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# Pentamethylcyclopentadienyl ruthenium: an efficient catalyst for the redox isomerization of functionalized allylic alcohols into carbonyl compounds

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ABSTRACT

The catalytic activity of the ruthenium(II) complex $[RuCp*(CH_3CN)_3][PF_6]$ **1** in the transposition of allylic alcohols into carbonyl compounds, in acetonitrile, is reported. This catalyst has proven to be able to catalyze the transformation of poorly reactive and/or functionalized substrates under smooth conditions.

## 1. Introduction

The concept of atom economy, that is, all atoms of the reactant end up in the final product, has emerged as an important tool and a desirable goal in chemistry.[1] Among the catalytic reactions dealing with this concept, considerable effort was devoted to the redox isomerization.[2] This catalytic reaction formally corresponds to the conversion, in a one-step process, of an allylic alcohol into a carbonyl compound via the oxidation of the alcohol and reduction of the alkene. Several metal complexes, mainly from the group 8, 9, and 10, were reported to perform this transformation.

Among a variety of ruthenium complexes used for this internal redox process,[2c] ruthenium(II) complexes with a cyclopentadienyl type ligand and ruthenium(IV) complexes featuring an allylic ligand have emerged as very efficient catalytic systems. The mononuclear $RuCpCl(PPh_3)_2$, $Ru(indenyl)Cl(PPh_3)_2$, $[RuCp(MeCN)_2(PR_3)]PF_6$, $[RuCp(MeCN)_3]PF_6$, RuCpCl(diphosphine) complexes have revealed good catalytic activities for the isomerization of aliphatic and aromatic allylic alcohols into ketones or aldehydes at 65–100 °C.[3] The binuclear ruthenium catalyst $[(Ru(CO)_2)_2(H)(C_5Ph_4OHOC_5Ph_4)]$,[4] $RuCp*Cl(Ph_2PCH_2CH_2NH_2\text{-}\eta^2\text{-}P,N)$,[5] and $Ru(C_5MePh_4)X(CO)_2$ (X=Br, Cl)[6] complexes were shown also to be active Cp-containing ruthenium catalysts. Ruthenium(IV) complexes bearing the bis(allyl) dodeca-2,6,10-triene-1,12-diyl (**L1**)[7a] or 2,7-dimethylocta-2,6-dien-1,8-diyl (**L2**)[7b] ligand in $RuCl_2$(**L1**) and $[RuCl_2(\mathbf{L2})]_2$, $RuCl_2(L)(\mathbf{L2})$ (L=CO, phosphine, $^t$BuNC, MeCN, $PhNH_2$), and $[RuCl(\mathbf{L2})(MeCN)_2]SbF_6$ have also shown very high turnover frequencies in the redox isomerization of allylic alcohols into carbonyl compounds, both in organic solvent and in water at 75 °C.

In conjunction with our work on $\eta^3$-allyl-ruthenium(IV) species as catalyst in allylic transformation,[8,9] we discovered that, starting from cinnamyl chloride derivatives and phenylboronic acid in the presence of $[RuCp*(MeCN)_3]^+$ as catalyst precursor, the reaction gives rise to the branched allylic alcohols, as the major isomer.[9] From electron-rich cinnamyl chloride derivatives, this process led, directly at room temperature, to propiophenones via a subsequent redox isomerization of the branched allylic alcohol intermediates.[10] In light of these results and encouraged by the mild conditions required for this redox isomerization, we decided to study this process with our catalyst system. Here we report our preliminary results showing the good activity of the stable $[RuCp*(MeCN)_3][PF_6]$ **1** in the isomerization of allylic alcohols to saturated carbonyl compounds. A large variety of substrates can be isomerized very efficiently using these conditions and the regioselectivity of this new process was also demonstrated. Finally, a mechanistic study using a labeled compound was also carried out.

