Asymmetric Hydrogenation Catalyzed by Bis(dimethylglyoximato)cobalt(II)-Optically Active Amine Complex

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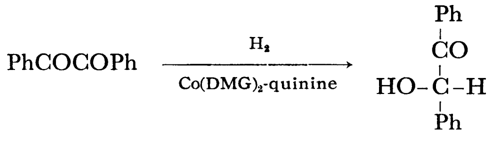
We reported that cyanocobalt - optically active amine complexes catalyze asymmetric hydrogenation.[1)] It has been concluded that rigid conformational fixation and proximity of asymmetric grouping to the reaction center result in higher optical yield, but at the same time there is the drawback that the close and rigid grouping prevents coordination of substrate.

In order to overcome this, we sought a system in which a polyfunctional asymmetric substance bound to ligand could draw the substrate into the reaction center with a weakly attractive force.

On the other hand, it has previously been reported that bis(dimethylglyoximato)cobalt(II) complex, Co-$(DMG)_2$, catalyzes hydrogenation of activated olefins, nitro-, azoxy-, and azo-benzenes, α-diketones, and α-keto carboxylic esters.[2,3)] This complex has polar groups around the metal which are suitable for the binding of asymmetric substances. Thus we used this complex with quinine (polyfunctional, optically active substance) in the hydrogenation of benzil.

Catalytic hydrogenation was carried out at room temperature under atmospheric pressure of hydrogen. The reaction mixture was poured into water and extracted with benzene or ether. The organic layer was successively washed with water, hydrochloric acid, sodium hydroxide solution and water. The organic layer was concentrated *in vacuo* to give crystals which were characterized as benzoin by IR and NMR spectra. It was shown by gas-liquid chromatography and thin layer chromatography that the crystals contained no substantial contaminant. Optical yield was calculated from the specific rotation of the product and that of the optically pure benzoin. The results are shown in Table 1. In every case S(+)-benzoin was predominant.



$$\mathrm{PhCOCOPh} \xrightarrow[\mathrm{Co(DMG)_2\text{-}quinine}]{H_2} \mathrm{HO{-}\overset{\overset{\displaystyle Ph}{|}\,\overset{|}{CO}}{\underset{\underset{\displaystyle Ph}{|}}{C}}{-}H}$$

TABLE 1. ASYMMETRIC HYDROGENATION OF BENZIL CATALYZED BY $Co(DMG)_2$-QUININE[a)]

Run	S/Co[b)]	B/Co[c)]	Solvent (ratio)[d)]	Yield (%)	$[\alpha]_D$[e)]	Optical Yield (%)
1	5	3	M	98.5	+10.3	8.7
2	20	3	M/B(1.4)	99	+27.8	23
3	50	3	M/B(1.07)	85	+33.5	28
4	20	1	M/B(1.4)	96.5	+29.7	25
5	20	2	M/B(1.4)	99	+30.2	25.5
6	20	2	M/B(0.43)	96.5	+50.1	42
7	20	2	THF	95.5	+42.6	36
8	20	2	THF/B(0.6)	97	+59	50
9	10	2	B	98	+72.7	61.5

a) In this series of experiments a solution of quinine containing 0.48 molar equivalent HCl was used.
b) Molar ratio of substrate to cobalt.
c) Molar ratio of base (quinine) to cobalt.
d) Ratio of solvents in volume; M = methanol; B = benzene.
e) Solvent; acetone, $c = 2$—5. Specific rotation of optically pure isomer, $[\alpha]_D$, ±118.5 (acetone, $c = 1$).[5)]

From the Table 1 it can be seen that increase in the molar ratio of substrate to cobalt or base causes no decrease in optical yield. The benzoin recovered after the treatment of racemic benzoin under the same conditions as in run 6 was found to be optically inactive. This indicates that the asymmetric synthesis is not due to a quinine-catalyzed isomerization(favored in S(+)-isomer) of racemic benzoin, but to the asymmetric induction at the stage of catalytic hydrogenation. Stereoselectivity of the asymmetric hydrogenation was sensitive to the polarity of the solvent. The reaction in benzene afforded maximum optical yield(61.5%). So far, this optical yield is the highest for homogeneous metal complex-catalyzed asymmetric syntheses.[4)] However, the asymmetric induction seems to occur through a mechanism different from our initial idea, *i. e.*, one equivalent of optically active amine is enough to bring about maximum asymmetric yield, and alkylcobalt complexes produced by the reaction of olefins with Co-$(DMG)_2$-Base and hydrogen have trans structure.[2)] Provided that the reduction of benzil proceeds through the same reaction mechanism as that of olefins, the reaction must take place at the trans site which can not interact directly with asymmetry of the base. This asymmetric reaction would be considered to be due to an induced asymmetry on the bis-dimethylglyoxime ring.

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