Abstract: We herein present the rapid palladium-catalyzed double bond isomerisation of allylic esters into their corresponding enol esters under mild conditions and with low catalyst loadings. The used binuclear palladium-complex outperforms all known isomerisation catalysts and exhibits a high functional group tolerance. The protocol can also be applied for allylic ethers, alcohols, amides as well as benzenes. It provides an advantageous approach to difficult accessible compounds starting from cheap and easy available materials.

**Pd-Catalyzed Double Bond Isomerisation of Allylic Esters**

Enol Esters

Enol esters are important as monomers in polymerisation reactions and as starting materials in the synthesis of chiral alcohols. Common synthetic pathways for enol esters are the addition of carboxylic acids to alkynes using expensive ruthenium catalysts and the waste intensive approaches via transesterification of vinylic acetates or the O-acylation of enols.

**Isomerisation of Allylic Esters**

Due to the large amount of easily available carboxylic acids and allylic alcohols, the isomerisation of allylic esters is potentially advantageous to known synthetic approaches. Unfortunately only a few examples of this almost thermodynamically neutral enol synthesis are known, requiring high amounts of transition metal catalysts such as ruthenium and iron.

We herein present an efficient palladium-catalyzed protocol for the double bond isomerisation of allylic esters into enol esters. A binuclear palladium-catalyst, that forms the active metal-hydride species in situ, allows the synthesis of a broad range of enol esters under mild reaction conditions, high functional group tolerance and catalyst loadings lower than 1 mol%.

**In Situ NMR Studies**

In situ NMR experiments in deuterated toluene show the rapid transformation of allyl benzoate into the isomeric mixture of the corresponding enol esters at room temperature. The complex also outperforms the known and established isomerisation catalysts.

**Scope of the Isomerisation Reaction**

The isomerisation protocol was successfully applied to different types of allyl benzoates, containing electron poor and rich respectively sterically demanding benzoic esters, heterocyclic and also alkyl esters such as fatty acids.

**Ongoing work**

Beside the rapid isomerisation of enol esters, the catalyst also shows high activity in the transformation of other allylic compounds such as allylic ethers, alcohols, amides and benzenes to synthesize the corresponding internal species under mild conditions and in high yields.

DFT-studies are in progress to gather insights into the mechanism and to obtain a better understanding of the unique catalytic performance. The now easily accessible enol esters are also applied in subsequent reactions such as cycloadditions and enantioselective hydrogenations.

Due to the high functional group tolerance, the isomerisation of double bonds offers a beneficial possibility for the late stage functionalisation in multi-step synthesis of natural products or comparatively complex target molecules.

**Literature and Further Reading**


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