NEW CHEMISTRY ON CATALYTIC RU-VINYLIDENES IN ACIDIC CONDITIONS

Carlos González-Rodríguez, Silvia G. Rubín, Jesús A. Varela, Carlos Saá*
Departamento de Química Orgánica y Unidad Asociada al CSIC Facultad de Química, Universidad de Santiago de Compostela
15782 Santiago de Compostela, Spain
qocsaa@usc.es

• Ru-vinylidenes.
Recent applications of catalytic Ru-vinylidenes includes the remarkable anti-Markovnikov hydration of terminal alkynes to give aldehydes1-2 and cycloisomerization of areynes.3 Also, catalytic Ru-allenylidenes have been used with great success in propargylic substitutions.4

• Reaction of α,ω-alkynals.
When we use different Ru-catalyzed in acetic acid with alkynal 1, cycloalkenes 2 and 3. Same results were obtained with alkynal 4 and tosylamide 5. The reaction of alkyn 6 gave the cycloisomer without descarboxylation and finally in the case of ketones, esters and nitriles only alkyne evolution were observed.

<table>
<thead>
<tr>
<th>Ru-Catalyzed</th>
<th>Product</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% CpRu(CH3CN)3PF6</td>
<td>2, 3 (9:1)</td>
<td>24</td>
</tr>
<tr>
<td>5% CpRu(CH3CN)3PF6</td>
<td>2, 3 (8:2)</td>
<td>5</td>
</tr>
<tr>
<td>5% CpRu(Ph3P)2Cl</td>
<td>2, 3 (8:2)</td>
<td>5</td>
</tr>
<tr>
<td>10% CpRu(CH3CN)3PF6</td>
<td>2</td>
<td>24</td>
</tr>
</tbody>
</table>

However, when bisphosphine ruthenium species was used the cycloisomer 7 was obtained as a sole product. This result and the deuteriation experiments conducted to proposed these mechanism of reaction. If the ligand of the ruthenium is a bidentate phosphine descarboxylation is not possible, and the product is an isomer.

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