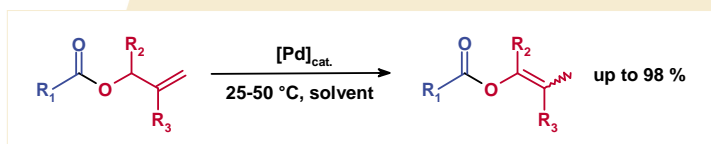


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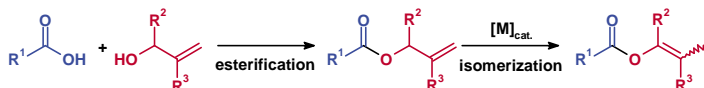


Herein, we report the development of a new catalyst system with a new level of reactivity. The optimized system allows the efficient isomerization of a broad range of allyl esters into the corresponding enol esters in the presence of < 1 mol% of a palladium catalyst and under very mild reaction conditions. Besides allyl esters, the protocol can also be applied for other unsaturated compounds such as olefins, allylic ethers, alcohols, amides and benzenes. It provides an advantageous approach to difficult accessible compounds starting from cheap and easy available materials.



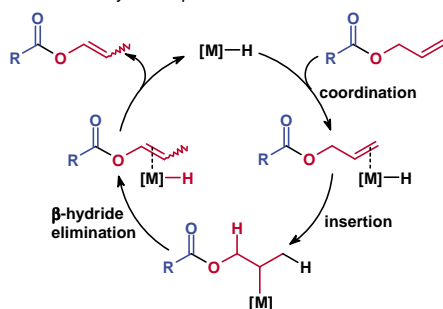
Application and Synthesis of Enol Esters

Enol esters are highly versatile key intermediates in organic transformations such as asymmetric hydrogenations,^[1] cycloadditions^[2] and polymerisation reactions.^[3] Compared to the traditional waste intensive multi-step methods,^[4] the transition metal catalyzed isomerization of alkenyl esters represents an environmentally benign alternative, since the allyl esters are accessible in a broad structural diversity from easily available carboxylic acids and allylic alcohols by a simple esterification reaction.

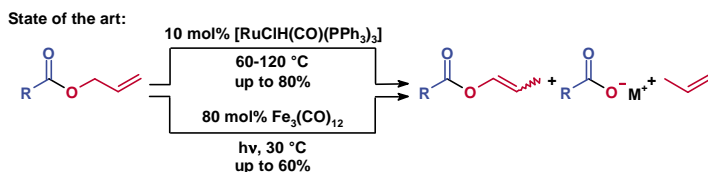


Isomerization of Allyl Esters to Enol Esters

For the isomerization of allylic compounds, a M-H species is involved, which can be utilized directly as a precursor or can be generated *in situ* in the reaction of the catalyst with the substrate. In the first step of the proposed mechanism, the metal-hydride species coordinates to the double bond. A C-H bond insertion takes place and a metal-alkyl species is formed. β -Hydride elimination leads to the desired isomerized product, regenerating the initial metal-hydride species.

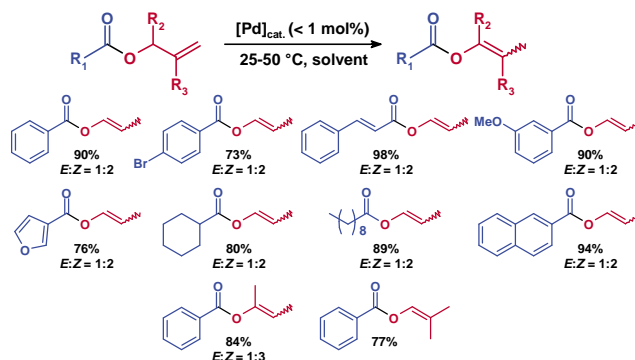


Only few examples of a successful metal catalyzed isomerization of allyl ester are known and require high loadings of ruthenium^[5a] or iron catalyst.^[5b] The biggest challenge of double-bond migration in allyl esters is the suppression of the O-C-allyl bond cleavage which releases propene and carboxylates as undesirable side products, where the latter often deactivate the catalyst.

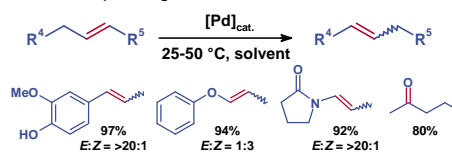


Scope of the Isomerization Reaction

After careful catalyst optimization, we identified a Pd/Bu₃P-based system, which allows isomerization of a broad range of allylic esters into enol esters under mild reaction conditions and at low catalyst loadings. Various electron-poor and electron-rich benzoic, heterocyclic and alkyl allyl esters were successfully converted to their corresponding enol esters in high yields.^[6]

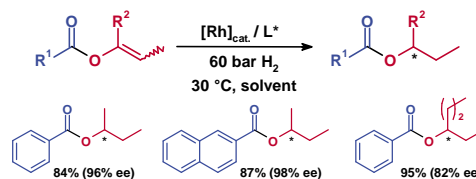


Besides the rapid isomerization of enol esters, the catalyst also shows high activity in the transformation of other allylic compounds such as allylic ethers, alcohols, amides and benzenes to the corresponding internal alkenes.



Enantioselective Hydrogenation of Enol Esters

The isomerization of allyl esters to enol esters derivatives opens a new entry to chiral esters via enantioselective hydrogenation. The asymmetric hydrogenation of obtained branched enol esters leads to the corresponding chiral esters in high yields and good selectivities (up to 98% ee).



Literature and Further Reading (see also www.chemie.uni-kl.de/goossen)

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We thank DFG (SFB-TRR 88 "3MET"), Umicore and NanoKat for financial support, the Landesgraduiertenförderung for fellowships and the MPI, Mülheim, for measurements.

