

Alkylhydridorhodium(III) Route for Isomerization and Hydrogenation of Unsaturated Alcohols with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ under Hydrogen

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Catalytic isomerization of unsaturated alcohols to the corresponding carbonyl compounds with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**2**) is faster under hydrogen (where hydrogenation also occurs to give saturated alcohols) than under nitrogen. The isomerization under hydrogen seems to occur through an alkylhydridorhodium(III) complex which also undergoes reductive elimination to give hydrogenation products, saturated alcohols. The isomerization under hydrogen is faster with **2** than with **1**, which is understood by acceleration of the last step, enol formation by PPh_3 dissociated from **2** and present in the reaction mixture when **2** is used as catalyst. Relative rates of the isomerization observed for different unsaturated alcohols are interpreted by steric effects of substituted groups and numbers of hydrogens to be abstracted by the rhodium of the intermediate, alkylhydridorhodium(III) to undergo the reductive elimination to give enol which is then rapidly converted into a carbonyl compound. It has been observed that the hydrogenation is relatively significant when reactions occur slowly whereas the isomerization is predominant when reactions proceed rapidly.

Introduction

Although most catalytic systems for the isomerization of unsaturated alcohols to the corresponding carbonyl compounds require high temperature to obtain high yields,¹ rhodium(I) complexes, $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)$ (**1**) and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**2**) catalyze the isomerization of unsaturated alcohols at room temperature under nitrogen.² The isomerization of unsaturated alcohols with **1** and **2** was reported to be initiated by a double bond migration followed by relatively fast ketonization of the intermediate, enol to the carbonyl compounds where an allylhydridorhodium(III) complex was suggested to be the intermediate for the first step (double bond migration).² During the investigation of more effective catalytic systems for the isomerization of unsaturated alcohols to carbonyl compounds, we have found that under hydrogen, the catalytic isomerization of unsaturated alcohols with **1** and **2** is faster than that under nitrogen, and the hydrogenation to give saturated alcohols also simultaneously occur (equation 1). In this paper, we wish to suggest an alkylhydridorhodium(III) complex as the intermediate for the first step (double bond migration) of the isomerization (as well as the hydrogenation) which also, like under nitrogen,² involves two steps, double bond migration and ketonization of enols (see equation 1). We also wish to discuss the relative rates of isomerization and hydrogenation with respect to the nature of catalysts **1** and **2** and substrates.

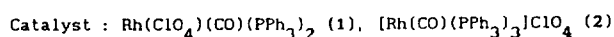
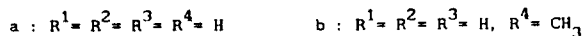
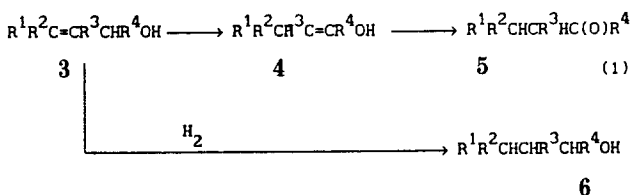


Table 1. Isomerization and Hydrogenation of Unsaturated Alcohols (6.0 mmol) with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) (0.2 mmol) and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**2**) (0.2 mmol) in CDCl_3 (5.0 ml) at 30 °C under Hydrogen. C = catalyst **1** or **2**. (In Parentheses are the Data Obtained under Nitrogen.)²

C	reactant	product	yield, % ^a	time, hr ^b
1	$\text{CH}_2 = \text{CHCH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CHO}$	69(63)	7(14)
2		"	83(95)	3(5)
		$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	12	
1	$\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{OH}^c$	$(\text{CH}_3)_2\text{CHCHO}$	100(100)	0.5(0.5)
2		"	100(100)	0.5(0.5)
1	$\text{CH}_2 = \text{CHCH}(\text{CH}_3)\text{OH}$	$\text{CH}_3\text{CH}_2\text{COCH}_3$	88(91)	20(43)
		$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$	12	
2		$\text{CH}_3\text{CH}_2\text{COCH}_3$	81(92)	5(10)
		$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$	17	
1	$\text{CH}_3\text{CH} = \text{CHCH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	64(64)	60(100)
2		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	20(78)	12(80)
		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	62	

^aConsiderable amounts of non-volatile oligimers were observed in cases where the total amount of products is far below the amount of the reactants. ^bElapsed time until the reactant (95%) disappeared in the reaction mixture. ^cReference 4.

