

Synthesis and derivatization of 2,5-bis(hydroxymethyl)furan

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INTRODUCTION

Biomass-derived C6-furanic platform chemicals are regarded as the most promising building blocks in biorefinery exploitation. 5-Hydroxymethylfurfural (HMF) is referred as a "sleeping giant" in consideration of its potential in bridging the gap from a fossil-based chemistry to a more sustainable one. HMF is a versatile substrate with enormous market potential as it can be easily converted into high value chemicals, materials and bio-based polymers. However, there are some limitations in developing an efficient HMF-based chemistry: its preferred solubility in water rather than in organic solvents, the absence of a cost-efficient scale-up synthesis, and well known HMF stability issue partially solved by the addition of specific stabilizers.

In our laboratory we have developed a new approach to HMF from D-Fructose using dimethyl carbonate as an extracting solvent in the presence of an acidic heterogenous catalyst. A rapid reduction from HMF to 2,5-bis(hydroxymethyl) furan (BHMF) was performed, using sodium borohydride as a reducing agent. This procedure made it possible to prepare a rather large amount of BHMF.

BHMF derivatization was also investigated. In particular, we have focused on BHMF etherification reaction to achieve 2,5-bis(alkoxymethyl) furans (BAMFs) – well-known biofuel candidates. Several catalysts were investigated; (mild) reaction conditions were optimized and thus employed for the preparation of a library of BAMFs (10 compounds). Products isolation and purification were addressed for each BAMFs.

Synthesis of HMF

	Solvent (mL)	TEAB (g)	Catalyst	Time (h)	5-Hydroxymethylfurfural	
D-fructose	DMC (20)	0.5	TBD	10% mol	5	0 %
Catalysts	DMC (20)	0.5	BF ₃ ·O(Et) ₂	10% mol	5	77 %
	DMC (20)	0.5	AlCl ₃	10% mol	5	54 %
	DMC (20)	0.5	TFA	10% mol	5	46 %
	DMC (20)	0.5	Amberlyst-15	10% wt.	5	77 %
Solvents	EtOAc (20)	0.5	Amberlyst-15	10% wt.	5	56 %
	EtOH (20)	0.5	Amberlyst-15	10% wt.	5	58 %
DMC/TEAB solvent system	DMC (10)	0.5	Amberlyst-15	10% wt.	5	53 %
	DMC (20)	0.1	Amberlyst-15	10% wt.	5	46 %
	DMC (20)	0	Amberlyst-15	10% wt.	5	0 %
	DMC (20)	0	Amberlyst-15	10% wt.	5	0 %

Reaction conditions: D-fructose (2.5 g); Conv. 100% in all experiments. Isolated yield.

Synthesis of BAMF

5-Hydroxymethylfurfural $\xrightarrow[\text{THF, r.t.}]{\text{NaBH}_4}$ 2,5-bis(hydroxymethyl)furan (77 %) $\xrightarrow[\text{ROH, 40 °C, 24 h}]{\text{Purolite CT26DR}}$ 2,5-bis(alkoxymethyl)furan (BAMF)

1 R = Me	60%	5	59%	6	57%	7	58%	8	70%	9	37%	10	41%	11	0%
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Reaction conditions: BHMF:ROH, 1.0:30.0 eq. mol.; Reactions were conducted on 0.25 g of BHMF. The substrate conversion was quantitative.

CONCLUSIONS

In conclusion, A new easy scalable approach to HMF employing DMC as reaction media is proposed. The optimized solvent system consists of a mixture of DMC and TEAB (99:1 mol ratio). TEAB favours the dissolution of D-fructose, while DMC is a good extraction solvent for the HMF that can be easily recovered from the reaction mixture by decantation and evaporation of the DMC. Furthermore, a simple and good yielding synthetic approach for the etherification of 2,5-bis(hydroxymethyl)furan in mild conditions using Purolite CT269DR (10% weight) as the catalyst is reported. A library of 10 BAMFs was prepared.

References

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