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Dimethyl isosorbide via organocatalyst N-methyl pyrrolidine: scaling up, purification and concurrent reaction pathways

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Dimethyl isosorbide (DMI) is a green replacement for conventional dipolar solvents as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) that are toxic and dangerous for human and environmental health. DMI is one of the simplest derivatives well-known bio-based platform chemical isosorbide, an anhydro sugar readily synthesised by D-sorbitol dehydration reaction. [1] The synthesis of DMI is mainly based on the etherification of bio-based platform chemical isosorbide in the presence of basic or acid catalyst employing different alkylating agent. Among them, dimethyl carbonate (DMC) is relevant thanks to its characteristics: good biodegradability and low toxicity. [2]

In this work, we report an extensive investigation on highly yielding methylation of isosorbide via DMC chemistry promoted by several nitrogen organocatalyst. [3] Reaction conditions were performed and then applied for the methylation of isosorbide epimers - isomannide and isoidide - and for preliminary scale-up test (10 g of isosorbide). Pure DMI, starting from mixture reaction, was obtained by both column chromatography and distillation at reduced pressure. Between all nitrogen used, N-methyl pyrrolidine (NMPy) demonstrated excellent behaviour as catalyst also for the one-pot conversion of D-sorbitol into DMI. Furthermore, for the first time, all seven methyl and carboxymethyl intermediates - observed during the etherification of isosorbide - were synthetized, isolated and characterised. This study allowed us to know more deeply the concurrent reaction pathways (methylation, methyl carbonylation and decarboxylation) leading to DMI and on the role played by NMPy in the methylation of isosorbide and in this way to propose a mechanism of conversion into isosorbide into DMI via DMC chemistry.

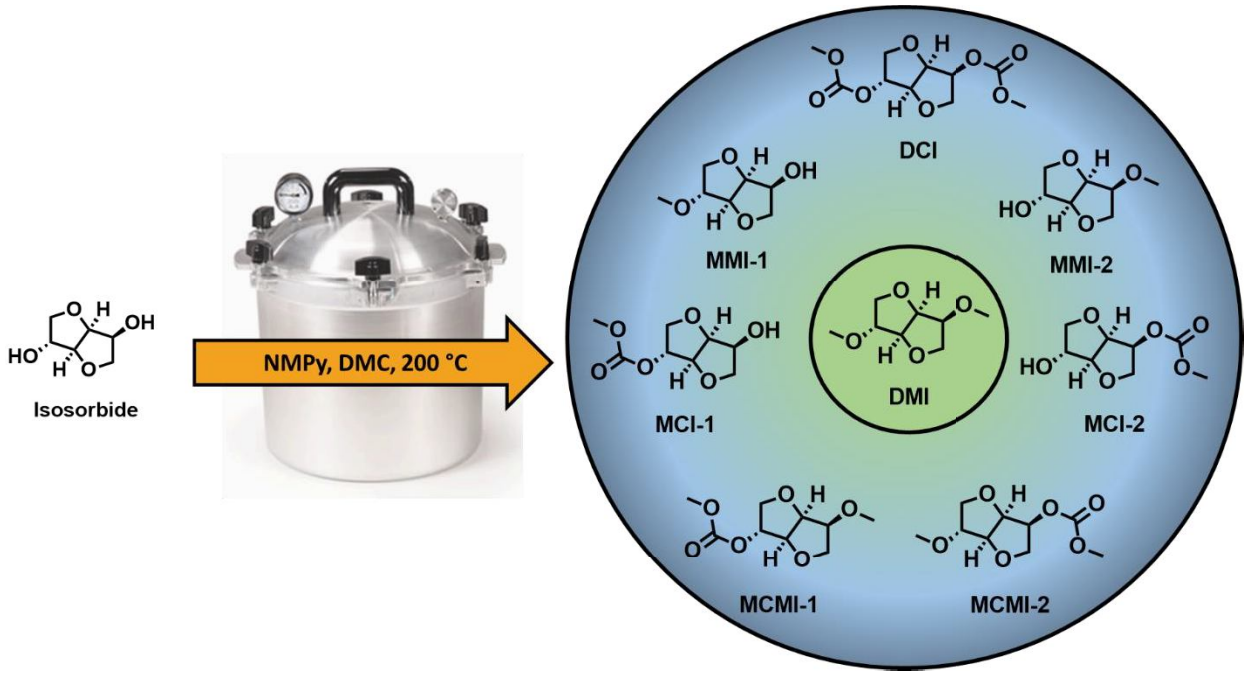

Figure 1. *Synthesis of dimethyl isosorbide (DMI) and reaction intermediates (MMI-1, MMI-2, MCI-1, MCI-2, MCMI-1, MCMI-2, DCI).*

References.

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