achieving a better $\sigma(SiSi)-\pi$ overlap, which is restricted by the cyclic structure.

Comparison of the MPI spectra of 1-3 leads us to the conclusion that 1 prefers the perpendicular conformation A at low temperatures.

The dihedral angles between an Si-Si bond and a benzene ring plane at the most stable conformations were estimated by MM2 force-field calculations for 1-3, as shown in Figure 2.[9] The MM2 calculations for 1 showed a shallow potential energy minimum at around A, together with another minimum at around B that was 1.3 kcal/mol higher in energy than A. The rotational barrier around the C_{ipso}-Si bond of 2 was calculated to be 1.5 kcal/mol, suggesting smooth rotation about the bond at room temperatures.

In conclusion, the present results are compatible with remarkable stereoelectronic effects on the absorption spectra of aryldisilanes as well as with the OICT model for the CT excited state of 1.

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Registry No. 1, 1130-17-2; 2, 40662-25-7; 3, 40662-22-4.

Stereoelectronic Control of Electron Transfer in the Oxidative Addition of $[py(dmgH)_2Co^I]^-Na^+$ to Carbohydrate Secondary Iodides

Bruce P. Branchaud*,[1] and Gui-Xue Yu

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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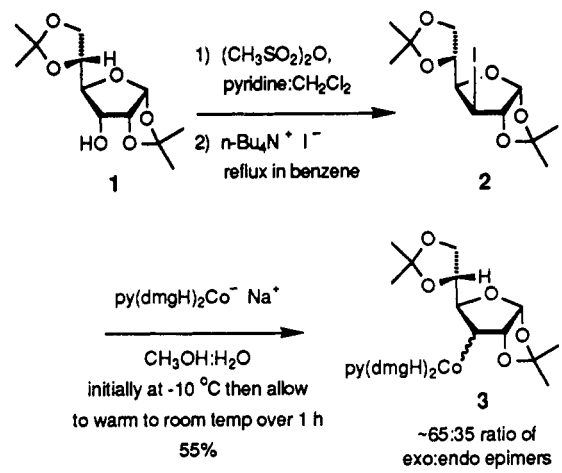
Summary: The relative rates of oxidative addition of secondary carbohydrate iodides **2**, **5**, and **7** with $[py(dmgH)_2Co^I]^-$, to form mixtures of diastereomeric alkyl cobaloximes **3** and **8**, are consistent with steric inhibition of the electron-transfer step. On the basis of these and previously reported observations, a unified mechanism for oxidative addition is proposed.

Organocobalt complexes have recently received attention in synthetic organic radical chemistry.[2,3] Organocobalt complexes can be formed by the oxidative addition of Co(I) complexes to alkyl, aryl, and vinyl halides. For such two-electron oxidative additions several mechanisms can be envisioned,[4] including (1) three-center cis addition, (2) S_N2 addition, (3) atom abstraction of halogen by one metal center followed by combination of the carbon-centered radical with another metal center, (4) inner-sphere electron transfer followed by caged radical-pair combination, (5) radical chains, and (6) outer-sphere electron transfer followed by combination of free carbon-centered radicals with a metal center. From the perspective of synthetic organic chemistry, it is usually adequate to distinguish between concerted mechanisms (1 and 2) and stepwise mechanisms (3-6), since such a simple distinction will cover most synthetically important aspects of stereochemistry and structure-reactivity relationships. Nevertheless, other more detailed aspects of reaction mechanism could have important consequences in using synthetic reactions in a predictable fashion. In this paper we report just such a case involving stereoelectronic control of electron transfer into carbon-halogen bonds.

Scheme I



We have been using alkylcobaloximes, $RCo^{III}(dmgH)_2py$ (dmgH = dimethylglyoxime monoanion; py = pyridine), for the development of new synthetic organic methodology.[2] Alkylcobaloximes are usually formed by the oxidative addition of $[py(dmgH)_2Co^I]^-$ to alkyl halides. In 1969 Schrauzer reported that the oxidative addition of $[py(dmgH)_2Co^I]^-$ with simple primary and secondary alkyl halides proceeded by an S_N2 mechanism.[5] This conclusion

(1) Fellow of the Alfred P. Sloan Foundation, 1987-1989.

