Efficient Isomerization of Allylic Alcohols to Saturated Carbonyl Compounds by Activated Rhodium and Ruthenium Complexes

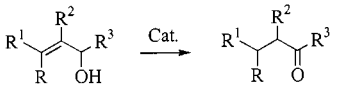
Ramalinga Uma,[a] Maxwell K. Davies,[a] Christophe Crévisy,[a] and René Grée*[a]

Keywords: Allylic alcohols / Isomerizations / Rhodium / Ruthenium

A range of readily available rhodium complexes of the general structures $Rh(PPh_3)_3^+ PF_6^-$ and $RhX(PPh_3)_3$ (X = H, Me, Ph) have been prepared and used in situ for the isomerization of allylic alcohols to their corresponding saturated carbonyl compounds. The isomerization of octen-3-ol, selected as a model, yielded octan-3-one in good yield. This reaction has been extended to the corresponding ruthenium complexes of the general structures $[RuCl(PPh_3)_3]^+ PF_6^-$, $RuXCl(PPh_3)_3$ and $RuX_2(PPh_3)_3$ (X = H, Me, Ph). It is noteworthy that many of these complexes have not been employed previously for this isomerization. The scope and efficiency of the process has been demonstrated by four representative complexes [$RhH(PPh_3)_3$, $RuH_2(PPh_3)_3$, $RuPh_2(PPh_3)_3$, $RuCl(PPh_3)_3^+ PF_6^-$] with a wide variety of allylic alcohols. The reaction of primary allylic alcohols in the presence of $RuCl(PPh_3)_3^+ PF_6^-$ in methanol yields aldehydes protected as their methyl acetals. Deuterium labelling experiments are in agreement with a 1,3-hydride shift mechanism.

Introduction

The conversion of allylic alcohols to saturated carbonyl compounds is a useful synthetic process, and conventionally sequential oxidation and reduction reactions are required for this process. A one-pot, catalytic transformation of allylic alcohols to saturated carbonyl compounds equivalent to an internal redox process (Scheme 1) is a conceptually attractive strategy. In this regard, a number of methods have been developed that harness the ability of transition metal complexes to migrate double bonds.[1] A few examples with asymmetric catalysis have been developed[2] with moderate[2a,2b] to good[2c] enantioselectivities. A double bond migration with an allylic alcohol results in the formation of an enol (or enolate) intermediate[3] which then tautomerizes to afford the saturated carbonyl compound. However, use of the catalysts has been restricted by the degree of substitution on the double bond and the harsh reaction conditions. Thus, there is a need to develop new efficient catalysts that are readily available, and easily prepared and used by organic chemists.



Scheme 1. Isomerization of allylic alcohols to ketones

In our study of enol/enolate intermediates from allylic alcohols catalyzed by transition metal complexes and their subsequent trapping,[4] we had to search for new catalytic species. It is known that Wilkinson's catalyst in THF does not perform the desired conversion efficiently. However, Boons has reported recently that Wilkinson's catalyst can be transformed by reaction with *n*BuLi to the active catalyst $RhH(PPh_3)_3$ **1,** which proved to be efficient for the deprotection of allyl ethers.[5] Therefore, we have started a research program the purposes of which are i) to check if this catalyst is also efficient in the isomerization of allylic alcohols, ii) to extend the reaction with related Rh or Ru catalysts and iii) to study the scope and limitation of such catalysts with regard to the substitution of the alcohols.

Results

Firstly, we verified the reactivity of **1** towards the isomerization of a simple model, octen-3-ol (**19**) (Table 1, entry 1). We prepared the hydrido complex **1** under the conditions described by Boons, that is, from Wilkinson catalyst and *n*Buli. The resulting catalyst (5 mol %) was used in situ and proved to be very efficient, a complete transformation was observed in 30−40 minutes. This prompted us to screen a variety of complexes for the isomerization.

Numerous examples in the literature demonstrate that if the Y group of the activator MY (Scheme 2) contains an available β-hydrogen, β-elimination occurs giving the metal hydride.[5,6a,6b,6c] The complex **1** can also be prepared by other well-established procedures using such activators. Therefore, in order to establish unambiguously the structure of the species involved in the process, we prepared **1** according to a known procedure using LDA as an activator,[6a] and we obtained a comparable result for the isomerization reaction (Table 1, entry 2).

If no β-hydrogen is readily available, the chloride [or the bromide in the case of $RhBr(PPh_3)_3$ is replaced by group Y to yield the σ-bonded Rh^I complex of the general formula $RhYL_3$ [6d−6g] (Scheme 2). It was of interest to check the potential of such derivatives as catalysts for the isomerization.

