

Stabilization of a simple enol, 2-methylprop-1-en-1-ol by triphenylphosphinerhodium(I) complexes

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Abstract

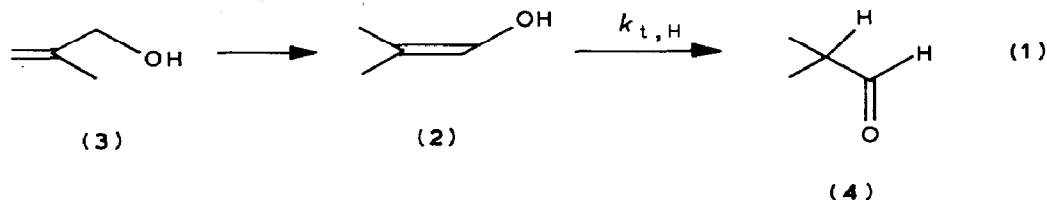
The rhodium(I) complexes, $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**1**), $[\text{Rh}(\text{CO})(\text{AsPh}_3)_3]\text{ClO}_4$ (**5**), $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**6**) and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$ (**7**) catalyze the isomerization of 2-methylprop-2-en-1-ol (**3**) to give 2-methylpropanal (**4**) at room temperature under nitrogen. During the isomerization (**3** $\rightarrow$ **4**), a large amount of the simple enol 2-methylprop-1-en-1-ol (**2**) was formed in the presence of **1**, but a somewhat lesser amount of **2** was formed in the presence of **6**. The rate of double bond migration (**3** $\rightarrow$ **2**) is greater in the presence of **6** than in the presence of **1**. A small amount of **2** was detected in the presence of **7** whereas no enol (**2**) was formed in the presence of **5**.

Introduction

The rapid generation and stabilization of enols are required so that their various properties can be characterised [1–16]. Rapid generation of enols has been achieved by the pyrolysis of cyclobutanol [1] or ethylene glycol [3], the hydrolysis of active precursors such as methoxy(vinyloxy)methyl acetate [4–6] or enolate salts [7,8], the photolysis of 5-hydroxy-2-pentanone [6], and double bond migration of 2-methylprop-2-en-1-ol with a rhodium(I) complex [9]. The stabilization of enols, on the other hand, is achieved either by introducing an appropriate substituent at the carbon–carbon double bond to hinder tautomerization to the carbonyl compound [10–14], or when the enol is kept in the presence of a rhodium(I) complex [9]. Transition metal-enol complexes were suggested as the intermediates in the isomerization of α,β -unsaturated alcohols to the carbonyl compounds although no evidence was obtained for the stabilization of enols [15,16].

Since the cationic rhodium(I) complex $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**1**) was found to be effective both for fast generation and stabilization of the simple enol 2-methylprop-1-en-1-ol (**2**) during the isomerization of 2-methylprop-2-en-1-ol (**3**) to 2-methylpro-

panal (4) (eq. 1) [9], related rhodium(I) complexes, $[\text{Rh}(\text{CO})(\text{AsPh}_3)_3]\text{ClO}_4$ (5), $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (6) and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$ (7) have been investigated in order to obtain more information on the generation and stabilization of the enol 2.



Result and discussion

It was found in this study that complex 5 also catalyzes the isomerization of 3 to give 4 (as does complex 1 [9]). Enol 2, however, was not detected during the isomerization in the presence of 5, whereas a significant amount of the enol 2 was observed in the presence of 1 as previously reported [9]. (Figure 1). This striking difference is certainly due to the stabilization of 2 by 1 but not due to the fast generation of 2 by 1 since the initial rate of disappearance of 2 (up to 50%) is somewhat greater in the presence of 5 than in the presence of 1 within the first 10 minutes, during which time a large amount of the enol 2 was detected though only in the presence of 1. It is also noticed in Fig. 1 that the enol 2 was detected immediately after 3 began to disappear, but the aldehyde 4 was not observed in the early stage of the reaction (up to ca. 5 min) although a large amount of 3 had already disappeared. On the other hand in the presence of 5, the appearance of the aldehyde 4 took place at the same rate as the disappearance of 2.

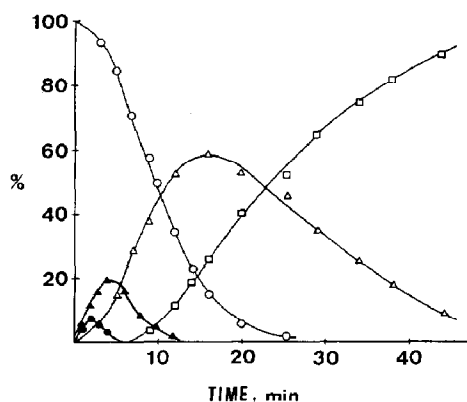


Fig. 1. Isomerization of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ (1.2 mmol) at 27°C under nitrogen in CDCl_3 (1.0 ml) in the presence of $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (0.04 mmol) ($\circ$ — $\circ$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$; $\triangle$ — $\triangle$, $(\text{CH}_3)_2\text{C}=\text{CHOH}$; $\square$ — $\square$, $(\text{CH}_3)_2\text{CHCHO}$), $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (0.04 mmol) ($\blacktriangle$ — $\blacktriangle$, $(\text{CH}_3)_2\text{C}=\text{CHOH}$) and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$ (0.04 mmol) ($\bullet$ — $\bullet$, $(\text{CH}_3)_2\text{C}=\text{CHOH}$). Data for $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ and $(\text{CH}_3)_2\text{CHCHO}$ with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$ are omitted for clarity.

