Asymmetric Reactions. IX. On the Catalytic Hydrogenation of Olefinic Compounds with Bis(dimethylglyoximato)cobalt(II)-base Complex[1)]

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Examination of the catalytic hydrogenation of twenty-one olefinic compounds with bis(dimethylglyoximato)-cobalt(II)-pyridine complex indicates that all $H_2C{=}C\langle^{Y}_{Y}$ type olefinic compounds having an electron-withdrawing and a weakly electron-donating substituent are reducible. Isolation and further hydrogenation of the alkyl complexes in the case of $H_2C{=}C\langle^{Y}_{Y}$ type olefinic compounds, and deuterogenation of α-phenylacrylophenone support the view that α-alkyl complexes are the intermediates in hydrogenation. It is concluded that the electron-withdrawing effect accelerates both the first (alkyl complex formation) and the second (reductive-cleavage of alkyl moiety) steps, while steric compression prevents the first step and accelerates the second step. The reaction mechanism is discussed.

Schrauzer and Windgassen reported that bis(dimethylglyoximato)cobalt(II)-base, $Co^{II}(DMG)_2B$, catalyzes the reductive methylation of amines and thiols with formaldehyde under hydrogen atmosphere,[2)] and that the formation of substituted alkyl and alkenylcobaloximes from $Co^{II}(DMG)_2B$ and alkenes or alkines is sometimes followed by reductive cleavage of the alkyl moieties as a side reaction.[3)] We have extended the hydrogenation to the homogeneous catalytic hydrogenation of reactive olefinic compounds, α-diketones, α-ketocarboxylic acid esters and unsaturated compounds carrying N=N or N=O double bond[4)] and also to their asymmetric hydrogenation with the use of Co^{II}-$(DMG)_2$-quinine complex.[5)] We have examined the electronic and steric effects of the substituents of olefinic compounds on their hydrogenation and on the nature of intermediate alkyl complexes, since they are important for making clear the mechanism of the asymmetric hydrogenation.

Results and Discussion

The reaction of the reduced cobaloximes with olefinic compounds having an electron-withdrawing substituent gives α-alkyl complexes (α-ACs) in nearly neutral medium and β-one in alkaline solution, the actually reacting species being considered to be the hydridocobaloxime; $HCo(DMG)_2B$, and cobaloxime(I); $[Co^{I}$-$(DMG)_2B]^-$, respectively.[3)] In order to clarify the limitation of the catalytic hydrogenation of olefinic compounds with $Co^{II}(DMG)_2$-pyridine, various substrates were hydrogenated in a slightly alkaline methanol or ethanol under the atmospheric pressure of hydrogen at room temperature. The results are summarized in Table 1, together with the previous ones.[4)]

It is apparent that; 1) monosubstituted ethylene compounds (**1**—**3**) are scarcely hydrogenated; 2) α,α-disubstituted compounds (**5**—**11**) ($H_2C{=}C\langle^{Y}_{Y}$), having an electron-withdrawing group (X: $COOCH_3$, COPh, CN) and a weakly electron-donating group (Y: CH_3, Phenyl, NHCOR, CH_2COOCH_3), are commonly hydrogenated very smoothly, but not α,β-disubstituted compounds (**12**—**14**) except for **15** in which both the substitutents are electron-withdrawing; 3) only trisubstituted ethylene compounds having two electron-withdrawing groups (**20**—**21**) are slowly hydrogenated.

The results indicate that the reactivity of olefinic compounds is controlled by electronic and steric effects of substituents. However, the interrelation between these effects and the reactivity is still ambiguous. The slow but successful hydrogenation of **15**, **20**, and **21** may be attributed to the electron deficiency of the ethylenic bond due to the substituents, but the large difference between compounds **5**—**11** and **12**—**14** seems to depend only on the position of both electron-withdrawing and donating substituents. For more detailed discussion, it is necessary to isolate alkyl complexes, and examine their reducibility. Acrylonitrile (**1**), methyl acrylate (**2**) and styrene (**3**) gave the same results as those by Schrauzer and Windgassen[3)] (Table 2). They stated that no product was obtained in the reaction of methacrylonitrile (**5**) with reduced cobaloxime under alkaline conditions.[3)] We have isolated the corresponding α-AC both under neutral and alkaline conditions.