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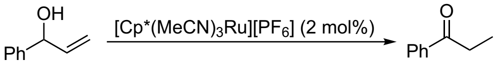
## 2. Results and discussion

Initially, we used the same reaction conditions that those described for the synthesis of propiophenones from electron-rich cinnamyl chloride:[10] acetonitrile as solvent, potassium carbonate (1.2 equiv) as base, and $[RuCp^*(MeCN)_3][PF_6]$ **1** (2 mol %) as catalyst. Then, from 1-phenylprop-2-en-1-ol **2a** (a less reactive substrate than the corresponding α-vinyl-alkyl alcohol[7]), the propiophenone was isolated in 88% yield after 7 h at room temperature (entry 1, Table 1). The importance of the base was clearly evidenced when the reaction was carried out only in presence of the catalyst with **2a** (entry 2, Table 1). Without any base, the starting material was mainly recovered accompanied with 5% of the expected ketone. We therefore sought to optimize the isomerization reaction conditions of **2a** in the presence of a catalytic amount of $[RuCp^*(MeCN)_3][PF_6]$ (Table 1). A decrease of the amount of base led to a drop of the yield and no improvement occurred when THF was the solvent (entries 3 and 4). However, the reaction rate was improved by increasing the reaction temperature (reflux of solvent), and the propiophenone **3a** was isolated with an almost quantitative yield (95%) in only 1 h (entry 5). Under these experimental conditions (temperature), the amount of $K_2CO_3$ can be reduced to 50 mol % without alteration of the yield (compare entries 5 and 6). In the presence of 10 mol % of base, the isomerization reaction still occurred but, then, the reaction time had to be increased to reach high yields (Table 1, entry 7). This decreasing reactivity might be due to the heterogeneous conditions. *More interestingly, it is to pointed out that* $[RuCp^*(MeCN)_3][PF_6]$*, unlike the less stable* $[RuCp(MeCN)_3][PF_6]$*, is still an efficient catalyst in presence of water. The reaction can be run in an aqueous solution of* $K_2CO_3$ *(2 M) in opened flask without any deleterious effect to furnish* ***3a*** *in 80% yield within 1 h* (entry 8). Then, distilled solvents are not required. Finally, stronger base such as potassium *tert*-butoxide, or organic base such as triethylamine, could also be used in this isomerization and provided comparable yields (entries 9–10). Given that potassium carbonate is not expensive, easy to handle, and to remove from the reaction medium, all the other catalytic reactions have been carried out with this base in refluxing acetonitrile.

To evaluate the scope and limitation of **1**, the study has been extended to a variety of α-arylallylic alcohols. The results are summarized in Table 2. Except for the phenyl ring bearing a nitro function in *ortho* position (**3b**), all the ketones were isolated in nearly quantitative yields. Neither the steric hindrance nor the electronic effect of the substituent has an influence on the efficiency of this redox isomerization. The lowest reactivity of **2b** might be explained either by an intramolecular hydrogen bond, which renders the hydrogen less acidic, or by a coordination of the nitro group on the ruthenium center, which decreases its activity.

**Table 1**
Optimization of the reaction conditions



**2a** **3a**

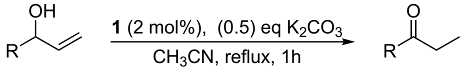
| Entry[a] | Base (equiv) | Temp (°C) | Solvent | Time (h) | Yield[c] (%) |
|---|---|---|---|---|---|
| 1 | $K_2CO_3$ (1.2) | rt | $CH_3CN$ | 7 | 88 |
| 2 | — | rt | $CH_3CN$ | 7 | 5 |
| 3 | $K_2CO_3$ (0.5) | rt | $CH_3CN$ | 7 | 50 |
| 4 | $K_2CO_3$ (0.5) | rt | THF | 7 | 52 |
| 5 | $K_2CO_3$ (1.2) | Reflux | $CH_3CN$ | 1 | 95 |
| 6 | $K_2CO_3$ (0.5) | Reflux | $CH_3CN$ | 1 | 95 |
| 7 | $K_2CO_3$ (0.1) | Reflux | $CH_3CN$ | 1 | 60 |
| 8[b] | aq $K_2CO_3$ (1.2, 2 M) | Reflux | $CH_3CN$ | 1 | 80 |
| 9 | *t*-BuOK (0.5) | Reflux | $CH_3CN$ | 1 | 95 |
| 10 | $Et_3N$ (0.5) | Reflux | $CH_3CN$ | 1 | 94 |

