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The Continuous Acid-Catalysed Etherification of Aliphatic Alcohols Using Stoichiometric Quantities of Dialkyl Carbonates

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Abstract:

A range of methyl and ethyl ethers of aliphatic alcohols have been synthesized cleanly in high yield by reacting the corresponding alcohol with dimethyl carbonate or diethyl carbonate over the solid acid catalyst, γ-alumina. The reaction could be conducted at ambient pressure without the need for the large excess of dialkyl carbonate as previously reported in the literature. If the reaction was conducted at high pressure, the conversion of the starting alcohol was greatly reduced. However, high pressure CO_2 can be used as the solvent without significant reduction in yield. This has implications for tandem reactions.

Introduction

Aliphatic methyl ethers are important compounds in synthetic organic chemistry and have applications as fuel additives and solvents.[1−4] Typically, methyl ethers of aliphatic alcohols are synthesized using the Williamson ether synthesis which uses highly toxic reagents such as dimethyl sulfate and methyl halides and generates stoichiometric quantities of inorganic salt.[5−7]

Dimethyl carbonate (DMC) has received much attention as an alternative methylating agent as it has low toxicity, is biodegradable, and has been used to perform methylation and carboxymethylation reactions with a wide variety of nucleophiles.[8−16] However, there are relatively few examples of the synthesis of aliphatic ethers *via* DMC in the literature to date. For example, Selva et al.[17] have successfully methylated several benzyl-type alcohols with a similar method using Y- and X-faujasites as catalysts at high temperature under autogenic pressure in an autoclave. They suggest that the methylation and carboxymethylation reactions occur simultaneously over this catalyst and at elevated temperatures the methyl carbonate undergoes decarboxylation, so that the methyl ether is the sole observed product of the reaction. This method is batch mode and requires a very large excess of DMC (>30 mol equiv) which wastes materials and energy due to the heating and cooling of the excess reagents which are not consumed by the reaction.

Tundo et al.[18,19] have reported the synthesis of methyl ethers from aliphatic alcohols using DMC but only *via* adopting a two-step process. They have proposed that due to their harder nature, aliphatic hydroxyl groups will only react with the harder carbonyl group of DMC to afford methyl carbonates; methyl ethers can then be obtained by decarboxylation of this methyl carbonate. This two-step procedure has been carried out in multipot and one-pot batch reactions. Both methods required an excess of DMC >4 and >18 mol equiv for multipot and one-pot, respectively, to drive the formation of the methyl carbonate.

Tundo et al.[19] have also reported a continuous flow method for the synthesis of methyl ethers, where a mixture of the alcohol and DMC (3 mol equiv) are continuously passed over a column of basic alumina at 180 °C and atmospheric pressure to yield ~90% of the methyl ether. Such continuous methods are preferable to the batch methods, especially when scale up of production needs to be considered.

Recently, we reported the continuous methylation of 1-octanol with DMC with a variety of heterogeneous acid catalysts at high pressure using supercritical CO_2 ($scCO_2$) as the solvent.[20] This method allowed the use of lower amounts of DMC (2 mol equiv) whilst maintaining a high yield (86%) of the methyl ether, with the best-performing catalyst being an acidic γ-alumina. This method was applied successfully to a range of aliphatic alcohols and diols, and it was also shown that DMC could be used for clean esterification and *N*-methylation reactions.[20]

Here we evaluate our original process[20] at several different reaction conditions and show that a range of primary and

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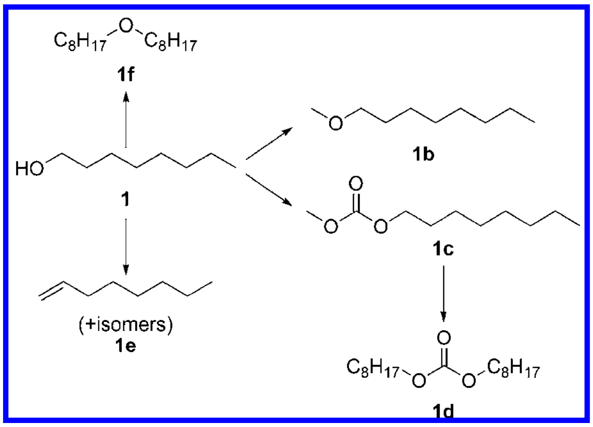
Scheme 1. **Reaction of 1-octanol (1) with DMC**



secondary aliphatic alcohols can be successfully methylated in a continuous process which operates at ambient pressure and uses stoichiometric amounts of DMC, thus potentially saving energy and material costs associated with our original process. This concept is also extended to ethylation reactions by using diethyl carbonate (DEC) as the alkylating agent. Additionally, the effect of the pressure on the reaction outcome has been investigated, and we show that an increase in pressure leads to a significant decrease in yield; however, this can be overcome by using $scCO_2$ as the solvent.