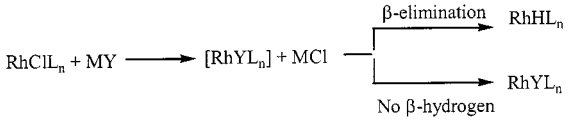
[a] Laboratoire de Synthèses et Activations de Biomolécules, UMR CNRS 6052, ENSCR,
35700 Rennes, France
Fax: (internat.) +33−(0) 2 99 87 13 84
E-mail: gree@ensc-rennes.fr

  1434−193X/01/0816−3141 $ 17.50+.50/0

Table 1. Active rhodium catalysts for the isomerization of octen-3-ol **19** to octan-3-one (octan-3-one is the only compound detected by ^1H and ^{13}C NMR of the crude reaction mixtures except for entries 3 and 9, where transformation was incomplete)

Entry[a]	Formation of active catalyst, Solvent	Catalyst	Conversion, time
1	$RhCl(PPh_3)_3$ + 1 equiv. *n*BuLi, THF	$RhH(PPh_3)_3$ (**1**)	100, 30−40 min
2	$RhCl(PPh_3)_3$ + 1 equiv. LDA, THF	$RhH(PPh_3)_3$ (**1**)	100, 45 min
3	$RhCl(PPh_3)_3$ + 1 equiv. MeMgBr, THF	$RhMe(PPh_3)_3$ (**2**)	40, 24 h
4	$RhCl(PPh_3)_3$ + 1 equiv. PhMgBr, THF	$RhPh(PPh_3)_3$ (**3**)	100, 24 h
5	$RhCl(PPh_3)_3$ + 1 equiv. MeLi, THF	**2**	100, 30−40 min
6	$RhCl(PPh_3)_3$ + 1 equiv. PhLi, THF	**3**	100, 30−40 min
7	$RhCl(PPh_3)_3$ + 1 equiv. Li-TMP[b], THF	$RhTMP(PPh_3)_3$ (**4**)	100, 30−40 min
8	$RhClCO(PPh_3)_2$ + 1 equiv. PhLi,[6g] THF	$RhPhCO(PPh_3)_2$ (**5**)	100, 40−50 min
9	$RhClCO(PPh_3)_2$ + 1 equiv. *n*BuLi, THF	$RhHCO(PPh_3)_2$ (**6**)	40, 4 h
10	Commercial $RhHCO(PPh_3)_3$,[7] THF	$RhHCO(PPh_3)_3$ (**7**)	100, 60−70 min
11	$RhCl(PPh_3)_3$ + 1 equiv. K_2CO_3, THF		100, 30−40 min
12	$RhCl(PPh_3)_3$ + 1 equiv. $AgPF_6$, MeOH	$Rh(PPh_3)_3^+$, PF_6^- (**8**)	100, <10 min

[a] In all experiments 5 mol % of the catalyst was used and the isomerization reaction was performed at reflux of the solvent. − [b] TMP = 2,6-tetramethylpiperidine.



Scheme 2. Reactivity of Wilkinson's Cat with metal base MY

Therefore, we extended our studies to activators with no available β-hydrogen, such as MeLi and PhLi, and also to other complexes (entries 3−10, Table 1) which lead to catalysts of the general structure $RhYL_n$. The catalysts **2**−**7** were screened in the conversion of octen-3-ol **19** to octan-3-one (entries 3−10). The preparation of complexes **2** and **3** from either Wilkinson's catalyst and Grignard reagents[6f] or from $RhBr(PPh_3)_3$ and organolithium or Grignard reagents[6e] have been reported in the literature. The first method (entries 3 and 4, Table 1) gave catalysts **2** and **3** which can perform the transformation. The organolithium reagents are more reactive and readily available. Therefore they reduced the reaction time in the preparation of **2** and **3**, and the isomerization reaction proved to be considerably faster (entries 5 and 6). With the complex $RhClCO(PPh_3)_2$, we assumed from the results reported above that the reaction with the organolithium reagent occurs in the same manner[6g] and that the structures of the active catalysts are those reported in Table 1 (entries 8, 9). With these catalysts an improvement in reactivity was seen when the activator was changed from *n*BuLi to PhLi.

