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# **Electronic Supplementary Information (ESI) for:**

Acid-catalysed carboxymethylation, methylation and dehydration of

alcohols and phenols with dimethyl carbonate under mild conditions

Saimeng Jin, Andrew J. Hunt, James H. Clark and Con R. McElroy\*

Green Chemistry Centre of Excellence, Department of Chemistry, The University of York, Heslington, York, YO10 5DD, UK. Tel: +44(0)1904324456; E-mail: rob.mcelroy@york.ac.uk

## **1** Experimental Process

#### Materials

1-Butanol 99.8%, 2-butanol 99%, *tert*-butanol 99%, 1-octanol 99%, 2-decanol 98%, phenol 99%, 3-nitrophenol 99%, *m*-cresol 99%, cyclohexanol 99%, dimethyl carbonate (DMC) 99%, *p*-toluenesulfonic acid monohydrate 98.5%, aluminium chloride 99%, iron (III) chloride 97%, ethyl acetate 99.7%, anhydrous magnesium sulphate 99.5%, methanol 99.9%, analytical standard anisole, 3-nitroanisole 99%, cyclohexene 99.0%, dichloromethane 99.8%, acetone 99.9%, silver (I) oxide 99%, iodomethane 99.5%, toluene 99.9% and chloroform-d (CDCl<sub>3</sub>, 99.8% D) were purchased from Sigma-Aldrich. (±)-2-octanol 97% was purchased from Acros Organics. 4A molecular sieves, 3-methylanisole 99% and methyl phenyl carbonate 97% were purchased from Alfa Aesar. Sulphuric acid >95% and n-heptane (HPLC grade) was purchased from Fisher Scientific.

# General experimental procedure for reaction of an alcohol or phenol with dimethyl carbonate

To a 100 cm<sup>3</sup> round bottom flask placed on a multi-point reflux reactor (Radleys, RR98073) was added 6.00 mmol limiting reagent (1-butanol, 2-butanol, *tert*-butanol, 1-octanol, ( $\pm$ )-2-octanol, phenol, 3-nitrophenol, *m*-cresol, 2-decanol or cyclohexanol) followed by 240.00 mmol DMC. To this was then added the relevant acid (*p*-toluenesulfonic acid monohydrate, sulphuric acid, aluminium chloride or iron (III) chloride) at catalytic (0.30 mmol) or stoichiometric (6.00 mmol) loading before heating to reflux with agitation. After the required time (19 or 60 h), the reaction was stopped, cooled to room temperature and filtered. GC and GC-MS samples of the reactants in DMC were taken prior to removal of the solvent under reduced pressure (Heidolph, VV2000) to yield the crude product. In the case of reactions of 1-butanol atmospheric distillation was required due to volatility of the reactant. The crude product was washed with distilled water (3 x 10 cm<sup>3</sup>), and the organic phases combined and dried with magnesium sulphate. Removal of the solvent after filtering yielded the product, which was then analysed by FT-IR and <sup>1</sup>H-NMR.

All Lewis acid catalysed/mediated reactions were run in the presence of molecular sieves to eliminate water.

The dehydration reactions of 2-butanol with stoichiometric FeCl<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> were carried out in closed systems and any gasses produced during reaction were collected and a 10 cm<sup>3</sup> Luer lock gas tight syringe (SGE Analytical Science) was utilised to obtain GC-MS.

#### General experimental procedure for dehydration of a secondary alcohol in heptane

As shown in general experimental procedure for reaction of an alcohol or phenol with dimethyl carbonate with the exception that the reactants were either 2-decanol or cyclohexanol, n-heptane (240.00 mmol) was used in place of DMC and the reaction carried out at 90 °C as opposed to reflux.

Conversion (%) and selectivity (%) were calculated by GC and/or <sup>1</sup>H-NMR. Each experiment was conducted at least twice in order to obtain the average experimental values.

#### **GC-FID** analysis

In this research, an Agilent 6890N gas chromatography with a flame ionisation detector (GC-FID) was used in order to analyse the reaction results. The GC-FID possessed a ZB5HT capillary column (30 m×250  $\mu$ m×0.25  $\mu$ m nominal, max temperature 400 °C) at 20.2 psi constant pressure. The carrier gas used in the GC-FID was helium with flow rate at 2.0 ml/min in constant flow mode. The split ratio used was 5:1. Typically, the initial oven temperature was held at 50 °C for 4 minutes. After that, the temperature was then increasing by 10 °C per minute to 300 °C and maintained at 300 °C for 10 minutes. The temperature of injector was set at 300 °C and the temperature of the flame ionisation detector was held at 340 °C. Some of the GC peaks were directly identified by comparing to standard samples or the purified products. Each of the GC samples was consisted of 20~40 mg product mixture and 1.5 ml dichloromethane or toluene or acetone as GC solvent.

