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

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Abstract

The rhodium(I) complexes, $[Rh(CO)(PPh_3)_3]ClO_4$ (**1**), $[Rh(CO)(AsPh_3)_3]ClO_4$ (**5**), $Rh(ClO_4)(CO)(PPh_3)_2$ (**6**) and $Rh(ClO_4)(CO)(AsPh_3)_2$ (**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** → **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** → **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 geneneration of enols has been achieved by the pyrolysis of cyclobutanol [1] or ethylene glycol [3], the hydrolysis of active precusors 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 $[Rh(CO)(PPh_3)_3]ClO_4$ (**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-

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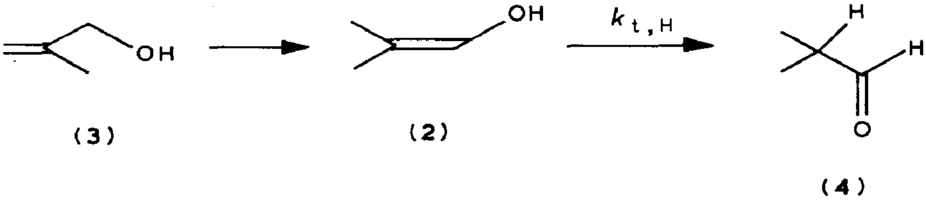
panal (4) (eq. 1) [9], related rhodium(I) complexes, $[Rh(CO)(AsPh_3)_3]ClO_4$ (5), $Rh(ClO_4)(CO)(PPh_3)_2$ (6) and $Rh(ClO_4)(CO)(AsPh_3)_2$ (7) have been investigated in order to obtain more information on the generation and stabilization of the enol 2.



(1)

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 disappearence 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 appearence of the aldehyde 4 took place at the same rate as the disappearence of 2.

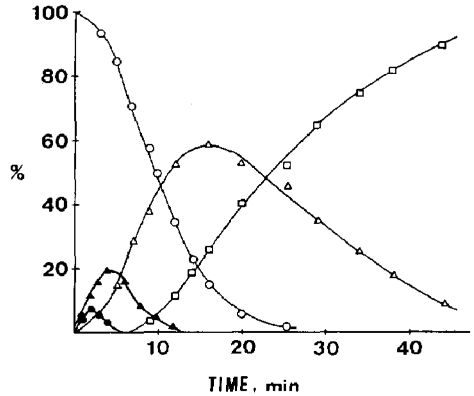


Fig. 1. Isomerization of $CH_2{=}C(CH_3)CH_2OH$ (1.2 mmol) at 27 °C under nitrogen in $CDCl_3$ (1.0 ml) in the presence of $[Rh(CO)(PPh_3)_3]ClO_4$ (0.04 mmol) (○——○, $CH_2{=}C(CH_3)CH_2OH$; △——△, $(CH_3)_2C{=}CHOH$; □——□, $(CH_3)_2CHCHO$), $Rh(ClO_4)(CO)(PPh_3)_2$ (0.04 mmol) (▲——▲, $(CH_3)_2C{=}CHOH$) and $Rh(ClO_4)(CO)(AsPh_3)_2$ (0.04 mmol) (●——●, $(CH_3)_2C{=}CHOH$). Data for $CH_2{=}C(CH_3)CH_2OH$ and $(CH_3)_2CHCHO$ with $Rh(ClO_4)(CO)(PPh_3)_2$ and $Rh(ClO_4)(CO)(AsPh_3)_2$ are omitted for clarity.

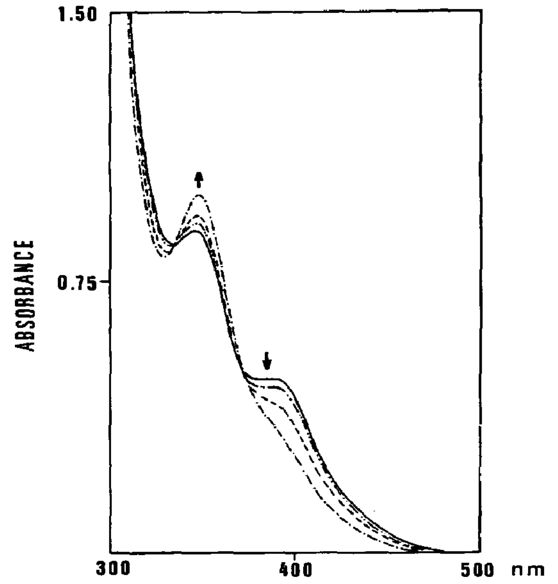


Fig. 2. Electronic absorption spectral changes during the isomerization of $CH_2=C(CH_3)CH_2OH$ to $(CH_3)_2CHCHO$ with $[Rh(CO)(PPh_3)_3]ClO_4$ in $CHCl_3$ at 27 °C under nitrogen. Cell path length = 1.0 cm. ———, $[Rh(CO)(PPh_3)_3]ClO_4$ (3.0×10^{-4} *M*); ··–··–··, 30 min; — — —, 1 h; ·–·–·, 6 h after the addition of $CH_2=C(CH_3)CH_2OH$ ($CH_2=C(CH_3)CH_2OH/Rh = 30$).

