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## Solketal: a key molecule in glycerol chemistry?

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### PURPOSE OF THE ABSTRACT

Although the biodiesel boom is over, the issue of bioglycerol valorization remains relevant today, also because FAME production is still quite appropriate route for biofuel generation. Efforts made towards development of bioglycerol valorization routes today afford bioglycerol to be converted into epichlorohydrine and 1,2-propylene glycol on an industrial scale. Besides these highly demanded chemicals, glycerol is a feed for synthesis of acetals, ketals, ethers and esters. Among them, valuable fuel components, green solvents, hydrotropes, emulsifiers, surfactants and food additives are found. Therefore, search of new and optimization of already existing approaches for bioglycerol valorization is today of interest.

First of all, purification of crude glycerol by distillation consumes significant quantities of heat; thus, it would be better to avoid this step and to use crude bioglycerol for further conversion. Second, glycerol is a highly polar, thermally unstable compound with high boiling point, almost insoluble in many organic solvents. These properties arouse problems during chemical modification finally influencing the operational costs. In the present communication, we propose some alternative routes for overcoming the aforementioned problems by building the concept of solketal as a key intermediate in bioglycerol chemistry. Direct solketal synthesis from crude bioglycerol has been studied; peculiarities of synthesis aroused by the presence of water and impurities have been described. It has been determined, that for this reaction the choice of the proper catalyst is vital [1]. Further, we demonstrate that compared to glycerol, solketal is much better feed for synthesis of various glycerol derivatives.

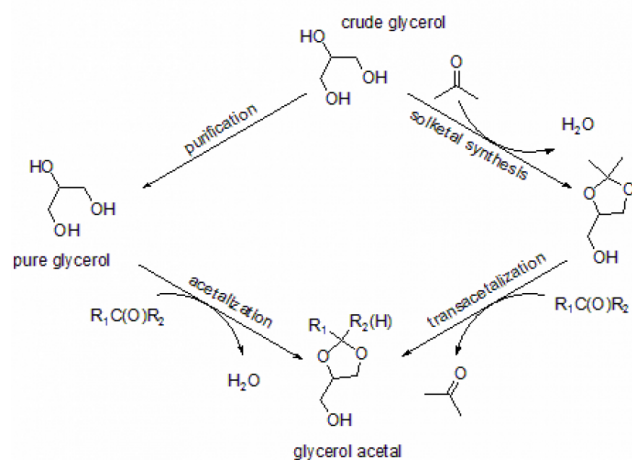
Reaction of higher acetals and ketals with glycerol is hindered by immiscibility of glycerol and lipophilic carbonyl compounds as well as by water release, being a potential reason of catalyst deactivation. In contrast, synthesis of the same compounds by transacetalization of solketal (Fig. 1) proceeds more efficiently than the direct acetalization: the reaction rates are always higher; the equilibrium yields are equal or higher, and in the transacetalization heterogeneous catalysts could be efficiently applied. Besides, a surprising regulation has been revealed: the reaction rate of transacetalization could be enhanced by temperature increase with no decrease in equilibrium yield. Moreover, as in transacetalization acetone is released instead of water, a green synthetic protocol has been developed: by stripping the acetone from the reaction volume the thermodynamical equilibrium is pushed towards the target product, could be obtained (purity up to 99%) in one pot synthesis; no excess of carbonyl compound or product purification is required [2]. Analogously to transacetalization, synthesis of glycerol esters from solketal is conducted more efficiently, than starting from glycerol. The approach is especially interesting for esterification of glycerol with higher lipophilic carbonic acids.

Interesting options are offered by catalytic hydrogenation of solketal. First, mild hydrogenation in the presence of bifunctional catalytic system (Pd + solid or soluble acid) yields glycerol isopropyl ethers with regioselectivities between isomers unreachable by direct etherification [3]. Second, upon copper-catalyzed solketal hydrogenolysis the mixtures of isopropanol and 1,2-propylene glycol could be obtained (Fig. 2). Under the same conditions, solketal is hydrogenolyzed with higher (compared to glycerol) rate and comparable selectivity. Higher volatility of solketal makes it possible to conduct the process in the vapor phase, thus providing extra possibilities for reaction intensification.

Together the results of the study demonstrate that solketal could be considered as a key intermediate for synthesis of valuable glycerol derivatives.

The work has been performed within the State program of the TIPS RAS.

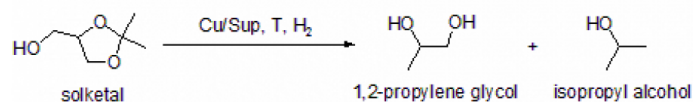
## FIGURES



**FIGURE 1**

Figure 1

Potential synthetic strategies from crude glycerol to acetals (ketals) with higher carbonyl compounds.



**FIGURE 2**

Figure 2

Reaction scheme of solketal hydrogenolysis yielding 1,2-propylene glycol and isopropyl alcohol

## KEYWORDS

bioglycerol | solketal | propylene glycol | hydrogenolysis

## BIBLIOGRAPHY

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