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HOMOGENEOUS HYDROGENATION OF ALDEHYDES TO ALCOHOLS CATALYZED BY $RuCl_2(PPh_3)_3$

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$RuCl_2(PPh_3)_3$ was found to be a good catalyst for the hydrogenation of aliphatic aldehydes to alcohols under mild conditions. Aromatic aldehydes were reduced to benzyl alcohols without hydrogenolysis. Ketones and nitro groups were not reduced under the same conditions.

Homogeneous catalytic hydrogenation is regarded as a useful technique of organic synthesis. Reduction of carbonyl groups is an important synthetic method and homogeneous hydrogenation of carbonyl groups has been carried out with a few catalysts. A typical example is smooth reduction of ketones by cationic rhodium complexes.[1,2] Also $RhCl(C_8H_{12})PPh_3$ was used for the reduction of ketones.[3] However, rhodium complexes can not be used for the reduction of aldehydes, because easy decarbonylation of aldehydes takes place.[4] It has been shown that homogeneous hydrogenation of aldehydes to alcohols was possible with $IrH_3(PPh_3)_3$.[5,6] In hydroformylation of olefins, aldehydes are sometimes reduced to alcohols by cobalt carbonyl.[7] Also bis(dimethylglyoximato)cobalt was used for the reduction of α-diketones.[8]

Ruthenium complexes are useful catalyst for the hydrogenation of functional groups. Reduction of cyclic acid anhydrides to give lactones was catalyzed by $RuCl_2(PPh_3)_3$.[9,10] Also nitro compounds were hydrogenated to amines with the same complexes.[11] Reduction of ketones and ketoximes was carried out by using $H_4Ru_4(CO)_8$[DIOP].[12] As a related reaction, transfer hydrogenation of aldehydes catalyzed by $RuH_2(PPh_3)_4$ has been reported.[13]

We now wish to report the homogeneous hydrogenation of aldehydes to alcohols with $RuCl_2(PPh_3)_3$ as catalyst under mild conditions. The hydrogenation of aldehydes was carried out in benzene at 50-80°C under initial hydrogen pressure of 10 atm. Under these conditions, both aliphatic and aromatic aldehydes were reduced to alcohols completely. Results of the hydrogenation are shown in table 1. The reaction was very slow at room temperature, but proceeded smoothly above 70°C. Higher pressures seem to accelerate the reaction, but the initial pressure of 10 atm is sufficient as a laboratory process. Hydrogenation of aldehydes in the coexistence of ketones such as 2-heptanone and benzophenone was carried out. Only aldehydes were reduced completely and no reduction of the ketones was observed. It is known that nitrobenzene is reduced to aniline with the same catalyst under severe conditions.[11] Thus a mixture of benzaldehyde and

nitrobenzene was subjected to the reduction. Formation of benzyl alcohol was observed, but nitrobenzene remained intact. Also it should be pointed out that benzaldehyde derivatives are reduced to benzyl alcohols without hydrogenolysis. In a typical example, benzaldehyde (2.12 g, 20 mmol) and $RuCl_2(PPh_3)_3$ (96 mg, 0.1 mmol, 0.5 mol%) in benzene (20 ml) were placed in an autoclave, which was charged with hydrogen to 20 atm. The hydrogenation was carried out at 80°C for 20 hr. The autoclave was cooled and the pressure decrease to 13.5 atm was observed. Distillation of the reaction mixture afforded benzyl alcohol at 105°C/22 Torr (1.84 g, 85.3%).

Table 1. Reduction of Aldehydes

Substrate	(g)	Catalyst (mg)	Reaction temp(°C)	Reaction time(h)	H_2 (atm)	Yield(%) of alcohol by GC	Yield(%) of alcohol isolated(g)
Octanal	0.641	24	50	60	10	100	
	2.56	96	70	36	10	100	83.2 (2.17)
Decanal	2.34	72	80	32	20	100	92.0 (2.18)
Benzaldehyde	2.14	72	80	20	20	100	85.3 (1.84)
	2.12	72	50	65	20	100	84.0 (1.81)
p-Methylbenzaldehyde	0.60	24	50	72	10	100	
p-Methoxybenzaldehyde	0.681	24	70	72	10	90.7	
p-Chlorobenzaldehyde	0.70	24	70	68	10	92	
Benzaldehyde Benzophenone	0.35 0.55	24	70	48	10	100[a]	
Benzaldehyde 2-Heptanone	0.32 0.34	19	70	54	10	100[a]	
Nitrobenzene Benzaldehyde	0.42 0.32	24	70	30	10	100[b]	

a. No reduction of the ketone was observed.

b. No reduction of nitrobenzene was observed.

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