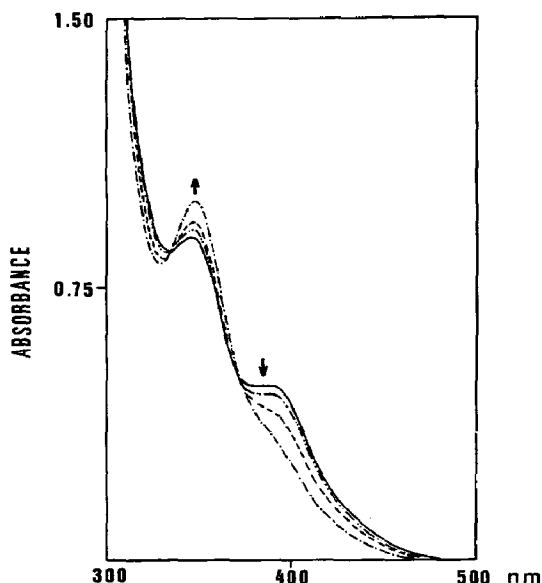


Fig. 2. Electronic absorption spectral changes during the isomerization of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ to $(\text{CH}_3)_2\text{CHCHO}$ with $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ in CHCl_3 at 27°C under nitrogen. Cell path length = 1.0 cm. —, $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ ($3.0 \times 10^{-4} \text{ M}$); ·····, 30 min; — — —, 1 h; ·-·-·, 6 h after the addition of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}/\text{Rh} = 30$).

Complexes **6** and **7** also catalyze the isomerization (**3** $\rightarrow$ **4**), and the enol **2** was detected during the isomerization although the amounts of the enol **2** were considerably less than that formed in the presence of **1** (Fig. 2). This observation also clearly indicates that complex **1** stabilizes **2** more effectively than **6** and **7** since the rates of disappearance of **3** in the presence of **6** and **7** were greater than that in the presence of **1** in the initial stages of the reaction, until more than 60% of the starting material **3** had disappeared.

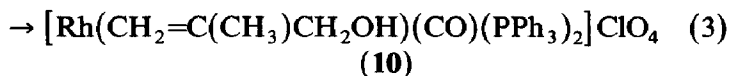
We now know that the triphenylphosphine complexes (**1** and **6**) are more effective than the triphenylarsine complexes (**5** and **7**) in the stabilization of the enol **2**. Investigation of the reactions of **3** with **1** or **6** may provide valuable information on the nature of the stabilization of **2** by **1** or **6**. The metal complexes isolated from the reactions of **3** with **1** on **6** were found to be **1** and a mixture of **1** and **6**, respectively. It is known that complex **6** reacts with alcohols (**L**) to give the cationic complexes $[\text{Rh}(\text{L})(\text{CO})(\text{PPh}_3)_2][\text{ClO}_4]$ (eq. 2) [17,18]. The but-2-en-1-ol



(**L** = CH_3OH [17], $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ [18])

complex, $[\text{Rh}(\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH})(\text{CO})(\text{PPh}_3)_2][\text{ClO}_4]$ (**8**) was isolated from CH_2Cl_2 solution and found to contain $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ coordinated through the oxygen atom but not through the olefinic system [18], whereas the presence of the methanol complex, $[\text{Rh}(\text{CH}_3\text{OH})(\text{CO})(\text{PPh}_3)_2][\text{ClO}_4]$ (**9**), was confirmed in CH_3OH but was not isolated [17]. Changes in the electronic absorption spectra suggest that complex **6** reacts with an excess of **3** (**3**/**Rh** = 30) in solution, initially to form the predominant $[\text{Rh}(\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH})(\text{CO})(\text{PPh}_3)_2][\text{ClO}_4]$ (**10**) (eq. 3).