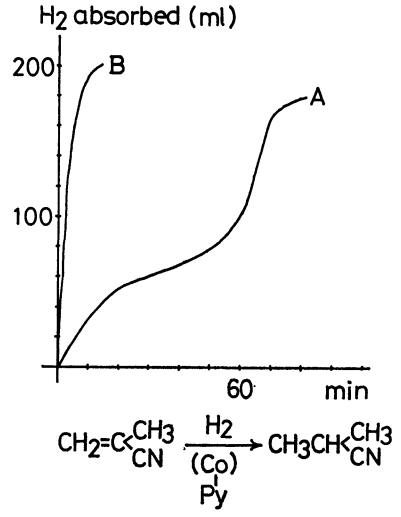
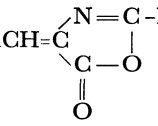


Fig. 1. Hydrogen absorption in the hydrogenation of methacrylonitrile under weakly (A) and strongly (B) alkaline conditions.
Conditions: substrate 7.5 mmol, S/Co=1.9; NaOH/Co=2.8 (A), 3.7 (B).

Table 1. Catalytic hydrogenation of various olefinic compounds with $Co^{II}(DMG)_2$-pyridine

No.	Substrates	S/Co[a]	Reaction[b] time	Products (yield)
1	$CH_2=CHCN$	1	—	—[c]
2	$CH_2=CHCO_2CH_3$	1	—	—[c]
3	$CH_2=CHPh$	4	—	—[c]
4	$CH_2=C(Ph)CH_3$	5	3 day	Recovered
5	$CH_2=C(CN)CH_3$	3.5	4.3 hr	$CH_3CH(CH_3)CN$ (87%)
6	$CH_2=C(CH_3)CO_2CH_3$	10	2 hr	$CH_3CH(CH_3)CO_2CH_3$ (98.5%)
7	$CH_2=C(Ph)CO_2CH_3$	1	1 hr	$CH_3CH(Ph)CO_2CH_3$ (69%)
8	$CH_2=C(CO_2CH_3)CH_2CO_2CH_3$	4	1 hr	$CH_3CH(CH_2CO_2CH_3)CO_2CH_3$ (100%)
9	$CH_2=C(CO_2CH_3)NHAc$	7	30 min	$CH_3CH(NHAc)CO_2CH_3$ (42%)[d]
10	$CH_2=C(CO_2CH_3)NHCOBzl$	3.5	17 min	$CH_3CH(NHCOBzl)CO_2CH_3$ (70%)
11	$CH_2=C(Ph)COPh$	2	15 min	$CH_3CH(Ph)COPh$ (80%)
12	$CH_3CH=CHCO_2CH_3$	10	4 days	Recovered
13	$PhCH=CHCO_2CH_3$	2	4 days	Recovered
14	$PhCH=CHCOCH_3$	7	4 days	Recovered
15	$EtO_2CCH=CHCO_2Et$	4	3 days	$EtO_2CCH_2CH_2CO_2Et$ (69%)
16	$CH_3CH=C(CH_3)CO_2CH_3$	3	1 day	Recovered
17	$PhCH=C(NHBz)CO_2CH_3$	1	1 day	Recovered
18	$PhCH=C(NHC_6H_{11})CO_2CH_3$	1	1 day	Recovered
19		1	2 days	$PhCH_2CH(NHBz)CO_2CH_3$ (7.3%) and **17**
20	$PhCH=C(CN)CO_2Et$	10	8 hr	$PhCH_2CH(CN)CO_2Et$ (80%)
21	*t*-$BuCH=C(Ac)CO_2Et$	3	24 hr	*t*-$BuCH_2CH(Ac)CO_2Et$

a) S/Co; molar ratio of substrate (S) to catalyst (Co). b) Time required for the absorption of theoretical amount of hydrogen. c) Molecular hydrogen was consumed only for formation of the alkyl complex. d) As the hydrogenated material was soluble in water, the yield was lowered.

Table 2. Isolation of alkyl complexes and hydrogenation of α-alkyl complexes

No.	Substrate	Alkyl complex (AC)[a]		Hydrogenation	Alkyl group in α-AC	Autocatalyzed[c] Hydrogenation	Catalytic Hydrogenation[d]
		Neutral	Alkaline				
1	$CH_2=CHCN$	α-AC	β-AC	None	$-CH(CN)CH_3$	None	Fast
2	$CH_2=CHCO_2CH_3$	α-AC	β-AC	None	$-CH(CH_3)CO_2CH_3$	Slow	Fast
3	$CH_2=CHPh$	α-AC	α-AC	None	$-CH(Ph)CH_3$	None	None
5	$CH_2=C(CH_3)CN$	α-AC	α-AC	Relatively slow	$-C(CH_3)(CN)CH_3$	Fast	Very fast
11	$CH_2=C(Ph)COPh$	—	(α-AC)[b]	Very fast	$-C(Ph)(COPh)CH_3$	—	—

