Catalytic Isomerization of Allyic Alcohols to Carbonyl Compounds with $Rh(ClO_4)(CO)(PPh_3)_2$ and $[Rh(CO)(PPh_3)_3]ClO_4$

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Four coordinated rhodium(I) complexes, $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) and $[Rh(CO)(PPh_3)_3]ClO_4$ (**2**) catalyze the isomerization of allylic alcohols to the corresponding carbonyl compounds at room temperature under nitrogen. The isomerization is faster with **2** than with **1**, which is understood in terms of relative ease of the last step of the catalytic cycle, the reductive elimination of enol. Relative rates of the isomerization with **1** and **2** for different allylic alcohols are also explained by the relative ease of the enol elimination step in part. The first step of the catalytic cycle, the complex formation of the allylic alcohol through the π-system of the olefinic group of the allylic alcohol and the following step, formation of hydridoallyl complex also seem to affect the over-all rate of the isomerization.

Introduction

Isomerization of allylic alcohols to the corresponding carbonyl compounds has been observed in the presence of various transition metal complexes.[1] The isomerization required high temperature for most catalytic systems, or the yields were poor[1k] and a cocatalyst was needed[1d] when the reaction occured at room temperature. Double bond migration of allylic alcohols has been suggested as the initial step of the isomerization (eq. 1) in most studies although the intermediate, enol had never been detected until quite recently.[2] In this paper, we wish to report the isomerization of allylic alcohols to the carbonyl compounds with four-coordinated rhodium(I) complexes, $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) and $[Rh(CO)(PPh_3)_3]ClO_4$ (**2**) at room temperature under nitrogen and discuss the relative rates of the isomerization with respect to nature of catalysts and substrates.

$$\underset{\mathbf{3}}{R^1R^2C{=}CR^3CHR^4OH} \longrightarrow \underset{\mathbf{4}}{R^1R^2CHCR^3{=}CR^4OH} \longrightarrow \underset{\mathbf{5}}{R^1R^2CHCR^3HC(O)R^4} \quad (1)$$

a : $R^1{=}R^2{=}R^3{=}R^4{=}H$ b : $R^1{=}R^2{=}R^3{=}H$, $R^4{=}CH_3$

c : $R^1{=}R^2{=}R^4{=}H$, $R^3{=}CH_3$ d : $R^1{=}R^3{=}R^4{=}H$, $R^2{=}CH_3$

Experimental

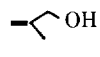
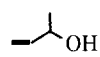
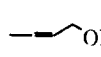
Materials. $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) and $[Rh(CO)(PPh_3)_3]ClO_4$ (**2**) were prepared by the literature methods.[3] Allylic alcohols were purchased from either Aldrich or Fluka and used without further purification. Products were analyzed by ^1H NMR (Varian 60 MHz, EM-360) and GC (Varian 3700).

Isomerization of Allylic Alcohols. A 0.2 mmole (0.16 g) of $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) (or 0.2 g of $[Rh(CO)(PPh_3)_3]ClO_4$, (**2**) was dissolved in $CDCl_3$ (5.0 m*l*) solution of allylic alcohol (0.2 mmol) and stirred at 30 °C under nitrogen. A part of the reaction mixture was taken from the reactor and analyzed by ^1H NMR and GC at intervals until all of the allylic alcohol disappeared. Separation of volatile materials from the reaction mixture by vacuum distillation yielded a mixture of non-volatile metal complex and oligomers which were analyzed by ^1H NMR.

Results of Discussion

Table 1 summarizes the catalytic isomerization of allylic alcohols with **1** and **2**. It is noticed that the rates are mostly faster with **2** than with **1**, and 2-methylprop-2-en-1-ol (**3c**), among the four simple allylic alcohols, undergoes the isomerization most rapidly. The reaction is believed to occur according to equation 1 since it is already known that the intermediate, enol (**4c**) was detected during the isomerization of **3c** to **5c** with **1**[4] and **2**.[2]

