

Upgrade of glycerol derivatives: the selective catalytic etherification of glycerol formal and solketal with dialkyl carbonates

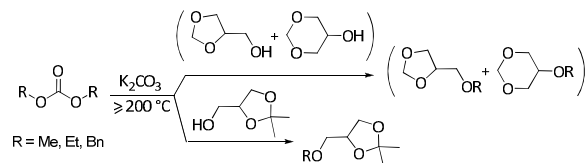
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Introduction

The massive surplus of glycerol from biodiesel productions, has fuelled an extensive research activity aimed at the conversion of both glycerol and its derivatives into energy and chemicals [1]. In this context, acetals such as glycerol formal (GlyF) and solketal are valuable and commercially available glycerol synthons. This paper reports a novel green method for the etherification of both GlyF and solketal using unconventional and non toxic dialkyl carbonates (dimethyl-, diethyl-, and dibenzyl carbonate) as alkylating agents, and K_2CO_3 as a catalyst (Scheme 1).



Scheme 1

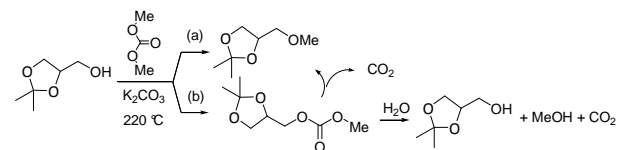
The reaction proceeds with a very high selectivity (up to 100%). However, results prove that final products form via simultaneous etherification, transesterification and decarboxylation processes. These observations have allowed the formulation of a mechanistic hypothesis.[2] Overall, this investigation not only describes a clean synthesis of high-added value chemicals from renewable acetals, but it unlocks a potential also for preparative purposes on a multigram scale.

Experimental

In a typical procedure, a mixture of GlyF (or solketal), dialkyl carbonate (DAIC: dimethyl-, diethyl-, dibenzyl-carbonate) and K_2CO_3 was set to react in a stainless steel autoclave (200 mL) heated at 200–220 °C, for 15–80 hours. The molar ratio substrate:DAIC:catalyst was 1:20:1.2. Experiments were scaled up to 5 g of reactant acetals. O-alkyl ethers were obtained with selectivity up to 99% and excellent yields (86–99% by GC).

Results/Discussion

The selective formation of *O*-alkyl ethers from the reactions of GlyF and Solketal with dialkyl carbonates catalyzed by K_2CO_3 , is an unexpected reaction since, under basic catalysis, alcohols are reported to react with dialkyl carbonates to form transesterification and not alkylation products. Under the investigated conditions, this study has demonstrated that beyond the methylation process (Scheme 2, a: case of solketal), the transesterification of both GlyF and Solketal with DAICs also takes place, but the so-formed carboxyalkyl derivatives follow an intermediate-like behavior. Experiments provide evidence that such carboxyalkyl compounds undergo parallel decarboxylation and hydrolysis processes (Scheme 2, b: case of solketal).



Scheme 2

The course of the reaction of solketal with dimethylcarbonate (DMC) is shown in Figure 1.

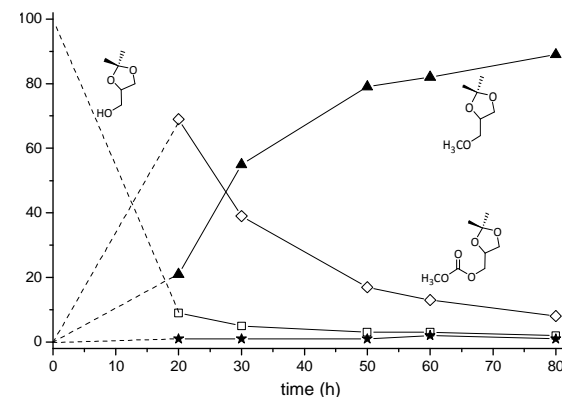


Figure 1. The reaction of Solketal with DMC carried out at 220 °C

Although these reactions are rather energy intensive, they have a genuine green potential since the use of non toxic DAICs is coupled to renewable-derived acetals/ketals in a catalytic procedure with no additional solvents.

References

1. M. Pagliaro and M. Rossi, "Future of Glycerol: New Usages for a Versatile Raw Material" RSC Publishing, Cambridge, UK, 2008,
2. M. Selva, V. Benedet and M. Fabris *Green Chem.*, **14**, 188–200 (2012)