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Sodium Borohydride Reduction of Cobaloxime Complexes. An Electron-Transfer, Free-Radical Process

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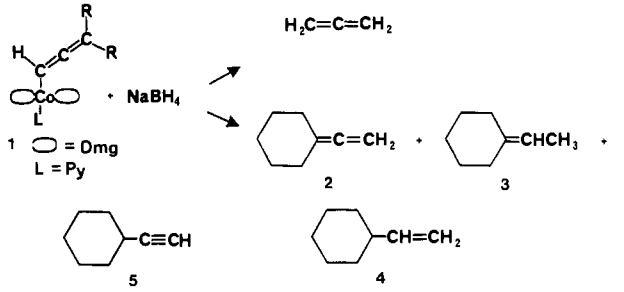
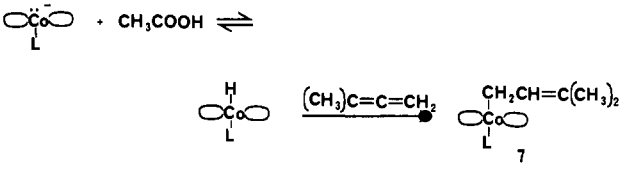
In 1969 Collman and co-workers[1] reported that allenylcobaloxime complexes undergo reductive removal of the allenyl group on treatment with sodium borohydride. The reduction of **1** (R = H) produced only allene, while the reduction of **1**



[R = $-(CH_2)_5-$] produced a mixture of six products, of which only **2–4** were isolated and identified. Products **3** and **4** represent overreduction of **2**, or possibly ethynylcyclohexane (**5**). We have extended the original work to include the reduction of other allenyl- and propargylcobaloxime complexes.

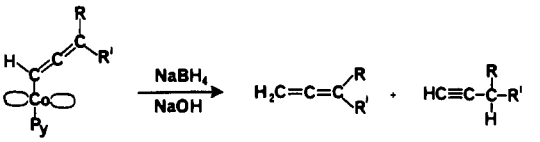
Preliminary studies indicated that the overreduction occurs via hydrocobaltation of the initially formed allene (or alkyne) followed by reduction of the intermediate complex. For example, 1,1-dimethylallene (**6**) undergoes hydrocobaltation by bis(dimethylglyoximato)(pyridine)cobalt(I) anion in the presence of acetic acid to form complex **7**. Under the reaction



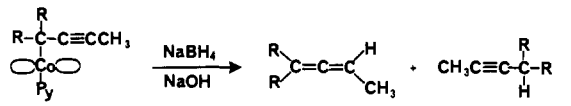
conditions originally described[1] the hydrocobaltation of **6** occurs to a lesser extent, and can be completely repressed, in the presence of added sodium hydroxide. These data are consistent with the presence of the equilibrium shown in the above equation involving the formation of the hydridocobalt complex. Thus, the reduction of the allenyl- and propargylcobaloxime complexes can be carried out in the presence of added base, which represses the overreduction of the initially formed products.

The reduction of **1** (R = H) produces only allene, consistent with the earlier observations. The reduction of the allenyl complexes **8a** and **8b** and the propargyl complex **9a** produces mixtures of the substituted allene *and* alkyne (see Table I). The reduction of **9b** produces only the alkyne. The allylcobaloxime complex **7** undergoes reduction to produce a 10:1 mixture of **10** and **11**.

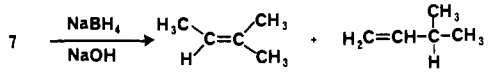
The product distributions observed in the reductions of the allenyl- and propargylcobaloxime complexes correspond reasonably well with those observed in the free-radical chain reduction of propargyl chlorides with tributyltin hydride[3] (see Table I), suggesting that the reduction of the cobaloxime complexes involves the formation of the allenyl–propargyl



