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Tandem isomerization/Claisen transformation of allyl homoallyl and diallyl ethers into γ,δ-unsaturated aldehydes with a new three component catalyst $Ru_3(CO)_{12}$/imidazolinium salt/Cs_2CO_3

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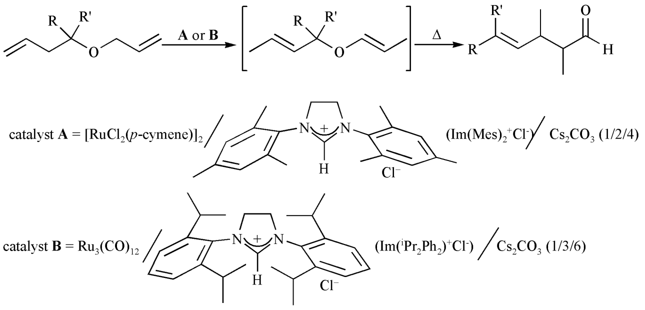
The three component catalyst $Ru_3(CO)_{12}$/1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride/Cs_2CO_3 (molar ratio 1 : 3 : 6) successively promotes both allyl to vinyl isomerization and Claisen rearrangement from allyl homoallyl and diallyl ethers to selectively afford γ,δ-unsaturated aldehydes.

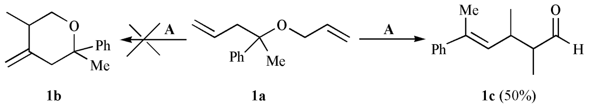
The [3,3]-sigmatropic rearrangement of allyl vinyl ethers, first described by Claisen in 1912,[1] represents a powerful tool for the synthesis of γ,δ-unsaturated aldehydes.[2] Different pathways have been used to generate the starting vinyl ethers *via* organometallic intermediates or acid-catalyzed reactions,[3] which actually revealed the difficulty to introduce the vinyl ether group. Ruthenium complexes have been used to carry out olefin isomerization, especially that of allyl into vinyl derivatives.[4,5] On the other hand $RuCl_2(PPh_3)_3$[6] has been shown to convert, at high temperature (*ca.* 150 °C), diallyl ethers into γ,δ-unsaturated aldehydes and ketones, whereas iridium catalysts perform related reactions under milder conditions.[7]

Our current interest in ruthenium catalyzed formation of C=C bonds *via* alkene metathesis reaction[8] has recently led us to report a new *in situ* generated three component catalytic system for the formation of five-membered rings[9] based on a ruthenium source $[RuCl_2(p\text{-cymene})]_2$, a bulky imidazolinium salt with Cs_2CO_3 (catalyst **A**). An attempt to explore the use of this catalytic system for the synthesis of larger rings, from etherated dienes, did not lead to the metathesis or cycloisomerization compound but to the tandem isomerization/Claisen rearrangement product. We now report that catalyst of type **A** and especially the more efficient novel catalytic system $Ru_3(CO)_{12}$/imidazolinium salt/Cs_2CO_3 (catalyst **B**) successively lead to the *in situ* allyl to vinyl isomerization of allyl homoallyl or diallyl ethers and to the corresponding Claisen rearrangement affording γ,δ-unsaturated aldehydes (Scheme 1).

The ether **1a** with 1,7-diene structure was first reacted for 16 h at 80 °C in toluene in the presence of catalyst **A**, based on 2.5 mol% of ruthenium $[RuCl_2(p\text{-cymene})]_2$/$(Mes)_2$imidazolinium chloride ($Im(Mes)_2{}^+Cl^-$)/$Cs_2CO_3$ (molar ratio 1 : 2 : 4) (Scheme 2). The diene **1a** was not converted into the expected cycloisomerization product **1b**[9] but gave a mixture of diastereoisomeric γ,δ-unsaturated aldehydes **1c** in 50% yield. It was shown that the transformation does not occur in the absence of one of these three catalyst components.



Scheme 1



1b **1a** **1c** (50%)

catalyst **A** ($[RuCl_2(p\text{-cymene})]_2$ / $Im(Mes)_2{}^+Cl^-$ / Cs_2CO_3 (1/2/4)), toluene, 80°C, 16h

Scheme 2

Starting from this initial observation, a better catalytic system was discovered by changing the nature of ruthenium source and the type of imidazolinylidene ligand. Indeed, $RuCl_3{\cdot}xH_2O$ and $Ru_3(CO)_{12}$ were also evaluated in the presence of 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride ($Im(^iPr_2Ph)_2{}^+Cl^-$), 1,3-bis-mesitylimidazolinium chloride ($Im(Mes)_2{}^+Cl^-$) or tricyclohexylphosphine ligand with Cs_2CO_3 at various temperatures. The results of the selective transformation of the diene **1a** are gathered in Table 1.