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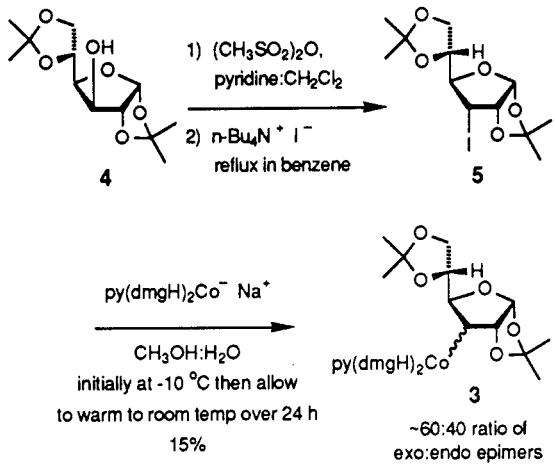
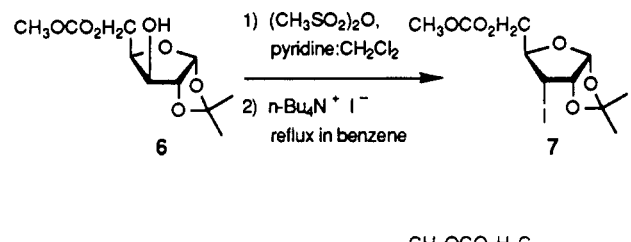
Scheme II

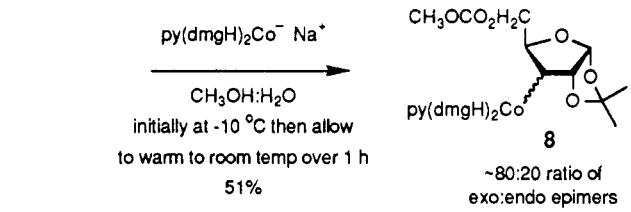


was based on substrate structural effects on reaction rates and not on stereochemical studies. In 1970 Jensen used stereochemistry as a probe of mechanism to show that oxidative addition of $[py(dmgH)_2Co^I]^-$ to secondary cyclohexyl bromides proceeded by an S_N2 mechanism.[6] In 1980 Tada used "5-hexenyl" radical-alkene cyclizations to probe for radical intermediates in the oxidative addition of $[py(dmgH)_2Co^I]^-$ to primary sulfonate esters, chlorides, bromides, and iodides.[7] These studies found an S_N2 mechanism for primary sulfonate esters, a steady progression from S_N2 to an electron-transfer (radical) mechanism on going from chlorides to bromides to iodides, and that steric hindrance favored electron transfer over S_N2. In 1980 Tada used stereochemistry and "5-hexenyl" radical-alkene cyclizations to show that oxidative addition of $[py(dmgH)_2Co^I]^-$ to 2-substituted cyclohexyl bromides and iodides proceeded by an electron-transfer (radical) mechanism.[8] Tada disputed one of Jensen's results, but most of Jensen's work appears incontrovertible.

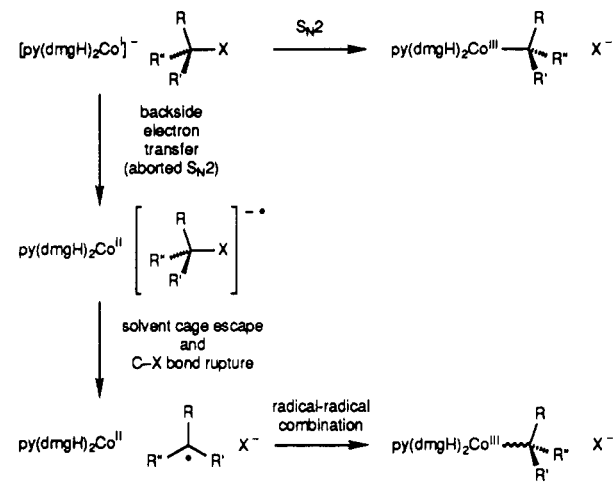
In connection with our synthetic work on developing new C–C bond constructions on carbohydrates using cobaloxime-mediated radical chemistry,[2,9] we were interested in preparing carbohydrate secondary cobaloximes. Iodides **2**[10] and **5**[10] were prepared according to a literature procedure (Schemes I and II).[11] Iodide displacement of the triflate group in this procedure is known to proceed with inversion of stereochemistry by an S_N2 mechanism. We obtained stereochemically homogeneous[12] epimeric iodides **2** and **5** as expected. When **2** was treated with $NaCo^I(dmgH)_2py$, oxidative addition proceeded smoothly within 1 h to provide **3** as a ~65:35 mixture of epimers at the carbon–cobalt bond in 55% isolated yield (Scheme I).[13,14]

Scheme III





Scheme IV



In contrast, treatment of **5** with $NaCo^I(dmgH)_2py$ led to a slow reaction, still very incomplete after 24 h, and a low ~15% isolated yield of **3** as a ~60:40 mixture of epimers at the carbon–cobalt bond (Scheme II).[13,14] Unreacted iodide **5** was recovered from the reaction in ~70% yield,

(6) Jensen, F. R.; Madan, V.; Buchanan, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1414.

