New ruthenium-catalyzed cyclization reactions

Carlos González-Rodríguez, Jesús A. Varela, Luis Castedo, Carlos Saá*
Departamento de Química Orgánica, Facultad de Química,
Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain
carlos.gonzalez.rodriguez@usc.es; carlos.saa@usc.es

Acknowledgement: This work was supported by the M.E.C. (CTQ2005-08613), Consolider Ingenio 2010 (CSD2007-00006) and the Xunta de Galicia (2007/XA084). C.G.R. and J.A.V. also thanks the M.E.C. for a FPI fellowship and a Ramón y Cajal research contract, respectively.

References:

• Decarbonylative cyclization of terminal alkynes

We have recently described the Ru-catalyzed decarbonylative cyclization of terminal 5- and 6-alkynes and 5-alkynes 1 to cycloalkenes 2 in moderate to excellent yields (Scheme 1).

The likely mechanism of the cyclization involves the formation of Ru(II) vinylidene species I, which upon nucleophilic addition of the acetic acid affords the vinyl Ru species II. Next, an aldol-type condensation gives the acyl Ru-hydride III, which after decarbonylation followed by reductive elimination affords the observed cycloalkenes 2 (Scheme 2).

• Decarbonylative cyclization of 1,6-diyynes

When 1,6-terminal and monosubstituted diyynes 4 were subjected to the Ru/AcOH conditions, exa-alkylidencyclopentane derivatives 5 were obtained in moderate to good yields.

The proposed mechanism starts with the formation of ruthenium vinylidene V which undergoes nucleophilic addition of AcOH to afford vinyl Ru-hydride VI which, through a [3+2]-type cycloaddition, leads to cyclic carbene Ru-hydride VII. Reductive elimination of AcOH to cyclic carbene VIII, followed by another nucleophilic attack of AcOH gives acyl Ru-hydride IX. Reductive opening of the ruthenacycle IX followed by oxidative addition of AcOH with concomitant decarbonylation of X leads to the Ru-hydride XI, which after reductive elimination affords the observed cyclopentanone derivatives 5 (Scheme 5).

• Cycloisomerization of terminal alkynes

Cycloisomerization of alkynes and alkynes 1 to α,β-unsaturated aldehydes 3 was achieved using CpRu(dppm)Cl as catalyst (Scheme 3). In this case no decarbonylation takes place due to the bidentate nature of dppm ligand, being favored the reductive elimination of III'.

• Decarbonylative cyclization of 1,6-diyynes

When disubstituted 1,6-diynes 6a or 1,7-diynes 6b were used, dienylacetates 7 were obtained by trapping ruthenacycle-biscarbene4 intermediate XII with AcOH (Scheme 6).

Scheme 1

Scheme 2

Scheme 3

Scheme 4

Scheme 5

Scheme 6