Isomerization of Allyl-Aryl Ethers Catalyzed by Ruthenium Complexes

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Alkyl-propenyl and aryl-propenyl ethers are interesting substrates for, among others, synthesis of heterocyclic systems [1], cycloaddition reactions [2] and are thoroughly investigated monomers and co-monomers [3]. Isomerization of allyl to propenyl ethers is also the key step of protection and following deprotection of amino and hydroxyl groups [4]. The most convenient method of propenyl ether synthesis consists in isomerization of appropriate, easy to synthetize, allyl ethers. The following have been used as isomerization catalysts: bases [5], zeolites [6], supported metals [7] and, particularly, transition metal complexes. Ruthenium [8–12], rhodium [13,14], iridium [15], palladium [16], chromium [17], molybdenum [18], iron [19] and platinum [20] complexes have been applied.

This article describes a convenient and universal method of synthesis of various aryl-propenyl ethers from appropriate allyl ethers via isomerization in the presence of [RuClH(CO)(PPh\textsubscript{3})\textsubscript{3}] as the catalyst. Relations between the structure of the ethers and their reactivity in the isomerization, as well as the double bond migration mechanism have been analyzed.

Propenyl ethers have been obtained by isomerization of respective allyl ethers:

\[
\text{ArO} = \text{CH}_3 + \text{ArO} = \text{CH}_3
\]

Experimental procedure: allyl ether, 0.1–1.3% mol [RuClH(CO)(PPh\textsubscript{3})\textsubscript{3}], benzene (1 cm\textsuperscript{3} per 2 mmol of ether) were stirred and heated at 50–60°C for 2–16 h under argon atmosphere. Afterwards benzene was evaporated \textit{in vacuo}. Propenyl ethers were sep-
parated from the catalyst by: vacuum distillation, vacuum sublimation, column chromatography or adsorption of [Ru] on diatomaceous earth. The following propenyl ethers were obtained (conversion of allyl ethers, determined by 1H NMR or GC-MS was 100%, selectivity was 100%, isolated yield in parentheses): Ar = X-C₆H₄, X = H (94); α-, p-Cl (90, 95); α-, p-Br (90, 92); α-, p-NO₂ (90, 91); α-, p-Me (93, 95); α-, p-MeO (90, 90); p-NC (90); p-H₂N (91); p-OHC- (90); α-(MeO)₂CH (93); p-MeCONH (90); p-HOCH₂ (94); p-ArOOC (95); α-CH₂CH=CH₂ (91); a) α-, p-OCH₂CH=CH₂ (95); a) – both allyl groups have isomerized to their propenyl counterparts. When: Ar = X-C₆H₄, X = o-, m-OHC-, p-HOOC, p-MeOOC, Ar = Cl₅C₆, 2,4,6-triallyloxy-1,3,5-triazynyl yields of propenyl ethers were moderate or low. In all isomerization reactions Z isomer was the main product (Z/E = 1.2÷25). As proved above, the elaborated method of synthesis of aryl-propenyl ethers is very versatile. It is important that neither the presence of phenol (even p-nitrophenol) nor traces of water inhibit catalytic process. Even such substituents as NH₂, OH, CN, MeCONH can be attached to the benzene ring. It is advantageous to transform the ethers with CHO group to derivatives with CH(OMe)₂ group. As far as ethers with COOR group are concerned, R has to be an aryl group for the bond migration to occur. It is supposed that low reactivity of some ethers (Ar = Cl₅C₆, 2,4,6-triallyloxy-1,3,5-triazynyl) in the reaction of double bond migration is the effect of their strong coordinating character. On the other hand, when X = CHO, COOH, COOMe, oxidative addition of C-H, C-O or O-H to [Ru] takes place. The influence of the substituent X attached to the benzene ring (X-C₆H₄-OAllyl) on the rate of the double bond migration has been examined. Competitive reactions method has been applied for the research, as is shown in Scheme. No Hammett’s type correlation between double bond migration rate and substituent’s constant has been observed, as it emerges from the table below. Only the coordinating substituents (p-CN, p-MeCONH, o-MeO, o-O₂N) reduce the reaction rate. Relatively stable complexes (of a probable structure of 1 or 2) are formed in the reaction media, hence the decrease of the isomerization rate of PhOAllyl and X-C₆H₄OAllyl. Such complexes are not very stable, because all ethers undergo quantitative isomerization in higher temperatures.

Scheme

\[
\begin{align*}
\text{PhOAllyl} & \quad \text{X-C₆H₄-OAllyl} \\
\text{[RuCl(H(CO)(PPh₃)₃],} & \quad C₆D₆, 40ºC, 2h
\end{align*}
\]
Isomerization of allyl-aryl ethers catalyzed by ruthenium complexes

<table>
<thead>
<tr>
<th>X (C₆H₅OAllyl)</th>
<th>X (XC₆H₄OAllyl)</th>
<th>X (C₆H₅OAllyl)</th>
<th>X</th>
<th>X (XC₆H₄OAllyl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43 H</td>
<td>43 o-Cl</td>
<td>45 o-Me</td>
<td>55</td>
<td>45 o-Me</td>
</tr>
<tr>
<td>42 o-Cl</td>
<td>40 p-Cl</td>
<td>12 o-MeO</td>
<td>48</td>
<td>12 o-MeO</td>
</tr>
<tr>
<td>41 p-Cl</td>
<td>48 o-Br</td>
<td>30 p-MeO</td>
<td>50</td>
<td>30 p-MeO</td>
</tr>
<tr>
<td>48 o-Br</td>
<td>55 p-Br</td>
<td>2 o-NO₂</td>
<td>4</td>
<td>2 o-NO₂</td>
</tr>
<tr>
<td>50 p-Br</td>
<td>4 p-CN</td>
<td>42 p-NO₂</td>
<td>48</td>
<td>31 p-NO₂</td>
</tr>
<tr>
<td>4 p-CN</td>
<td>29 p-COMe</td>
<td>24 p-MeCONH</td>
<td>55</td>
<td>12 p-MeCONH</td>
</tr>
</tbody>
</table>

It was also found that modification of the catalyst precursor affects positively neither the rate nor the selectivity of isomerization. This has been carried out on a model isomerization reaction of allyl-(o-bromophenyl) ether with complexes of a general formula of [RuClH(CO)L₃], where L = PPh₃, AsPh₃, PEt₃, P(o-tolyl)₃ or P(1-naphthyl)₃. It leads also to the conclusion that double bond migration follows the hydride mechanism, as in the case of isomerization of simple alkenes [9]. In the reaction of a mixture of allyl-phenyl and (α-d₂-allyl)-trityl ethers with [RuClH(CO)(PPh₃)₃] as the catalyst, an intermolecular deuterium transfer from deuterated trityl ether to phenylpropenyl ethers — the products of isomerization of allyl-phenyl ether — has been observed. The occurrence of the deuterium shift has been proved by GC-MS analysis of the products of these cross-over reactions. Moreover, a mixture of deuterated and non-deuterated propenyl-trityl ethers has been observed. This eliminates such mechanisms, as: hydride-π-allyl, hydride-synchronic, carbene. The fact that (Z)-1,2-diphenylethen isomerizes easily to (E)-1,2-diphenylethen with [RuClH(CO)(PPh₃)₃] in 60°C (after 2 h) does also support the conclusion that the isomerization follows the hydride mechanism.

REFERENCES