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Asymmetric Reactions. V. Homogeneous Hydrogenation of Unsaturated Compounds Catalyzed by Bis(dimethylglyoximato)cobalt(II)[1]

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Schrauzer and Windgassen[2] reported that stable metal-alkyl complexes are formed in the reaction of bis(dimethylglyoximato)cobalt(II) complex and certain olefines under hydrogen atmosphere, and that in some cases reduction products are obtained concurrently. Reductive methylation of amines and mercaptanes with formaldehyde and hydrogen catalyzed by bis(dimethylglyoximato)cobalt(II) was also reported by the same investigators.[3]

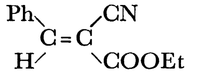
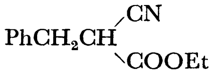
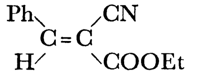
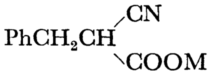
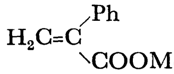
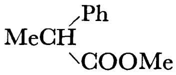
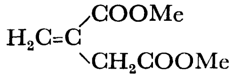
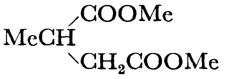
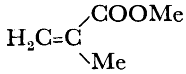
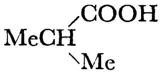
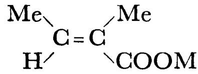
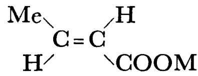
As a part of studies on the asymmetric reduction using optically active metal complexes,[4,5] we have tried to obtain a suitable metal-alkyl complex by the reaction of bis(dimethylglyoximato)cobalt(II) with several unsaturated compounds under hydrogen atmosphere. However, no metal-alkyl complex but the reduction product could be obtained.

We wish to report that bis(dimethylglyoximato)-cobalt(II) is a useful catalyst for reduction of activated olefines, unsaturated nitrogen compounds, α-diketones and α-keto acid esters.

Experiments were carried out under atmospheric pressure of hydrogen at room temperature, and the products were confirmed by mixed melting point and/or IR and NMR spectra. The results are summarized in Tables 1 and 2.

It can be considered that both steric and electronic

Table 1. Hydrogenation of olefines catalyzed by bis(dimethylglyoximato)cobalt

Run	Substrate	S/Co[b]	Reaction time[c]	Products (Yield)
1	 $\mathrm{Ph(H)C{=}C(CN)(COOEt)}$	2	7 hr	 $\mathrm{PhCH_2CH(CN)(COOEt)}$ (89%)[a]
2	 $\mathrm{Ph(H)C{=}C(CN)(COOEt)}$	10	8 hr	 $\mathrm{PhCH_2CH(CN)(COOMe)}$ (80%)
3	 $\mathrm{H_2C{=}C(Ph)(COOMe)}$	1	1 hr	 $\mathrm{MeCH(Ph)(COOMe)}$ (69%)
4	 $\mathrm{H_2C{=}C(COOMe)(CH_2COOMe)}$	4	1 hr	 $\mathrm{MeCH(COOMe)(CH_2COOMe)}$ (100%)
5	 $\mathrm{H_2C{=}C(COOMe)(Me)}$	10	2 hr	 $\mathrm{MeCH(COOH)(Me)}$ (98.5%)
6	 $\mathrm{Me(H)C{=}C(Me)(COOMe)}$	3	1 day	recovered
7	 $\mathrm{Me(H)C{=}C(H)(COOMe)}$	10	4 days	recovered

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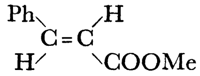
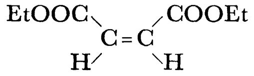
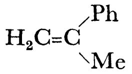
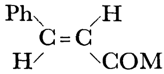
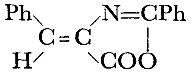
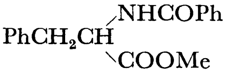
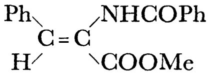
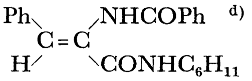
[1] This work was presented at the 23rd Annual Meeting of the Chemical Society of Japan, April., 1970.

[2] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **89**, 1999 (1967); G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

[3] G. N. Schrauzer and R. J. Windgassen, *Nature*, **214**, 492 (1967).