8a R=H, R'=CH_3
8b R=R'=CH_3



9a R=R=H
9b R=R=CH_3

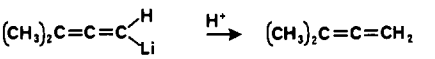


10 **11**

resonance-hybrid free radical **12**. This is not consistent with

12

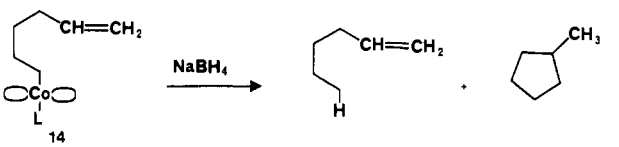
the previously proposed mechanism for the reduction of alkylcobaloxime and alkylcobalamine complexes with zinc, dithionite, or sodium borohydride, which has been proposed to occur by the protonation of intermediate alkylcarbanions, in most cases the anionic center not being stabilized.[4] In the reduction of the allenyl- and propargylcobaloximes this cannot be the case. The protonation of 1,1-dimethyl-3-lithioallene (**13**) produces *only* 1,1-dimethylallene,[5] not a mixture of allene



13 **6**

and alkyne as is observed in the present study. Theoretical calculations on the allenyl and propargyl anion system indicate that the former is more stable, and hence the dominant contributor, than the latter by 6 kcal/mol.[6]

In order to test for the possible formation of free radicals in the reduction of other alkylcobaloxime complexes, the 1-(5-hexenyl)cobaloxime complex **14** was prepared.[7] Reduction



14

of **14** with sodium borohydride produces a mixture of 1-hexene *and* methylcyclopentane in a 44:56 ratio. The 5-hexen-1-yl radical is known to undergo ring closure to the cyclopentylmethyl radical with a first-order rate constant of 1.0×10^5 s^{-1} at 25 °C.[8] The corresponding 5-hexen-1-yl anion does *not* undergo ring closure and, in fact, has been used as a probe for electron-transfer reactions in Grignard reactions.[9] It is,

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(7) An attempt was also made to prepare the (cyclopropylmethyl)cobaloxime complex from cyclopropylmethyl bromide. The results of this experiment will be reported separately.
(8) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355. Schmid, P.; Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1979**, *11*, 333.
(9) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545.

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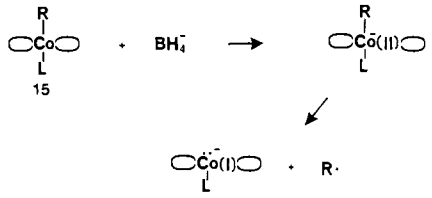
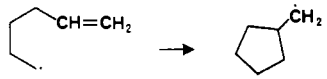
Table I. Alkyne:Allene Product Ratios from the Reduction of Cobaloxime Complexes (A) and Propargyl Chlorides with Tributyltin Hydride (B)

cobaloxime complex	propargyl chloride	A	B
1	$ClCH_2C{\equiv}CH$	<0.05	5.9
9a	$ClCH_2C{\equiv}CCH_3$	1.5	25
8a	$ClCH(CH_3)C{\equiv}CH$	1.1	4.5
8b	$ClC(CH_3)_2C{\equiv}CH$	2.1	1.7
9b	$ClC(CH_3)_2C{\equiv}CCH_3$	>100	>20

Scheme I



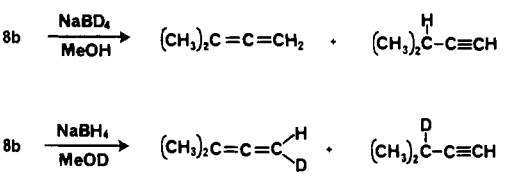
obvious that the reduction of **14** results in the initial formation of the 5-hexen-1-yl radical, which undergoes partial ring closure before further reaction.



A reduction mechanism consistent with the present data is illustrated in Scheme I. We believe that the reduction process is initiated by an electron transfer from borohydride to the cobaloxime complex, producing a Co(II) complex that undergoes homolytic cleavage to form the reduced Co(I) complex and an organic free radical. Single electron-transfer reactions have been observed previously between metal hydrides (AlH_3 and BH_3) and aromatic ketones,[10] between complex metal hydrides ($LiAlH_4$) and aromatic hydrocarbons,[11] in the reduction of substituted pyridine *N*-oxides by potassium tri-*sec*-butylborohydride,[12] and, most cogently, in the reduction of d^6 and d^7 organoiron cations by lithium aluminum hydride and sodium borohydride.[13]