Anisole, 3-nitroanisole, 3-methylanisole, methyl phenyl carbonate and cyclohexene were used as standards in order to confirm retention times of the target products.

#### **GC-MS** analysis

For liquid sample analysis, during this research, gas chromatograph-mass spectrometry (GC-MS) was conducted on a Perkin Elmer Clarus 500 GC along with a Clarus 560 S quadrapole mass spectrometer. The instrument was installed with a DB5HT capillary column (30 m×250  $\mu$ m×0.25  $\mu$ m nominal, max temperature 430 °C). The carrier gas used in the GC-MS was helium with flow rate at 1.0 ml/min, and the split ratio was 10:1. The injector temperature was held at 330 °C. In general, the initial temperature of oven was remained at 50 °C for 4 minutes. Afterwards, the temperature was then ramped with a rate of 10 °C per minute to 300 °C and maintained for 10 minute. The Clarus 500 quadrapole mass spectrum was conducted in electron ionisation (EI) mode at 70 eV with the source temperature and the quadrapole both at 300 °C. The m/z mass scan was at the range of 40 to 640 m/z. The data was collected by the PerkinElmer enhanced TurboMass (Ver. 5.4.2) chemical software. Some of the compounds were identified by direct comparison of the standard mass spectrum provided in the NIST library (Ver. 2.0). Each of the GC-MS samples was consisted of 20~40 mg product mixtures and 1.5 ml dichloromethane or toluene or acetone as GC solvent.

For gas sample analysis, the mass spectrometry was a Waters GCT Premier time of flight (TOF) instrument connected to an Agilent 7890 GC system. The column was an Agilent HP-

AL/S 30 m, 0.25 mm diameter, 5 um film thickness column. GC method was used as follows: the start temperature was remained at 100 °C for 1 minutes. Next, the temperature was then ramped with a rate of 5 °C per minute to 135 °C and held for 2 minutes. The data was collected by the Masslynx 4.1 (Ver. 4.1) software. Each of the GC-MS samples was consisted of 0.5 ml gas sample from the experiment.

Anisole, 3-nitroanisole, 3-methylanisole, methyl phenyl carbonate and cyclohexene were used as standards in order to confirm fragmentation patterns of the target products.

#### **FT-IR** analysis

A Bruker Vertex 70 FT-IR which was fitted with a Specac Golden Gate ATR possessing a diamond top plate analysis window was used for the IR analysis in this research. This FT-IR equipment was operated by Opus software (Ver. 5.5). The spectrum was scanned at a range of 4000-600 cm<sup>-1</sup>. The scan numbers of background and sample were both 64, and the resolution was 2 cm<sup>-1</sup>.

#### <sup>1</sup>H-NMR analysis

The <sup>1</sup>H-NMR spectrum results of samples in this research were recorded by a JEOL JNM-ECS 400 MHz spectrometer. Typically, 100 mg sample from the experiment was dissolved in 1 ml chloroform-d. 16 scans were used for the <sup>1</sup>H-NMR testing. The data of <sup>1</sup>H-NMR was processed and analysed by ACD/NMR Processor Academic Edition software (Ver. 12.01).

#### Control experiments for all the substrates investigated in this research

Control experiments run in the absence of catalyst were conducted for all reactants discussed in this research, results are listed in Table S1. This demonstrates that acidic catalysts are vital for the carboxymethylation, methylation and dehydration reactions.

Entry	ROH	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>				
1	1-Butanol	0	0				
2	2-Butanol	0	0				
3	1-Octanol	0	0				
4	2-Octanol	0	0				
5	2-Decanol	0	0				
6	Cyclohexanol	0	0				
7	tert-Butanol	0	0				
8	3-Nitrophenol	0	0				
9	Phenol	0	0				
10	<i>m</i> -Cresol	0	0				
<sup><i>a</i></sup> Reaction conditions: ROH/DMC or n-heptane = 6.00 mmol : 240.00 mmol; $T = 90$ °C; Reaction time 19 h. <sup><i>b</i></sup>							

**Table S1**. The results of control experiments run in the absence of catalyst for all the substrates investigated in this research<sup>*a*</sup>

# Experimental results for the reactions between *tert*-butanol and DMC in the presence of various acid catalysts

The experimental data for reactions of *tert*-butanol, DMC and various acid catalysts is listed in Table S2. This implies that tertiary alcohols cannot be carboxymethylated by DMC under the acidic conditions described.

