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Synthesis of Commodity Chemicals via Sustainable Olefin Metathesis

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PURPOSE OF THE ABSTRACT
Synthesis of Commodity Chemicals via Sustainable Olefin Metathesis

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Olefin metathesis is a powerful and versatile green method in synthetic organic and polymer chemistry. These reactions - in general - are very selective and require mild reaction conditions as well as low catalyst loadings.[1] Cross metatheses of a non-edible vegetable oil, the tung oil or eleostearic acid (ESA) methyl ester (1) with cis-1,4-diacetoxy-2-butene (2) using Hoveyda-Grubbs (3-HG2), Grubbs second or third generation catalysts (3-G2 or 3-G3), followed by Pd/C catalysed hydrogenation, gives methyl 11-acetoxy-undecanoate (4) as a polyester raw material, 1,6-hexanediol diacetate (5), the precursor of 1,6-hexanediol polyurethane monomer and heptyl acetate as a fragrance (6) in 51-99% yields. The one-pot isomerisation of the isolated double bonds containing vegetable oils such as linolenic acid methyl ester (7) using RuHCl(CO)(PPh3)3 catalyst followed by in-situ cross-metathesis (CM) of the reaction mixtures with 2 using 3-G2 leads also to the formation of 5 and the homologs of 4 and 6. Thus, in the latter approach, the key step of the synthesis of 5 is the one-pot isomerization of the isolated double bonds of 7 into conjugated ones in combination with a subsequent cross-metathesis using cross-coupling agent 2. An emerging, new class of catalysts, the cyclic alkyl amino carbene (CAAC) ligand containing ruthenium complex family has recently appeared showing superior activity and stability in olefin metathesis reactions (TONs > 100.000).[2,3] The recent developments of environmental benign solvent soluble, new generation CAAC olefin metathesis catalyst systems and their application in sustainable catalysis will be presented.

FIGURES

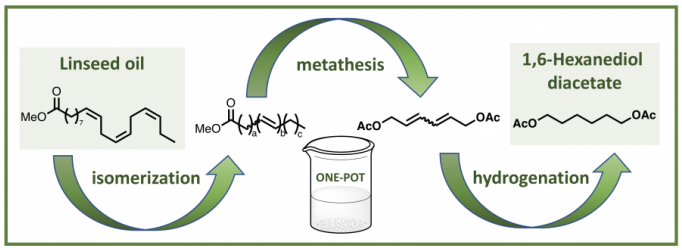

FIGURE 1

Sustainable catalysis

General concept for polyurethane precursor synthesis from renewable resources via ISOMET reaction.

FIGURE 2

KEYWORDS

Olefin metathesis | ISOMET reaction | Renewable resources | CAAC ligands

BIBLIOGRAPHY