Reductive Etherification of Fatty Acids or Esters with Alcohols using Molecular Hydrogen

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Abstract

Mixtures of fatty acids and aliphatic alcohols are converted into the corresponding long-chain ethers at 70 bar H_2 in the presence of a ruthenium/triphos catalyst and the Brønsted acid trifluoromethanesulfonimide. Valuable long-chain ether fragrances, lubricants, and surfactants are thus accessible from renewable sources via a one-step synthesis. The reaction protocol allows the conversion of various fatty acids and esters both in pure form and as mixtures, for example, tall oil acids or rapeseed methyl ester (RME). Even the mixed triglyceride rapeseed oil, purchased from a grocery store, was cleanly converted in one step.
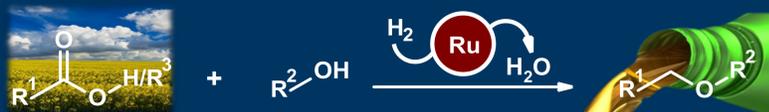
Introduction

Fatty acids like stearic, oleic, and linoleic acid are a highly desirable renewable feedstock, as they are available in vast amounts from natural oils and fats.[1] Moreover, they represent an ideal starting material for the production of long-chain alkyl ethers, that are highly demanded for industrial applications, e.g. in fragrances, lubricants, and surfactants,[2] due to their low melting points and viscosities.[3] Known etherification methods, e.g. the Williamson ether synthesis, condensation of alcohols or the reductive etherification of aldehydes/ketones, posses major drawbacks, as they produce stoichiometric salt waste, are not selective for the unsymmetrical ethers or require additional steps.

The most desirable synthetic path is the direct reduction of esters (ideally triglycerides), but this usually requires waste-intensive reagents, such as silanes or $BF_3/LiAlH_4$.[4] Replacing these reagents by molecular H_2, the least expensive and most sustainable reducing agent, would be clearly advantageous.

Fatty Acid Mixtures and Esters

Fatty acids/esters naturally occur as a mixture with different chain length and degree of saturation. With our method, we are able to convert these mixtures, like tall oil or rapeseed methyl ester, to one single compound without preceding purification. Most interestingly, also triglycerides, e.g. rapeseed oil purchased in a grocery store, can be converted to butyl octadecyl ether in high yields.
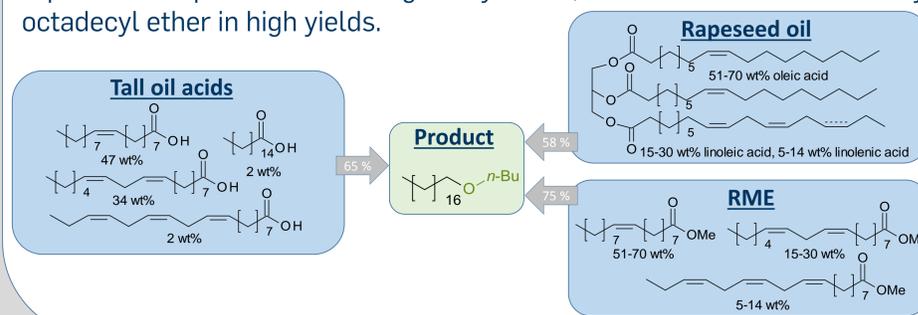
Scope of the Reductive Etherification

A particularly effective catalyst system for the hydrogenation of carboxylic acid derivatives is the combination of a ruthenium(II) center with the tridentate triphos ligand.[5] After careful optimization, a catalyst system consisting of 3 mol% (cod)Ru(met)$_2$, 3 mol% triphos and 10 mol% HNTf$_2$ revealed as optimal for the conversion of fatty acids/esters with aliphatic alcohols at 70 bar initial hydrogen pressure and 180°C.[6]
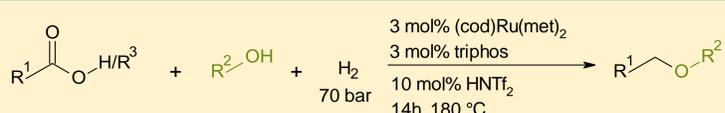

Mechanistic Investigations

We hypothesized, that this transformation can either proceed via hydrogenation of butyl stearate, that should be available in large quantities in the reaction mixture, as HNTf$_2$ catalyzes the esterification very efficiently, or via condensation of two alcohols. Indeed, comparable yields were achieved from stearic acid and 1-butanol, n-butyl stearate, or stearyl alcohol and 1-butanol.
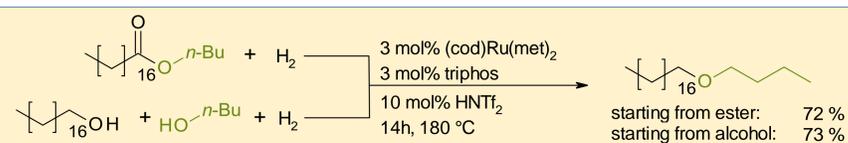
These results are in agreement with the mechanism proposed by Beller.[5] After acid catalyzed ester formation, coordination of the Ru-complexe takes place, followed by a hydride transfer affording the hemiacetal. Ether formation can then be achieved either by hydrogenation of the hemiacetal or via reduction to the alcohol followed by condensation of two alcohols.
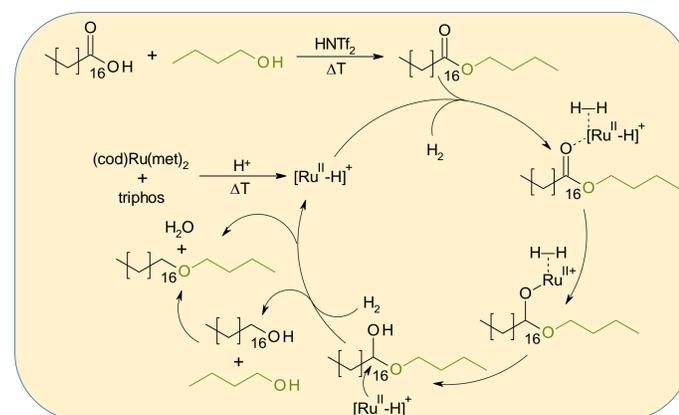
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