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Acid-catalysed carboxymethylation, methylation and dehydration of alcohols and phenols with dimethyl carbonate under mild conditions†

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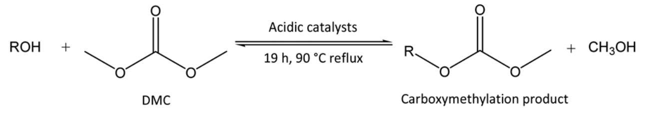
Dimethyl carbonate (DMC) chemistry has been extended to include acid-catalysed reactions of different aliphatic alcohols and phenols. For the first time, *p*-toluenesulfonic acid (PTSA), H_2SO_4, $AlCl_3$ and $FeCl_3$ have been shown to aid carboxymethylation for primary aliphatic alcohols at catalytic loadings with quantitative conversion and selectivity. For carboxymethylation of secondary alcohols, stoichiometric PTSA and catalytic $AlCl_3$ both gave quantitative conversion and selectivity. Stoichiometric $FeCl_3$ and H_2SO_4 promoted dehydration of linear aliphatic alcohols. Additionally $FeCl_3$ catalysed methylation of cyclohexanol, whilst $AlCl_3$ resulted in methylation of phenolic compounds. This research expands the range of potential application for DMC in green chemistry.

Introduction

Dimethyl carbonate (DMC) is an established solvent and a green reagent which continues to attract attention. It readily biodegrades in the atmosphere[1] and is non-toxic.[2] It can be synthesised by many methods and processes.[3–7] DMC has shown extensive applications as a solvent,[8] including in pharmaceutically relevant synthesis[9] and in biocatalysis.[10] In fact, owing to its properties, a recent solvent guide has classified DMC in the greenest "recommended" bracket.[11] Additionally, supercritical DMC has been shown to give a non-catalytic, reagent free route to biodiesel and glycerol carbonate.[12] Significantly, DMC is a green substitute for highly toxic and hazardous compounds such as (a) dimethyl sulphate (DMS) and halohydrocarbon (CH_3X, X = I, Br, Cl) in methylation reactions and (b) phosgene ($COCl_2$) in carboxymethylation (methoxycarbonylation) reactions.

Nowadays, most DMC mediated carboxymethylation reactions are base catalysed. Potassium carbonate is one of the most common basic catalysts used in DMC carboxymethylation and methylation reactions with alcohols and phenols.[13–15] Reaction of the highly hindered secondary alcohols of isosorbide with DMC under reflux results in carboxymethylation in the presence of a weak base or methylation with a strong base.[16] Potassium *tert*-butoxide was also discovered to give excellent conversion and selectivity towards unsymmetrical carbonates from primary and secondary alcohols and DMC.[17] 1,5,7-Triazabicyclo[4.4.0] dec-5-ene (TBD) was also applied as a basic catalyst for the carboxymethylation of primary through to tertiary alcohols and for the production of polycarbonates from diols and DMC.[18] The f-block base lanthanum(III) isopropoxide has been reported as an excellent catalyst for the carboxymethylation of primary, secondary and tertiary alcohols in high yield.[19] Beyond base catalysis, the ionic liquid 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride was found to be an activated reaction medium for the synthesis of non-symmetrical dialkyl carbonates,[20] while enzymatic carboxymethylation of alcohols has also been reported.[21] However, there is very limited literature on acid catalysed (Brønsted or Lewis acid) carboxymethylation or methylation of aliphatic alcohols/phenolic compounds with DMC.

Herein, for the first time Brønsted and Lewis acids including sulfuric acid, iron(III) chloride, *p*-toluenesulfonic acid (PTSA) and aluminium chloride have been used to catalyse the carboxymethylation and/or methylation reactions for various alcohols and phenols. Scheme 1 shows the general carboxymethylation reaction used in this study, while Scheme 2 illus-



Scheme 1 The acid-catalysed DMC carboxymethylation reaction for different ROHs at 90 °C under normal pressure.