The transfer of an electron from borohydride to the cobaloxime complex would produce a Co(II) complex, which, on the basis of known photochemical reactions of cobaloxime complexes, should undergo homolytic cleavage of the Co–C bond. Irradiation of alkylcobaloxime complexes in the ligand-to-cobalt charge-transfer band results in the formal formation of an alkylcobalt(II) complex.[14] Such complexes undergo loss of an alkyl radical competitive with hydrogen atom abstraction from the O–H of the belt dimethylglyoximato ligands.[14,15] The controlled potentiometric reduction of cobaloxime(III) complexes produces Co(II) complexes that give rise to similar results.[16]

A critical question is from what do the intermediate radicals abstract a hydrogen atom. The reduction of **8b** with sodium borodeuteride in methanol does not result in the incorporation of deuterium in the 1,1-dimethylallene or 3-methyl-1-butyne. Interestingly, the reduction of **8b** with sodium borohydride in methanol-*d* results in the quantitative introduction of deuterium to form 3-deuterio-1,1-dimethylallene and 3-deuterio-3-methyl-1-butyne. Abstraction of a hydrogen atom



from methanol-*d* should preferentially involve abstraction of a hydrogen atom from a C–H bond and not a deuterium atom from the O–D bond for thermodynamic reasons. Two experimentally indiscriminable possibilities exist. The cobalt(I) anionic complex formed after loss of the organic free radical could become deuterated by transfer of a deuteron from methanol-*d* which in turn is abstracted by the free radical. Such radical abstraction reactions have been observed with benzylcobaloxime complexes.[17] However, kinetic considerations suggest that such is not the case as it appears that the hydrogen (deuterium) atom transfer occurs between the Co–organic radical pair within the solvent cage before cage–solvent reactions occur. Alternatively, exchange of OH by OD in the dimethylglyoximato ligands, a rapid exchange reaction, would also provide a source of deuterium for the free radical to abstract. Such abstraction reactions have been observed in photochemical reactions[15] but have not been demonstrated with Co(I) complexes.

A final question concerning the proposed mechanism is whether the reaction proceeds via the base-on complex **15** or via the base-off complex. The addition of an electron to the base-on complex would occur to the lowest lying, unoccupied σ^* MO.[18] This should result in a weakening of the Co–C bond, thus facilitating Co–C bond homolysis. Following loss of the base ligand, the electron will add to one of the π-type hybrids, which although more energetically favorable, should have little effect on the Co–C bond strength. Qualitatively, when the reduction is carried out in the presence of a 50-fold molar excess of pyridine, the reaction appears to occur somewhat more slowly, suggesting that the base-off complex is involved in the electron-transfer step. Further studies are required on more kinetically manageable systems in order to clarify this point.

The results of this study seriously question whether alkylcarbanions are formed in the reduction of alkylcobaloxime and alkylcobalamine complexes with sodium borohydride.[19,20]

Experimental Section

Reduction of the Cobaloxime Complexes. To 300 mg of the cobaloxime complex suspended in 20 mL of degassed methanol containing 100 mg of sodium hydroxide at 0 °C under a nitrogen atmosphere was added 50 mg of finely ground sodium borohydride. The solution immediately turned dark blue. The volatile products were swept out of the reaction mixture in a stream of nitrogen bubbled through the solution and were condensed in a trap cooled in a dry ice–acetone bath. The condensed volatile fractions were dissolved in deuteriochloroform, and the NMR spectra were recorded. All products were identified by their simple, characteristic NMR spectral patterns. Ratios of products were determined by integration of the NMR spectra.

Hydrocobaltation of 1,1-Dimethylallene. Bis(dimethylglyoximato)(pyridine)cobalt chloride (300 mg, 0.75 mmol) was

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(19) The reduction of **14** with dithionite and thiophenoxide produces only 1-hexene. The mechanism of these reduction reactions is not clear, and faster radical–clock containing systems must be prepared and studied.
(20) The reduction reactions reported in ref 4 can all be rationalized on the basis of an electron-transfer, free-radical-intermediate process including the reported acyl migration reactions. Migrations of carbonyl functions in radical reactions have been reported previously (Jorgenson, M. J.; Thacher, A. F. *Chem. Commun.* **1969**, 1030. Hart, H.; Shih, E.-M. *J. Org. Chem.* **1976**, *41*, 3377).

