Carpe Diene!

Europium-catalyzed [3,3] and [5,5] rearrangements of aryl-pentadienyl ethers

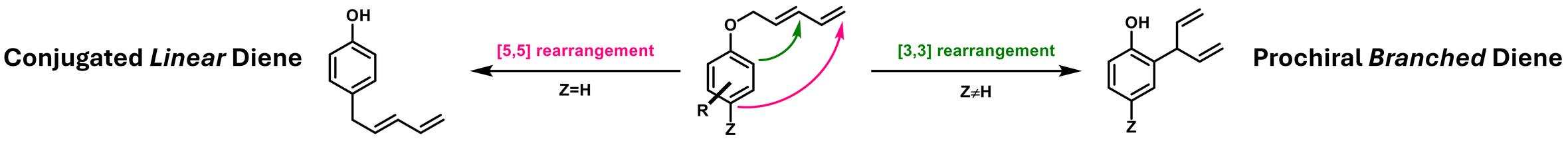
Maximilian Kaiser, Michael Steinacher, Florian Lukas, Peter Gärtner

Institute of Applied Synthetic Chemistry, TU WIEN, 1060 Vienna, Austria

Introduction

In contrast to the well-studied aryl-allyl ether rearrangement, the corresponding **aryl-dienyl ethers** have been greatly overlooked. Harsh reaction conditions of the scarce literature precedents severely limit the applicability of such a transformation. With this work we achieved the establishment of a reliable method for the rearrangement of aryl-pentadienyl ethers into synthetically versatile products.

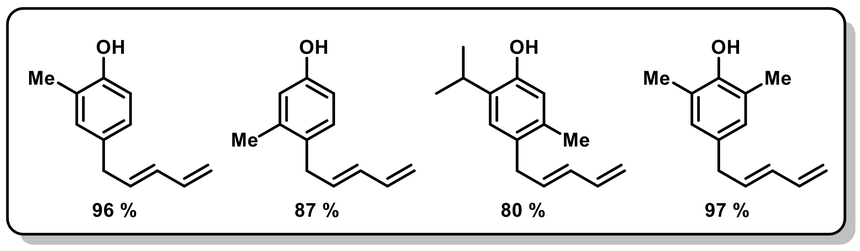
The rearrangement of aryl-pentadienyl ethers was realized by Eu^{3+} catalysis applying ***5 mol % EuFOD in toluene at 110 °C***. The reaction proceeds regioselectively and is solely directed by the Z-substituent in *para* position. This guiding element allowed the formation of either **conjugated linear dienes** or **prochiral branched dienes**.



[5,5] Rearrangement: Z= H

In case of an unsubstituted *para*-position (Z=H) the rearrangement of aryl-pentadienyl ethers selectively delivers the *para*-alkylated product in good to excellent yields. The scope with respect to aromatic substitution patterns is broad ranging from alkyl and O-protection groups to halides, ketones, aldehydes and nitro compounds.

