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Short communication

Stereoselective Palladium(II)-Catalyzed Oxycarbonylation of Unsaturated Polyols

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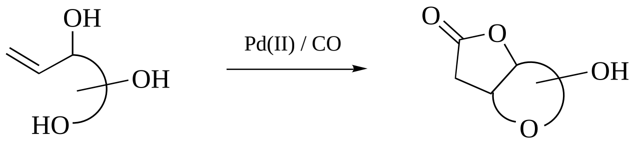
Abstract

The general approach to optically active anhydroalditols, a class of compounds that have proven most versatile intermediates for C-nucleosides / C-glycosides syntheses is presented. Our entry into this field features the palladium(II)-catalyzed oxycarbonylation of unprotected enitols as key step.

The total syntheses of some natural styryl-lactones [(+)-goniofufurone, (+)-7-*epi*-goniofufurone and (+)-goniopypyrone] have been developed, using oxycarbonylation as key step.

Keywords: oxycarbonylation, palladium(II)-chloride catalysis

The complexity of polyfunctionalized molecules of many natural products has stimulated more and more synthetic organic chemists in the research of new methods to introduced functionalities. In this context, the control of regio- and stereochemistry in simultaneous creation of contiguous stereogenic centers is of particular importance. The functionalization of double bond promoted by an electrophile is one of the most used reactions in organic synthesis. Among these, palladium(II)-assisted oxycarbonylation of unsaturated polyols constitute an effective method for constructing oxygen heterocycles.



Scheme 1. *Palladium(II)-catalyzed oxycarbonylation of unsaturated polyols.*

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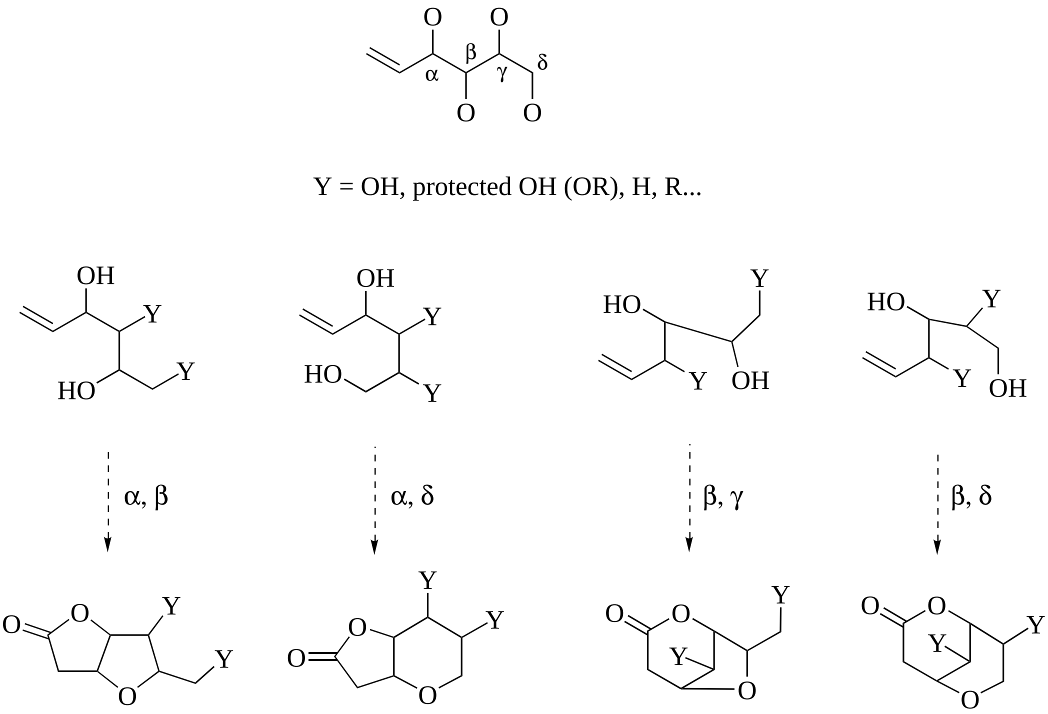


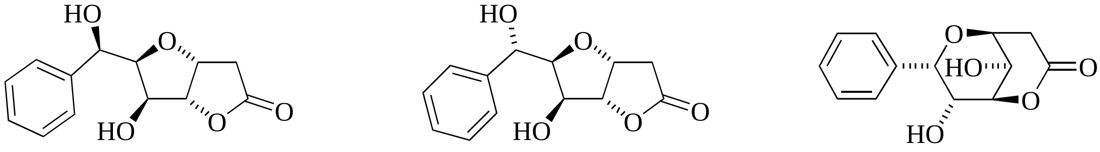
A [3.3.0]

B [4.3.0]

C [3.2.1]

D [3.3.1]

Scheme 2. *Possible courses of bicyclization of unsaturated tri- and tetrols.*



1 (+)-goniofufurone

2 (+)-7-*epi*-goniofufurone

3 (+)-goniopypyrone

Scheme 3. *Structures of natural (+)-goniofufurone* ***1****, 7-(+)-epi-goniofufurone* ***2*** *and (+)-goniopypyrone* ***3****.*

We present here a general approach to optically active anhydroalditols, a class of compounds that have proven most versatile intermediates for C-nucleosides / C-glycosides syntheses. Our entry into this field features the palladium(II)-catalyzed oxycarbonylation of chiral enitols as the key step.

We have studied regio- and stereoselectivity of this reaction with optically active 4-pentenitols (-triols) and 5-hexenitols (-tetrols), thereby two (**A**, **C**) resp. four (**A**, **B**, **C**, **D**) bicyclic lactones with various but defined stereochemistry could be expected.

It has been shown that C_5- and C_6- enitols with unprotected hydroxy groups undergo Pd(II)-catalyzed O-cyclization and carbon monoxide addition, to yield 3,6-anhydro-2-deoxy-1,4-glyconolactones (type **A**; [3.3.0]) with high regio-preference and excellent *threo* selectivity (concerning the newly formed stereocentre at C-3). [1]

The total syntheses of some natural styryl-lactones [(+)-goniofufurone **1**, (+)-7-*epi*-goniofufurone **2** and (+)-goniopypyrone **3**] have been developed, using oxycarbonylation as key step. [2, 3]

References

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3. Gracza, T.; Jäger V. *Synthesis* **1994**, *12*, 1359.