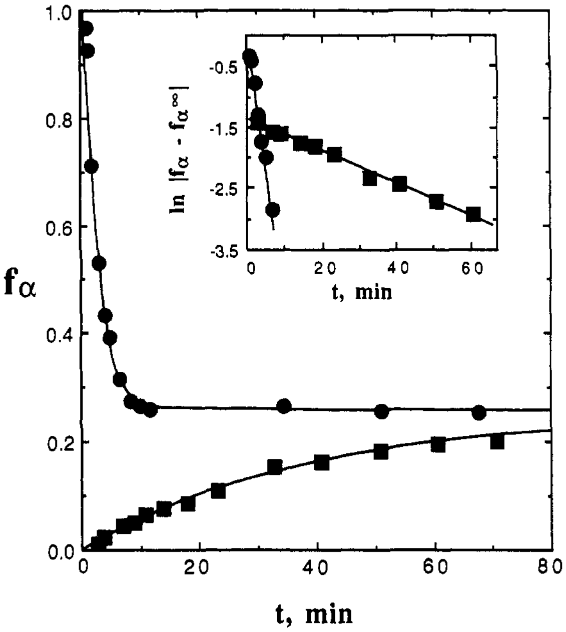

Figure 1. Plot of the fraction of CH_3Cbi present as the α diastereomer, f_α, vs time, for the anaerobic photoisomerization of α-CH_3Cbi (●) and β-CH_3Cbi (■). The solid lines were calculated from a simple first-order rate law and the rate constants listed in Table I. Inset: Semilogarithmic plots of these kinetic data. The solid lines are linear regression lines, slope $= -0.443 \pm 0.015$ m^{-1}, intercept $= -0.333 \pm 0.045$, and $r^2 = 0.994$ for α-CH_3Cbi (●) and slope $= -0.0260 \pm 0.0007$ m^{-1}, intercept $= -1.41 \pm 0.02$, and $r^2 = 0.994$ for β-CH_3Cbi (■).

The diastereomeric CF_2HCbi's, $NCCH_2Cbi$'s, and CF_3CH_2Cbi's similarly underwent facile, photoinduced isomerization under the same conditions.[18,19] In the photolytic steady state, 25–30% of the α diastereomer was obtained and the final composition was independent of the diastereomer which was

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(4) Abbreviations: $(H_2O)_2Cbi$, diaquocobinamide; β-RCbi, β-alkylcobinamide (the organic ligand is in the "upper" axial ligand position); α-RCbi, α-alkylcobinamide (the organic ligand is in the "lower" axial ligand position); β-RCbl, β-alkylcobalamin (the organic ligand is in the "upper" axial ligand position, and the nucleotide is coordinated in the "lower" axial ligand position in neutral solution); α-RCbl, α-alkylcobalamin (the organic ligand is in the "lower" axial ligand position, and the pendent nucleotide cannot coordinate).

(5) Factor B is a mixture of the diastereomeric cyanoaquocobinamides, α-CN-β-$(H_2O)Cbi$ and α-H_2O-β-(CN)Cbi, synthesized by a modification[6] of the method of Renz.[7]

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(8) CF_3Cbi's and CF_2HCbi's are obtained simultaneously from reductive alkylation of factor B with CF_3I due to reductive defluorination of the CF_3Cbi's.[2,3]

(9) Brown, K. L.; Zou, X. *Inorg. Chem.*, in press.

(10) Under even stronger (400-W tungsten lamp at 20 cm), more prolonged illumination, all complexes undergo dealkylation.

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(12) Nonthermodynamic photostationary states have been successfully exploited for the synthesis of thermodynamically disfavored geometrical isomers of olefins, including *trans*-cyclooctene[13] and *cis*-2,2,5,5-tetramethyl-3-hexene.[14]

(13) (a) Inoue, Y.; Takamuka, S.; Kunitomi, Y.; Sukurai, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1672. (b) Inoue, Y.; Takamuka, S.; Sukurai, H. *Synthesis* **1977**, 111.