We then tried to extend the reaction to other type of activators. Bäckvall[1a] has reported that the isomerization reaction of allylic alcohols by ruthenium dichloride catalysts can be activated in the presence of potassium carbonate. We tried to activate the Wilkinson's catalyst in such a way and obtained a comparable result (entry 11). Finally, on the basis of other analogous reactions in the literature,[8] we propose that under the conditions reported in entry 12 the silver salt $AgPF_6$ undergoes a salt elimination reaction with $RhCl(PPh_3)_3$ to give AgCl (removed by filtration) and $[(PPh_3)_3Rh]^+PF_6^-$ **8**, which proved to be a very efficient catalyst.

We then extended our studies to the related ruthenium catalysts (Table 2). By analogy with the rhodium complexes, we postulate that activation of $RuCl_2(PPh_3)_3$ with one or two equivalents of MY would give catalysts **9**−**14**. Once again, no difference in reactivity was observed between **9** prepared under these conditions (entry 1) and the catalyst obtained by a known procedure[9] (entry 2). All the ruthenium catalysts show a comparable reactivity with the related rhodium complexes. A change in ligand was also investigated. For example, the replacement of the triphenylphosphane for tri-*n*-butylphosphane resulted in an active catalyst **15** with comparable results,[10] in spite of the difference in steric and electronic factors between the two ligands. With the additive K_2CO_3 (entry 10), we obtained only a low yield and a slow rate of conversion contrary to the literature report.[1a]

From catalysts **1**−**16**, derivatives **1**, **12** and **14** were chosen for further studies with a range of allylic alcohols as they are readily available and easily prepared. The complex **16** was also investigated as a representative cationic species. Alcohols **19**−**35** (Figure 1) were carefully chosen to model a large variety of substitution patterns and to increase the scope of this reaction which is usually restricted to a relatively narrow panel of substrates. The results are listed in Table 3.

The three complexes **1**, **12** and **14** were equally effective for alcohols **19**, **20**, **21** and **25**, with 100% conversion over approximately 30−40 min, and equally ineffective with propargylic alcohols **29**, **34** and **35**, 1,3-diene **28** and primary alcohol **30** (no isomerization). From the result in entry 18, it can be concluded that the presence of a propargylic alcohol completely inhibits the reaction, though the reason for this observation is not clear.

Although **16** is equally effective for the transformation of **19** and **20**, a quick investigation revealed a different behavior for this complex. The most striking difference in activity was observed with *trans*-dodec-2-en-1-ol **30** (entry 12). Catalysts **1, 12** and **14** were inactive with **30**, whereas the corresponding saturated acetal **36** (Figure 2) was

Table 2. Active ruthenium catalysts for the isomerization of octen-3-ol (**19**) to octan-3-one (octan-3-one is the only compound detected by ^1H and ^{13}C NMR of the crude reaction mixtures expect for entry 10, where transformation was incomplete)

Entry[a]	Formation of active catalyst, Solvent	Catalyst	Conversion, time
1	$RuCl_2(PPh_3)_3$ + 1 equiv. *n*BuLi, THF	$RuClH(PPh_3)_3$ (**9**)	100, 60−70 min
2	$RuCl_2(PPh_3)_3$ + 20 equiv. Et_3N, THF[9]	$RuClH(PPh_3)_3$ (**9**)	100, 60−70 min
3	$RuCl_2(PPh_3)_3$ + 1 equiv. LDA, THF	$RuClH(PPh_3)_3$ (**9**)	100, 45 min
4	$RuCl_2(PPh_3)_3$ + 1 equiv. MeLi, THF	$RuClMe(PPh_3)_3$ (**10**)	100, 60−70 min
5	$RuCl_2(PPh_3)_3$ + 1 equiv. PhLi, THF	$RuClPh(PPh_3)_3$ (**11**)	100, 60−70 min
6	$RuCl_2(PPh_3)_3$ + 2 equiv. *n*BuLi, THF	$RuH_2(PPh_3)_3$ (**12**)	100, 30−40 min
7	$RuCl_2(PPh_3)_3$ + 2 equiv. MeLi, THF	$RuMe_2(PPh_3)_3$ (**13**)	100, 30−40 min
8	$RuCl_2(PPh_3)_3$ + 2 equiv. PhLi, THF	$RuPh_2(PPh_3)_3$ (**14**)	100, 30−40 min
9	Isolated $RuH_2(PnBu_3)_4$,[10] THF	$RuH_2(PnBu_3)_4$ (**15**)	100, 30−40 min
10	$RuCl_2(PPh_3)_3$ + 1 equiv. K_2CO_3, THF[b]		25, 6 h
11	$RuCl_2(PPh_3)_3$ + 1 equiv. $AgPF_6$, MeOH	$RuCl(PPh_3)_3^+ PF_6^-$ (**16**)	100, <10 min

[a] In all experiments 5 mol % of the catalyst was used and the isomerization reaction was performed at reflux of the solvent. – [b] Bäckvall's conditions (ref.[1a]).