Complexes **6** and **7** also catalyze the isomerization (**3** → **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 disappearence 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 $[Rh(L)(CO)(PPh_3)_2[ClO_4$ (eq. 2) [17,18]. The but-2-en-1-ol

$$Rh(ClO_4)(CO)(PPh_3)_2 + L \rightarrow [Rh(L)(CO)(PPh_3)_2]ClO_4 \qquad (2)$$

$$(L = CH_3OH\ [17],\ CH_3CH{=}CHCH_2OH\ [18])$$

complex, $[Rh(CH_3CH{=}CHCH_2OH)(CO)(PPh_3)_2]ClO_4$ (**8**) was isolated from CH_2Cl_2 solution and found to contain $CH_3CH{=}CHCH_2OH$ coordinated through the oxygen atom but not through the olefinic system [18], whereas the presence of the methanol complex, $[Rh(CH_3OH)(CO)(PPh_3)_2]ClO_4$ (**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 $[Rh(CH_2{=}C(CH_3)CH_2OH)(CO)(PPh_3)_2]ClO_4$ (**10**) (eq. 3).

$$\underset{(6)}{Rh(ClO_4)(CO)(PPh_3)_2} + \underset{(3)}{CH_2{=}C(CH_3)CH_2OH}$$

$$\rightarrow \underset{(10)}{[Rh(CH_2{=}C(CH_3)CH_2OH)(CO)(PPh_3)_2]ClO_4} \quad (3)$$

It is well-known that the four-coordinated rhodium(I) complexes $RhA(CO)(PPh_3)_2$ 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**, $[Rh((CH_3)_2CHCHO)(CO)(PPh_3)_2]^+$ (**11**), since it is known that $[RhL(CO)(PPh_3)_2]^+$ (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 unambiguousely due to **1** and **6**, respectively. The dissociation of PPh_3 from **1** (eq. 4) was to be significant this work: $K = [\mathbf{6}][PPh_3]/[\mathbf{1}] = 3.6 \pm 0.1) \times 10^{-4}$ *M* at 30 °C in $CHCl_3$. Figure 2 shows that complex **1** and **10** coexist in the solution containing excess of **3** (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**.

$$\underset{(1)}{[Rh(CO)(PPh_3)_3]ClO_4} \rightleftharpoons \underset{(6)}{Rh(ClO_4)(CO)(PPh_3)_2} + PPh_3 \quad (4)$$

$$\underset{(1)}{[Rh(CO)(PPh_3)_3]ClO_4} + \underset{(3)}{CH_2 = C(CH_3)CH_2OH} \rightleftharpoons$$

$$\underset{(10)}{[RhCH_2{=}C(CH_3)(CH_2OH)(CO)(PPh_3)_2]ClO_4} + PPh_3 \quad (5)$$

It is now possible to state that double bond migration, 3 → 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** → **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 tautomerization, **2** → **4** since the tautomerization (**2** → **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

$Rh(ClO_4)(CO)(PPh_3)_2$ and $[Rh(CO)(PPh_3)_3]ClO_4$ were prepared by published methods [17]. $Rh(ClO_4)(CO)(AsPh_3)_2$ and $[Rh(CO)(AsPh_3)_3]ClO_4$ were prepared by the reactions of $RhCl(CO)(AsPh_3)_2$ with $AgClO_4$ and of $Rh(ClO_4)(CO)(AsPh_3)_2$ with $AsPh_3$ in the same manner as those for $Rh(ClO_4)(CO)(PPh_3)_2$ and $[Rh(CO)(PPh_3)_3]ClO_4$ [17,21]. $CH_2{=}C(CH_3)CH_2OH$ was used as purchased from Fluka.

Dissociation constant measurement

The dissociation constant for the reacton, $[Rh(CO)(PPh_3)_3]ClO_4 \rightleftharpoons Rh(ClO_4)(CO)(PPh_3)_2 + PPh_3$ was measured as described previously [22].

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

The reaction with $[Rh(CO)(PPh_3)_3]ClO_4$ is described as a typical example of the procedure used. $[Rh(CO)(PPh_3)_3]ClO_4$ (40.6 mg, 0.04 mmol) in $CDCl_3$ (1.0 ml) was mixed with 86.5 mg (1.2 mmol) of $CH_2{=}C(CH_3)CH_2OH$ 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 ($CH_2{=}C(CH_3)CH_2OH$ (**3**) → $(CH_3)_2C{=}CHOH$ (**2**) → $(CH_3)_2CHCHO$ (**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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