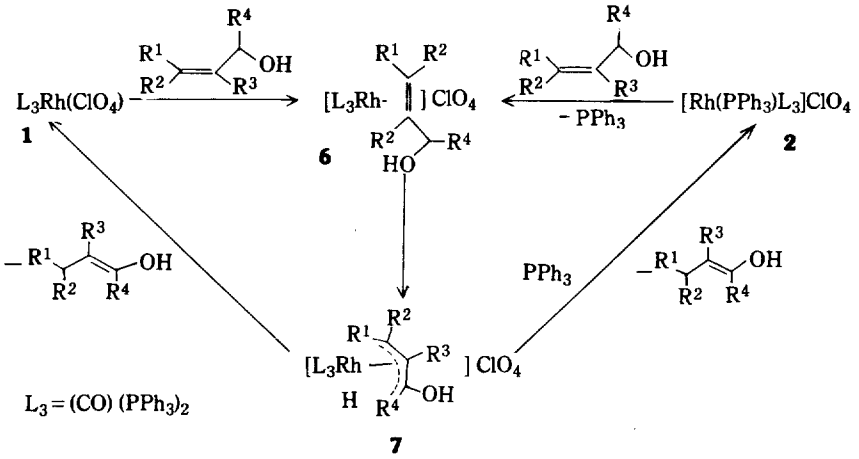
Table 1. Isomerization of Allylic Alcohols (6.0 mmol) to Carbonyl Compounds with $Rh(ClO_4)(CO)(PPh_3)_2$ (1) (0.2 mmol) and $[Rh(CO)(PPh_3)_3]ClO_4$ (2) (0.2 mmol) in $CDCl_3$ (5.0 m*l*) at 30 °C

catalyst	reactant	product	yield(%)	time(hr)[a]
1			63[b]	14
2			95	5
1			100	0.5
2			100	0.5
1			91[b]	43
2			92[b]	10
1			64[b,c]	100
2			78[b,c]	80

[a] Elapsed time until the reactant disappeared in the reaction mixture. [b] Considerable amount of non-volatile oligomers were observed. [c] Small amounts (6-8%) of the dehydrogenation product ($CH_3CH{=}CHCHO$) were also observed.

The perchlorato group of complex **1** is readily replaced by an alcohol[3a] and the dissociation of one PPh_3 from complex **2** to give **1** is so significant that the concentration of **1** is actually higher than that of **2** in chloroform.[4] Interaction between rhodium and the π-system of the olefinic group of an allylic alcohol is certainly expected for **1** and **2** to catalyze the double bond migration. Accordingly it is quite reasonable to assume that an allylic alcohol replaces the ClO_4 group in **1** and PPh_3 in **2** to give the allylic alcohol complex **6** (Scheme 1) in the presence of an excess alcohol. Since the isomerization (eq. 1) occurs under nitrogen, complex **6** may undergo intramolecular oxidative addition to form π-allylhydridorhodium (III) complex, **7** which then produces an enol by reductive elimination. The enol then is readily isomerized to the corresponding carbonyl compounds.

The faster reaction rates with complex **2** than with **1** (Table 1) may be understood in terms of relative ease of the



Scheme 1. Suggested Reaction Pathways for the Isomerization (double bond migration) of Allylic Alcohols with $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) and $[Rh(CO)(PPh_3)_3]ClO_4$ (**2**) under Nitrogen.

last step, reductive elimination of **7** to give enol and **1** (or **2**) since the formation of **6** in the reaction of **1** should be faster than that of **2**, and the second step, **6** ⟶ **7** should make no difference between the rates with **1** and **2**. Triphenylphosphine (PPh_3) dissociated from **2** and present in the solution would facilitate the enol elimination in the isomerization with **2** whereas no such effect is expected in the reaction with **1**.

A part of relative reaction rates for different alcohols (Table 1) may also be explained by the relative ease of the enol elimination step: the faster rates for 2-methylprop-2-en-1-ol (**3c**) than those of prop-2-en-1-ol (**3a**) may be due to the steric effect of methyl group which facilitates the enol elimination from **7**.

Slower rates for the secondary alcohol, **3b** than those for **3c** may be understood by the numbers of hydrogens to be abstracted to rhodium to form **7**:**3b** has only one hydrogen to be transferred to rhodium to form hydridoallylrhodium complex, **7** while **3c** (and other alcohols) has two such hydrogens.

It is not surprising to notice that rates for the inner olefinic alcohol, **3d** are slower than those for the terminal olefinic alcohols, **3a, 3b** and **3c**. This is probably because the formation of both **6** and **7** is unfavorable for **3d** compared with other terminal olefinic alcohols.

In summary, the relative rates of the isomerization of allylic alcohols to the corresponding carbonyl compounds with **1** and **2** are understood in terms of relative ease of the last step, reductive elimination of enol (**7** ⟶ **1** (or **2**) + enol) as well as the formation of olefin complex, **6** and hydridoallyl complex, **7**.

Acknowledgement. Authors wish to thank the Korea Science and Engineering Foundation and the Ministry of Education for the financial support to this study.

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