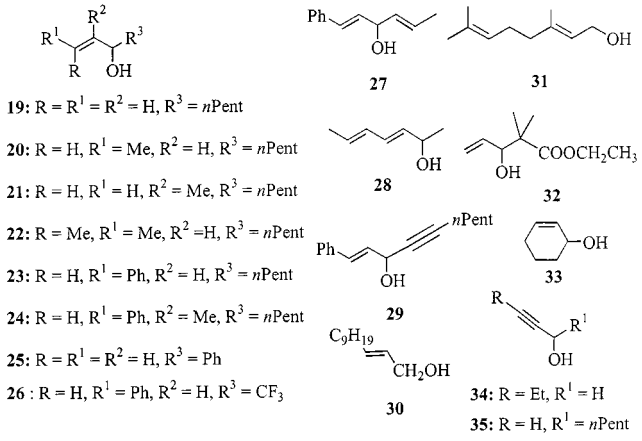


Figure 1. Alcohols **19**−**35**.

formed with catalyst **16**. Presumably, **16** behaves as a Lewis acid, and as the reaction is performed in methanol, concomitant acetalization occurs. This catalytic system could therefore be useful when sensitive aldehydes are formed, as they can be protected in situ. When the reaction of **30** was performed with catalysts **1**, **12** and **14** in methanol, no reaction was observed and when the solvent was changed from methanol to THF with catalyst **16**, the reaction does not proceed. With conjugated systems **23** and **29**, the Lewis acid behavior of **16** dominates, thus the substrate becomes activated towards nucleophilic attack and results in the corresponding allylic ether **37** and a mixture (67:23:10) of allylic ethers **(*E*+*Z*)-38a** and **38b**, respectively. However, the two reactions exhibit a different regioselectivity, the driving force for the formation of **38a** is probably the formation of a conjugated enyne.

Overall, catalyst **1** is active for the transformation of 1,1- and 1,2-disubstituted allylic alcohols (e.g: **22**, **24**), this has been reported for very few cases in the literature[3,11] (entries 4, 6). It is also noteworthy that for the first time the isomerizations of 1,2-disubstituted allylic alcohol **24** and functionalized substrate **32** (entries 6 and 14) are reported. The isomerization of derivative **26** is also reported for the first time, this is a particularly challenging case as the electron-withdrawing trifluoromethyl group was expected to inhibit the oxidation of C-1 (entry 8). Among the four catalysts studied, complex **1** is the most effective in the transformation of geraniol to citronellal which is, according to the literature,[1d][11b,12] also a challenging case (entry 13). Surprisingly, catalysts **1** and **12** are far more efficient with the aromatic conjugated model **23** although the reasons for this are not immediately apparent. Finally, in the case of the diallylic alcohol **27**, the nonconjugated double bond is selectively reduced to give **39** (entry 9).

A number of mechanisms have been proposed for this process, one involves the transfer of molecular hydrogen to the activated double bond, the hydrogen is formed from the oxidative addition and subsequent elimination of the alcohol on the low valent transition metal.[1a,13] The transformation of deutero allylic alcohol **41** (>90% deuterium content) by catalysts **1**, **3**, **9**, **12,** and **14** does not give any compounds with the D atom on the C-2 (*d*-**43**), and thus the former mechanism is excluded (Scheme 3). Other mechanisms proposed require π-coordination of the alkene to the metal, which then facilitates a 1,3 hydride shift, to yield an enol/enolate or π-oxyallyl intermediate.[1b,3][11c,14]

When the catalyst is a rhodium complex (**1** or **3**) no significant loss of deuterium content is observed (Table 4). When the catalyst is a ruthenium complex (**9**, **12** or **14**), some loss in deuterium content is observed during the reaction. The extent of the deuterium loss depends on the ligand on the catalyst (Table 4). The explanation of these results will require more detailed studies on the reactivity of such catalysts.

Conclusion

In conclusion, we have developed a range of effective catalysts for the conversion of allylic alcohols to their corresponding saturated carbonyl compounds. These active catalysts are easily prepared in one step, from off-the-shelf starting materials, and can be used in situ. Though known catalysts **1**,[6c] **2**,[6f] **3**,[6f] and **9**[15] have been isolated in a pure form, it proved to be far more convenient to prepare

Table 3. Yields in the reactions of complexes **1**, **12**, **14** and **16** with various allylic alcohols.