Experimental

Materials and Instruments. $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**2**) were prepared by the literature methods.³ Unsaturated alcohols were purchased from either Aldrich or Fluka and used without further purification. Products of isomerization and hydrogenation were analyzed by ¹H NMR (Varian 60 MHz, EM-360) and GC (Varian 3700).

Catalytic Reactions. These reactions were followed in the same manner as previously described for the isomerization of unsaturated alcohols² except that the reactions in this study were carried out under hydrogen.

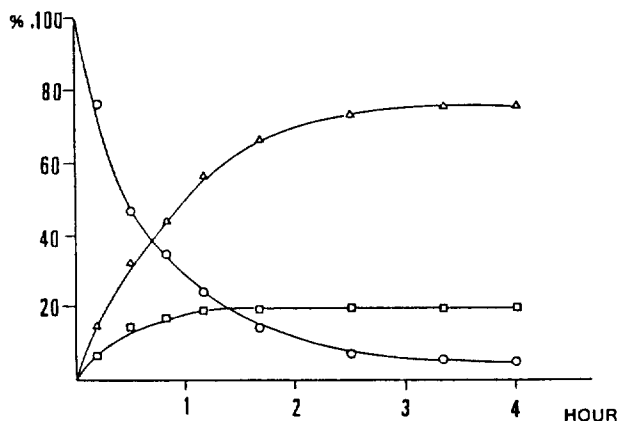
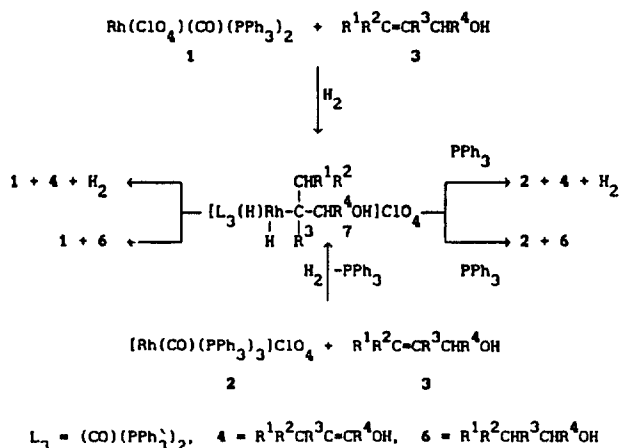


Figure 1. Catalytic Reactions of $\text{CH}_2 = \text{CHCH}_2\text{OH}$ (6.0 mmol) with $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (0.2 mmol) in CDCl_3 (5 ml) at 30°C under Hydrogen (P_{H_2} + vapor pressure of solution = 1 atm). $\text{CH}_2 = \text{CHCH}_2\text{OH}$, \circ - \circ - \circ ; $\text{CH}_3\text{CH}_2\text{CHO}$, \triangle - \triangle - \triangle ; $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, \square - \square - \square .



Scheme 1. Suggested Reaction Pathways for the Isomerization (double bond migration) and Hydrogenation of Unsaturated Alcohols with $[\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2]$ (1) and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (2) under Hydrogen.