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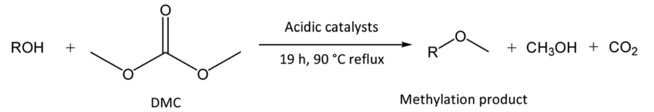
† Electronic supplementary information (ESI) available: Experiment process, ^{1}H-NMR spectra, FT-IR spectrum and GC-MS profile of products. See DOI: 10.1039/c6gc01826b



Scheme 2 The acid-catalysed DMC methylation reaction for different ROHs at 90 °C under normal pressure.

trates the possible general methylation reaction equation at 90 °C. Crucially use of acid catalysts will aid in expanding the potential range of substrates for DMC chemistry to include those that cannot currently be investigated using traditional base catalysed DMC chemistry, such as acidic substrates.

Results and discussion

Carboxymethylation products obtained by Brønsted acid catalysis

In order to investigate acid catalysed DMC carboxymethylation chemistry, PTSA and H_2SO_4 were selected as typical Brønsted acid catalysts. Table 1 shows the conversion and selectivity towards carboxymethylation products synthesised from different primary and secondary alcohols in the presence of DMC and catalytic (0.05 equivalents) or stoichiometric (1.00 equivalent) loadings of catalyst.

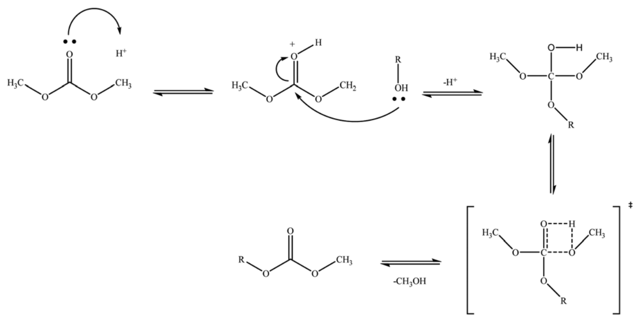
According to Table 1, catalytic loading of PTSA resulted in carboxymethylation of primary alcohols (entries 1 and 3, Table 1). Under similar conditions, PTSA also promoted carboxymethylation of secondary alcohols with high selectivity but reduced conversion (entries 2 and 4, Table 1). When stoichiometric loading of PTSA was employed, the conversion and selectivity towards carboxymethylation for all primary and secondary alcohols became quantitative (entries 1–4, Table 1).

Sulphuric acid was selected as a representative low cost inorganic acid catalyst. When catalytic laoding of sulphuric acid was applied, reactions of all alcohols occurred with high selectivity, with good conversions for primary alcohols (entries 1 and 3, Table 1), but only moderate conversion for secondary alcohols (entries 2 and 4, Table 1). Under stoichiometric loading of H_2SO_4, the conversion of both primary and secondary alcohols became quantitative (entries 1–4, Table 1). In the case of primary alcohols, selectivity was exclusively towards carboxymethylation, however, for secondary alcohols only dehydration to the resultant alkene was observed (GC-MS spectrum is provided in the ESI†). This is as a result of increased stability of the intermediate carbonium ion of secondary alcohols as compared to primary alcohols during acid catalysed dehydration.[22] Under such conditions, stoichiometric H_2SO_4 had been shown to be an excellent reagent for the dehydration of secondary alcohols. This is significant as dehydration of secondary aliphatic alcohols is generally conducted at higher temperatures. Specifically, dehydration of 2-octanol has been reported utilising a molybdenum complex at 150 °C,[23] while heterogeneous Al_2O_3-ZrO_2 required very high temperatures of 280 °C.[24]

Traditional base catalysed DMC chemistry with OH functionality proceeds through deprotonation to form a strong nucleophile prior to attack upon the carbonyl (carboxymethylation) or methyl (methylation) carbon of the alkyl carbonate. A possible mechanism of Brønsted acid catalysed carboxymethylation reaction for alcohols is given in Scheme 3 and is based on the proposed Brønsted acid catalysed transesterification mechanism.[25] Under acidic conditions, the lone pair of the DMC carbonyl picks up a free proton from solution, before undergoing nucleophilic attack from the alcohol. After losing a proton, the hemiketal intermediate forms and then eliminates methanol to yield the carboxymethylation product.

Carboxymethylation products obtained by Lewis acid catalysis

$AlCl_3$ and $FeCl_3$ were selected as common and low cost Lewis acids for the study of the effects of such catalysts in DMC chemistry.



Scheme 3 The possible mechanism of Brønsted acid catalysed carboxymethylation between DMC and alcohols.

