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DISMUTATION OF ALLYL ALCOHOLS TO ALKENES AND α,β-UNSATURATED ALDEHYDES ON THE INTERACTION WITH Ni(cod)$_2$ IN THE PRESENCE OF LIGANDS

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Allyl alcohols RCH=CHCH$_2$OH (R = H, CH$_3$, C$_6$H$_5$) are converted into corresponding alkenes RCH=CHCH$_3$, α,β-unsaturated aldehydes RCH=CHCHO, and water by the interaction with bis(1,5-cyclooctadiene)nickel Ni(cod)$_2$ in the presence of ligands under mild conditions. The formation of the products is explained by assuming oxidative addition of the alcohol to nickel involving O-H or C-OH bond cleavage.

Reduction and oxidation of alcohols to hydrocarbons and aldehydes have been widely studied by organic chemists. Recently it has been reported that certain transition metal compounds catalyze the disproportionation of allyl alcohols to the corresponding alkenes and aldehydes.[1,2] However, the reactions require high temperatures and the selectivity is not high. In the course of our studies on nickel-promoted C-O bond activation of organic compounds[3] we found that allyl alcohols were dismutated to alkenes and aldehydes on the interaction with bis(1,5-cyclooctadiene)nickel Ni(cod)$_2$ in the presence of a ligand under mild conditions.

Table shows the products of the reaction of allyl alcohols with Ni(cod)$_2$ in the absence or in the presence of a ligand. The reaction of allyl alcohol with a mixture of Ni(cod)$_2$ and PPh$_3$ (PPh$_3$/Ni = 2.2) at 30°C affords C$_3$H$_6$, Ni(CH$_2$=CHCHO)(PPh$_3$)$_2$, and water in a 1 : 1 : 1 ratio and their yields based on Ni(cod)$_2$ are almost quantitative (No. 1):

$$2CH_2{=}CHCH_2OH + Ni(cod)_2 + 2PPh_3 \longrightarrow \underset{1}{CH_2{=}CHCH_3} \;:\; \underset{1}{Ni(CH_2{=}CHCHO)(PPh_3)_2} \;:\; \underset{1}{H_2O} \qquad (1)$$

The amount of C$_3$H$_6$ and H$_2$O were determined by gas chromatography and Ni(CH$_2$=CHCHO)(PPh$_3$)$_2$ was characterized by IR and NMR.[4]

The reaction in the presence of PCy$_3$ or PMe$_2$Ph gives similar results, although in these cases a part of acrylaldehyde was polymerized. In contrast to the reaction in the presence of the phosphine ligands, the reaction in the presence of 2,2'-bipyridine (bpy) gives more than 1 mol of C$_3$H$_6$ per Ni(cod)$_2$. The difference in the yield between the reactions in the presence of PPh$_3$ and bpy seems to be attributable to the difference in the stability of the Ni-acrylaldehyde complexes; Ni(CH$_2$=CHCHO)(PPh$_3$)$_2$ is so stable that it does not catalyze further dismutation of allyl alcohol, whereas acrylaldehyde attached to Ni(bpy) is easily converted into its polymer and therefore the remaining Ni(bpy) catalyzes further dismutation of allyl alcohol.

Table Products of the Reactions of Allyl Alcohols with $Ni(cod)_2$ in the Absence or in the Presence of Ligands.