It is well-known that the four-coordinated rhodium(I) complexes $\text{RhA-Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2 + \text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$

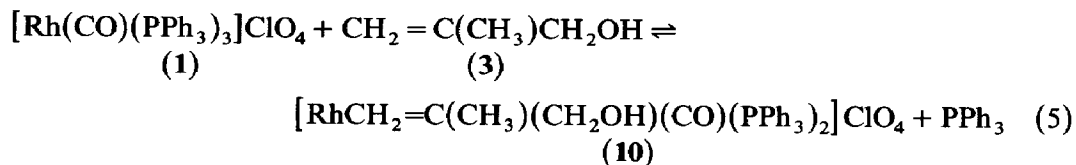


$(\text{CO})(\text{PPh}_3)_2$ show an absorption band in the visible region which shifts with respect to the ligating atom of A [19] and the band appears at 350–360 nm (ϵ 2600–4000) when A is a ligand that coordinates through the oxygen atom [19,20]. A slight increase in absorbance and very slight shift to the shorter wavelength of the absorption band takes place when an excess of 3 is added to a solution of 6 and indicates the formation of another four-coordinated rhodium(I) complex 10 in which 3 is coordinated through the oxygen. No further spectral changes were observed for several hours during which 3 isomerized completely to give 4. The absorption band at ca. 350 nm of the final solution after several hours is certainly not due to 10 but to the rhodium complex of 4, $[\text{Rh}((\text{CH}_3)_2\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]^+$ (11), since it is known that $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]^+$ (L = aldehyde) are readily formed by the reaction of 1 and L and show an absorption band at 350–360 nm [20].

The reaction of 1 with 3 is rather complicated. The electronic spectrum of 1 in CHCl_3 shows two absorption bands at 397 and 352 nm which are unambiguously due to 1 and 6, respectively. The dissociation of PPh_3 from 1 (eq. 4) was to be significant this work: $K = [\text{6}][\text{PPh}_3]/[\text{1}] = 3.6 \pm 0.1 \times 10^{-4} M$ at 30°C in CHCl_3 . Figure 2 shows that complex 1 and 10 coexist in the solution containing excess of 3

$$\begin{array}{ccc} [\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4 \rightleftharpoons \text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2 + \text{PPh}_3 & & (4) \\ (1) & & (6) \end{array}$$

(3/Rh = 30) (eq. 5) until the isomerization of 3 to 4 is nearly completed. The band at ca. 350 nm observed after 6 h (Fig. 2) is also due to 11 since 3 was converted completely into 4 within 5 h under the same experimental conditions. It is certain that complex 1 and 10 coexist in the presence of 3 (3/Rh = 30) but complex 11 is



the predominant species in the presence of 4 (4/Rh = 30). This could be explained in terms of relative affinities of the aldehydes carbonyl group and alcohol hydroxyl group for rhodium(I). In short, complex 10 is the only species in a mixture containing 6 and an excess 3, whereas complex 10 and 1 coexist in a mixture containing 1 and an excess of 3.

It is now possible to state that double bond migration, $3 \rightarrow 2$, is faster in the presence of 6 than in the presence of 1 (in fact it is best in the presence of 1 and 6) (Fig. 1), whereas the stabilization of the enol 2 is more significant in the presence of 1 (also best in the presence of 1 and 6) than in the presence of 6 (Fig. 1). Complex 6 catalyzes double bond migration ($2 \rightarrow 4$) which occur by more rapid formation of 10 than 1 does, while complex 1 stabilizes the enol 2 more effectively than does complex 6. The rhodium complexes 1 and 6 do not seem to catalyze the tautomeri-

zation, $2 \rightarrow 4$ since the tautomerization ($2 \rightarrow 4$) is considerably faster in the absence of rhodium complex **1** or **6** [9].

Although fast interactions between enol **2** and the rhodium complex(es) may account for the stabilization of a more than stoichiometric amount of enol **2** by **1** (and **6**), the nature of this stabilization remains obscure and is currently under investigation.

Experimental

Methods

^1H NMR and electronic absorption spectra were measured on Varian 60 MHz (EM-360A) and Shimadzu UV-240 instruments. A standard vacuum line and Schlenk type glassware were used in handling the metal complexes.

Materials

$\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ were prepared by published methods [17]. $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$ and $[\text{Rh}(\text{CO})(\text{AsPh}_3)_3]\text{ClO}_4$ were prepared by the reactions of $\text{RhCl}(\text{CO})(\text{AsPh}_3)_2$ with AgClO_4 and of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$ with AsPh_3 in the same manner as those for $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ [17,21]. $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ was used as purchased from Fluka.

Dissociation constant measurement

The dissociation constant for the reaction, $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4 \rightleftharpoons \text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2 + \text{PPh}_3$ was measured as described previously [22].

Isomerization of 2-methylprop-2-en-1-ol

The reaction with $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ is described as a typical example of the procedure used. $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (40.6 mg, 0.04 mmol) in CDCl_3 (1.0 ml) was mixed with 86.5 mg (1.2 mmol) of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ in a 25 ml round bottom flask and ca. 0.5 ml of the reaction mixture was immediately transferred into an NMR tube which was sealed with a rubber cap and Teflon tape under nitrogen at 27°C . The isomerization ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ (**3**) $\rightarrow$ $(\text{CH}_3)_2\text{C}=\text{CHOH}$ (**2**) $\rightarrow$ $(\text{CH}_3)_2\text{CHCHO}$ (**4**)) was followed by measuring ^1H NMR spectral changes in the δ 4.5–10 region during the reaction over which a fast scanning for integration of the signals of **2**, **3** and **4** took 33 s. Detailed ^1H NMR spectral data for **2**, **3** and **4** are to be found in ref. 9.

Acknowledgements

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