suspended in 20 mL of degassed methanol containing 100 mg of sodium hydroxide at 0 °C and was reduced with 50 mg of sodium borohydride. 1,1-Dimethylallene (0.8 mmol) was added, followed by the dropwise addition of glacial acetic acid until the solution turned orange-red. Ice water (100 mL) was added, resulting in the formation of orange-red crystals. The crystals were collected by filtration and were recrystallized from methanol–water. ^{1}H NMR ($CDCl_3$): δ 1.15 (br, s, 3 H), 1.25 (br s, 3 H), 2.10 (s, 12 H), 2.43 (d, J = 9.43 Hz, 2 H), 5.00 (br t, J = 9.43 Hz, 1 H), 7.29 (m, 2 H), 7.69 (m, 1 H), 8.55 (m, 2 H).

Anal. Calcd for $C_{18}H_{28}CoN_5O_4$: C, 49.42; H, 6.46; N, 16.01. Found: C, 49.11; H, 6.48; N, 15.86.

Preparation of 5-Hexen-1-ylcobaloxime (14). To a solution of 0.1 g of sodium hydroxide in 25 mL of methanol under an argon atmosphere was added 0.5 g (1.3 mmol) of bis(dimethylglyoximato)(pyridine)cobalt(III) chloride, followed by the addition of 60 mg (1.6 mmol) of sodium borohydride. The dark blue reaction mixture was stirred for 5 min and cooled to −20 °C, and 215 mg of 1-bromo-5-hexene was added. The reaction mixture was allowed to come to room temperature and was stirred for 1 h. Ice water (200 mL) was then added, and the mixture was allowed to stand overnight in the refrigerator. The orange-brown crystals (30%) were collected and recrystallized from methanol–water; mp >170 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.93 (m, 2 H), 1.28 (m, 2 H), 1.62 (m, 2 H), 1.97 (m, 2 H), 2.15 (s, 12 H), 4.87 (dd, J = 10.16, 1.66 Hz, 1 H), 4.92 (dd, J = 13.50, 1.66 Hz, 1 H), 5.73 (ddt, J = 10.16, 13.50, 6.74 Hz, 1 H), 7.32 (dd, J = 4.86, 7.50 Hz, 2 H), 7.73 (t, J = 7.50 Hz, 1 H), 8.59 (d, J = 4.86 Hz, 2 H).

Anal. Calcd for $C_{19}H_{30}CoN_5O_4$: C, 50.55; H, 6.70; N, 15.51. Found: C, 50.37; H, 6.47; N, 15.26.

Sodium Borohydride Reduction of 14. To a solution of 20 mg of sodium hydroxide and 216 mg (0.5 mmol) of **14** in 20 mL of methanol at 25 °C under an argon atmosphere was added 120 mg (3.2 mmol) of sodium borohydride. The reaction mixture was stirred for 30 min, and the volatiles were then removed on a vacuum line. The volatile fraction was analyzed by GC using a 24-ft DEGS column at 80 °C showing the presence of 1-hexene and methylcyclopentane (by comparison of retention times with authentic samples) in a 0.80:1.00 ratio.

An identical reduction was carried out, and the organic phase was diluted with ice water and extracted with a small volume of deuteriochloroform. The deuteriochloroform extract was repeatedly washed with cold water and was dried over $MgSO_4$. The ^{1}H NMR spectrum of the extract displayed a triplet at δ 0.88 for 1-hexene (Sadtler No. 3427, δ 0.89) and a doublet at δ 0.96 for methylcyclopentane (Sadtler No. 3436, δ 0.97).

Reduction of Bis(dimethylglyoximato)(3,3-dimethylallen-1-yl)(pyridine)cobalt (8b, R = R′ = CH_3) with Sodium Borodeuteride in Methanol. To a solution of 300 mg of **8b** (R = R′ = CH_3) and 0.15 g of sodium hydroxide in 10 mL of methanol under an argon atmosphere was slowly added an excess (100%) of sodium borodeuteride. A stream of argon was slowly bubbled through the reaction mixture and passed through 1 mL of deuteriochloroform cooled in a dry ice–carbon tetrachloride bath. The NMR spectrum of the deuteriochloroform solution contained only a triplet methyl resonance for 1,1-dimethylallene and a doublet methyl resonance for 3-methyl-1-butyne. The methynyl CH resonance of 3-methyl-1-butyne was clearly evident.