Entry[a][b][c]	Alcohol	Catalyst **1**	Catalyst **12**	Catalyst **14**	Catalyst **16**
1	**19**	91%	91%	90%	89%
2	**20**	92%	92%	90%	90%
3	**21**	96%	95%	93%	-
4	**22**	89%	no reaction[d]	no reaction[d]	-
5	**23**	89%	95%	70%[e]	**37**[f], 90%
6	**24**	**40**[f], 96%	**40**[f], 98%	no reaction[d]	-
7	**25**	92%	90%	89%	-
8	**26**	69%	n.a.[g]	-	-
9	**27**	**39**[f], 78%	no reaction[d]	no reaction[d]	-
10	**28**	no reaction[d]	no reaction[d]	no reaction[d]	-
11	**29**	no reaction[d]	no reaction[d]	no reaction[d]	**38a**(*E*+*Z*)+**38b**[f], 98%
12	**30**	no reaction[d]	no reaction[d]	no reaction[d]	**36**[f], 72%
13	**31**	61%[h]	-	40%[i]	-
14	**32**	88%	71%[j]	-	-
15	**33**	-	35%[k]	-	-
16	**34**	no reaction[d]	no reaction[d]	no reaction[d]	no reaction[d]
17	**35**	no reaction[d]	no reaction[d]	no reaction[d]	no reaction[d]
18	**19** + **35**	no reaction[d]	no reaction[d]	-	-

[a] In all reactions the starting material was completely consumed unless otherwise stated. Consumption of starting material was confirmed by analyses of ^{1}H NMR spectra of crude reaction mixtures. – [b] All the reactions were conducted at solvent reflux and complete in less than 3 hours. – [c] Except **29**, **38a** and **38b** all compounds (**19**–**40**) were known, and gave ^{1}H, ^{13}C NMR spectra in accordance with literature data. – [d] The starting material was intact. – [e] Based on recovered starting material (90% conversion). – [f] See Figure 2. – [g] A maximum of 40% conversion can be obtained. – [h] Based on recovered starting material (50% conversion). – [i] Based on recovered starting material (45% conversion). – [j] Based on recovered starting material (75% conversion). – [k] Based on recovered starting material (40% conversion).

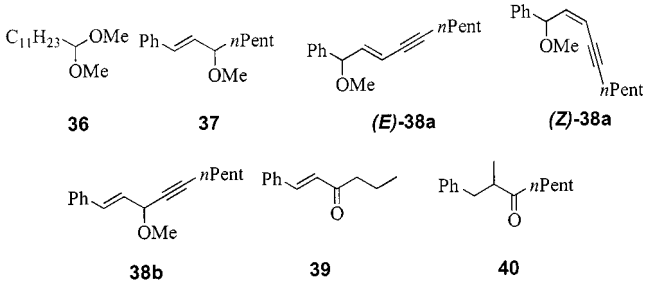
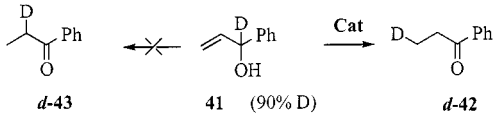


Figure 2. Structure of compounds **36**–**40**.



Scheme 3. Isomerization of deutero allylic alcohol **41**.

Table 4. Isomerization of deutero allylic alcohol **41**

Entry	Catalyst	Deuterium content (%)	Overall yield (%)
1	**1**	90	85
2	**3**	90	99
3	**9**	60	90
4	**12**	75	85
5	**14**	80	90

and use them in situ since they are very sensitive towards oxygen and water. Our procedure does not require any special equipment or expertise and can be easily carried out by an organic chemist.

Scope and limitations studies show that catalyst **1** is efficient for the isomerization of a wide range of substrates. In addition, the catalyst **16** transforms nonconjugated primary alcohols, into the corresponding aldehydes, and protects them in situ. Finally, the extension to catalysts which can bring about asymmetric induction could in principle be developed.[2]

Experimental Section

General: All reactions were carried out under dry nitrogen or argon. Standard syringe techniques were employed for the transfer of dry solvents and air-or moisture-sensitive reagents. – IR spectra were recorded on a Nicolet 205 FT-IR spectrophotometer and absorption bands are given in cm^{-1}. – NMR spectra were obtained at 400 MHz (^{1}H) or 100 MHz (^{13}C) on a Bruker ARX 400 instrument using deuteriochloroform as solvent. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (δ = 0) or to an internal standard of residual protons in the solvent. – High-resolution mass spectra (HRMS) were measured at the "Centre Régional de Mesure Physique de l'Ouest" on a Varian MAT 311 spectrometer operating at 70 eV. – Merck silica gel 60H was used for column chromatography. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Methanol was freshly distilled from sodium. Petroleum ether (40–60 °C) and diethyl ether were distillated before use.