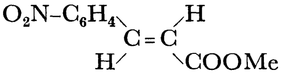
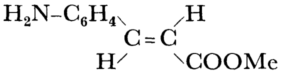
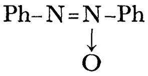
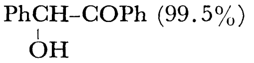
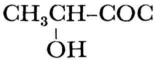
[4] Asymmetric Reactions. IV., Y. Ohgo, S. Takeuchi, and J. Yoshimura, This Bulletin, **43**, 505 (1970).

[5] S. Takeuchi, Thesis for M.Sc., Tokyo Institute of Technology, March, 1969.

8		2	4 days	recovered
9		4	3 days	$EtOOCCH_2CH_2COOEt$ (69%)[a]
10	$H_2C=CHPh$	4	3 days	recovered
11		5	3 days	recovered
12		7	4 days	recovered
13		1	2 days	 (7.3%) MBAC (3%)
14	 (MBAC)	1	1 day	recovered
15	 [d]	1	3 days	recovered

a) Solvent; ethanol, in systems except for a) methanol was used.
b) S/Co; molar ratio of substrate to catalyst (Co).
c) Time required for the completion of reaction for the reaction mixture to be left standing.
d) C_6H_{11}=cyclohexyl

Table 2. Hydrogenation of unsaturated compounds containing hetero atoms catalyzed by bis(dimethylglyoximato)cobalt (II)

Run	Substrate	S/Co[a]	Reaction time[b]	Products (yield)
16		2	1 hr	 (78%)
17	$PhNO_2$ (2.4 g)	7	5 days	PhNHNHPh $PhNH_2$ (1.5 g)
18	 $Ph-N=N(\rightarrow O)-Ph$	3	45 min	Ph-N=N-Ph (76%)
19	Ph-N=N-Ph	5	29 min	PhNHNHPh (99%)
20	PhCOCOOEt	10	80 min	 $PhCH(OH)-COOMe$ (98%)
21	PhCOCOPh	10	35 min	 $PhCH(OH)-COPh$ (99.5%)
22	$CH_3COCOCH_3$	10	24 hr	 $CH_3CH(OH)-COCH_3$[c]

a) S/Co: molar ratio of substrate to catalyst (Co).
b) Time required for the completion of reaction or for the reaction mixture to be left standing.
c) Biacetyl adsorbed a theoretical amount of hydrogen, but only a small amount of acetoin was obtained because of an unsuitable isolation procedure.

factors have an effect on the reactivity. As shown in Table 1, olefines which have electron defficient double bond were catalytically reduced by hydrogen. However, the olefines having no electron-withdrawing group were not reduced. Steric factors do not seem to be so important as electronic ones. From this viewpoint, methyl *p*-nitrocinnamate was considered to be catalytically reducible. However, it was found that the C–C double bond of this compound was not reduced, but the nitro group was reduced to give amino group contrary to anticipation (Table 2). Nitrobenzene was also reduced to give aniline and hydrazobenzene. Azobenzene and azoxybenzene gave hydrazobenzene, but a prolonged treatment for isolation and purification afforded azobenzene. This implies that hydrazobenzene is catalytically oxidized by oxygen during the course of isolation. Nitroalkanes were not reduced under mild conditions. α-Diketones and α-keto acid esters were also reduced easily. Studies on the reduction mechanism are now in progress.

Experimental

$CoCl_2\cdot 6H_2O$ (0.708 g, 0.03 mol) was dissolved in 50 m*l* of methanol or ethanol, and to the solution was added 0.690 g of dimethylglyoxime (0.06 mol) with stirring under nitrogen atmosphere for 5 min. To this solution was added a solution of 0.28 g of sodium hydroxide (0.07 mol), pyridine (0.23 g) and substrate (1—10 equivalent to cobalt) successively. Stirring was then stopped. The vessel containing the solution was purged with hydrogen, and the solution was again stirred under hydrogen atmosphere at room temperature. After absorption of the theoretical amount of hydrogen, the reaction mixture was diluted with water containing a small amount of acetic acid and extracted with ether or methylene chloride. The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The resulting products were confirmed by mixed melting point (incase of crystals) and/or IR and NMR spectra. The results are shown in Tables 1 and 2.