Sulfamic acid catalyzed synthesis of solketal and glycerol ketals and acetals under microwave-assisted conditions

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Introduction

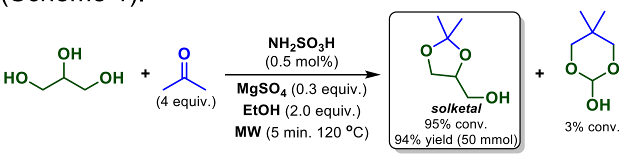
The search for greener methods and feedstock from renewable sources grows fast and mightily all over the world, and its use is essential for the sustainable development. It appears strongly in the fuels industry, where there is a high demand for alternatives to the use of fossil fuels. Among the most promising renewable fuels is biodiesel, which is made from a diverse mix of feedstocks, including oils and fats, through a transesterification reaction.[1] The main residue from biodiesel synthesis is glycerol, which accounts for 10% of every gallon of biodiesel produced.[2] Therefore, the demand of high value-added products made from glycerol increases constantly.

In this context, solketal, which is the glycerol/acetone ketal, is a relevant and well researched compound, which is important in the synthesis of many compounds, including biologically active ones.[3] Also, it is known that solketal reduces the gum formation in gasolines (with and without ethanol) and increases the octane number up to 2.5 points in the gasoline without ethanol.[4]

Based on these facts, we explored the properties of sulfamic acid as acid catalyst in the ketalization and acetalization reaction of glycerol under microwave heating.

Results and Discussion

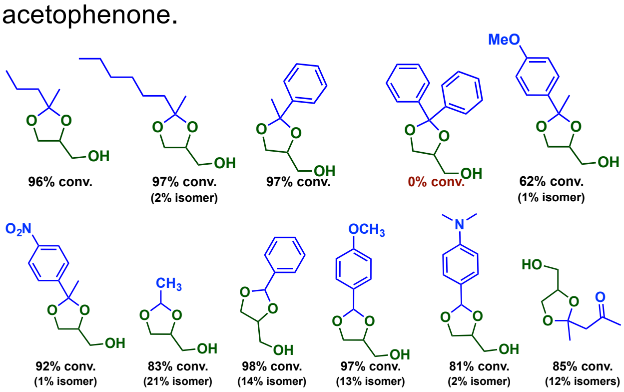
The present study aimed to investigate the best method and conditions for the synthesis of ketals and acetals from glycerol, mainly solketal, using a mono-mode laboratory instrument (Anton Paar, Monowave 300). We evaluated different temperatures, reaction time, cosolvents and catalyst loading to achieve the maximum conversion (Scheme 1).



Scheme 1. Reaction of glycerol with acetone catalyzed by sulfamic acid under microwave heating.

The optimized method afforded the conversion of glycerol in high selectivity (95% conversion for solketal and 3% for the known isomer 4,4-dimethyl-3,5-dioxacyclohexanol) after 5 minutes at 120 °C, in the presence 0.5 mol% of sulfamic acid. The addition of 2.0 equivalents of methanol increased the solubility of glycerol in the acetone and $MgSO_4$ was applied to trap the water formed in the course of the reaction.

We applied the same methodology for the synthesis of glycerol ketal and acetals as shown in Scheme 2. The ketals and acetals were obtained with excellent overall conversions, except for acetophenone.



Scheme 2. Ketals and acetals obtained by $NH_2SO_3H/MgSO_4$ system under microwave heating.

Conclusões

In summary, the present methodology represents a simple and efficient green method for glycerol acetylation and ketalization. Good to excellent yields were achieved in a short time. We believe that this methodology will be a valuable addition to the existing methods in the field of acetals/ketals production and mainly in the synthesis of solketal.

Agradecimentos

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