General Procedure for the Isomerization of Allylic Alcohols to Corresponding Ketones with Catalyst 1: To a stirred suspension of $(PPh_3)_3RhCl$ (46 mg, 0.05 mmol, 5 mol %) in 5–10 mL of dry THF, under an atmosphere of nitrogen, was added one equivalent (32 μL, 0.05 mmol) of *n*BuLi (1.6 M solution in hexane) at room temperature. A wine red solution was quickly formed and this mix-

ture was allowed to react for about 10−15 min before a solution of the allylic alcohol **19** (154μL, 1 mmol) in dry THF was added. The reaction mixture was heated at reflux and the progress of the reaction was monitored by thin layer chromatography. Upon completion of isomerization, the reaction mixture was cooled to ambient temperature and THF removed under reduced pressure. The crude reaction mixture was purified by column chromatography (silica gel, pentane/ether, 9:1) to afford pure octan-3-one.

General Procedure for the Isomerization of Allylic Alcohols to Corresponding Ketones with Catalyst 12: To a stirred suspension of $(PPh_3)_3RuCl_2$ (48 mg, 0.05 mmol, 5 mol %) in 5−10 mL of dry THF, under an atmosphere of nitrogen, were added two equivalents (63 μL, 0.1 mmol) of *n*BuLi (1.6 M solution in hexane) at room temperature. A wine red solution was quickly formed and this mixture was allowed to react for about 10−15 min before a solution of the allylic alcohol **19** (154 μL, 1 mmol) in dry THF was added. The reaction mixture was heated at reflux and the progress of the reaction was monitored by thin layer chromatography. Upon completion of isomerization, the reaction mixture was cooled to ambient temperature and THF removed under reduced pressure. The crude reaction mixture was purified by column chromatography (silica gel, pentane/ether, 9:1) to afford pure octan-3-one.

General Procedure for the Isomerization of Allylic Alcohols to Corresponding Ketones with Catalyst 16: To a mixture of $(PPh_3)_3RuCl_2$, (48 mg, 0.05 mmol, 5 mol %) and $AgPF_6$ (13 mg, 0.05 mmol) in a Schlenk tube was added 5−10 mL of freshly distilled MeOH and refluxed in the dark, under an atmosphere of nitrogen, for 2 hours. The reaction mixture was cooled to room temperature during which time the precipitated silver salts settled. The supernatant solution was filtered through a small Celite pad under nitrogen using Schlenk equipment. To the filtrate was added allylic alcohol (154 μL, 1 mmol) in MeOH (3 mL) and refluxed under a nitrogen atmosphere. The progress of the reaction was monitored by thin layer chromatography and upon completion, the reaction mixture was cooled to room temperature. Removal of MeOH under reduced pressure and column chromatography (silica gel, pentane/ether, 9:1) afforded pure octan-3-one.

(*E*)-1-Phenyldec-1-en-4-yn-3-ol (29): FT-IR (neat): $\tilde{\nu}$ = 3350 cm^{-1} (OH), 2235, 1947, 1877, 1802, 1599, 1495, 1451. − ^{1}H NMR: δ = 0.90 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.27−1.42 (m, 4 H, CH_2), 1.54 (pent, *J* = 7.2 Hz, 2 H, CH_2), 2.23 (br. s, 1 H, OH), 2.25 (dt, *J* = 2.0, 7.1 Hz, 2 H, CH_2-CC), 5.04 (br. s, 1 H, C*H*OH), 6.29 (dd, *J* = 6.1, 15.8 Hz, 1 H, C*H*−CH-OH), 6.74 (br. d, *J* = 15.8 Hz, 1 H, C*H*=CH−CHOH), 7.22−7.41 (m, 5 H, Ph). − ^{13}C NMR: δ = 14.0, 18.8, 22.2, 28.3, 31.1, 63.1, 79.1, 87.5, 126.8, 128.0, 128.6, 128.8, 131.4, 136.2. − HRMS (*m*/*z*) calcd. for $C_{16}H_{20}O$: 228.1514; found 228.1520.

