ISGC2022

N°101 / OC
TOPIC(s) : Clean reactions / Homogenous, heterogenous and biocatalysis

Tungsten-based Tandem Catalysis for the direct oxidative carboxylation of olefins into cyclic organic carbonates

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PURPOSE OF THE ABSTRACT

Cyclic organic carbonates (COCs) actually assumed the role of greener alternatives to common fossil-based chemicals owing to their biodegradability, lack of toxicity and high boiling points, which find applications as lithium battery electrolytes, solvents, plasticizers and intermediates for polymers.

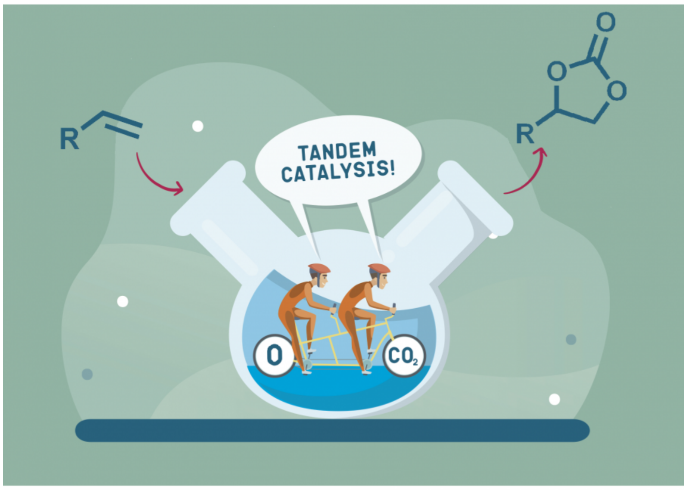
The most widely explored synthesis of COCs involves CO2 fixation into epoxides. However, while CO2 is a renewable feedstock, one cannot overlook that the use of epoxides as starting materials is neither sustainable, nor safe, nor green. Epoxides are not renewable compounds which synthesis poses issues related to low atom economy, environmental impact and costs connected with their purification and isolation along with their potential mutagenicity. With a view to sustainability, health and safety, it would be therefore highly recommended to avoid the use of these reactants.

In this context, one-pot Tandem approach could solve issues related to the handle of highly toxic compounds: these procedures represent a green approach towards process intensification as they are intrinsically simpler compared to the conventional stepwise processes, do not require intermediate isolation/workup, and are generally more efficient in terms of use of materials.

The synthesis of COCs is an attractive reaction susceptible of a tandem approach through the direct oxidative carboxylation (DOC) of olefins via a consecutive oxidation reaction (preferably with a green oxidant, e.g. H2O2 or O2) followed by CO2 insertion as renewable carbonyl source (Figure 1) avoiding intermediate work-up, isolation and handling of epoxides.[1] Moreover, olefinic substrates are widely available on the chemical market, generally less toxic with respect to the corresponding epoxides and may be of natural origin or directly obtained from processing renewable feedstocks.

We therefore explored the identification of a catalytic system capable of being active for the tandem oxidation/CO2 insertion reactions. Tungstate catalysts are well established for olefin epoxidations, while their catalytic activity for CO2 insertion into epoxides is our more recent discovery.[2] This dual reactivity of tungstate prompted us to investigate the feasibility of a general method suitable for the purpose. Each of the two steps was studied in the presence of the ammonium tungstate ionic liquid catalyst ? [N8,8,8,1]2[WO4] ? obtained via a benign procedure starting from ammonium methylcarbonate ionic liquids. An assisted tandem approach was optimized on 1-decene as model substrate, using H2O2 as benign oxidant, [N8,8,8,1]2[WO4] as catalyst and phosphoric acid as promoter, while the addition of 1 atm CO2 and tetrabutyl ammonium iodide after completion of the first step without any intermediate work-up afforded a 94% yield in decene carbonate. The scope of the reaction was demonstrated for 8 primary olefins with C6?C16 alkyl chain lengths (Figure 2a-b) [3], but our approach was furtherly simplified and refined for the DOC of a renewable -based olefin such as methyl oleate. In this case, methyl oleate carbonate was obtained in 99% yield and high retention of cis-configuration starting from methyl oleate using hydrogen peroxide and CO2 in a biphasic system in the presence of [N8,8,8,1]2[WO4] with KBr as the sole co-catalyst (Figure 2c).[4] The tungstate ammonium ionic liquid has a crucial multifunctional role in the tandem reaction: in the first step, it promotes epoxidation of the olefin in the biphasic mixture by activating hydrogen peroxide; in the second step, it activates CO2 for insertion into the epoxide while at the same time controlling the stereochemistry with exclusive formation of the cis-carbonate and serving as phase transfer catalyst enabling the use of a simple and economic alkali halide as co-catalyst for the epoxide ring opening. This multifaceted catalytic activity represents a clear innovation in the use of tungsten-based catalysis but also in the synthesis of COCs.

FIGURES



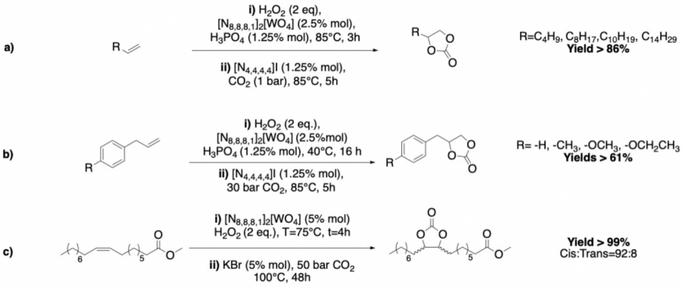


FIGURE 1

Figure 1

Direct oxidative carboxylation of olefins

FIGURE 2

Figure 2

Assisted Tandem Catalysis procedures for the direct synthesis of COCs from different olefinic substrates: a) C6-C16 terminal alkylic olefins; b) aromatic olefins; c) Methyl oleate

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KEYWORDS

Tandem Catalysis | CO2 fixation | Cyclic Carbonates | Ionic liquids

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