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Olefin isomerization by a ruthenium carbenoid complex. Cleavage of allyl and homoallyl groups

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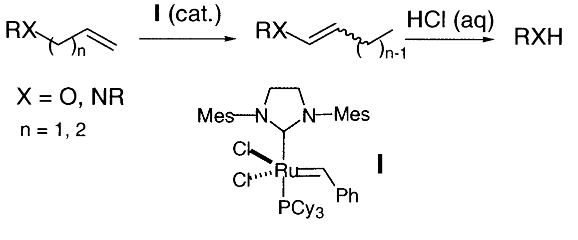
Abstract—Ruthenium–carbenoid catalysts such as Grubbs' complex **I** mediate efficiently the isomerization of β,γ-unsaturated ethers and amines to the corresponding vinyl ethers and enamines. This reaction can be useful in the deprotection of allyl and homoallyl ethers as well as amines. © 2002 Elsevier Science Ltd. All rights reserved.

Various metal complexes act as efficient catalysts for the isomerization of β,γ-unsaturated oxygen and nitrogen containing compounds. These complexes can be used for the isomerization and deprotection of allylic ethers and amines.[1,2] The most frequently used catalysts for this purpose are palladium,[3] iridium(I),[4] ruthenium(II)[5,6] and rhodium complexes,[7,8] including Wilkinson's catalyst.[7a] The reaction is completed usually by acid hydrolysis or by oxidation of the resulting enol ether or enamine. Other methods are also known including the use of *t*-BuOK[9] or oxidative conditions such as DDQ,[10] SeO_2,[11] NBS/*hv*[12] ozone[13] or OsO_4/$NaIO_4$ systems.[14] Here, we report that a ruthenium–carbenoid catalyst such as **I** (2nd generation Grubbs' catalyst)[15] is able to mediate isomerization of *O*- and *N*-allyl as well as *O*-homoallyl groups to produce the corresponding enol ethers and enamines. The resulting enol ethers and enamines can be transformed to the corresponding alcohols and amines by acidic work-up (Scheme 1).



Scheme 1.

When allyl ether **1** was treated with catalyst **I** (3%) in methylene chloride at room temperature for 12 h and subsequently with an aqueous HCl solution (2N), the corresponding alcohol **6** was obtained in 90% yield. Similar results were obtained when **2**, **3** and **5** were treated under the same conditions. The corresponding alcohols **7**, **8** and **10** were isolated in a range of 75–95% yield. The aryl vinyl ether **9** derived from **4** was shown considerably more stable than the corresponding aliphatic ones and was isolated in 78% yield when the acidic treatment was omitted. The results are summarized in Scheme 2.

The isomerization reaction (cat. **I**, 3–8%, rt, 12 h) also took place when the allyl group was substituted at the C-3 and C-2 positions as in compounds **11** and **12** which were transformed to the corresponding indanol **10** in 92 and 82% yield, respectively (Scheme 3). For these compounds, the enol products were isolated in 30 and 78% yield, respectively, when the acidic treatment was omitted (Scheme 3). However, when the double bond was disubstituted at C-3, as in compound **13**, the starting material was recovered unchanged (Scheme 3).

When the allylic chain was substituted at C-1, a dramatic effect on the isomerization was observed as exemplified by ether **17** which was converted to the corresponding homoallylic ether **18**. Furthermore, alcohol **19a** was converted to ketone **20** in 26% yield and to dimer **21** (40% yield) which corresponds to the cross-metathesis product. However, no isomerization was observed when the corresponding benzyl ether **19b** was submitted to these reaction conditions and the dimer was the only isolated product (Scheme 4).

Keywords: alkenes; isomerization; protecting groups.