[a] Conditions: 0.5 mmol of allylic alcohol, 0.25 mmol of potassium carbonate, 0.01 mmol of catalyst (2 mol %) in 1.3 mL of solvent.

[b] Conditions: 0.5 mmol of allylic alcohol, 0.01 mmol of catalyst (2 mol %), 0.5 mL of aqueous solution of $K_2CO_3$ (2 M) in 1 mL of solvent.

[c] Isolated yields after purification on silica gel.

**Table 2**
Redox isomerization of various 1-arylprop-2-en-1-ols



**2** **3**

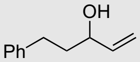
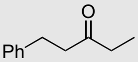
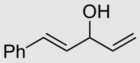
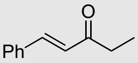
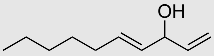
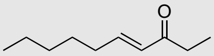
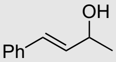
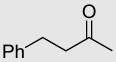
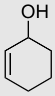
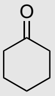
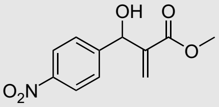
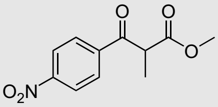
| Entry[a] | Products | R | Yield[b] (%) |
|---|---|---|---|
| 1 | **3a** | Ph | 95 |
| 2 | **3b** | 2-$NO_2$-$C_6H_4$ | 33 |
| 3 | **3c** | 4-$NO_2$-$C_6H_4$ | 96 |
| 4 | **3d** | Br-$C_6H_4$ | 99 |
| 5 | **3e** | 4-MeO-$C_6H_4$ | 99 |
| 6 | **3f** | 4-F-$C_6H_4$ | 98 |
| 7 | **3g** | 2,4,6-$(Me)_3$-$C_6H_2$ | 97 |
| 8 | **3h** | 2,4,6-$(MeO)_3$-$C_6H_2$ | 98 |
| 9 | **3i** | 2-Naphthyl | 99 |
| 10 | **3j** | 1-Naphthyl | 99 |

[a] Conditions: 0.5 mmol of allylic alcohol, 0.25 mmol of potassium carbonate, 0.01 mmol of catalyst (2 mol %) in 1.3 mL of solvent.

[b] Isolated yields after purification on silica gel.

Having in hand an efficient process for the synthesis of aromatic ketones, the reactivity of complex $[RuCp^*(MeCN)_3][PF_6]$ **1** was evaluated with other substituted allylic alcohols (Table 3). Isomerization of aliphatic allylic alcohols bearing an unsubstituted vinyl group under previous experimental conditions was

**Table 3**
Isomerization of a variety of allylic alcohols catalyzed by $[RuCp^*(MeCN)_3][PF_6]$[a]

| Entry[a] | Substrate | Product | Yield[b] (%) |
|---|---|---|---|
| 1 |  **2k** |  **3k** | 94 |
| 2 |  **2l** |  **3l** | 82 |
| 3 |  **2m** |  **3m** | 77 |
| 4 |  **2n** |  **3n** | 85 |
| 5 |  **2o** |  **3o** | 96 |
| 6 |  **2p** |  **3p** | 84 |

[a] Conditions: 0.5 mmol of allylic alcohol, 0.25 mmol of potassium carbonate, 0.01 mmol of catalyst (2 mol %) in 1.3 mL of acetonitrile, reflux, 1 h.

[b] Isolated yields after purification on silica gel.