Results and Discussion

Data for the catalytic reactions of unsaturated alcohols with 1 and 2 under hydrogen are given in Table 1, and Figure 1 shows the reaction curves for $\text{CH}_2 = \text{CHCH}_2\text{OH}$ (3a) with 2. It is evident in Table 1 and Figure 1 that the isomerization is faster under hydrogen than under nitrogen. This observation suggests that somewhat different reaction pathways for the isomerization under hydrogen from those under nitrogen.² Accordingly, one may readily assume the mechanism involving an alkylhydridometal complex for the catalytic reactions with 1 and 2 under hydrogen while an allylhydridometal complex was suggested as the intermediate under nitrogen.² It has been found, in separate experiments, that the hydrogenation of saturated carbonyl compounds to saturated alcohols with 1 and 2 under the atmospheric pressure of hydrogen at 30°C is so slow that no detectable amounts of the products (saturated alcohols) are obtained for 24 hours. It is, therefore, conceivable that the isomerization and the hydrogenation with 1 and 2 under hydrogen occur simultaneously and the saturated alcohols in Table 1 are not the hydro-

genation products of the isomerization products, carbonyl compounds. A considerable amount of a simple enol, $(\text{CH}_3)_2\text{CH} = \text{CHOH}$ (4c)⁴ was actually detected during the isomerization of 3c to 5c with 1 and 2 under hydrogen.⁵

Now, the data in Table 1 may simply be explained by the reaction pathways in Scheme 1. In fact, we have already suggested an alkylhydridorhodium(III) species (like 7 in Scheme 1) as the intermediate for the isomerization of 3c to $(\text{CH}_3)_2\text{CHCHO}$ (5c) with 1 under hydrogen⁶ and hydrogenation of 3-phenylprop-2-en-1-ol to 3-phenylpropanol with 2 under hydrogen.⁷ Then the isomerization products, 4 rapidly undergo the ketonization to produce the corresponding carbonyl compounds as we have suggested.^{4,6}

Scheme 1 also readily explains the hydrogenation products, 6 (see Table 1) since the saturated alcohols, 6 and 1 (or 2) would be simply the reductive elimination products of 7. Relative rates of the isomerization and hydrogenation for different unsaturated alcohols (data in Table 1) with 1 and 2 may be understood according to the suggested reaction pathways in Scheme 1.

It is seen in Table 1 that the isomerization under hydrogen is faster with 1 than with 2 as observed for the reactions under nitrogen.² This may be understood in terms of relative ease of the last steps ($7 \rightarrow 1 + 4 + \text{H}_2$ and $7 + \text{PPh}_3 \rightarrow 2 + 4 + \text{H}_2$) since the formation of 7 in the reaction of 1 with 3 could not be slower than that in the reaction of 2 with 3. (It is well-known that the perchlorato group of 1 is so readily replaced by an alcohol to give $[\text{Rh}(\text{alcohol})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ^{3c} and the dissociation of PPh_3 from 2 to produce 1 is so significant that the concentration of 1 is actually higher than that of 2 in chloroform.^{4b} In the reactions with 2, the production of carbonyl compounds, 4 would evidently be accelerated by PPh_3 dissociated from 2 and present in the reaction mixture while in the reactions with 1, no such effect is expected.

A part of relative rates of the isomerization for several unsaturated alcohols with 1 and 2 (Table 1) may be rationalized by the relative ease of the last step (formation of enol, 4) as shown in the previous paper;² the faster rates for $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ (3c) than those for $\text{CH}_2 = \text{CHCH}_2\text{OH}$ (3a) seem to be due to the steric effect of the methyl group of 3c which would facilitate the enol formation from 7.

The fact that the rates of the isomerization of secondary alcohol, $\text{CH}_2 = \text{CHCH}(\text{CH}_3)\text{OH}$ (3b) are slower than those of $\text{CH}_2 = \text{CHCH}_2\text{OH}$ (3a) (Table 1) could be understood by the numbers of hydrogens to be abstracted to rhodium to produce 4: there is only one hydrogen for rhodium in 7 to abstract to give 4 when $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{CH}_3$ while two hydrogens are available for rhodium in 7 to yield 4 when $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$. The slowest rates for the inner olefinic alcohol, 3d are unambiguously interpreted by the difficulty of forming 7 compared with the other terminal olefinic alcohols in Table 1.