(*E*)-1-Methoxy-1-phenyldec-2-en-4-yne [(*E*)-38a], (*Z*)-1-Methoxy-1-phenyldec-2-en-4-yne [(*Z*)-38a] and (*E*)-3-Methoxy-1-phenyldec-1-en-4-yne (38b). − Compound (*E*)-38a: ^{1}H NMR: δ = 0.88 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.23−1.62 (m, 6 H, CH_2), 2.26 (dt, *J* = 7.0, 2.3 Hz, 2 H, CC−CH_2), 3.31 (s, 3 H, OCH_3), 4.62 (br. d, *J* = 6.8 Hz, 1 H, C*H*−OCH_3), 5.71 (ddt, *J* = 16.0, 2.3, 1.3 Hz, 1 H, CH=C*H*-CC), 6.08 (dd, *J* = 16.0, 6.8 Hz, 1 H, CH(OCH_3)−C*H*=CH), 7.22−7.41 (m, 5 H, Ph).

Compound (*Z*)-38a: ^{1}H NMR: δ = 0.91 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.23−1.62 (m, 6 H, CH_2), 2.38 (dt, *J* = 6.9, 2.3 Hz, 2 H, CC−CH_2), 3.38 (s, 3 H, OCH_3), 5.28 (br. d, *J* = 9.0 Hz, 1 H, C*H*−OCH_3), 5.65 (ddt, *J* = 10.5, 2.3, 0.8 Hz, 1 H, CH=C*H*-CC), 5.88 (dd, *J* = 10.5, 9.0 Hz, 1 H, CH(OCH_3)−C*H*=CH), 7.22−7.41 (m, 5 H, Ph).

Compound 38b: ^{1}H NMR: δ = 0.90 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.23−1.62 (m, 6 H, CH_2), 2.28 (dt, *J* = 5.0, 2.0 Hz, 2 H, CC−CH_2), 3.41 (s, 3 H, OCH_3), 4.67 (ddt, *J* = 6.0, 2.0, 1.5 Hz, 1 H, C*H*−OCH_3), 6.25 (dd, *J* = 16.0, 6.0 Hz, 1 H, Ph−CH=C*H*), 6.76 (d, *J* = 16.0 Hz, 1 H, Ph-C*H*), 7.22−7.41 (m, 5 H, Ph).

Compounds (*E*)-38a + (*Z*)-38a + 38b: ^{13}C NMR: δ = 13.9, 13.95 (2), 18.7, 19.3, 19.4, 22.1, 22.15, 28.25, 28.3, 28.35, 31.0 (2), 31.05, 55.3, 56.3, 56.4, 71.4, 76.7, 76.75, 78.2, 80.5, 83.6, 88.4, 91.7, 96.3, 111.8, 126.2, 126.7, 126.8, 127.5, 127.7, 127.9, 128.4, 128.45 (2), 132.7, 136.2, 140.2, 141.0, 141.3, 141.5. − HRMS (*m*/*z*) calcd. for $C_{17}H_{22}O$: 242.1671, found 242.1671.

Acknowledgments

We thank P. Guenot (CRMPO, Rennes) for performing mass spectral experiments. We thank CNRS and Ministry of Education and Research for the award of a research associate position to R. U.

[1] For representative examples using different metals see: [1a] J.-E. Bäckvall, U. Andreasson, *Tetrahedron Lett.* **1993**, *34*, 5459−5462. − [1b] B. M. Trost, R. J. Kulawiec, *J. Am. Chem. Soc.* **1993**, *115*, 2027−2036. − [1c] Y. Sasson, G. L. Rempel, *Tetrahedron. Lett.* **1974**, *47*, 4133−4136. − [1d] D. Baudry, M. Ephritikhine, H. Felkin, *Nouv. J. Chim.* **1978**, *2*, 355−356. − [1e] R. Damico, T. J. Logan, *J. Org. Chem.* **1967**, *32*, 2356−2358. − [1f] R. W. Goetz, M. Orchin, *J. Am. Chem. Soc.* **1963**, *85*, 1549−1550. − [1g] C. Slugovc, E. Rüba, R. Schmid, K. Kirchner, *Organometallics* **1999**, *18*, 4230−4233. − [1h] N. Iranpoor, E. Mottaghinejad, *J. Organomet. Chem.* **1992**, *423*, 399−404 and references therein.

