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RHODIUM CATALYZED α-METHYLATION OF KETONES WITH CARBON MONOXIDE-WATER-FORMALDEHYDE SYSTEM

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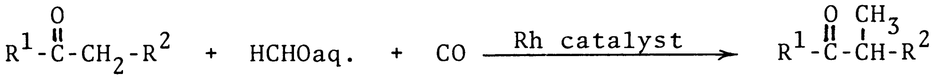
α-Methylation of ketones is catalyzed by rhodium chloride with aqueous formaldehyde under pressures of carbon monoxide at 180°C. Cyclohexanone and acetophenone gave mono- and dimethylated ketones in good yields.

Certain metal carbonyl derivatives(L_nMCO) are reactive toward water and hydroxide ion to give metal hydride species(L_nMH) via L_nMCO_2H, strongly suggesting that a metal-coordinated carbonyl may be used for generation of hydrogen via a metal hydride by the reaction with water.$^{1)}$ Recently, several reports have demonstrated that rhodium complexes combined with water and carbon monoxide are effective for reduction of several organic compounds such as nitrobenzenes.$^{2)}$ In the present study, we have found that rhodium chloride is an excellent catalyst for α-methylation of ketones with aqueous formaldehyde under high pressures of carbon monoxide, following the scheme.



$$R^1\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}CH_2\text{-}R^2 \;+\; HCHOaq. \;+\; CO \xrightarrow{\text{Rh catalyst}} R^1\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}\overset{\overset{\large CH_3}{|}}{CH}\text{-}R^2$$

Typically, a mixture of rhodium chloride($RhCl_3 \cdot 3H_2O$)(10 mg), cyclohexanone(4 ml), a certain amount of aqueous formaldehyde(37%), ethanol(20 ml) and triethylamine(5 ml) was stirred at 70 atm(initial pressure of carbon monoxide) at 180°C for 4 hr in a 100 ml stainless autoclave. Products such as 2-methyl- and 2,6-dimethylcyclohexanone were analyzed by GLPC.

Some representative results are shown in Table.

Rhodium trichloride is effective for the α-methylation of such ketones as cyclohexanone, acetone and acetophenone. Cyclohexanone gave 2-methyl- and 2,6-dimethylcyclohexanone in moderate yields. High molar ratios of formaldehyde/cyclohexanone are favorable for the dimethylation. Acetone gave a mixture of methylated products

Table. The α-Methylation of Ketones by Rhodium Catalyst[a]

Exp. No.	Ketone	Molar Ratio[b]	Products Yield (%)	Distribution of Products (%) Mono-methylated	Di-methylated
1	Cyclohexanone	1.05	42	70[c]	30[c]
2	Cyclohexanone	2.0	43	50	50
3	Cyclohexanone	3.1	31	19	81
4	Cyclohexanone	4.2	31	14	86
5	Acetone	4.9	2[d]	-	-
6	3-Pentanone	3.3	13[d]	-	-
7	Acetophenone	3.3	54	19[e]	81[e]

a) $RhCl_3 \cdot 3H_2O$ 10 mg, ketone 2-4 ml, ethanol-triethylamine 20 ml-5 ml, at 180°C, at 70 atm(initial pressure of carbon monoxide) for 4 hr.

b) Formaldehyde/ketone.

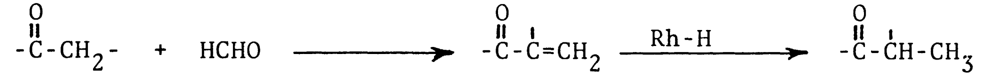
c) 2-Methyl- and 2,6-dimethylcyclohexanone, respectively.

d) 2,4-Dimethyl-3-pentanone. Other products could not be identified by GLPC.

e) Propiophenone and isobutyrophenone, respectively.

but only 2,4-dimethyl-3-pentanone, tetramethylated acetone, was identified by GLPC. 3-Pentanone also gave 2,4-dimethyl-3-pentanone. Acetophenone was converted into propiophenone and isobutyrophenone in fairly good yields.

These results show that the α-methylation of ketones can be catalyzed by rhodium chloride with a carbon monoxide-water-formaldehyde system. This reaction appears to involve the hydrogenation of vinyl ketone derivatives, condensates of ketones with formaldehyde.[3] The hydrogen used for the hydrogenation appears to come from water via rhodium hydride which is generated by the reaction of some rhodium carbonyls with water.



$$-\overset{O}{\overset{\|}{C}}-CH_2- + HCHO \longrightarrow -\overset{O}{\overset{\|}{C}}-\overset{|}{C}=CH_2 \xrightarrow{Rh\text{-}H} -\overset{O}{\overset{\|}{C}}-\overset{|}{C}H-CH_3$$

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