Reduction of Bis(dimethylglyoximato)(3,3-dimethylallen-1-yl)(pyridine)cobalt (8b, R = R′ = CH_3) with Sodium Borohydride in Methanol-*d*. In a solution of sodium methoxide (prepared by the addition of 50 mg of sodium to the methanol-*d*) in 8 mL of methanol-*d* 200 mg of **8b** (R = R′ = CH_3) was reduced with an excess (50%) of sodium borohydride under an argon atmosphere. A stream of argon was bubbled through the reaction solution and passed through 1 mL of deuteriochloroform in a dry ice–carbon tetrachloride cooling bath. The NMR spectrum of the deuteriochloroform solution showed a methyl doublet for 1,1-dimethylallene, and a methyl doublet (C–H coupling) and methyl triplet (C–D coupling) for 3-methyl-1-butyne in a 0.11:0.89 ratio.

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Registry No. 1 (R = H), 42568-33-2; **7**, 42568-31-0; **8a**, 42568-34-3; **8b**, 42568-35-4; **9a**, 42568-38-7; **9b**, 92490-51-2; **10**, 513-35-9; **11**, 563-45-1; **14**, 42568-40-1; $ClCH_2C{\equiv}CH$, 624-65-7; $ClCH_2C{\equiv}CCH_3$, 3355-17-7; $ClCH(CH_3)C{\equiv}CH$, 21020-24-6; $ClC(CH_3)_2C{\equiv}CH$, 1111-97-3; $ClC(CH_3)_2C{\equiv}CCH_3$, 999-79-1; $NaBH_4$, 16940-66-2; bis(dimethylglyoximato)(pyridine)cobalt chloride, 23295-32-1; 1-hexene, 592-41-6; methylcyclopentane, 96-37-7; 1,1-dimethylallene, 598-25-4; 3-methyl-1-butyne, 598-23-2; 1-methylallene, 590-19-2; 1,1,3-trimethylallene, 3043-33-2; 1-butyne, 107-00-6; 2-butyne, 503-17-3; 4-methyl-2-pentyne, 21020-27-9; 1-bromo-5-hexene, 2695-47-8.

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Mechanism of Oxidation of Mandelic Acid by Fenton's Reagent

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The oxidation of organic substrates by Fenton's reagent (Fe^{2+}–H_2O_2, Fe^{2+}–$S_2O_8^{2-}$, Cu^{2+}–$S_2O_8^{2-}$, and related systems) presents unusual complexity at the molecular level.[1] The role of the hydroxyl radical and sulfate radical anion as primary oxidants has been recognized. The ferryl radical (FeO^{2+} or $Fe(OH)^{3+}$) has been implicated in biological oxidations.[2] The mechanistic conflict boils down to one of oxidation due to OH· and SO_4^{-}·, vis-a-vis oxidation by an Fe^{IV} intermediate.

The intermediacy of an Fe^{IV} species was postulated in the oxidative decarboxylation of phenylglyoxylic acid (PGA).[3] Recently Walling and co-workers addressed this problem in the oxidation of mandelic acid.[4] The choice of mandelic acid was unique in the sense that it formed a stable 1:1 complex with Fe^{2+} offering an opportunity to detect intramolecular oxidation by higher valent Fe^{IV} species. In addition to the usual hydroxyl radical reaction, Walling proposed a cage reaction of the OH· radical that could not be eliminated by hydroxyl radical traps. Shinra[5] has proposed the intermediacy of PGA to account for the formation of benzoic acid in the oxidation of mandelic acid by the Cu^{2+}/Ag^{+}–$S_2O_8^{2-}$ system. Walling considered PGA an unlikely intermediate. Benzoic acid was thought to arise due to oxidation of benzaldehyde. Mandelic acid seemed important to us in another respect. One-electron oxidants cleave the C–C bond, giving exclusively benzaldehyde.[6] Two-electron oxidation involving C–H cleavage should give the keto acid, i.e. PGA.

In Walling's work, benzaldehyde was the major product (the highest reported yield being 66%). Benzoic acid (5%) and ring-hydroxylated mandelic acids (3.5%) were the other products in the oxidation. Strangely enough, 25% of the material balance was still missing. We were intrigued by the

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