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(16) Daikh et al.[17] have shown that the cobalt-to-carbon benzyl group migration of the B_{12} model complex $C_6H_5CH_2-Co^{III}[C_2(DO)(DOH)pn]I$ (benzyliodo(2,10-diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diol)cobalt(III)) is formed in 100% yield in the photostationary state while thermal equilibrium provides 60% of this isomer.

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(18) For the $NCCH_2Cbi$'s, the least reactive of these compounds, irradiation for the length of time necessary to achieve the steady state caused some net dealkylation (ca. 15% after 5.3 half-times of irradiation of the α diastereomer).

(19) The CF_3Cbi's were extremely resistant to anaerobic photolysis. Under much stronger illumination (400-W tungsten lamp at 20 cm for 1 h) substantial dealkylation occurred, with only a small amount of isomerization.

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Table I. Observed Rate Constants and Stationary-State Compositions for the Photoinduced Isomerization of α- and β-Alkylcobalt Corrins[a]

compd	f_α[b]	f_α[c]	10^3k,[d] s^{-1}
α-CH_3Cbi	0.26	0.04	7.35
β-CH_3Cbi	0.25		0.442
α-CF_3CH_2Cbi	0.30	0.87	4.30
β-CF_3CH_2Cbi	0.33		0.215
α-CF_2HCbi	0.26	0.98	3.36
β-CF_2HCbi	0.24		0.942
α-$NCCH_2Cbi$[e]	0.27	0.73	1.74
β-$NCCH_2Cbi$[e]	0.30		0.160
α-CH_3CH_2Cbi	0.25	<0.02	17.4
β-CH_3CH_2Cbi	0.29		0.448
α-CH_3Cbl[f]	0.10	0.03	1.11
β-CH_3Cbl[f]	0.14		3.90
α-CH_3CH_2Cbl[g]	0.075	<0.02	4.50
β-CH_3CH_2Cbl[g]	0.097		1.50

[a] Anaerobic solutions (0.05–0.25 mM) of alkylcobalt corrinoid were illuminated for various periods of time with a 3-V lamp (powered by a dc transformer) at a distance of 38 cm. [b] Fraction of the product as the α diastereomer in the photostationary state. Reaction mixture composition was determined by integration of HPLC chromatograms at 254 nm and at 350 nm after correction for differences in molar absorptivity.[2,3,21,39] [c] Fraction of the product as the α diastereomer from synthesis by reductive alkylation.[2,3] [d] From the slopes of semilogarithmic plots of the approach to the photostationary state (see Figure 1). [e] Some decomposition occurs under these conditions.[18] [f] pH 1.2. Some decomposition occurs by the time the stationary state is achieved.[36] [g] pH 1.2. Some decomposition occurs by the time the stationary state is achieved.[24]

photolyzed (Table I). The rate constants for the photoinduced isomerization of the α-RCbi's decreased in the order CH_3 > CF_3CH_2 > CF_2H > $NCCH_2$, and the rate constant for approach to the steady state starting from the α diastereomer of a given RCbi was 3.5–20-fold larger than that for the β diastereomer (Table I). Thus, for R = CF_2H, $NCCH_2$, and CF_3CH_2, for which the equilibrium-controlled distribution of products resulting from reductive alkylation provides only small amounts of the β diastereomer,[2] substantial amounts of this isomer can be obtained by photoinduced isomerization of the α diastereomer.

