

Converting wastes into added value products: from glycerol to glycerol carbonate, glycidol and epichlorohydrin using environmentally friendly synthetic routes

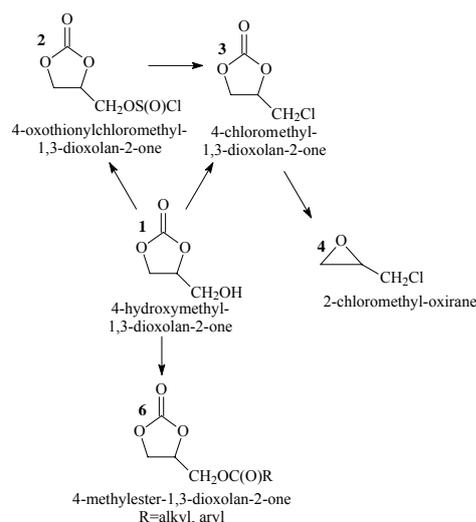
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Introduction

Glycerol carbonate is a multifunctional compound usable in several fields of chemical industry. It was synthesized *via* a non-phosgene route using low cost and high available starting reagents like glycerol and CO₂ [1] or urea [2] in presence of a heterogeneous catalyst. In order to expand its applications, it was efficiently converted into an added value series of new or known derivatives through the functionalization of the –OH moiety, using high yield and high selectivity synthetic routes not affecting the carbonate functionality [3].

Experimental

Synthesis of glycerol carbonate **1** was performed for direct carboxylation of glycerol using CeO₂/Al₂O₃ and CeO₂/Nb₂O₅ mixed oxide as catalyst or by glycerolysis of urea using γ-ZrP as catalyst. The functionalization of glycerol carbonate were carried out in different ways depending on the target product; in particular 4-oxothionylchloromethyl-1,3-dioxolan-2-one **2** was obtained by thionyl chlorination, 4-chloromethyl-1,3-dioxolan-2-one **3** by desulfurization of **2** or by direct chlorination of **1**, 2-chloromethyloxirane **4** by decarboxylation of **2**, 4-phenoxyethyl-1,3-dioxolan-2-one **5** by etherification base-catalyzed of **3**, 4-methylbenzoate-1,3-dioxolan-2-one **6a** and 4-phenylacetate-1,3-dioxolan-2-one **6b** by esterification of **1** with acyl chlorides.



Scheme 1. Products of functionalization of glycerol carbonate

Results and Discussion

The CeO₂ based catalysts, that we have found to be active in the carboxylation of methanol and ethanol afforded a good performance also in the direct carboxylation of glycerol in a biphasic system using tetra(ethyleneglycol)dimethylether-TEGDME as solvent under 5 MPa of CO₂. The conversion of glycerol into glycerol carbonate was equal to 2.5 % with an apparent TON of 8 in each of the three consecutive cycles of reaction. After a few cycles a total conversion of 10% glycerol was observed. Urea can be considered an activated form ($\Delta G = -334$ kJ/mol) of CO₂ ($\Delta G = -395$ kJ/mol). γ-ZrP is active in catalysing the glycerolysis of urea to afford **1** very selectively with a *ca.* 80 % conversion of glycerol. The catalyst shows a good recoverability under the reaction conditions at least for a few cycles. Glycerol carbonate obtained in such phosgene-free and organic-carbonate-free routes has been cleanly converted into a few derivatives, as reported in Scheme 1, shows the compounds obtained through the functionalization of the hydroxymethyl moiety –CH₂OH of **1**. Table 1 shows the main results obtained in the derivatization of **1**.

Table 1: Products of functionalization of glycerol carbonate

Starting reagent	Product	T, t	Yield
1	2	40 °C, 1h	> 99 %
2	3	60 °C, 3 h	> 99 %
2	4	vac. dist.	> 99 %
5	3	reflux, 3 h	54 %
6	1	reflux, 3 h	> 99 %

Conclusions

Heterogeneous systems were used to convert glycerol into glycerol carbonate using CO₂ or urea. The same carbonate was functionalized and converted into added value products.

The high yield and mild reaction conditions (very often close to the ambient conditions) make the environmentally friendly synthetic approach described in this work of potential applicative interest. All compounds prepared were fully characterized.

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References

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