aminium ion catalyzed reactions is clearly limited.

In conclusion, our results illustrate that cation radical mechanisms for isomerizations in Brønsted acids + dioxygen have not been rigorously excluded. Although the mechanism of the electron-transfer step is not fully understood, it likely involves a substrate–dioxygen charge-transfer complex.[7] Finally, we should warn that an analogous mechanistic dilemma may arise for Lewis acid promoted reactions. Many Lewis acids are known to promote one-electron oxidation (e.g. $SbCl_5$, $AlCl_3$, and BF_3).[4] It will be interesting to see how general the Brønsted acid and Lewis acid promoted electron-transfer reactions are.

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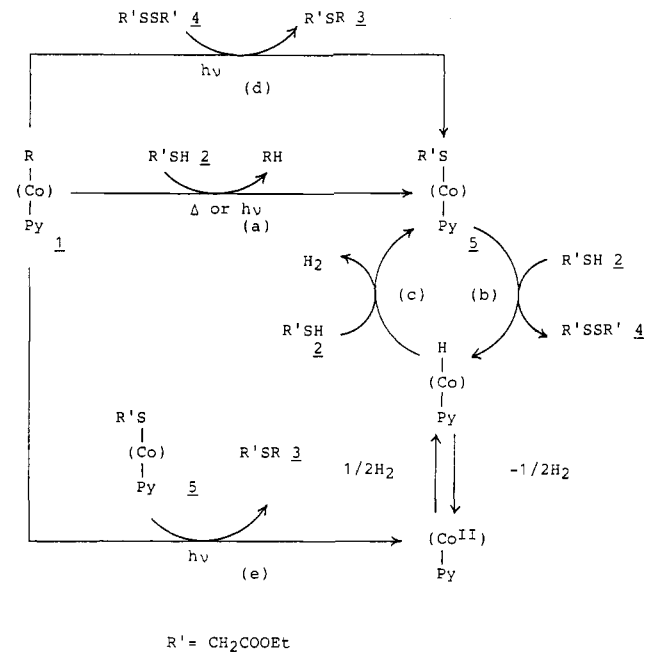
Homolytic Alkyl Group Transfer Reaction of Photoactivated Alkylcobaloximes into Thiols

Summary: Alkyl groups of alkylcobaloximes were transferred to alkylthiols by irradiation of alkylcobaloxime and thiol under anaerobic conditions; a radical route via homolytic substitution between alkylcobaloxime and disulfide, formed during the reaction, is proposed.

Sir: Currently, the reactivity of C–Co bond in alkylcobaloxime has received much attention as a stable organometallic reagent and also as a cobalamin (vitamin B_{12}) model.[1] We have investigated[2] the chemical reactivity of photoactivated alkylcobaloxime. The dealkylative substitution reaction of alkylcobaloxime has frequently been utilized in organic syntheses.[1c,3] Particularly, the reaction of organocobalt complexes with thiols has received much attention with respect to the function of methionine synthetase, a cobalamin (vitamin B_{12}) dependent enzyme.[4] It has not been shown, however, whether the methyltransfer reaction of the enzymic reaction proceeds in a radical or in an ionic manner. Schrauzer et al. have suggested[4a,b] the ionic mechanism in the methionine formation reaction with methylcobaloxime and homocysteine in alkaline media. The attempted[4a] homolytic alkyl-transfer reaction of alkylcobaloxime to alkylthiol has failed so far.

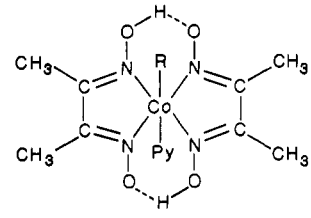
Scheme I



R'= CH_2COOEt

In this paper, we present the first successful example involving the homolytic alkyl-transfer reaction from alkylcobaloxime to some thiols induced by the cleavage of C–Co bond in alkylcobaloxime by irradiation with a visible light.