No.	Allyl Alcohol (mmol)	$Ni(cod)_2$ (mmol)	Ligand a) (mol/Ni)	Solv (ml)	Temp (°C)	Time (hr)	Products (mol/mol $Ni(cod)_2$)		
							Alkene	α,β-Unsaturated Aldehyde,b)	Others
1	$CH_2{=}CHCH_2OH$ 6	1.6	PPh_3 2.2	THF 2	30	48	C_3H_6 0.97	$Ni(CH_2{=}CHCHO)L_2$ d) 0.93	H_2O 0.92
2	$CH_2{=}CHCH_2OH$ 15	0.8	PCy_3 1.0	—	30	48	C_3H_6 0.51	c), polymer of acrylaldehyde	H_2O
3	$CH_2{=}CHCH_2OH$ 15	0.9	$MPMe_2Ph$ 2.0	—	30	48	C_3H_6 0.93	c), polymer of acrylaldehyde	H_2O
4	$CH_2{=}CHCH_2OH$ 18	1.1	bpy 1.0	THF 2	30	7	C_3H_6 4.0	polymer of acrylaldehyde	
5	$CH_2{=}CHCH_2OH$ 15	1.2	—	—	30	11	C_3H_6 0.10		Ni-metal
6	$CH_3CH{=}CHCH_2OH$ 7	0.8	PPh_3 2.1	THF 2	30	48	$\underline{t}\text{-}C_4H_8$ 0.44 $\underline{c}\text{-}C_4H_8$,0.15 $1\text{-}C_4H_8$,0.03	$Ni(CH_3CH{=}CHCHO)L_2$ d) 0.51	H_2O 0.51
7	$C_6H_5CH{=}CHCH_2OH$ 6	1.6	PPh_3 2.2	THF 2	30	48	$C_6H_5CH{=}CH_2$ 0.09 $C_6H_5CH{=}CHCH_3$ 0.53	$Ni(C_6H_5CH{=}CHCHO)L_2$ 0.30 + $C_6H_5CH{=}CHCHO$ trace	H_2O
8	$CH_2{=}CHCH_2OH$ 5 + $CH_3CH{=}CHCH_2OH$ 5	1.4	PPh_3 2.0	THF 2	50	6	C_3H_6 0.90 $\underline{t}\text{-}C_4H_8$ 0.001	Mixture of nickel-α,β-unsaturated aldehyde complexes	
9	$CH_2{=}CHCH_2OH$ 5 + $C_6H_5CH{=}CHCH_2OH$ 5	1.1	PPh_3 2.0	THF 2	50	6	C_3H_6 0.24 $C_6H_5{=}CH_2$ 0.57 $C_6H_5CH{=}CHCH_3$ 0.38	Mixture of nickel-α,β-unsaturated aldehyde complexes	
10	$CH_2{=}CHCH_2OH$ 4.4 + $CH_2{=}C(CH_3)COCH_3$ 15	0.6	PPh_3 2.0	-	80	8	C_3H_6 1.3		$(CH_3)_2CHCOCH_3$ 4.9

a) PPh_3=triphenylphosphine, PCy_3=tricyclohexylphosphine, PMe_2Ph=dimethylphenylphosphine, bpy=2,2′-bipyridine.

b) L stands for the ligand employed.

c) Formation of Ni-acrylaldehyde complex(es) is shown by IR spectrum. However, isolation of the complex was not possible due to the contamination with polymer.

d) Yield after crystallization.

Polymerization of vinyl compounds catalyzed by Ni-bpy complexes in the presence of a trace amount of air has been observed.$^{5)}$ The dismutation of allyl alcohol also proceeds in the absence of ligand to some extent accompanied by formation of metallic nickel (No. 5).

The reaction of $CH_3CH=CHCH_2OH$ yields an equilibrated mixture of <u>trans</u>-C_4H_8, <u>cis</u>-C_4H_8, and 1-C_4H_8 together with $Ni(CH_3CH=CHCHO)(PPh_3)_2$ and H_2O. $C_6H_5CH=CHCH_2OH$ is also dismutated to $C_6H_5CH=CHCH_3$ and $C_6H_5CH=CHCHO$ on interaction with $Ni(cod)_2$ in the presence of PPh_3 and a part of $C_6H_5CH=CHCHO$ further undergoes decarbonylation reaction to give $C_6H_5CH=CH_2$ and $Ni(CO)(PPh_3)_3$. The competitive experiment between $CH_2=CHCH_2OH$ and $RCH=CHCH_2OH$ ($R=CH_3$, C_6H_5) indicates that the reactivity of the alcohol increases with increase in the electron-withdrawing ability of the $RCH=CHCH_2$- group. This trend agrees with our previous observation that the rate of the acyl-O bond cleavage of carboxylic esters by Ni(0)-complexes increases with increase in the electron-withdrawing ability of RCO- and R'O- groups in RCOOR'.$^{3)}$

