“New Cyclizations Catalyzed by Ruthenium Carbenes”

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Previous Work

We have recently described a mild procedure based on a novel tandem Ru-catalyzed carbene addition to terminal alkynes/insertion into Csp²-H bonds in alkynyl acetals, ethers and amines to form complex spiro and fused bicyclic compounds by 1,5- or 1,6-hydride shift/cyclization sequence.1

1,5-hydride shift

1,6-hydride shift

Aldehyde Cyclization via Ruthenium Carbone Intermediates

We now report similar Ru-catalyzed cyclizations of 5-alkynals to give the interesting dithydropyranes 5a as exclusive or major products. Minor amounts of vinyloxiranes 5b were also isolated.2,3 Ether or isopropanol were chosen as solvents depending on the nature of the starting material (entries 1 and 6).

Mechanistic Proposal

The catalytic transformation of alkynal derivatives with (trimethylsilyl)diazomethane in the presence of Cp²RuCl(cod) could be understood supposing the initial formation of ruthenium carbone species I. Oxidative coupling to give a metalacylcobutene followed by opening of this species would lead to the ruthenium vinyl carbene II. This intermediate could undergo a nucleophilic attack to the carbene, followed by a [β-hydrogen elimination to give the ruthenium species IV. Reductive elimination from IV would lead to the observed dithydropyran 5a. On the other hand, vinyl ruthenium carbene III could undergo a reductive elimination affording to the vinyloxirane 5b.

Acknowledgement: This work was supported by MICINN [Projects: CTQ 2011-28258, Consolider Ingenio 2010 (CSD 2007-00006)] and the Xunta de Galicia (CI 2011/054). F.C. thanks to Xunta de Galicia for a predoctoral contract.