A mixture of alkylbis(dimethylglyoxymato)pyridinecobalt(III) (1)[5] (1.5 mmol), ethyl mercaptoacetate (2) (1 mmol), and 15 mL of CH_2Cl_2 in a Schlenk tube was deoxygenated and replaced with argon gas by the freeze–pump–thaw technique. The reaction vessel was irradiated



alkylbis(dimethylglyoxymato)pyridinecobalt(III)
R = methyl (**1a**), benzyl (**1b**); py = pyridine

with a tungsten lamp (400 W) for 24 h at 35 °C. The reaction proceeds according to eq 1, and the results are summarized in Table I. Product yield and conversion were determined by NMR.[6]

$$\underset{\mathbf{2}}{HSCH_2CO_2Et} \xrightarrow[h\nu]{RCo(DH)_2py\ (1)} \underset{\mathbf{3}}{RSCH_2CO_2Et} + \underset{\mathbf{4}}{(SCH_2CO_2Et)_2} \quad (1)$$

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(6) Product yield was determined by the ^1H NMR peak area of organic products, which were separated from the reaction mixture by a silica gel column with a $CHCl_3$ solvent. Conversion was also determined by the ^1H NMR peak area of the reaction mixture: ^1H NMR ($CDCl_3$): δ 3.28 (d, 2 H, $HSCH_2CO_2Et$, **2**), 2.20 (s, 3 H, $CH_3SCH_2CO_2Et$, **3a**), 3.08 (s, 2 H, $PhCH_2SCH_2CO_2Et$, **3b**), 3.60 (s, 4 H, $(SCH_2CO_2Et)_2$, **4**), 2.30 (s, 12 H, CH_3 of **5**).

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Table I. Reaction of Photoactivated Alkylcobaloxime and Ethyl Mercaptoacetate[a]

run	cobaloxime	temp, °C	time, h	yield, % 3	yield, % 4	conversion, %
1	**1a**	35	24	3	27	79
2	**1b**	35	24	52	15	100
3		35	48	61	6	100
4		-20	24	55	18	100
5[b]		-20	24	0	76	76

[a] Conditions: alkylcobaloxime, 1.5 mmol; thiol, 1.0 mmol; CH_2Cl_2, 15 mL; tungsten lamp (400 *W*), distance from lamp to reaction vessel 20 cm, under an argon atmosphere. [b] Dark reaction.

In every case, both ethyl 2-(alkylthio)acetate (**3**) and bis[(ethoxycarbonyl)methyl] disulfide (**4**) were obtained (runs 1-4). Methylcobaloximine (**1a**) showed a lower reactivity than benzylcobaloxime (**1b**) (run 2) because of its higher dissociation energy[1b] of the Co-C bond and instability of methyl radical formed. The yield of sulfide **3** increased by extending the reaction (run 3). The reaction proceeded similarly even at a low temperature under irradiation (run 4), but in the dark, the reaction at low temperature failed to give the sulfide **3** and the only product was disulfide **4** (run 5). Besides **3** and **4**, a considerable amount of [[(ethoxycarbonyl)methyl]thio]bis(dimethylglyoxymato)pyridinecobalt(III) **5** was detected in the reaction mixture by the ^1H NMR measurement. Similarly, benzyl-transfer reaction occurred when **1b** was treated with other thiols such as benzenethiol, α-toluenethiol, and 2-mercaptoethanol.[7]

The reaction course was assumed as in Scheme I by considering below additional results and discussions.

In the first step of this reaction (path a), the abstraction of hydrogen by an alkyl radical formed from thermal- or photoactivated alkylcobaloxime gives alkane and (alkylthio)cobaloxime **5**. In the case of the reaction of benzylcobaloxime (**1b**) and thiol **2**, a slight amount of toluene was detected by gas chromatography.[8] The bimolecular homolytic substitution reaction between **1** and **2**, which is an assumed path of direct alkyl sulfide formation, will not occur for high dissociation energy of RS-H bond.[9]

(Alkylthio)cobaloxime **5** prepared from sodium thiolate and chloro(pyridine)cobaloxime[5] worked as a catalyst for the formation of disulfide **4** from **2**,[10] where **5** worked catalytically just as (phenylthio)cobaloxime has been reported[11] to catalyze the hydrogen evolution and diphenyl disulfide formation from benzenethiol under irradiation. The result of the disulfide formation in Table I would be ascribed this catalytic reaction. In the second step, the cobaloxime **5** reacts with **2** (path b) to give **4** and hydridocobaloxime, of which further reaction with **2** gives **5** and hydrogen (path c).