(7) Tada, M.; Okabe, M. *Chem. Lett.* **1980**, 201.

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(10) 1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranose (**1**), 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**4**), and 5-*O*-carbomethoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**6**) are commercially available from Pfanstiehl. Compounds **2** and **5** are known and were characterized by ^1H NMR and ^{13}C NMR data and by ^1H NMR comparison with literature data.[11]

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

(12) For compounds **2**, **5**, and **7** only a single diastereomer was observed by ^1H NMR spectroscopy. By this criterion they were judged to be stereochemically homogeneous.

(13) Compound **3** is a new compound. ^1H NMR ($CDCl_3$) for the major isomer (exo, 3*S*): δ 0.87 (m, 1 H, H-3), 1.21–1.44 (group of s, 12 H, CH_3's from isopropylidene), 2.06–2.18 (group of s, 12 H, CH_3's from dmgH ligands), 3.41 (t, 1 H, H-6), 3.61 (t, 1 H, H-6), 4.22 (d, 1 H, H-4), 4.49 (m, 1 H, H-2), 4.61 (t, 1 H, H-5), 5.42 (d, 1 H, H-1), 7.30 (m, 2 H), 7.71 (m, 1 H), 8.54 (m, 2 H), 18.30 (broad s, 2 H, O–H–O bridge). ^1H NMR ($CDCl_3$) for the minor isomer (endo, 3*R*): δ 1.21–1.44 (group of s, 12 H, CH_3's from isopropylidene), 2.06–2.18 (group of s, 12 H, CH_3's from dmgH ligands), 3.02 (m, 1 H, H-3), 4.03 (m, 1 H, H-4), 4.15 (m, 2 H, H-6), 4.34 (m, 1 H, H-5), 4.84 (d, 1 H, H-2), 5.20 (d, 1 H, H-1), 7.30 (m, 2 H), 7.71 (m, 1 H), 8.54 (m, 2 H), 18.30 (broad s, 2 H, O–H–O bridge). ^{13}C NMR ($CDCl_3$) for the diastereomeric mixture: δ 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 were superimposed). A sample which was purified by regular silica gel column chromatography and eluted with deoxygenated 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.

(14) The formation of diastereomeric cobaloximes is known to be a result of the oxidative-addition mechanism and not the result of subsequent cobaloxime isomerization by reversible carbon–cobalt bond homolysis for two reasons. First, reactions in the dark give the same product ratios as those performed under room light. Second, the cobaloxime diastereomers are stable for months under ambient light and temperature conditions and require thermolysis or photolysis to cause isomerization to a different ratio of products. The results of these thermal and photochemical isomerization studies will be reported elsewhere.

providing a nearly complete mass balance.

The slow reaction of **5** with $[py(dmgH)_2Co^I]^-$ is quite surprising. A reasonable explanation might be that electron transfer into the C–I bond proceeds by backside donation into the larger lobe of the C–I antibonding orbital and that steric hindrance from the C5–C6 chain with the isopropylidene group was inhibiting the reaction. To test this idea, we examined a substrate with less steric hindrance. Iodide **7** was prepared according to a literature procedure (Scheme III).[10-12,15] When **7** was treated with $NaCo^I(dmgH)_2py$, oxidative addition proceeded smoothly within 1 h to provide **8** as a ~80:20 mixture of epimers at the carbon–cobalt bond in 51% isolated yield (Scheme III).[14,16] The rapid reaction of **7** was almost as surprising as the slow reaction of **5**. We worried that the structure shown for **7** was not correct, that its epimer had been formed by a double iodide displacement, and that the epimer was causing the rapid reaction. To rule out this possibility, the structure of **7** was determined by X-ray crystallography,[17] verifying that the stereochemistry shown in **7** is correct.