Table 1 The experimental results of carboxymethylation products ($ROCO_2Me$) synthesised from different ROHs with DMC promoted by catalytic amount (0.05 equivalent) or stoichiometric amount (1.00 equivalent) of Brønsted acid PTSA or H_2SO_4 at 90 °C[a]

		Catalytic PTSA		Stoichiometric PTSA		Catalytic H_2SO_4		Stoichiometric H_2SO_4	
Entry	ROH	Conv.[b] (%)	Sel.[b] (%)	Conv.[b] (%)	Sel.[b] (%)	Conv.[b] (%)	Sel.[b] (%)	Conv.[b] (%)	Sel.[b] (%)
1	1-Butanol	>99	>99	>99	>99	94 ± 2	>99	>99	>99
2	2-Butanol	65 ± 3	>99	>99	>99	52 ± 4	>99	>99	0[c]
3	1-Octanol	>99	>99	>99	>99	>99	>99	>99	>99
4	2-Octanol	28 ± 2	>99	>99	>99	41 ± 3	>99	>99	0[c]

[a] Reaction conditions: ROH/DMC/PTSA or H_2SO_4 = 6.00 mmol : 240.00 mmol : 0.30/6.00 mmol; T = 90 °C; reaction time 19 h. [b] Conversions and selectivity were calculated by ^{1}H-NMR and GC. [c] Selectivity >99% towards dehydration products.

Table 2 The experimental results of carboxymethylation products ($ROCO_2Me$) synthesised from different ROHs with DMC promoted by catalytic amount or stoichiometric amount (1.00 equivalent) of Lewis acid $AlCl_3$ or $FeCl_3$ at 90 °C[a]

		$AlCl_3$				$FeCl_3$	
Entry	ROH	Conv./Sel.[b] (%) (0.01 equivalent)	Conv./Sel.[b] (%) (0.05 equivalent)	Conv./Sel.[b] (%) (0.20 equivalent)	Conv./Sel.[b] (%) (1.00 equivalent)	Conv./Sel.[b] (%) (0.05 equivalent)	Conv./Sel.[b] (%) (1.00 equivalent)
1	1-Butanol	>99/99	>99/>99	>99/>99	>99/>99	>99/>99	>99/>99
2	2-Butanol	77 ± 4/>99	>99/98	>99/>99	>99/99	88 ± 2/>99	>99/0[c]
3	1-Octanol	99 ± 1/>99	>99/99	>99/>99	>99/>99	>99/>99	>99/>99
4	2-Octanol	8 ± 1/>99	>99/>99	>99/>99	>99/51[d]	74 ± 3/99	>99/0[c]
5	3-Nitrophenol	0/0	0/0	20 ± 3/76	83 ± 1/29	9 ± 4/>99	9 ± 3/>99
6	Phenol	0/0	0/0	42 ± 5/94	85 ± 2/33	0/0	0/0
7	*m*-Cresol	0/0	0/0	14 ± 4/97	90 ± 2/56	0/0	0/0

[a] Reaction conditions: ROH/DMC = 6.00 mmol : 240.00 mmol; T = 90 °C; reaction time 19 h. [b] Conversions and selectivity were calculated by ^{1}H-NMR and GC. [c] Selectivity >99% towards dehydration products. [d] Selectivity 49% towards dehydration products.

Table 3 The experimental results of methylation products (ROMe) synthesised from different phenols with DMC promoted by catalytic amount (0.20 equivalent) or stoichiometric amount (1.00 equivalent) of $AlCl_3$ at 90 °C[a]

		Catalytic amount (0.20 equivalent) of $AlCl_3$	Stoichiometric amount (1.00 equivalent) of $AlCl_3$
Entry	ROH	Conv./Sel.[b] (%)	Conv./Sel.[b] (%)
1	3-Nitrophenol	20 ± 3/24	83 ± 1/71
2	Phenol	42 ± 5/6	85 ± 2/67
3	*m*-Cresol	14 ± 4/3	90 ± 2/44

[a] Reaction conditions: ROH/DMC/$AlCl_3$ = 6.00 mmol : 240.00 mmol : 1.20/6.00 mmol; T = 90 °C; reaction time 19 h. [b] Conversions and selectivity were calculated by ^{1}H-NMR and GC.

