Master2 project – 2023

Exploring the chemistry of vinylene carbonates

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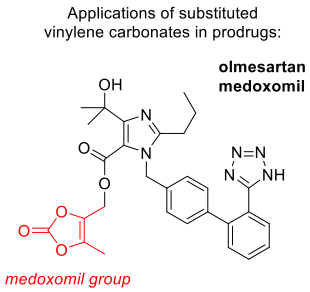
Context: Organic carbonates are currently the subject of intense research efforts, notably due to their general innocuity and biodegradability. In this broad field, the chemistry of vinylene carbonates (VCs) is considerably underdeveloped but has a significant potential in terms of applications. For example, vinylene carbonate (1,3-dioxol-2-one) can be used as an electrolyte additive in lithium batteries or as a monomer to prepare poly(vinylene carbonate). Moreover, functionalized vinylene carbonates are key compounds to prepare medoxomil groups that are used as a cleavable function in prodrugs.



Previous work: Vinylene carbonates are traditionally prepared from α-hydroxyketones and a source of carbonyl such as phosgene, triphosgene or 1,1'-carbonyldiimidazole (CDI). However, these reagents are either toxic or very expensive. In this context, we have recently developed new organocatalytic methods using diphenylcarbonate as a cheap and safe carbonyl source to prepare vinylene carbonates either from α-hydroxyketones[1] or directly from aldehydes.[2] Moreover, we have also demonstrated that VCs can be prepared using dimethyl carbonate[3] or bisphenol A-polycarbonate[4], simultaneously leading to the depolymerization of this polymer notably contained in compact disks. With several clean and handy routes to VCs in hands, we would like now to explore further the chemistry of vinylene carbonates (Figure 1).

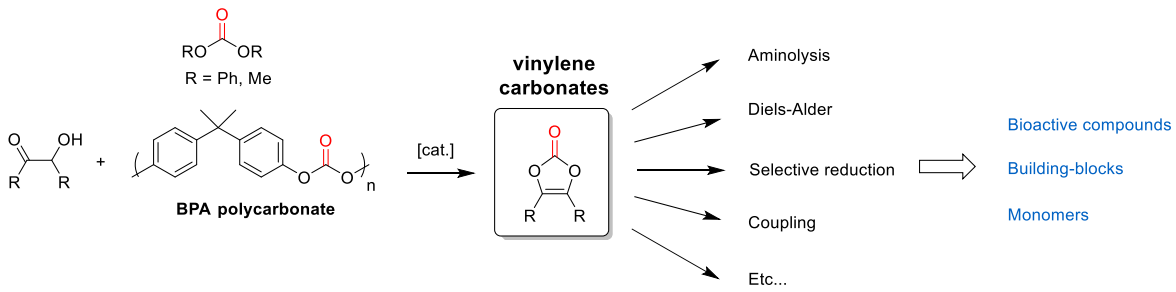


Figure 1. Synthesis and applications of vinylene carbonates.

M2 Project: The aim of this M2 project is to explore the chemistry of vinylene carbonates. In that sense, the project is quite open. Some reactions such as aminolysis, Diels-Alder, reduction, coupling will be first explored but others will be also considered. The project will be later oriented depending on the preliminary results. The target compounds are either bioactive compounds, building-blocks or monomers. The development of (organo)catalytic methods will be encouraged in the respect of Green Chemistry principles (non toxic solvents, solvent-free conditions, original activation modes, etc.).

Interested applicants are welcomed to meet us to discuss this project further.

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[1] Organocatalytic synthesis of substituted vinylene carbonates. K. Onida, A. Haddleton, S. Norsic, C. Boisson, F. D'Agosto, N. Duguet, *Adv. Synth. Catal.* **2021**, *363*, 5129–5137 (link).
[2] Direct synthesis of vinylene carbonates from aromatic aldehydes. K. Onida, L. Ibrahimli, N. Duguet, *Eur. J. Org. Chem.* **2022**, e202200153 (link).
[3] Synthesis of vinylene carbonates using dimethyl carbonate as a carbonyl source. K. Onida, N. Duguet, *manuscript in preparation*.
[4] Chemical upcycling of poly(bisphenol A carbonate) to vinylene carbonates through organocatalysis. K. Onida, M. Fayad, N. Duguet, *manuscript in preparation*.