a) For example, α- and β-AC of acrylonitrile imply $CH_3(CN)CHCo(DMG)_2$-pyridine and $CNCH_2CH_2Co(DMG)_2$-pyridine, respectively. b) The structure was deduced from the result of deuterogenation. c) Hydrogenation only with molecular hydrogen. d) Hydrogenation with $Co^{II}(DMG)_2$-pyridine and molecular hydrogen in slightly alkaline methanol solution.

Hydrogenation of **5** under weakly alkaline conditions proceeds stepwise, while under strongly alkaline conditions very smoothly (Fig. 1). The presence of α-AC was easily proved by the NMR spectrum, and the α-AC was isolated by concentrating the reaction mixture after the reaction had been interrupted at the first stage when a half-equimolar amount of hydrogen was absorbed. In the case of dimethyl itaconate (**8**) under alkaline conditions, a small amount of β-AC was obtained, and the yield was increased to 30% under strongly alkaline conditions by use of a large excess of imidazole as the axial base.

All β-AC described above could not be hydrogenated even in the presence of excess $Co^{II}(DMG)_2B$ or palladium-charcoal. Both the results with β-AC and **5** strongly indicate that the α-AC is the actual intermediate in the hydrogenation. Since AC could not be detected in all other cases in which the hydrogenation proceeded very fast, deuterogenation of α-phenylacrylphenone (**11**) under deuterium atmosphere in slightly alkaline methanol-d_1 was examined. The ratio of deuterium on β-carbon to that on α-carbon of the corresponding saturated product was determined by NMR spectrum to be about 2.3. This also indicates that the deuterogenation of **11** proceeds *via* α-AC, as in a similar reaction with pentacyanocobaltate.[6] Thus, it is con-

cluded that α-ACs are formed in both neutral and alkaline solution in the cases of $H_2C{=}C\langle^{Y}_{Y}$ type olefinic compounds.

Autocatalytic and catalytic hydrogenation of thus isolated α-ACs was examined (Table 2). Hydrogenation in the absence of catalyst (autocatalytic hydrogenation) of α-AC from **5** proceeded relatively fast, while that of α-AC from **2** slowly. α-ACs from **5**, **1**, and **2** were hydrogenated much faster in the presence of Co^{II}-$(DMG)_2B$ than in the absence of the catalyst. The results show that their reactivity is in the order **5**>**2**>**1**>**3**, indicating that the bulkiness (steric compression including DMG ring) of substituents causes the sequence of the former three. The remarkable stability of α-AC from **3**, inspite of the greater bulkiness of phenyl group than that of methoxycarbonyl group or cyano group, suggests that the electron-withdrawing effect of substituents plays a more decisive role than the steric one. Thus, it can be concluded that both the electron-withdrawing effect and steric compression of substituents accelerate the second step (reductive cleavage) of the hydrogenation, the former playing a more important role.

On the other hand, compounds **4**, **12**—**14**, and **16**—**18** gave neither the saturated product nor the corresponding α-AC. If we compare these compounds with **1**—**3**, **5**—**11**, **20**—**21**, respectively, in structure, we realize the higher electron density of the former. **20** and **21** were hydrogenated more slowly than **5**—**11**, though they have two electron-withdrawing substituents. If they undergo hydrogenation via α-ACs, the α-ACs from **20** and **21** would be more unstable than those of **5**—**11**. Thus, the slow rate may be attributed to the steric hindrance in the formation of α-ACs. It can be considered that the electron-withdrawing effect of substituents accelerates the formation of alkyl complex, and the steric compression of substituents prevents it and the electron-withdrawing effect should overcome the steric hindrance to give α-AC.

It is thus concluded that the electron-withdrawing effect accelerates both the first (alkyl complex formation) and the second (reductive cleavage of the alkyl moiety) steps, while steric compression prevents the first step and accelerates the second step as shown schematically in Fig. 2.

In the first stage, electronic effect (E) and steric effect (S) make $\Delta G_1^{\neq}$ smaller by lowering the free energy of transition state and greater by elevating it, respectively. In the second stage, though it is not evident how E and S affect the transition state, both E and S make $\Delta G_2^{\neq}$ lower by elevating the potential energy of alkyl complex.