Because of the nonequilibrium stationary state achieved,[20] photoinduced isomerization can potentially provide access to compounds not otherwise obtainable. Thus, during reductive alkylation of factor B with CH_3CH_2Br, no trace of the α diastereomer is found,[2] the product distribution attained under synthesis conditions overwhelmingly favoring the β diastereomer for this alkyl group. Nonetheless, anaerobic photolysis of β-CH_3CH_2Cbi under the conditions described above rapidly produces a new RCbi in 25% worked-up yield, which is readily characterized as the previously unknown α-CH_3CH_2Cbi. Thus, the UV–visible spectrum of this compound[21] has the same relationship to that of β-CH_3CH_2Cbi as seen in the other pairs of diastereomeric RCbi's;[1,2] i.e., the spectra are quite similar, except that the longest wavelength transition (or α band) is significantly red-shifted (34 nm). In addition, irradiation of β-$CH_3{}^{13}CH_2Cbi$[22] produced α-$CH_3{}^{13}CH_2Cbi$, the ^{13}C NMR resonance of which occurred at 19.40 ppm ($^1J_{H-C}$ = 143.2 Hz, $^2J_{H-C}$ = 7.9 Hz). This resonance is 3.7 ppm upfield from that of β-$CH_3{}^{13}CH_2Cbi$, similar to the upfield shifts of 1.9–4.1 ppm previously observed for the α-carbon resonances of six α-$ROCH_2CH_2Cbi$'s relative to their β diastereomers.[23] Furthermore, both pairs of ^{13}C-enriched and unlabeled compounds were further characterized by FAB MS, unambiguously demonstrating the isomeric relationship between each pair of diastereomers.[24] Finally, reirradiation of the isolated α-CH_3CH_2Cbi produced the same steady-state mixture of α- and β-CH_3CH_2Cbi's as photolysis of the β diastereomer, and the β diastereomer thus produced was indistinguishable from that obtained by reductive alkylation of factor B with CH_3CH_2Br. In fact, the α diastereomer of CH_3CH_2Cbi was the most reactive of the α-RCbi's and was 39-fold more reactive than β-CH_3CH_2Cbi (Table I).

Photolysis of simple alkylcobalt corrinoids is well-known to involve photohomolysis of the Co–C bond to produce a caged radical pair (i.e., $R^\bullet$ and Co^{II}).[27-31] In the absence of oxygen (or other radical scavengers) or sources of abstractable hydrogens, net photodealkylation is extremely slow,[32] the recombination of $R^\bullet$ and Co^{II} within the solvent cage being quite efficient.[33] For cobinamides, which lack an axial nucleotide, recombination can evidently occur at either the α or β face of the cobalt corrin. However, as previously observed by Alelyunas et al.[35] for α-(2-oxo-1,3-dioxolan-4-yl)cobalamin, anaerobic photolysis of α-CH_3Cbl in neutral, aqueous solution gave 100% isomeration to the β diastereomer. As suggested by Alelyunas et al.,[35] this is due to the fact that in neutral solution, cob(II)alamin is base-on ($pK_{base-off} = 3.10$),[3] so that the coordinated nucleotide blocks the α face and recombination can occur only at the β face. This is demonstrated by the observation that anaerobic photolysis of β-CH_3Cbl at pH 1.2, where the axial nucleotide of cob(II)alamin is dissociated and protonated, produces a stationary state mixture of 14% α-CH_3Cbl and 86% β-CH_3Cbl.[36] The same photostationary state is achieved when α-CH_3Cbl is photolyzed under the same conditions (Table I).[36] Since only minuscule amounts of α-CH_3Cbl are obtained by reductive alkylation at low pH, photoinduced isomerization at low pH is of substantial synthetic utility for the synthesis of α-RCbl's as well.

We have consequently exploited this method to obtain the previously unknown α diastereomer of CH_3CH_2Cbl. Anaerobic photolysis of β-CH_3CH_2Cbl at pH 1.2 provided α-CH_3CH_2Cbl in approximately 10% yield (Table I).[37,38] Preparation of this complex permits the complete spectral analogy among the four ethylcobalt corrinoids previously demonstrated for other alkylcobalt corrinoids.[1,2,23] Thus, the UV–visible spectrum of β-CH_3CH_2Cbl[39]

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(20) Recent work[9] suggests that, at thermal equilibrium, the RCbi's are 4–7% α diastereomer for all R groups considered here.

(21) α-CH_3CH_2Cbi: λ (log ε) 478 (4.00), 378 (3.93), 306 (4.38), 265 nm (4.36). β-CH_3CH_2Cbi: λ (log ε) 444 (3.94), 384 (3.98), 303 (4.43), 264 nm (4.33).