**Table S2.** Experimental results for the reactions between *tert*-butanol and DMC catalysed by different acidic catalysts<sup>a</sup>

Entry	Catalysts	Catalytic loading		Stoichiometric loading				
		Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)	Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)			
1	PTSA	0	0	0	0			
2	$H_2SO_4$	0	0	0	0			
3	AICI <sub>3</sub>	0	0	0	0			
4	FeCl <sub>3</sub>	0	0	0	0			
<sup><i>a</i></sup> Reaction conditions: ROH/DMC/catalyst = 6.00 mmol : 240.00 mmol : 0.30/6.00 mmol; <i>T</i> = 90 °C; Reaction								
time 19 h. <sup>b</sup> Conversions and selectivity were calculated by <sup>1</sup> H-NMR and GC.								

# 2 Characterisation of structures of products

1 Butyl methyl carbonate

 $\left[C_{4}H_{8}\right]^{+}$ 

Butyl methyl carbonate



Figure S1. Mass spectrum (EI) of butyl methyl carbonate

This mass spectrum (EI) of butyl methyl carbonate obtained in this experiment was in accordance with the standard mass spectrum reported in the literature.<sup>1</sup>



Figure S2. <sup>1</sup>H-NMR of butyl methyl carbonate

<sup>1</sup>H-NMR (400 MHz,  $CDCI_3$ ):  $\delta$  = 0.90 (t, *J* = 7.32 Hz, 3H, CH<sub>3</sub>), 1.36 (m, *J* = 7.36 Hz, 2H, CH<sub>2</sub>), 1.61 (m, *J* = 7.32 Hz, 2H, CH<sub>2</sub>), 3.74 (s, 3H, CH<sub>3</sub>), 4.10 (t, *J* = 6.60 Hz, 2H, CH<sub>2</sub>) ppm



Figure S3. FT-IR of butyl methyl carbonate

 $CH_3$  group C-H stretching bands 2961 cm<sup>-1</sup> and 2876 cm<sup>-1</sup>, ester C=O stretching band 1747 cm<sup>-1</sup>,  $CH_3$  group C-H bend band 1443 cm<sup>-1</sup> and ester C-O stretching band 1258 cm<sup>-1</sup>



2 sec-Butyl methyl carbonate

Figure S4. Mass spectrum (EI) of sec-Butyl methyl carbonate

This mass spectrum (EI) of *sec*-Butyl methyl carbonate obtained in this experiment was in accordance with the standard mass spectrum reported in the literature.<sup>1</sup>



Figure S5. <sup>1</sup>H-NMR of sec-Butyl methyl carbonate

<sup>1</sup>H-NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 0.92 (t, J = 7.32 Hz, 3H,  $CH_3$ ), 1.26 (d, J = 6.44 Hz, 3H,  $CH_3$ ), 1.61 (m, 2H,  $CH_2$ ), 3.76 (s, 3H,  $CH_3$ ), 4.69 (m, J = 6.40 Hz, 1H, CH) ppm 3 Methyl octyl carbonate



Figure S6. Mass spectrum (EI) of methyl octyl carbonate



Figure S7. <sup>1</sup>H-NMR of methyl octyl carbonate

<sup>1</sup>H-NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 0.84 (t, *J* = 6.96 Hz, 3H, CH<sub>3</sub>), 1.17-1.40 (m, 10H, CH<sub>2</sub>), 1.63 (m, *J* = 6.56 Hz, 2H, CH<sub>2</sub>), 3.74 (s, 3H, CH<sub>3</sub>), 4.09 (t, *J* = 6.60 Hz, 2H, CH<sub>2</sub>) ppm



Figure S8. FT-IR of methyl octyl carbonate

 $CH_3$  group C-H stretching band 2958 cm<sup>-1</sup>,  $CH_2$  group C-H stretching band 2928 cm<sup>-1</sup> and 2858 cm<sup>-1</sup>, normal saturated ester group C=O stretching band 1750 cm<sup>-1</sup>,  $CH_3$  group C-H deformation band 1444 cm<sup>-1</sup> and ester C-O stretching band 1264 cm<sup>-1</sup>

### 4 Methyl octan-2-yl carbonate







Figure S10. <sup>1</sup>H-NMR of methyl octan-2-yl carbonate

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.86 (t, *J* = 6.44 Hz, 3H, CH<sub>3</sub>), 1.26 (d, *J* = 6.40 Hz, 3H, CH<sub>3</sub>), 1.27-1.68 (m, 10H, CH<sub>2</sub>), 3.75 (s, 3H, CH<sub>3</sub>), 4.74 (m, *J* = 6.40 Hz, 1H, CH) ppm





Figure S11. Mass spectrum (EI) of anisole

In this research, the structure of corresponding product was also confirmed to be anisole *via* comparing to the standard anisole sample by GC.