Table 2 illustrates the conversion and selectivity of different alcohols towards carboxymethylation in the presence of catalytic and stoichiometric loading of $AlCl_3$ or $FeCl_3$. Selectivity and conversion of primary alcohols is quantitative regardless of acid loading being catalytic or stoichiometric (entries 1 and 3, Table 2). In the case of secondary alcohols, selectivity remains high at catalytic loadings, but conversion drops (entries 2 and 4, Table 2). At a stoichiometric loading however $FeCl_3$, and to a lesser extent $AlCl_3$, result in dehydration of the secondary alcohol to the relevant alkenes (entries 2 and 4, Table 2).

In addition to the aliphatic alcohols, three phenols were also investigated; phenol, *m*-cresol and 3-nitrophenol. The methyl group on *m*-cresol has electron-donating hyperconjugation effect while the nitro group on 3-nitrophenol has electron-withdrawing inductive effect. These three substrates were selected to observe the effect of electron density upon the reactivity of phenol in these methylation reactions.

When reacting phenols with DMC in the presence of $AlCl_3$ at 0.01 and 0.05 molar equivalents, no reaction was observed, however at 0.20 equivalents or stoichiometric loading, both carboxymethylation and methylation took place (entries 5–7, Table 2 and entries 1–3, Table 3). At 0.2 equivalents of $AlCl_3$ conversion is moderate to low but selectivity is high towards carboxymethylation, while increasing to stoichiometric loadings drastically increases conversion but decreases selectivity (entries 5–7, Table 2). However, with regard to methylation, employing stoichiometric $AlCl_3$ enables good selectivity towards 3-nitroanisole and anisole, and reasonable selectivity to 3-methylanisole (entries 1–3, Table 3).

Employing hard–soft acid–base (HSAB)[26,27] theory to explain the experimental results, softer nucleophiles prefer to react with the softer methyl carbon (lower positive charge) on the DMC to obtain the methylation product, while the harder nucleophilic reagents prefer to react with the harder centre carbon (higher positive charge) of DMC to form the corresponding carboxymethylation product.[14] In this study the order of hardness for the phenols is *m*-cresol > phenol > 3-nitrophenol, with selectivity towards methylation products following this trend (entries 1–3, Table 3). This indicated that reactions between DMC and phenols in the presence of stoichiometric $AlCl_3$ gave similar methylation results to base catalysed reactions but with much improved conversion.[14] However when employing 0.2 equivalent of $AlCl_3$, selectivity is significantly towards carboxymethylation for all three reactions regardless of the softness of the nucleophile (entries 5–7, Table 2). This is in contrast to base catalysed reactions.[14]

In order to investigate the impact of extended reaction time the stoichiometric $AlCl_3$ reactions were repeated but run for 60 h (Table 4). In comparison to 19 h reactions, conversion remains constant (within statistical error) while selectivity towards methylation increases. This suggests carboxymethylation of the phenols occurs first but this reaction is reversible so constantly reforming small quantities of the substrates (Scheme 1). Methylation proceeds much more slowly but is irreversible (Scheme 2) and results in the production of methanol, pushing the carboxymethylation equilibrium to the left. Therefore, the longer a reaction is run, the greater the degree of methylation observed.

As $AlCl_3$ can lead to highly acidic and toxic contaminated aqueous wastes,[28,29] a second safer Lewis acid, $FeCl_3$ was also investigated. According to Table 2, quantitative conversions and selectivity of primary alcohols were attained under both catalytic and stoichiometric conditions (entries 1 and 3,

Table 4 The experimental results of methylation products (ROMe) and carboxymethylation products ($ROCO_2Me$) synthesised from different phenols with DMC promoted by stoichiometric amount (1.00 equivalent) of $AlCl_3$ at 90 °C for 60 h[a]

Entry	ROH	Conv.[b] (%)	Sel. (%) ROMe	Sel. (%) $ROCO_2Me$
1	3-Nitrophenol	84 ± 3	88	12
2	Phenol	88 ± 1	85	15
3	*m*-Cresol	92 ± 3	62	38

[a] Reaction conditions: ROH/DMC/$AlCl_3$ = 6.00 mmol : 240.00 mmol : 6.00 mmol; T = 90 °C; reaction time 60 h. [b] Conversions and selectivity were calculated by ^{1}H-NMR and GC.