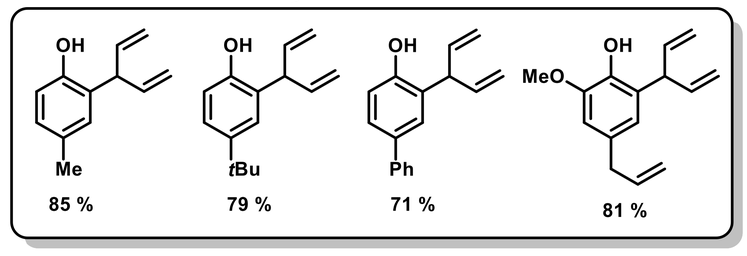
Alkyl substituents

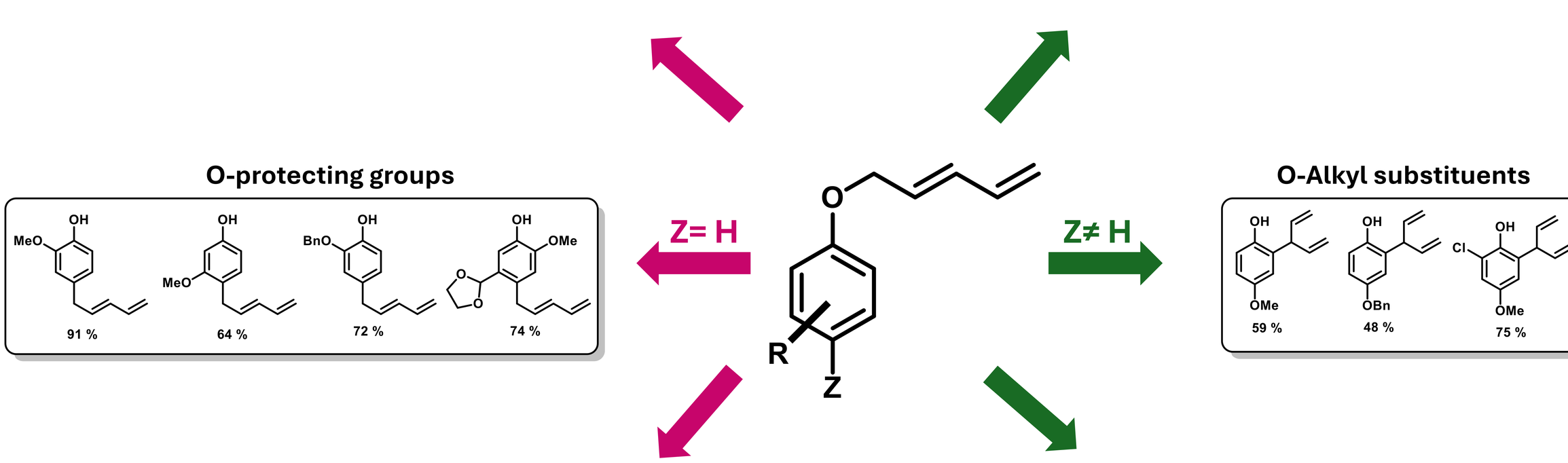


[3,3] Rearrangement: Z≠ H

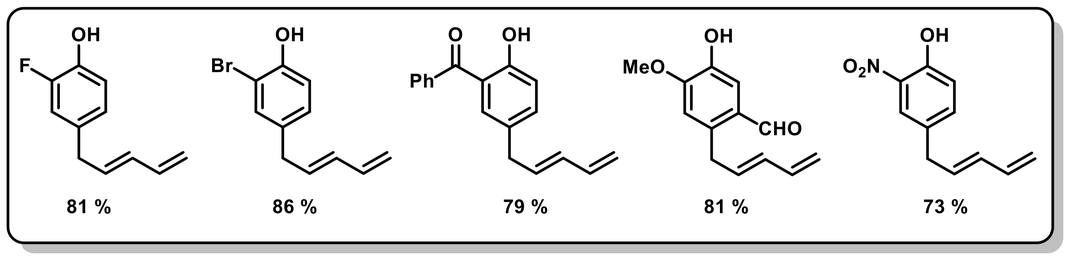
In case of a substituted *para*-position (Z≠H) the rearrangement of aryl-pentadienyl ethers selectively forms an *ortho*-alkylated prochiral branched diene product in good to excellent yields. The scope with respect to aromatic substitution patterns includes alkyl and O-alkyl groups as well as halides, aldehydes and nitriles.

Alkyl substituents

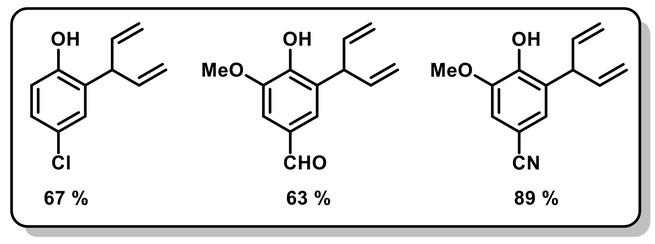




Functional groups



Functional groups



- ✓ Fully regioselective
- ✓ High yields
- ✓ Broad scope
- ✓ High functional group tolerance
- ✓ Rapid access to highly functionalized compounds

Acknowledgement

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