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Ruthenium Complex Catalyzed Selective Deoxygenation of Ketoximes to Ketimines

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$Ru_3(CO)_{12}$ showed high catalytic activity for the deoxygenation of various ketoximes to the corresponding ketimines under carbon monoxide pressure (20 kg/cm^2). For the deoxygenation of propiophenone oxime, ethyl phenyl ketimine was obtained in 100 % yield. On the other hand, heptanal oxime which was aldoxime was dehydrated under the same reaction conditions to the corresponding nitrile in 32% yield.

Since organic molecules including azomethine group (i.e., $>C=N-$) are important as both synthetic and biologic intermediates, various approaches for the construction of the azomethine group have been reported.1) As for the synthesis of ketimines, which can be used to regenerate the parent ketones,2) examples are those including the reaction of ketones with ammonia using potassium hydroxide,3) and the decomposition of nitrile - Grignard complex by dry HCl, anhydrous ammonia4) or absolute methanol.5) More intriguing and simple method is deoxygenation of ketoximes using transition metal complexes such as $TiCl_3$,6) chromous (II) acetate,7) peroxopalladium,8) $Fe(CO)_5$9,10) and $Fe_2(CO)_9$.10) However, a stoichiometric or excess amount of transition metal complexes is always indispensable for all of these reactions and true *catalytic* deoxygenation of ketoximes to ketimines has not yet been reported.

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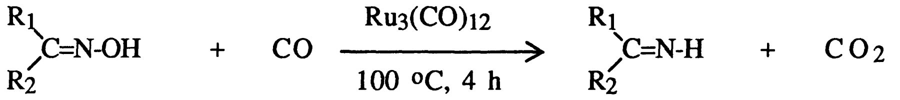
In the course of our study on ruthenium complex catalysis,[11] we found that $Ru_3(CO)_{12}$ showed high catalytic activity for the deoxygenation of ketoximes to ketimines using carbon monoxide as a reducing reagent (Eq.1); preliminary results of which we now report here.



$$\overset{R_1}{\underset{R_2}{>}}C{=}N\text{-}OH + CO \xrightarrow[100\ ^{\circ}C,\ 4\ h]{Ru_3(CO)_{12}} \overset{R_1}{\underset{R_2}{>}}C{=}N\text{-}H + CO_2 \qquad (1)$$

In a typical procedure, a mixture of ketoxime (5.0 mmol), $Ru_3(CO)_{12}$ (0.10 mmol) and benzene (5.0 ml) was heated in a 50 ml stainless steel autoclave with stirring at 100 °C for 4 h under 20 kg/cm^2 of carbon monoxide. All products were isolated by Kugelrohr distillation, and satisfactory spectroscopic and analytical data for them were obtained.

Activity of several catalyst precursors was examined with propiophenone ketoxime as the substrate and summerized in Table 1.

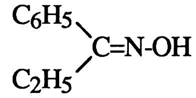
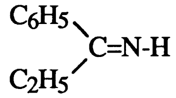
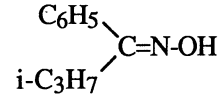
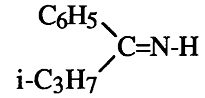
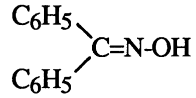
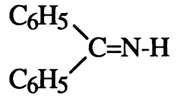
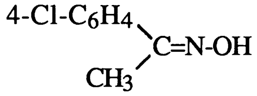
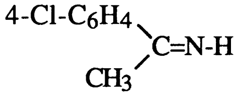
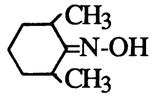
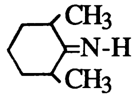
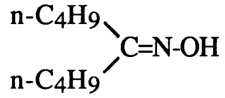
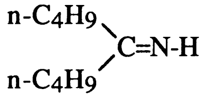
Table 1. Activity of Several Catalyst Precursors[a)]