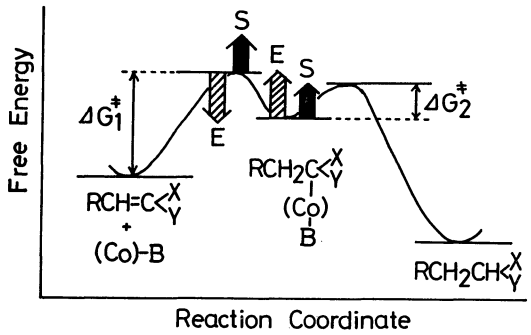


Fig. 2. Schematic presentation of electronic (E) and steric (S) effects of substituents on the hydrogenation.

Nonreactivity of **1**—**2** and **3** would be explained by the absence of steric and electronic acceleration in the second step, respectively, while that of **4** or **12**—**14** by the insufficient electronic acceleration, in the first step. In the hydrogenation of $H_2C{=}C\langle^{X}_{Y}$ type olefinic compounds both electron-withdrawing and steric compression effects of the substituents tend to lower the activation energy of both the two steps, leading to smooth hydrogenation.

On the mechanism of the hydrogenation, Schrauzer and Windgassen stated that the reductive cleavage is apparently catalyzed by cobaloxime(I), which exists in equilibrium with hydridocobaloxime.[3] It is thus understandable that the rate of hydrogenation of olefinic compounds is faster in alkaline solution than in neutral solution as in the case of **5**.

When **5** reacts predominantly with the hydridocobaloxime to form relatively stable α-AC[7] the equilibrium may shift to the hydridocobaloxime, and the concentration of cobaloxime(I), which acts as a reductant of the α-AC, becomes smaller. However, when the alkalinity of the solution becomes higher, the equilibrium shifts to cobaloxime(I) and the rate of of the formation of α-AC decrease, and consequently, the reductive cleavage of the α-AC by cobaloxime(I) will become effective. The mechanism of the hydrogenation is shown in Fig. 3.

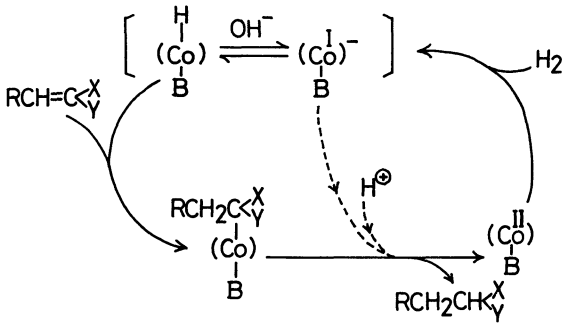


Fig. 3.

Experimental

Catalytic Hydrogenation of Various Olefinic Compounds in the Presence of Pyridino Bis(dimethylglyoximato)cobalt(II). Dimethylglyoxime (0.48 g, 4 mmol) was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.5 g, 2 mmol) in methanol or ethanol, and the mixture was stirred under nitrogen atmosphere for a few min. Aqueous sodium hydroxide (1 ml of 4.87 M, 4.9 mmol), pyridine (0.16 g, 2 mmol) and a substrate (1-10 equivalent to cobalt) were successively added. The flask was purged with hydrogen gas and the solution was then stirred under the atmospheric pressure of hydrogen at room temperature. After absorption of the theoretical amount of hydrogen, the reaction mixture was diluted with water and extracted with ether or methylene chloride. The organic layer was washed with water, dried over anhydrous sodium

sulfate, and concentrated to give the corresponding product which was purified and confirmed by IR and NMR spectra.

Hydrogenation in neutral solution was carried out in a similar way, except for the use of cobaltous acetate in place of cobaltous chloride and sodium hydroxide.

Isolation of α-Cyanoisopropylcobaloxime. Methacrylonitrile (0.25 g, 3.7 mmol) was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.5 g, 2 mmol), dimethylglyoxime (0.48 g, 4 mmol) in aqueous sodium hydroxide (1 ml of 4.87 M solution) and pyridine (0.16 g, 2 mmol). The resulted solution was shaken under hydrogen atmosphere until *ca.* 19 ml (0.9 mmol) of hydrogen was absorbed (6 min). The solvent was then removed *in vacuo* to give crude α-cyanoisopropylcobaloxime (0.9 g). The crude complex showed a sharp absorption of cyano-group at 2200 cm^{-1} in IR spectrum, and characteristic methyl-proton signals (isopropyl; δ 0.7, singlet, 6H; DMG; δ 2.0, singlet, 12H) in NMR spectrum. The complex could not be recrystallized, because it decomposed in ether or chloroform to give black complex whose IR spectrum showed no absorption of CN and alkyl groups. The complex was obtained even when 1.2 ml of aqueous sodium hydroxide (4.87 M solution) was used. Smooth hydrogenation occurred when 1.5 ml of aqueous sodium hydroxide (4.87 M solution) was used.

