ISGC 2022

N°193 / OC
TOPIC(s) : Biomass conversion / Polymers or composites

Angelica Lactones: renewable intermediates for the synthesis of monomers and polymers

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PURPOSE OF THE ABSTRACT

There are many ways to achieve the ambitious goal of switching from a petrol- to a renewable-based chemical economy. Platform chemicals, a concept developed in the last decade, indicates a range of compounds that can be synthetized from renewable resources in high yield by chemical or fermentative synthesis.[1] Levulinic acid (LA), which can be obtained by degradation of lignocellulose in the presence of an acid catalyst, is a prominent example of this category. Several compounds have been prepared starting from LA, such as solvents, fuels, and herbicides;[2] methyl vinyl ketone can be prepared by decarbonylation of LA via the intermediate ?-angelica lactone (?AL).[3] ?AL is a very interesting compound: it has been used as jet-fuel precursor and monomer in photo- and cationic-vinyl polymerizations.[4] Our group has investigated the reactivity of the C-C double bond to introduce new transformations that can widen the spectrum of chemicals accessible from ?AL.[5]

The first approach involved the isomerization to the corresponding ?,?-unsaturated lactone, ?AL. The latter has been previously used in the synthesis of fuels and monomer for acrylate-like polymers.[4d, 6] A 90% ?-enriched mixture was obtained under solvent-free conditions, in the presence of catalytic amounts of base (Fig. 1a). Diels-Alder reaction with different dienes was then performed, among them cyclopentadiene showed the best results. Upon ring-opening metathesis polymerization using Grubbs 2nd generation catalyst, a new bio-based polymer was prepared. A number of green solvents were effective, being ethyl acetate the most promising due to its safety and low toxicity. Functionalized norbornenes are known as useful monomers for polyelectrolytes, shape-memory materials and adhesives.[7] The hydrophobicity of the material is reduced in comparison with the analogous poly-norbornene. Moreover, the polymer can form films with good transparency, that could be employed as optical wave guides or transparent coating.

In the second approach, ozonolysis has been used to cleave the double bond of ?AL. Malonic acid (MA), as well as its mono- and diesters and oxopropionic acid (OA) derivatives were successfully synthetized under different experimental conditions. MA is an important intermediate for the synthesis of fine chemicals with an annual market of 20,000 ton/year, and can be used for the synthesis of specialty polyesters.[8] On the other hand, OA is an intermediate for the preparation of hydroxypropionates, intermediates for the synthesis of acrylonitrile and acrylic acid.[9] The choice of solvent and quenching can tune the reaction to the desired product, achieving good to high yields of MA and OA acetals (Fig. 1b).

FIGURES

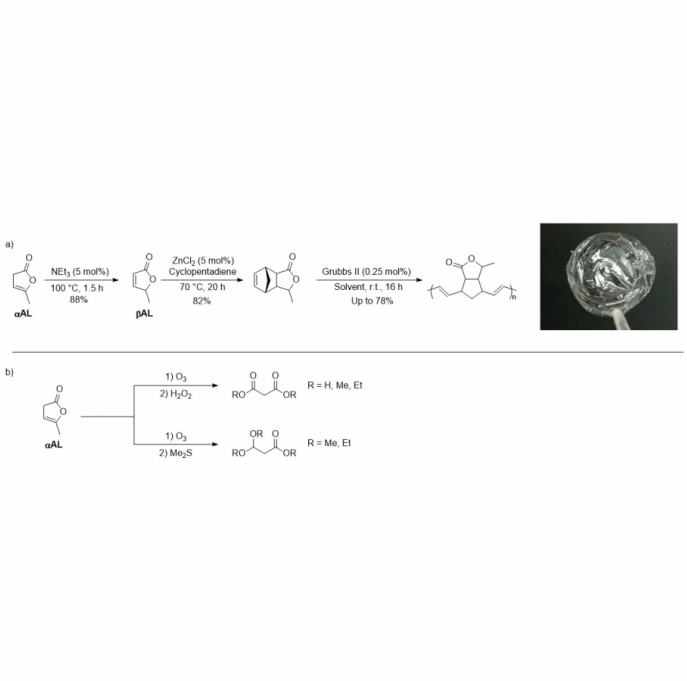

FIGURE 1
Fig. 1

FIGURE 2

KEYWORDS
Platform chemicals | Angelica Lactone | Ring-opening metathesis polymerization | Ozonolysis

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