[2] [2a] K. Tani, *Pure and Appl. Chem.* **1985**, *57*, 1845−1854. − [2b] S. Otsuka, K. Tani, *Synthesis* **1991**, 665−680. − [2c] K. Tanaka, S. Qiao, M. M.-C. Lo, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 9870−9871. − [2d] A kinetic resolution of an allylic alcohol has been studied by Noyori, see ref.[2e] − [2e] M. Kitamura, K. Manabe, R. Noyori, *Tetrahedron Lett.* **1987**, *28*, 4719−4720. − [2f] Very good results were also obtained for the enantioselective isomerization of allylic amines by Noyori, see ref.[2g]) − [2g] R. Noyori, H. Takaya, *Acc. Chem. Res.* **1990**, *23*, 345−350.

[3] S. H. Bergens, B. Bosnich, *J. Am. Chem. Soc.* **1991**, *113*, 958−967.

[4] C. Crévisy, M. Wietrich, V. Le Boulaire, R. Uma, R. Grée, *Tetrahedron Lett.* **2001**, *42*, 395−398.

[5] G. J. Boons, H. Burton, S. Isles, *Chem. Commun.* **1996**, 141−142.

[6] [6a] S. E. Diamond, F. Mares, *J. Organomet. Chem.* **1977**, *142*, C55−C57. − [6b] S. H. Strauss, S. E. Diamond, F. Mares, D. F. Shriver, *Inorg. Chem.* **1978**, *17*, 3064−3068. − [6c] D. K C. Dewhirst, W. Keim, C. A. Reilly, *Inorg. Chem.* **1968**, *7*, 546−552. − [6d] W. Keim, *J. Organomet. Chem.* **1967**, *8*, P25−P26. − [6e] M. Michman, M. Balog, *J. Organomet. Chem.* **1971**, *31*, 395−402. − [6f] W. Keim, *J. Organomet. Chem.* **1968**, *14*, 179−184. − [6g] L. S. Hegedus, S. M. Lo, D. E. Bloss, *J. Am. Chem. Soc.* **1973**, *95*, 3040−3042.

[7] [7a] The reaction was performed from commercial rhodium complex and according to a modified version of the procedure described by Strohmeier, see ref.[7b] − [7b] W. Strohmeier, L. Weigelt, *J. Organomet. Chem.* **1975**, *86*, C17−C19.

[8] S. G. Davies, J. P. McNally, A. J. Smallridge, *Adv. Organomet. Chem.* **1990**, *30*, 1−75.

[9] [9a] When catalyst **9** is prepared according to the procedure described by Wells (see ref.[9b]), it performs the desired isomerization reaction. Nevertheless, due to the large excess (20 equiv.) of triethylamine used for its preparation, it cannot be used for other reactions, for example it is not able to perform any isomerization−aldol condensation (see ref.[9c]). − [9b] B. Hud-

son, D. E. Webster, P. B. Wells, *J. Chem. Soc. Dalton* **1972**, 1204−1207. − [9c] R. Uma, M. Davies, C. Crévisy, R. Grée, *Tetrahedron Lett.* **2001**, *42*, 3069−3072.
[10] T.-a. Mitsudo, Y. Nakagawa, K. Watanabe, Y. Hori, H. Misawa, H. Watanabe, Y. Watanabe, *J. Org. Chem.* **1985**, *50*, 565−571.
[11] [11a] M. Kraus, *Collect. Czech. Chem. Commun.* **1972**, *37*, 460−465. − [11b] H. Bricourt, E. Monflier, J. F. Carpentier, A. Mortreux, *Eur. J. Inorg. Chem.* **1998**, 1739−1744. − [11c] I. E. Marko, A. Gautier, M. Tsukazaki, A. Llobet, E. Plantalech-Mir, C. J. Urch, S. M. Brown, *Angew. Chem. Int. Ed.* **1999**, *38*, 1960−1962.
[12] [12a] Iron pentacarbonyl failed to perform the isomerization of geraniol (see ref.[12b]). − [12b] H. Cherkaoui, M. Soufiaoui, R. Grée, *Tetrahedron* **2001**, *57*, 2379−2383.
[13] T. Naota, H. Takaya, S. I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599−2660, and references cited therein.
[14] [14a] F. G. Cowherd, J. L. Von Rosenberg, *J. Am. Chem. Soc.* **1969**, *91*, 2157−2158. − [14b] Y. Lin, X. Lu, *J. Organomet. Chem.* **1983**, *251*, 321−325.
[15] P. S. Hallman, B. R. McGarvey, G. Wilkinson, *J. Chem. Soc. (A)* **1968**, 3143−3150.

Received January 22, 2001
[O01033]