They show that $RuCl_2(p\text{-cymene})(PCy_3)$ only led to the isomerization of the allyl branch at 120 °C and gave the *Z* and *E* vinyl ether isomers $CH_2{=}CHCH_2C(Ph)(Me)OCH{=}CHCH_3$ **1d** (entry 1). The catalysts arising from $[RuCl_2(p\text{-cymene})]_2$ and each of the imidazolinium salts led to complete conversion of **1a** after 8 h but to the formation of vinyl ether **1d** and to the aldehydes **1c** (entries 2 and 3). $RuCl_3{\cdot}xH_2O$ with $Im(^iPr_2Ph)_2{}^+Cl^-$ after 6 h led to partial conversion into **1d** (22%) (entry 4). However, $Ru_3(CO)_{12}$ led to complete conversion of **1a** only after 1 h with both heterocyclic precursors but with 75% of aldehydes **1c** and 25% of **1d** with $Im(Mes)_2{}^+Cl^-$ and selectively to only the aldehydes **1c** with $Im(^iPr_2Ph)_2{}^+Cl^-$

Table 1 Catalytic transformation of the ether **1a**[a]

Entry	Ru source	Imidazolinium	Conversion (%)	Time/h	**1c**[b] (%)	**1d**[b] (%)
1	$RuCl_2(p\text{-cymene})(PCy_3)$	None	100	16	—	100
2	$[RuCl_2(p\text{-cymene})]_2$	$Im(Mes)_2{}^+Cl^-$	100	8	60	40
3	$[RuCl_2(p\text{-cymene})]_2$	$Im(^iPr_2Ph)_2{}^+Cl^-$	100	8	80	20
4	$RuCl_3{\cdot}xH_2O$	$Im(^iPr_2Ph)_2{}^+Cl^-$	22	6	—	22
5	$Ru_3(CO)_{12}$	$Im(Mes)_2{}^+Cl^-$	100	1	75	25
6	$Ru_3(CO)_{12}$	$Im(^iPr_2Ph)_2{}^+Cl^-$	100	1	100	—

[a] All reactions are performed at 120 °C in toluene using 5 mol% of ruthenium, imidazolinium chloride (5 mol%) and Cs_2CO_3 (10 mol%). [b] Determined by ^1H NMR.

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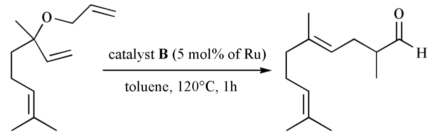
(entries 5 and 6). The above results show that the ruthenium catalysts easily isomerise the allyl to vinyl branch (entry 1) and then some of the complexes the homoallyl to allyl branch immediately followed by Claisen rearrangement (entries 2, 3, 5, 6). $Ru_3(CO)_{12}$ especially revealed the strong beneficial influence of the $Im(^iPr_2Ph)_2^+Cl^-$ precursor as catalyst **B** based on $Ru_3(CO)_{12}$ associated with the bulkier imidazolinium chloride appeared as the best catalyst system for the **1a** → **1c** transformation at 120 °C for one hour (entry 6). It was thus used under the same conditions for further applications.

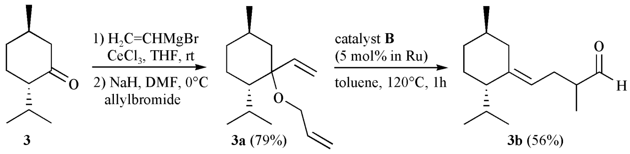
The *in situ* generated catalytic system **B** selectively transformed the triene derivative of linalool **2a** into the aldehyde **2b** in 87% yield, without the isomerization of the trisubstituted C=C bond (Scheme 3).



2a **2b** (87%)

Scheme 3

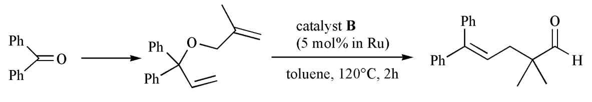
This conversion of allyl vinyl ethers to γ,δ-unsaturated aldehydes was used for the transformation of terpenoid derivatives modified by incorporation of five additional carbon atoms to create new fragrance properties. Starting from (−)-menthone **3**, the addition of vinyl Grignard followed by allylation of the corresponding alcohol afforded **3a** in 79% yield. This mixed diallyl ether was then converted, by using the catalytic system **B**, into the aldehyde **3b**, isolated in 56% yield (Scheme 4).



3 **3a** (79%) **3b** (56%)

Scheme 4

Analogously, the catalyst **B** transformed the easily made ether **4** to give the aldehyde **5** in 90% yield (Scheme 5). The overall two-step reactions allow the simple substitution of the oxygen atom of ketones by the $=CHCH_2C(R)_2CHO$ fragment.



4 **5** (90%)

Scheme 5

This new *in situ* generated catalytic system **B**, composed by commercially or easily available materials, represents a very efficient tool for the tandem isomerization/Claisen rearrangement of allyl ethers easily produced from ketones or alcohols, and constitutes a practical method for the synthesis of modified terpenoids. Moreover it offers another example of multiple catalytic functions of alkene metathesis ruthenium catalysts.

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