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(24) FAB MS was performed as described previously:[23] β-CH_3CH_2Cbi, *m/e* 1019.1 (calc, 1019.2); α-CH_3CH_2Cbi, *m/e* 1018.9 (calc, 1019.2); β-$CH_3{}^{13}CH_2Cbi$, *m/e* 1019.8 (calc, 1020.2); α-$CH_3{}^{13}CH_2Cbi$, *m/e* 1019.8 (calc, 1020.2).[25]

(25) As discussed elsewhere,[1,23,26] the parent ion for cationic RCbi's in positive ion FAB MS lacks an axial water ligand ($M^+ - H_2O$).

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(33) The cage efficiency, F_c,[34] for 5′-deoxyadenosylcobalamin has been estimated[34] to be 0.7 + 0.3 − 0.5 from the flash-photolysis studies of Endicott and Netzel.[31]

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(36) Starting from β-CH_3Cbl, approximately 20% decomposition occurred by the time the stationary state was achieved (17 min), while starting from the α diastereomer, ca. 40% decomposition occurred after 50 min.

(37) β-CH_3CH_2Cbl (184 mg, 0.135 mmol) was dissolved in 100 mL of 2% phosphoric acid (pH 1.2) and purged with argon for 1 h. The anaerobic solution was irradiated with a 9-V tungsten lamp at a distance of 5 cm for 90 min by which time the photostationary state had been achieved. After neutralization, the solution was desalted by chromatography on Amberlite XAD-2[6] and the α- and β-CH_3CH_2Cbl's were separated by semipreparative HPLC.[2,23] The recovered yield of α-CH_3CH_2Cbl was 22 mg (12%).

(38) Starting from β-CH_3CH_2Cbl, approximately 50% dealkylation occurred by the time the stationary state was achieved (33 min), while starting from the α diastereomer, ca. 20% dealkylation occurred by the time the stationary state was reached (10 min).

undergoes the typical base-on/base-off transition between neutral solution and pH 0.3, and the spectrum of the base-off complex is virtually identical to that of β-CH_3CH_2Cbi above 300 nm (i.e., where the axial nucleotide is transparent). The newly obtained α-CH_3CH_2Cbl fails to show a base-on/base-off transition in the visible region upon acidification[39] (i.e., only UV spectral changes associated with protonation of the axial nucleotide[6] occur), and its spectrum is identical to that of α-CH_3CH_2Cbi[21] above 300 nm. The new compound was also characterized by FAB MS,[40] unambiguously demonstrating the isomeric relationship between the CH_3CH_2Cbl diastereomers. As was the case for the CH_3Cbl's, anaerobic photolysis of the newly obtained α-CH_3CH_2Cbl at pH 1.2 produced the same stationary-state mixture of diastereomers as photolysis of β-CH_3CH_2Cbl under these conditions (Table I). Similarly, at neutral pH, photolysis had no effect on β-CH_3CH_2Cbl (other than slow dealkylation), while α-CH_3CH_2Cbl was converted completely to the β diastereomer under this condition.

It is not clear if the photoinduced isomerization by recombination of $R^{\bullet}$ and Co^{II} observed here occurs within the solvent cage or via recombination of separated, free radicals, although available evidence favors the latter.[34,35,42] Alelyunas et al.[35] have obtained evidence from trapping experiments that free radicals are involved in the photoinduced isomerization of α-(2-oxo-1,3-dioxolan-4-yl)cobalamin to the β-diastereomer in neutral solution.[42] If it is correct that α/β isomerization in organocobalt corrinoids requires escape from the solvent cage prior to radical recombination, then the product distribution in the photolytic steady state represents kinetic control of the reaction of $R^{\bullet}$ with Co^{II}. This would suggest that the 2-3-fold preference of $R^{\bullet}$ for the β face of cob(II)inamide (Table I) reflects the greater steric congestion at the α face, due to the downward projecting b, d, and e propionamides and the secondary amide f side chain, than at the β face, which has only three upwardly projecting acetamide side chains. This line of reasoning is supported by the results of the photoinduced isomerization of the base-off RCbl's, where the preference for the β face is increased relative to the RCbi's (Table I), possibly due to the presence of the pendent, bulky dimethylbenzimidazole nucleotide in the former complexes. The mechanism of this synthetically useful photoisomerization is currently under further investigation.