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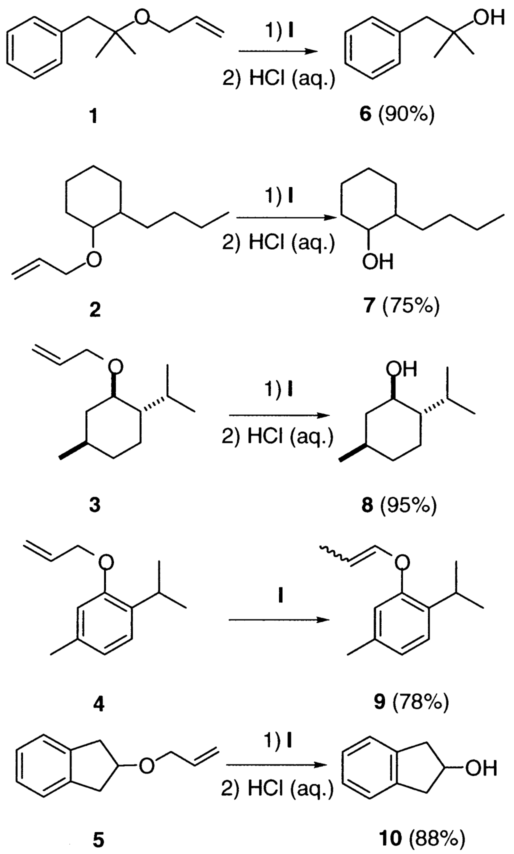
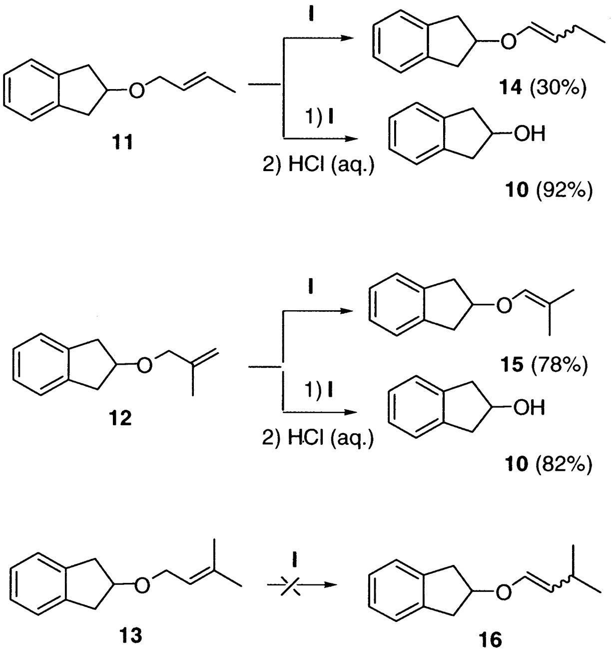


Scheme 2.



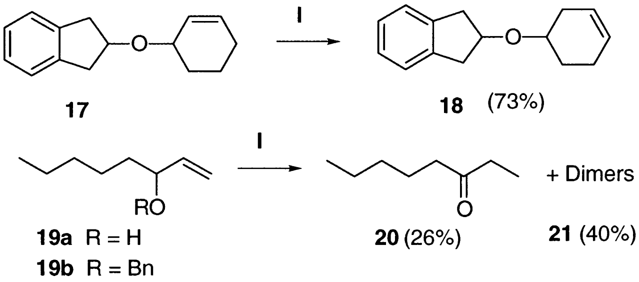
Scheme 3.

It is worth noting that the isomerization of olefins was not limited to allylic substrates. When the homoallylic derivative **22** was treated with the ruthenium catalyst **I**, a 1/1 mixture of *Z*/*E* isomers of vinyl ethers **23** was obtained and subsequently transformed under acidic conditions to the corresponding alcohol **24** in 63% overall yield (Scheme 5).

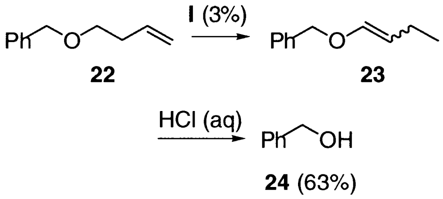
The isomerization conditions were also applied to allylamine derivatives. When tosyl allylamine **25** was treated with the ruthenium catalyst **I**, without acidic treatment, the dimer was formed, which corresponds to the cross-metathesis product, in 41% yield, and the enamine **28** in 21% yield. In the case of the benzyl allylamine **26**, the only product observed and isolated was the amine **29** (46% yield). These results suggest that the presence of basic nitrogen promotes rather the isomerization than the dimerization of olefins (Scheme 6).

The isomerization may occur analogously to that of related 16 electron Ru complexes, by hydrometallation followed by β-elimination.[6] The active catalyst is probably not complex **I**, but the corresponding hydrido derivatives formed in situ under the reaction conditions.

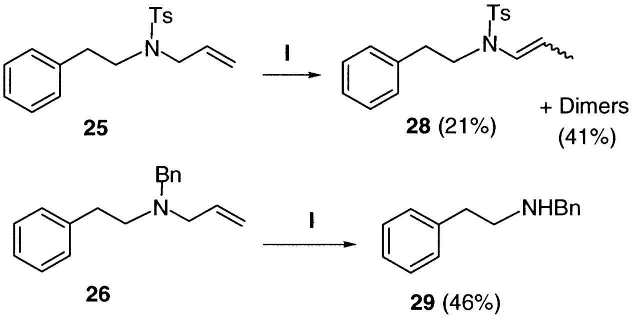
In summary, we have shown that $L_2X_2Ru{=}CHR$ complexes such as the Grubbs' complex **I** are able to mediate efficiently the isomerization of β,γ-unsaturated ethers and amines.[16] This reaction can be useful in preparing vinyl ethers and enamines, or to achieve the



Scheme 4.



Scheme 5.



Scheme 6.

deprotection of allyl and homoallyl ethers and amines. This process must be taken into consideration and can explain, in certain cases, the modest or low yields of cross-metathesis reactions as well as ring-closure metathesis reactions.

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