It is interesting to notice that the hydrogenation is relatively significant when reactions occur slowly (as for $\text{CH}_3\text{CH} = \text{CHCH}_2\text{OH}$) whereas the isomerization is predominant when reactions proceed rapidly (as for $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}_2\text{OH}$).

The ratio of isomerization product to hydrogenation product for each unsaturated alcohol may be affected by various factors such as relative stabilities of isomerization products to hydrogenation products and the numbers of hydrogens to

be abstracted by rhodium in **7**. Greater formation of hydrogenation products with **2** than that with **1** (Table 1) is explained in the same manner as discussed for isomerization above.

Finally, it should be mentioned that it is also possible to obtain a small amount of the carbonyl compounds (Table 1) via the allyhydridorhodium(III) intermediate even under hydrogen.

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Template Synthesis and Properties of Square Planar Nickel(II) and Copper(II) Complexes of 14 - Membered Hexaaza Macrocyclic Ligands with Various Alkyl Pendant Arms at the Uncoordinated Nitrogens

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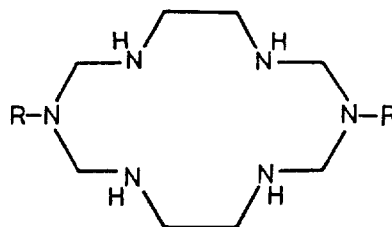
Square planar nickel(II) and copper(II) complexes of 14-membered macrocyclic ligands containing various alkyl pendant arms at the uncoordinated nitrogen atoms, 1,8-dipropyl, 1,8-dibutyl, 1,8-bis(2-methylpropyl), 1,8-bis(2-ethylhexyl), and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane have been prepared from the template condensation of ethylenediamine, formaldehyde, and appropriate primary amines in the presence of the metal ion. The spectroscopic and electrochemical properties of these complexes are similar to those of tetraaza macrocyclic complexes and are not affected significantly by the nature of the alkyl groups.

Introduction

Metal template syntheses often provide selective routes toward the products that are not obtainable in the absence of metal ion. Especially, template reactions involving formaldehyde and amines facilitate the preparation of saturated polyaza multidentate, macrocyclic, and macropolycyclic complexes.¹⁻⁷ The reactions are simple ("one pot reaction"), cheap, and high yielding.

Previously, we synthesized Ni(II) and Cu(II) complexes of fully saturated 14-membered hexaaza macrocyclic ligands A and B from the template condensation reaction of ethylenediamine, formaldehyde, and appropriate primary amines, and compared their properties with those of tetraaza macrocyclic complexes.⁵ Although it has been known that number of methyl groups at the carbon or nitrogen atoms of the tetraaza macrocyclic ligands affect the spectra and the electrochemical properties of the complexes,⁸⁻¹⁶ the effects of the nature of the alkyl groups on the properties of the complexes have rarely been studied. Therefore, we have been interested in the syntheses and comparison of the preproperties for the complexes of macrocyclic ligands C-G, 1,8-dipropyl,

1,8-dibutyl, 1,8-bis(2-methylpropyl), 1,8-bis(2-ethylhexyl), and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane, that contain various alkyl groups at the uncoordinated nitrogen atoms.



A: R = CH₃. B: R = CH₂CH₃. C: R = CH₂CH₂CH₃. D: R = CH₂CH₂CH₂CH₃. F: R = CH₂CH(CH₃)₂. F: R = CH₂CH(CH₂CH₃)CH₂CH₂CH₂CH₃. G: R = CH₂C₆H₅.

Experimental

Materials. All chemicals and solvents used in synthesis were of reagent grade and were used without further purification. Solvents used in spectral measurements were puri-