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(39) β-CH_3CH_2Cbl, base-on: λ (log ϵ) 511 (3.96), 345 (4.11), 314 (4.17), 266 nm (4.28). β-CH_3CH_2Cbl, base-off (pH 0.3): λ (log ϵ) 442 (3.91), 382 (3.95), 304 (4.44), 262 (4.49). α-CH_3CH_2Cbl (neutral solution): λ (log ϵ) 476 (4.01), 377 (3.96), 306 (4.38), 264 (4.33). α-CH_3CH_2Cbl (pH 0.3): λ (log ϵ) 476 (4.01), 378 (3.94), 306 (4.40), 265 (4.39).

(40) FAB MS was performed as described previously:[23] β-CH_3CH_2Cbl, *m/e* 1359.2 (calc, 1359.4); α-CH_3CH_2Cbl, *m/e* 1359.4 (calc, 1359.4).[41]

(41) As discussed elsewhere,[1,23] the parent ion for the zwitterionic RCbl's in positive ion FAB MS contains a proton from the matrix (*m*-nitrobenzyl alcohol). For the α-RCbl's, the axial water ligand is lost, so that the parent ion has the same mass for β-RCbl's (MH^+) and for α-RCbl's ($MH^+ - H_2O$).

(42) Similarly, the reversible, thermal cobalt-to-carbon migration of a benzyl radical in $C_6H_5CH_2$–$Co^{III}[C_2(DO)(DOH)pn]I$ (benzyliodo(2,10-diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diol)cobalt(III) is also known to involve escape from the solvent cage followed by recombination.[17]

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Preparation and X-ray Crystal Structure of K[Nd(O-2,6-*i*-$Pr_2C_6H_3)_4$]: A One-Dimensional Chain of Lanthanide Aryloxide Anions Joined by Bis(η^6-arene)–Potassium Interactions

Reports in the literature of the preparation of alkoxide,[1,2] and to a lesser extent aryloxide,[2,3] complexes of the lanthanide elements are numerous, and these complexes have received considerable attention in recent years as potential precursors to high-temperature superconductors, nonlinear optics, and optical fibers.[4] However, the amount of X-ray structural data available for these complexes is somewhat limited, and in the case of lanthanide aryloxide complexes, only the homoleptic species Ce(O-2,6-*t*-$Bu_2C_6H_3)_3$[3a] and Yb(O-2,6-$Ph_2C_6H_3)_3$[3c] and the Lewis base adducts $Na_3[La_2(O\text{-}4\text{-}MeC_6H_4)_6(THF)_5]$,[3b] Yb(O-2,6-$Ph_2C_6H_3)_3$-$(THF)_2$·THF,[3c] and Yb(O-2,6-*t*-Bu_2-4-$MeC_6H_2)_2(THF)_n$ (*n* = 2, 3)[3d] have been crystallographically characterized. Lappert and co-workers have also prepared a series of homoleptic $M(OAr)_3$ (Ar = 2,6-*t*-Bu_2-4-MeC_6H_2) derivatives of many of the lanthanide elements,[3e] yttrium, and scandium, the last of which has been structurally characterized.[3g]

One of the most general synthetic routes to metal alkoxides is the simple metathesis of a metal halide and an alkali-metal alkoxide. While this strategy has great utility in transition-metal chemistry, retention of the alkali metal and formation of "ate" or "double alkoxide" complexes can be a pervasive problem in the chemistry of actinide and lanthanide metals.[2] For alkoxide or aryloxide complexes, the most common type of alkali-metal interaction in "ate" complexes is between the electronegative oxygen atom and the alkali-metal cation, with donor solvent molecules often completing the coordination sphere.[2] This ubiquitous interaction type is illustrated qualitatively in I and has been observed in both early-transition-metal[5,6] and lanthanide[3f] aryloxide complexes. Notably rare are examples of "ate" complexes in which

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