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

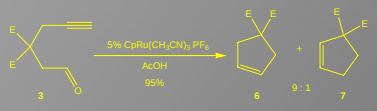
15782 Santiago de Compostela, Spain

qocsaa@usc.es

•Ru- vinilydenes.

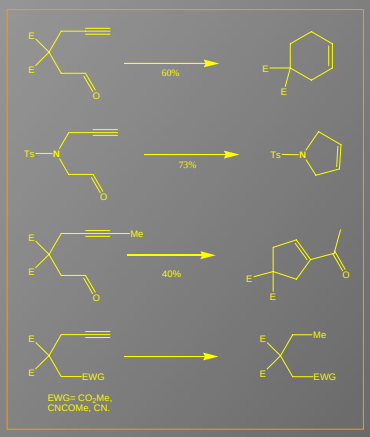
Recent aplications of catalytic Ru-vinylidenes includes the remarkable anti-Markovnikov hydration of terminal alkynes to give aldehydes[1,2] and cycloisomerization of arenynes.[3]

Also, catalytic Ru-allenylidenes have been used with great success in propargylic substitutions.[4]



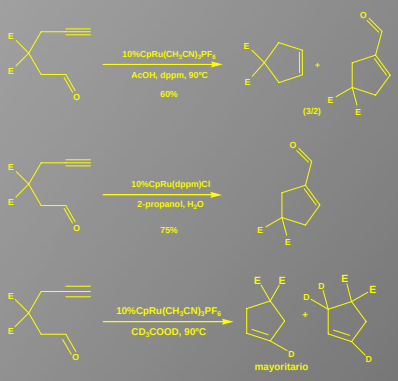
•Reaction of α,ω-alkynals.

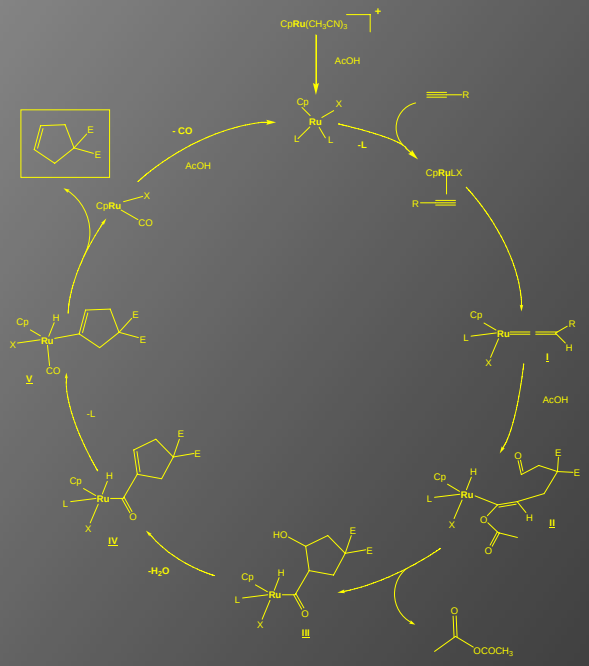
When we use different Ru-catalized in acetic acid wiht alkynal**1**, cycloalkenes **2** and **3.** Same results where obtained with alkynal **4** and tosylamide **5**.The reaction of alkyne **6** gave the cycloisomer without descarboxylation and finally in the case of ketones, esters and nitriles only akyne evolution where observed.



Ru Catalized	Product	Time/ (h)
5% $CpRu(CH_3CN)_3PF_6$	2, 3 (9:1)	24
5% $Cp^*Ru(CH_3CN)_3PF_6$	2, 3 (8:2)	5
5 % $Cp^*Ru(cod)Cl$	2, 3 (8:2)	5
10% $CpRuCl(Ph_3P)_2$	2	24

However, when bisphosphine ruthenium species was used the cycloisomer 7 was obtained as a sole product.This resuls and the deutheration experiments conduced 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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