Run	Catalyst/mmol		Conv.[b)]/%	Yield[b)]/%	Selectivity[c)]/%
1	$Ru_3(CO)_{12}$	(0.10)	100	100	100
2	$Ru(CO)_3(PPh_3)_2$	(0.30)	41	32	78
3	$Fe(CO)_5$	(0.46)	16	4	25
4	$Fe_3(CO)_{12}$	(0.10)	30	4	13
5	$RuCl_3{\cdot}nH_2O$	(0.30)	32	0	0
6	$RuCl_2(PPh_3)_3$	(0.30)	5	trace	-
7	$Co_2(CO)_8$	(0.15)	81	31	38
8	$Rh_6(CO)_{16}$	(0.05)	100	36	36

a) Propiophenone oxime (5.0 mmol), benzene (5.0 ml), CO 20 kg/cm^2, 100 °C 4 h. b) Determined by GLC. c) Selectivity = (Yield of ketimine / Conv. of ketoxime) x 100.

In the presence of a catalytic amount of $Ru_3(CO)_{12}$, propiophenone oxime was smoothly deoxygenated to give the corresponding ethyl phenyl ketimine in 100% yields. After the deoxygenation of propiophenone oxime (run 1), CO_2 was generated in 85% yield based on the amount of propiophenone oxime, together with the corresponding ketimine. This result indicates that carbon monoxide functioned as a reducing reagent. Other transition metal complexes such as $Ru(CO)_3(PPh_3)_2$, $Fe(CO)_5$,[9,10] $Fe_3(CO)_{12}$ (runs 2 - 4) showed some catalytic activity, but $RuCl_3 \cdot nH_2O$ and $RuCl_2(PPh_3)_3$ showed no catalytic activity under the present reaction conditions (runs 5,6). When $Rh_6(CO)_{16}$[12] and $Co_2(CO)_8$ were employed in the present reaction, the selectivities of the corresponding ketimines were low and several high boiling products were obtained (runs 7 and 8).

Table 2. Deoxygenation of Various Oximes[a)]

Run	Substrate	Product	Yield[b)]/%
9	 $(C_6H_5)(C_2H_5)C=N-OH$	 $(C_6H_5)(C_2H_5)C=N-H$	(100)[c)]
10	 $(C_6H_5)(i\text{-}C_3H_7)C=N-OH$	 $(C_6H_5)(i\text{-}C_3H_7)C=N-H$	91
11	 $(C_6H_5)_2C=N-OH$	 $(C_6H_5)_2C=N-H$	82
12	 $(4\text{-}Cl\text{-}C_6H_4)(CH_3)C=N-OH$	 $(4\text{-}Cl\text{-}C_6H_4)(CH_3)C=N-H$	77
13			75
14[d)]	 $(n\text{-}C_4H_9)_2C=N-OH$	 $(n\text{-}C_4H_9)_2C=N-H$	70
15[e)]	$n\text{-}C_6H_{13}CH=N-OH$	$n\text{-}C_6H_{13}CN$	32
16[f)]	$C_6H_5CH=N-OH$	C_6H_5CN	22

a) Oxime (5.0 mmol), $Ru_3(CO)_{12}$ (0.10 mmol), benzene (5.0 ml), CO 20 kg/cm^2, 100 °C, 4 h. b) Isolated yield. c) Determined by GLC. d) For 8 h. e) $n\text{-}C_6H_{13}CH=NH$ was not detected at all. f) At 150 °C.

Various ketoximes including aromatic, aliphatic and cyclic ketoximes were smoothly deoxygenated under the present reaction conditions to give the corresponding ketimines in 77 - 100% yields (Table 2). On the other hand, deoxygenation of aldoximes to the corresponding imines did not proceed at all and heptanal oxime and benzaldoxime were dehydrated to give heptanenitrile and benzonitrile in 32% and 22% yields respectively (runs 15 and 16). Similar rhodium catalyzed dehydration of aldoximes to the corresponding nitriles has also been reported by Kaneda et al.12)

Furthermore, O-benzyl propiophenone oxime and O-acetyl acetophenone oxime, which have no O-H bond, were not converted at all under the same reaction conditions as run 1. These results suggest that the initial step of the present deoxygenation reaction could be the cleavage of ketoxime O-H bond, and Wilkinson et al. reported the formation of $Ru(oximato)_2(PPh_3)_2$ with the O-H bond cleavage of ketoximes by $RuCl_2(PPh_3)_3$ and NaOH.13)

Mechanistic study and application of the present reaction are now in progress.

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