Disulfide **4** reacted with 1.5 M benzylcobaloxime (**1b**) at -20 °C under the irradiation condition to give sulfide **3** in 106% yield. Sulfide **3** would be formed by the bimolecular homolytic displacement reaction[12] of **1** and **4** (path d). Photoactivation is responsible for the decreased yield of disulfide by extending the reaction time (Table I, runs 2 and 3). In addition, the above result suggests the (alkylthio)cobaloxime **5** formed in the reaction is also reacted with benzylcobaloxime (**1b**) to give sulfide **3**. The equimolar reaction of **1b** and (alkylthio)cobaloxime **5** gave sulfide **3** in 14% yield under the same reaction condition. In parallel to the main path (d) for disulfide formation, path e is presumed to exist.

(7) Yield of benzyl sulfides; benzyl phenyl sulfide (51%), dibenzyl sulfide (38%), 2-benzylthioethanol (34%).

(8) Yield of toluene was determined to be 7% by GLC with *m*-xylene as an internal standard.

(9) The dissociation energy of RS-H (about 90 kcal/mol) is considerably higher than that of substrates (CCl_3Br, PhSSPh, RSO_2Cl, etc.) which can take place in homolytic displacement with alkylcobaloxime.

(10) The mixture of thiol **2** (1 mmol) and cobaloxime **5** (0.02 mmol) in CH_2Cl_2 (2 mL) were irradiated with W lamp to give disulfide **4** in 60% yield.

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Catalytic Asymmetric Induction in Enantioselective Conjugate Addition of Dialkylzincs to Enones[†]

Summary: Chiral complex derived in situ from nickel acetylacetonate and *N,N*-dibutylnorephedrine catalyzed the asymmetric addition of dialkylzinc reagents to enones to afford optically active β-substituted ketones in moderate enantiomeric excesses.

Sir: Increasing interest has been centered on *catalytic* asymmetric carbon-carbon bond forming reaction.[1] Although many methods have been reported on the asymmetric conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds,[2] all methods require at least a stoichiometric amount of chiral auxiliary. No attempts have been made in the area of *catalytic* asymmetric conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds.

During our continuing study on asymmetric 1,2-addition of dialkylzincs to aldehydes,[3] we found the first catalytic asymmetric conjugate addition of dialkylzincs to enones catalyzed by a chiral nickel complex. Chiral nickel catalyst **2** was prepared by stirring a mixture of nickel acetylacetonate [$Ni(acac)_2$] (1 equiv)[4] and either (1*S*,2*R*)-(-)- or (1*R*,2*S*)-(+)-2-(*N,N*-dibutylamino)-1-phenylpropan-1-ol (**1**) (*N,N*-dibutylnorephedrine) (1.2 equiv)[3c] in toluene (eq 1). Although we have not yet managed to prepare a characterizable chiral *N,N*-dibutylnorephedrinato complex of nickel, asymmetric conjugate additions with in situ generated chiral nickel complexes **2** have been encouraging (eq 2). As shown in Table I, conjugate addition of diethylzinc (**4b**) to chalcone (**3a**) using **2** [prepared from (1*S*,2*R*)-(-)-**1**] as catalyst [0.50 mol equiv to **3a**] afforded optically active (*R*)-(-)-1,3-diphenylpentan-1-one (**5b**) in 75% isolated yield and in 45% enantiomeric excess (ee) as determined by HPLC analysis using chiral column (Daicel Chiralcel OD) (Table I, entry 2). Without **2**, no

[†] A preliminary account of these results has been reported at the 56th National Meeting of the Chemical Society of Japan, Tokyo, 1988; Paper 1XII B37.

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