The significant observation in these results is that there appears to be a steric inhibition of electron transfer in comparing the reactivities of **2** vs **5** vs **7**. This may not be immediately obvious, but an inspection of hand-held molecular models and computer-generated MMX-minimized structural models[18] provides a satisfactory explanation. Models show that in-line backside attack on the C–I bond in **5** and **7** results in considerable steric hindrance from the adjacent C5–C6 chain with the isopropylidene group in **5** or C5 methyl carbonate group in **7**. Such steric hindrance should be especially important for the large $[py(dmgH)_2Co^I]^-$ with the square-planar array of the two dmgH ligands. The smaller C5 methyl carbonate group in **7** can swing out of the way to let $[py(dmgH)_2Co^I]^-$ approach, whereas the bulkier C5–C6 chain with the isopropylidene group in **5** cannot do the same. In-line backside attack by $[py(dmgH)_2Co^I]^-$ on the C–I bond in **2** also experiences steric hindrance, since the approach is from the endo face of the molecule, but the steric hindrance does not appear to be as great as for exo in-line backside attack by $[py(dmgH)_2Co^I]^-$ on the C–I bond in **5**.[19]

Coupling our observations with those previously reported in the literature[5-8] leads us to propose the unified mechanism for oxidative addition of alkyl halides with $[py(dmgH)_2Co^I]^-$ shown in Scheme IV. *We propose that all reactions begin by backside approach of* $[py(dmgH)_2Co^I]^-$ *toward the C–X bond and then steric effects and C–X bond effects (Cl vs Br vs I) determine whether a successful* S_N2 *reaction is achieved or the* S_N2 *process is aborted and an electron transfer ensues.* To our knowledge the results reported in this paper are the first observations of stereochemical preferences for electron transfer into carbon–halogen bonds. The approach we have used here, varying steric hindrance from a remote substituent as a probe of reaction at a locally otherwise unperturbed center, should be adaptable to the study of other types of electron-transfer processes.

Acknowledgment. This work was supported by NSF grant CHE 8806805. The GE QE-300 NMR spectrometer used in this work was purchased with funds provided by NIH grant RR 02336 and NSF grant CHE 8411177. The VG ZAB-2FHF MS and VG 12/253 Quad MS instruments used in this work were purchased with funds provided by NIH grant RR 03001, NSF grant DMB 8414627, and the M. J. Murdoch Charitable Trust.

(15) Iodide **7** is a new compound. ^1H NMR ($CDCl_3$): δ 1.38 (s, 3 H, isopropylidene CH_3), 1.56 (s, 3 H, isopropylidene CH_3), 3.81 (s, 3 H, methoxy CH_3), 3.88 (m, 1 H, H-3), 2.27–4.36 (m, 2 H, H-4, H-5), 4.57–4.66 (m, 2 H, H-2, H-5), 5.85 (d, 1 H, H-1). ^{13}C NMR ($CDCl_3$): δ 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.

(16) Cobaloxime **8** is a new compound. ^1H NMR ($CDCl_3$): δ 1.25–1.44 (group of singlets, 6 H, CH_3's from isopropylidene), 1.73 (m, 1 H, H-3), 2.09–2.18 (group of singlets, 12 H, CH_3's from dmgH ligands), 3.74–3.76 (two s, 3 H, CH_3 from methoxy), 4.09–4.89 (m, 4 H, H-2, H-4, H-5), 5.31-5.42 (two d, 1 H, H-1), 7.32 (m, 2 H), 7.73 (m, 1 H), 8.53 (m, 2 H), 18.15–18.24 (two broad s, 2 H, O–H–O bridge H). ^{13}C NMR ($CDCl_3$): δ 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 diastereomers, some carbon peaks are not recorded here). A sample which was purified by regular 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.

(17) The results of the X-ray crystallographic analysis of the structure of **7** will be reported in detail elsewhere.

(18) Calculations were done using PCMODEL version 4.25 on either Macintosh IIcx or SE/30 computers. PCMODEL is a product of Serena Software, Box 3076, Bloomington, IN 47402-3076. MMX is a version of the MM2 molecular mechanics program that has been enhanced by Serena Software.

(19) *cis*-Bicyclo[3.3.0]octane ring systems generally have an enormous difference in steric hindrance to approach from exo vs endo faces, with the exo approach highly favored. The C5–C6 side chain in **2** and **5** is known to significantly perturb this since reactions of the radical at C3, which could be produced from **2** or **5** or from homolysis of the C–Co bond in **3**, exhibits a modest 4:1 exo:endo selectivity in radical-alkene addition reactions and as low as a 1:1 exo:endo selectivity in radical-nitroalkyl-anion addition reactions. PCMODEL calculations show that the radical has a flattened-out conformation that is significantly different from that found in **2** and **5** and that the steric effects of the C5–C6 side chain should be larger in **2** and **5** than in the radical, further disfavoring an exo approach: (a) Reference 9. (b) Giese, B.; Gonzalez-Gomez, J. A.; Witzel, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 69.