Deuterogenation of α-Phenylacrylophenone. A solution of anhydrous cobaltous chloride (0.27 g, 2 mmol), dimethylglyoxime (0.48 g, 4 mmol), and α-phenylacrylophenone (2.8 g, 13.5 mmol) in 3.82 M sodium deuteroxide in dideuterium oxide (1.38 ml, 4.7 mmol of NaOD), pyridine (0.16 g, 2 mmol), and methanol-d_1 (30 ml) was shaken under deuterium atmosphere until 289 ml (13 mmol) of D_2 was absorbed 58 min). The reaction mixture was concentrated *in vacuo*, and the residue was extracted with ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated to give an oily product (2.4 g). The crude product was purified by vacuum distillation (124—126 °C/1 mmHg), and the main fraction (1.9 g) crystallized (mp 38.5—41 °C) on standing. NMR spectra of the crude and purified products showed relatively broad signals of α- and β-protons at δ 4.66 and δ 1.50, respectively. The ratio of integration of the signals of phenyl proton, α- and β-proton was 10 : 0.14 : 1.12 in the crude product and 10 : 0.15 : 1.07 in the purified product. The ratio of deuterium distribution in β-carbon to α-carbon was estimated to be 2.5 (crude) and 2.3 (purified), respectively.

Reductive Cleavage of Various Alkyl Complexes. a) Catalytic Cleavage. Catalytic cleavage was carried out in a similar manner to that for hydrogenation of olefinic compounds, except for the use of alkyl complexes instead of olefinic compounds as substrate. α-Phenylethylcobaloxime was recovered quantitatively after reaction for 4 days. α-Cyanoethylcobaloxime and α-methoxycarbonylethylcobaloxime underwent reductive cleavage within 1 hr to give propionitrile and methylpropionate, respectively. *b) Autocatalytic Cleavage.* α-Methoxycarbonylethylcobaloxime underwent reductive cleavage even in the absence of the catalyst when it was dissolved in methanol and stirred under hydrogen atmosphere at room temperature for 1 day. β-Alkyl complexes underwent no reductive cleavage.

β-Alkyl Complex from Dimethyl Itaconate. Dimethyl Itaconate (2.5 g, 1.6 mmol) was added to a catalyst solution (in MeOH) prepared from $CoCl_2 \cdot 6H_2O$ (2.5 g, 10 mmol), dimethylglyoxime (2.45 g, 20 mmol), aqueous sodium hydroxide (10 ml of 4.67 M solution, 47 mmol) and imidazole (4.22 g, 62 mmol), and the resulting solution was shaken under hydrogen atmosphere. After absorption of *ca.* 274 ml (12 mmol) of hydrogen within 26 min, the reaction mixture was poured into water and extracted with methylene chloride. The extract was washed with water, dried over calcium chloride, and concentrated to give an oily product which crystallized by scratching. The crude alkyl complex (1.7 g, 34%) was purified by recrystallization from methanol. Yellow crystals, mp 166 °C (167—168 °C dec.). Spectral data showed typical absorptions for β-alkyl complex; *i.e.*, characteristic absorption of ester (1720—1730 cm^{-1}) in IR and broad doublet signal at δ 2.45 ($Co-CH_2$; 2H) and broad multiplet (–CH–) and doublet ($-CH_2CO-$) at δ 2.3—1.9 (3H) in NMR spectrum.

Found: C, 42.29; H, 5.97; N, 16.49%. Calcd for $C_{18}H_{29}N_6O_8Co$: C, 41.87; H, 5.62; N, 16.28%.

When the amount of aqueous hydroxide and imidazole was decreased to about half (5 ml, 24 mmol) and one fourth (0.7 g, 10 mmol), respectively, the formation of alkyl complex was negligible.

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7) It is known that α-AC is formed by the reaction of 5 or 6 with hydridopentacyanocobaltate. (Ref. 6, p. 54).