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RHODIUM-CATALYZED HYDROGENATION OF ALDEHYDES BY CARBON MONOXIDE-WATER SYSTEM

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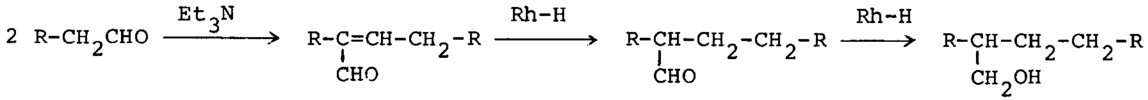
Our previous articles have indicated that a rhodium-carbon monoxide-water system can be employed for the α-methylation of ketones[1) and the N-alkylation of amines.[2) These reactions appeared to include a nucleophilic attack of water on a metal-coordinated carbonyl to give a metal hydride intermediate[3) which is active for the hydrogenation. Described herein are the results of the reductive dimerization of aldehydes having two α-hydrogens by a rhodium-carbon monoxide-water system.

$$\mathrm{L_nRh\text{-}CO} + \mathrm{H_2O} \longrightarrow \mathrm{L_nRhCOOH} \longrightarrow \mathrm{L_nRhH} + \mathrm{CO_2}$$



$$2\ \mathrm{R\text{-}CH_2CHO} \xrightarrow{\mathrm{Et_3N}} \mathrm{R\text{-}\underset{CHO}{C}{=}CH\text{-}CH_2\text{-}R} \xrightarrow{\mathrm{Rh\text{-}H}} \mathrm{R\text{-}\underset{CHO}{CH}\text{-}CH_2\text{-}CH_2\text{-}R} \xrightarrow{\mathrm{Rh\text{-}H}} \mathrm{R\text{-}\underset{CH_2OH}{CH}\text{-}CH_2\text{-}CH_2\text{-}R}$$

(1) (2) (3) (4)

(1)	R
1a	CH_3-
1b	CH_3CH_2-
1c	$CH_3CH_2CH_2$-

Typically, a mixture of rhodium chloride($RhCl_3 \cdot 3H_2O$)(10 mg), an aldehyde (50 mmol), moist ethanol(20 ml), water(5 ml) and triethylamine(5 ml) was stirred at 200°C under pressures of carbon monoxide(initial pressure, 50 atm) for 4 hr in a 100 ml stainless autoclave. Products were analyzed by GLC, IR and PMR spectroscopy.

Some representative results are shown in Table.

Although an active reaction species is not clear, rhodium chloride can be used as a catalyst for the reductive dimerization of aldehydes to alcohols at 200°C under pressures of carbon monoxide. Propanal gave 2-methylpentanol(4a) and 2-methylpentanal(3a) in good yields. Butanal gave 2-ethylhexanol(4b) and 2-

Table. Catalytic Hydrogenation of Aldehydes by Carbon Monoxide-Water System[a]

Run	Aldehyde	Product	Yield (%)
1	Propanal(1a)	2-Methylpentanol(4a)	30
		2-Methylpentanal(3a)	19
2	Butanal (1b)	2-Ethylhexanol (4b)	17
		2-Ethylhexanal (3b)	9
3	Pentanal(1c)	2-Propylheptanol(4c)	11[c]
		Pentanol	19
4	2-Methylpentanal(3a)	2-Methylpentanol(4a)	56 (28)[d]
5	2-Ethylhexanal (3b)	2-Ethylhexanol (4b)	68 (32)
6[b]	Benzaldehyde	Benzyl alcohol	34 (46)

a) $RhCl_3 \cdot 3H_2O$ 10 mg, an aldehyde 50 mmol, ethanol 20 ml, water 5 ml, triethylamine 5 ml, at 200°C, at 50 atm(initial pressure of carbon monoxide) for 4 hr.

b) In the absence of triethylamine.

c) Isolated yield.

d) Yields in parentheses: the starting aldehydes recovered.

ethylhexanal(3b). Pentanal gave 2-propylheptanol(4c). These results show that the hydrogenation of the aldehydes was accompanied by the aldol condensation and that the main reaction process was the hydrogenation of the condensates, α,β-unsaturated aldehydes(2). Triethylamine appeared to be a base catalyst for the condensation. This consideration was supported by the fact that 2-methylpentanal(3a) and 2-ethylhexanal(3b) were converted into 2-methylpentanol(4a) and 2-ethylhexanol(4b), respectively in fairly good yields by this procedure. Benzaldehyde also gave benzyl alcohol. These results show that aldehydes having no α-hydrogen or only one α-hydrogen can be derived into the corresponding alcohols by this method.[4] On the other hand, this procedure can be applied for the reductive dimerization of aldehydes having two α-hydrogens.

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