#### 6 Methyl phenyl carbonate

Figure S12. Mass spectrum (EI) of methyl phenyl carbonate

This mass spectrum (EI) of methyl phenyl carbonate obtained in this experiment was in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as

mentioned in the Experiment Process section and the reported mass spectrum in the literature.<sup>2</sup> In this research, the structure of corresponding product was also confirmed to be methyl phenyl carbonate *via* comparing to the standard methyl phenyl carbonate sample by GC.



7 3-Nitroanisole and methyl 3-nitrophenyl carbonate

Figure S13. Mass spectrum (EI) of 3-nitroanisole

In this research, the structure of corresponding product was also confirmed to be 3nitroanisole *via* comparing to the standard 3-nitroanisole sample by GC.



Figure S14. Mass spectrum (EI) of methyl 3-nitrophenyl carbonate

This mass spectrum (EI) of methyl 3-nitrophenyl carbonate obtained in this experiment was also in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section.



Figure S15. <sup>1</sup>H-NMR of product mixtures of 3-nitrophenol, 3-nitroanisole and methyl 3nitrophenyl carbonate

The main <sup>1</sup>H-NMR peaks in Figure S15. in the range of 0.000 ppm to 2.500 ppm, were from the 3-nitrophenol starting material.



### 8 3-Methylanisole and methyl *m*-tolyl carbonate



In this research, the structure of corresponding product was also confirmed to be 3methylanisole *via* comparing to the standard 3-methylanisole sample by GC.



Figure S17. Mass spectrum (EI) of methyl m-tolyl carbonate

This mass spectrum (EI) of methyl *m*-tolyl carbonate obtained in this experiment was also in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section.



# **Figure S18.** <sup>1</sup>H-NMR of product mixtures of *m*-cresol, methyl *m*-tolyl carbonate, 3methylanisole

The main <sup>1</sup>H-NMR peaks in Figure S18. in the range of 0.000 ppm to 2.000 ppm, were from the *m*-cresol starting material.

#### 9 Cyclohexene



Figure S19. Mass spectrum (EI) of cyclohexene

In this research, the structure of corresponding product was also confirmed to be cyclohexene *via* comparing to the standard cyclohexene sample by GC.

10 Methoxycyclohexane



Methoxycyclohexane



Figure S20. Mass spectrum (EI) of methoxycyclohexene

This mass spectrum (EI) of methoxycyclohexane obtained is in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section and the reported mass spectrum in the literature.<sup>3</sup> The GC retention time of this compound and methoxycyclohexane synthesised from cyclohexane and methyl iodide were identical.





Figure S21. Mass spectrum (EI) of 2-octene

This mass spectrum (EI) of 2-octene obtained in this experiment was also in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section and the reported mass spectrum in the literature.<sup>4,5</sup>

12 3-Octene





This mass spectrum (EI) of 3-octene obtained in this experiment was also in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section and the reported mass spectrum in the literature.<sup>5</sup>





Figure S23. Mass spectrum (EI) of 2-decene

This mass spectrum (EI) of 2-decene obtained in this experiment was also in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section and the reported mass spectrum in the literature.<sup>6-8</sup>



This mass spectrum (EI) of 3-decene obtained in this experiment was also in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section and the reported mass spectrum in the literature.<sup>5,8</sup>



Figure S25. Mass spectrum (EI) of 5-decene

This mass spectrum (EI) of 5-decene obtained in this experiment was also in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section and the reported mass spectrum in the literature.<sup>5</sup> 16 <sup>1</sup>H-NMR of products mixture of dehydration reaction of 2-decanol after removed DMC





Figure S26. <sup>1</sup>H-NMR of products mixture of dehydration reaction of 2-decanol

17 GC-MS of the gas produced in the experiment of 2-butanol reacted with stoichiometric  $\mbox{FeCl}_3$  or  $\mbox{H}_2\mbox{SO}_4$ 





This mass spectrums of 1-butene and (E/Z)-2-butene obtained in this experiment were also in accordance with the standard mass spectrum provided by NIST library (Ver. 2.0) as mentioned in the Experiment Process section.

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