Table 2). Good conversion and high selectivity of secondary alcohols were also obtained under catalytic loading (entries 2 and 4, Table 2). Reactions of secondary alcohols and DMC in the presence of stoichiometric loading of $FeCl_3$ resulted in quantitative conversion, but with selectivity exclusively towards dehydration to the respective alkene (entries 2 and 4, Table 2), as observed with stoichiometric H_2SO_4. Although H_2SO_4 is a well-known dehydrating agent,[30] stoichiometric $FeCl_3$ is not normally considered as such.

When forming alkyl carbonates through Brønsted or Lewis acid catalysed reactions between an aliphatic alcohol and DMC, the ease of attack follows the trend primary alcohol > short chain secondary alcohol > long chain secondary alcohol > tertiary alcohol. This is consistent with previously published base catalysed studies.[31] Regardless of the system employed, no acid catalysed reaction occurred between a tertiary alcohol (*tert*-butanol) and DMC (detail as shown in the ESI†).

During the investigation of reactions of phenols and DMC in the presence of catalytic or stoichiometric $FeCl_3$ (entries 5–7, Table 2), only very low conversion of 3-nitrophenol was observed with >99% selectivity towards methyl 3-nitrophenyl carbonate. Stoichiometric loading of H_2SO_4 resulted in *m*-cresol reacting with DMC to give methylation (selectivity 90%) and carboxymethylation (selectivity 10%) products, but at low conversion (16%). As such, phenols catalysed by stoichiometric amount of H_2SO_4 or $FeCl_3$ did not follow the HSAB theory, where the hardest *m*-cresol had a high selectivity towards its methylation product promoted by H_2SO_4, and the softest 3-nitrophenol had a near quantitative selectivity towards its carboxymethylation product under $FeCl_3$ (entry 5, Table 2). The mechanistic study of Lewis acid catalysed DMC chemical reactions is currently in progress. Of note is the need to run these Lewis acid reactions under anhydrous conditions to limit chlorination.

Lewis and Brønsted acid dehydration of cyclohexanol and 2-decanol in DMC and *n*-heptane

As mentioned above, stoichiometric $FeCl_3$ and H_2SO_4 both exhibited the ability to dehydrate secondary alcohols to their respective alkene with DMC as the reaction medium. In order to further investigate their ability to dehydrate secondary aliphatic alcohols as well as the influence of the solvent, cyclohexanol and 2-decanol were selected as the substrates and the reaction conducted in either DMC or *n*-heptane. *n*-Heptane was selected as comparable reactions could be conducted at 90 °C while still solubilising the substrates.

Table 5 demonstrates the results for the dehydration of cyclohexanol. When employing $FeCl_3$ as a reagent in DMC, conversion of cyclohexanol was quantitative, although the major product was methoxycyclohexane, with little dehydration to cyclohexene observed (entry 1, Table 5). In heptane, cyclohexene is the only product but with low conversion (entry 2, Table 5). It is obvious that under such conditions, dehydration of cyclohexanol in either DMC or *n*-heptane is difficult. Of interest is the methylation of an aliphatic, cyclic alcohol at low temperature with no carboxymethylation products observed. These reactions typically require the use of highly toxic methylation reagents such as CH_3I and DMS,[32,33] or very high reaction temperature (>170 °C) in the case of DMC.[34] Consequently, $FeCl_3$ in DMC under 90 °C can be used as a green system for the methylation of cyclohexanol to replace these undesirable reagents or conditions. Base catalysed reactions under similar conditions with cyclohexanol as the reactant generally gave poor conversion unless an ionic liquid was employed, with selectivity solely towards the carboxymethylation product.[35] This demonstrates that Lewis acids promote different reactions with DMC and alicyclic alcohols in comparison with base catalysts. Strangely stoichiometric loading of H_2SO_4 did not result in either methylation or carboxymethylation of cyclohexanol in DMC despite showing good activity in Table 1. However, in both solvents the dehydration product was obtained with high selectively but low conversion (entries 1 and 2, Table 5).

In the case of 2-decanol, either acidic reagent in DMC resulted in quantitative conversion of 2-decanol with selectivity exclusively towards a mixture of C_{10} alkenes (entry 1, Table 6, GC-MS and ^{1}H-NMR (400 MHz) spectrums provided in the ESI†). With heptane as the solvent, selectivity remained the same but with a lower conversion (entry 2, Table 6). Overall, DMC resulted in greater conversion of an aliphatic secondary alcohol than heptane during this process. This may be a simple solvent effect or as a result of the specific chemistry associated with DMC such as carboxymethylation followed by decarboxylation as opposed to straight dehydration.