The formation of propylene, acrylaldehyde, and water in a 1 : 1 : 1 ratio from allyl alcohol indicates that cleavage of both C-O and O-H bonds in allyl alcohol is taking place in the reaction. A straightforward mechanism to account for the reaction is to assume the oxidative addition of allyl alcohol involving the C-O bond cleavage to give allyl nickel hydroxide to which allyl alcohol may attack affording water and an allyl-allyloxonickel intermediate from which propylene and acrylaldehyde may be formed by β-hydrogen transfer (Scheme 1). A similar C-O bond cleavage of allyl alcohols by the interaction with Pd-catalysts to form π-allylpalladium intermediates has been postulated in the Pd-catalyzed carbonylation of allyl alcohols$^{6)}$ and allylation of diethylamine and acetylacetone.$^{7)}$

The alternative mechanism involves the first oxidative addition of allyl alcohol through O-H bond cleavage to give an allyloxonickel hydride followed by insertion of the allyl alcohol double bond into the Ni-H bond. If one invokes the β-OH abstraction followed by β-hydrogen transfer the reaction would give propylene, acrylaldehyde, and water (Scheme 2). A similar β-OH abstraction mechanism from allylic compounds has been presented previously.$^{8)}$

$$NiL_n + RCH=CHCH_2OH \longrightarrow \underset{I}{RCH=CHCH_2\text{-}NiL_n\text{-}OH} \text{ (or } \quad \text{---}NiL_n\text{-}OH \text{)} \qquad (1)$$

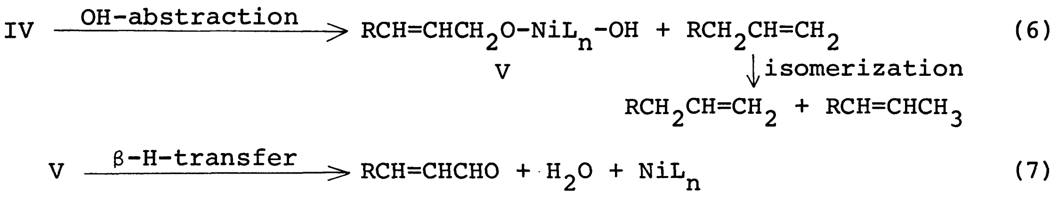
$$I + RCH=CHCH_2OH \longrightarrow \underset{II}{RCH=CHCH_2\text{-}NiL_n\text{-}OCH_2CH=CHR} + H_2O \qquad (2)$$

$$II \xrightarrow{\beta\text{-H-transfer}} RCH=CHCH_3 + RCH=CHCHO + NiL_n \qquad (3)$$

Scheme 1

$$NiL_n + RCH=CHCH_2OH \longrightarrow \underset{III}{RCH=CHCH_2O\text{-}NiL_n\text{-}H} \qquad (4)$$

$$III + RCH=CHCH_2OH \xrightarrow{\text{Insertion}} \underset{IV}{RCH=CHCH_2O\text{-}NiL_n\text{-}CH(CH_2R)CH_2OH} \qquad (5)$$



$$\mathrm{IV} \xrightarrow{\text{OH-abstraction}} \underset{\mathrm{V}}{RCH{=}CHCH_2O\text{-}NiL_n\text{-}OH} + RCH_2CH{=}CH_2 \qquad (6)$$

$$RCH_2CH{=}CH_2 \xrightarrow{\text{isomerization}} RCH_2CH{=}CH_2 + RCH{=}CHCH_3$$

$$\mathrm{V} \xrightarrow{\beta\text{-H-transfer}} RCH{=}CHCHO + H_2O + NiL_n \qquad (7)$$

Scheme 2

When the reaction of allyl alcohol was carried out in the same system in the presence of methyl isopropenyl ketone, a typical hydrogen acceptor, the formation of methyl isopropyl ketone was observed (No 10 in Table). The result is in favor of the mechanism involving the formation of allyloxonickel hydride (Scheme 2). The reactions of saturated alcohols and propagyl alcohol with Ni(cod)$_2$-ligand mixtures did not give any product noteworthy.

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