Table 5 The experimental results of products synthesised from cyclohexanol with stoichiometric $FeCl_3$ or H_2SO_4 in DMC or *n*-heptane at 90 °C[a]

		Stoichiometric $FeCl_3$ [b]	Stoichiometric H_2SO_4 [b]
Entry	Solvent	Conv./Sel.[c]/Sel.[d](%)	Conv./Sel.[c]/Sel.[d](%)
1	DMC	>99/12/88	9 ± 3/99/0
2	*n*-Heptane	35 ± 4/99/0	6 ± 2/99/0

[a] Reaction conditions: cyclohexanol/solvent/reagent = 6.00 mmol : 240.00 mmol : 6.00 mmol; T = 90 °C; reaction time 19 h. [b] Conversions and selectivity were calculated by ^{1}H-NMR and GC. [c] Towards cyclohexene. [d] Towards methoxycyclohexane.

Table 6 The experimental results of products synthesised from 2-decanol with stoichiometric $FeCl_3$ or H_2SO_4 in DMC or *n*-heptane at 90 °C[a]

		Stoichiometric $FeCl_3$	Stoichiometric H_2SO_4
Entry	Solvent	Conv./Sel.[b] (%)	Conv./Sel.[b] (%)
1	DMC	>99/99	>99/99
2	*n*-Heptane	80 ± 4/99	90 ± 3/99

[a] Reaction conditions: 2-decanol/solvent/reagent = 6.00 mmol : 240.00 mmol : 6.00 mmol; T = 90 °C; reaction time 19 h. [b] Conversions and selectivity were calculated by ^{1}H-NMR and GC, selectivity towards decene.

For the purpose of study, control reactions for every substrate and solvent were carried out in the absence of any catalyst. In each case negligible conversion of alcohols or phenols was observed. Therefore, the acid played a vital role for the reaction between OH functionality and DMC (details are provided in the ESI†).

This work highlights several major advantages of acid-catalysed DMC chemistry including, expanding the range of substrates that can be reacted with DMC to include acids. This was previously impossible due to acid–base neutralisation reactions of the substrate and catalyst which would occur. The acid catalysts used in this study have comparable or lower market prices than the common base catalysts used in existing DMC chemistry.[36] This is especially true in the case H_2SO_4 which is a widely available, cheap inorganic catalyst that will offer a cost effective alternative to base catalysed DMC processes. The Lewis acids $AlCl_3$ and $FeCl_3$ while employed homogeneously in this work, could potentially be used to form heterogeneous ion-exchanged clays which would open up numerous options to further green this chemistry.[37,38]

Many strong bases (sodium methoxide[16] and potassium *tert*-butoxide[17]) are hydroscopic, hazardous to handle and have an energy intensive synthesis due to the electrolytic production of the corresponding alkali metals.[39] In comparison, all acidic catalysts bar $AlCl_3$ investigated in this research are less hazardous, have lower energy requirements for production and are not significantly affected by water. In the future PTSA can be potentially replaced by bio-based organic acidic catalysts such as *p*-cymene sulphonic acid (PCSA),[40] which would expand the application of green bioderived catalysts in DMC chemistry.

Conclusion

In summary, this research explored employing acids as catalyst or reagents in the reaction of alcohols or phenols with DMC as a new area of dialkyl carbonate green chemistry. The authors believe that for the first time Brønsted and Lewis acids have been observed to promote carboxymethylation of alcohols with quantitative or near quantitative conversion and selectivity and methylation or carboxymethylation of phenols with improved conversion and tuneable selectivity in comparison to base catalysed reactions. Of note was the high activity of $AlCl_3$ even at low loadings suggesting that greener reusable, heterogeneous aluminium catalysts may be practical. Stoichiometric loading of $FeCl_3$ or H_2SO_4 resulted in dehydration of secondary alcohols, with better results in DMC than in *n*-heptane. Overall, the system of $FeCl_3$ and DMC has the potential to be applied to substrates that have previously been difficult to dehydrate. In addition, $FeCl_3$ and DMC have been found to be a good green methylation system for cyclohexanol under mild conditions.

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