Results and Discussion

Reactions at Ambient Pressure. In all our experiments, reactions were carried out in an automated continuous reactor equipped with online gas liquid chromatography (GLC) analysis as described in the Experimental Section. To determine if DMC could be used as a methylating agent in stoichiometric amounts at ambient pressure, the methylation of 1-octanol (**1**), Scheme 1, was chosen as a model reaction, as it is a well-understood reaction which formed the basis of our previous studies.[20]

A solution of DMC and **1** (1:1 molar ratio of DMC:**1**) was pumped at 0.2 mL/min at ambient pressure over a fixed bed of γ-alumina, which we have already shown to be an excellent catalyst for this reaction in $scCO_2$.[20] The temperature of the reactor was gradually increased from 100 to 250 °C, and GLC samples were taken periodically so that the effect of the increasing temperature on the product composition could be determined, as shown by Figure 1.

At low temperatures (<120 °C) **1** underwent transesterification with DMC to form octyl carbonate (**1c**) which, as the temperature was increased (>150 °C), underwent further transesterification with **1** to generate dioctyl carbonate (**1d**). Small amounts of the desired methyl ether, 1-methoxyoctane (**1b**), were also formed at these low temperatures. As the temperature of the reaction was increased (>160 °C) both overall conversion of **1** and selectivity towards **1b** increased markedly so that the yield of **1b** increased rapidly with increasing temperature, reaching a maximum yield of >99% at around 220 °C. Above this temperature unimolecular dehydration of **1** to form 1-octene and its isomers (**1e**) occurs, lowering the yield of **1b**. Small amounts (<10%) of dioctyl ether (**1f**), which is formed from the bimolecular dehydration of **1**, were also detected at high temperatures (>180 °C). Interestingly this product composition versus temperature profile is very similar to those observed previously when the reaction was performed at 100 bar with the same organic feed rate but with an additional 1 mL/min CO_2.[20] This result confirms that high yields of aliphatic methyl ethers can be obtained when using DMC as the methylating agent in stoichiometric quantities, at ambient pressure and with no solvent. The catalyst lifetime was tested in a separate experiment with the temperature held at 220 °C, and a solution of **1** and DMC was pumped at 0.2 mL/min over a fixed bed of γ-alumina at ambient pressure; the yield of **1b** remained constant at around 90% for a period of greater than 110 h.

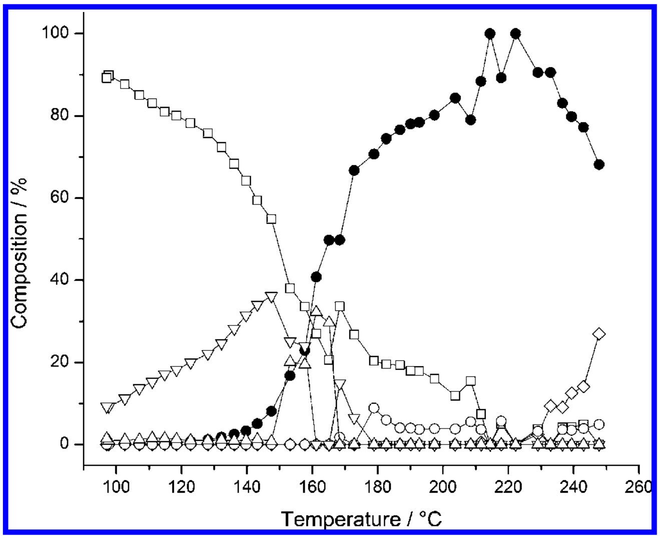
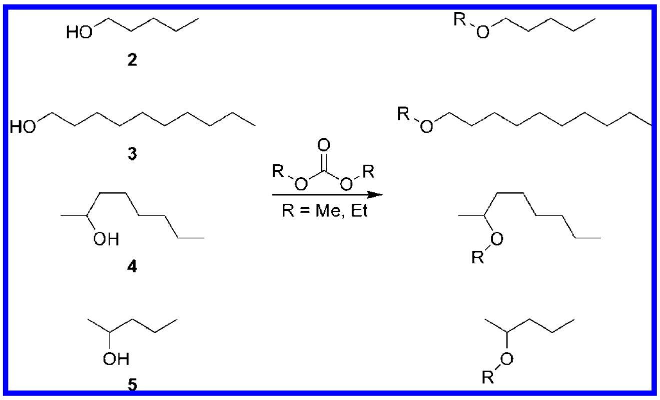


Figure 1. **Plot showing the effect of temperature on the reaction of 1 with DMC (1:1 molar ratio). Liquid reagents pumped at 0.2 mL/min, 10 cm^3 tubular reactor packed with γ-alumina catalyst, ambient pressure. Traces are labeled as follows: □ 1, ● 1b, ▽ 1c, △ 1d, ◇ 1e, ○ 1f.**

Scheme 2. **Alkylation of aliphatic alcohols with DMC and DEC at ambient pressure**



Consequently, the scope of this ambient pressure route was further investigated by attempting the alkylation of several aliphatic alcohols with both DMC and DEC, Scheme 2.

In all experiments the substrate alcohol and the dialkyl carbonate (DAC) were mixed to form a 1:1 molar solution which was pumped at 0.2 mL/min over a fixed bed of γ-alumina catalyst at ambient pressure. The temperature of the preheater and reactor were initially set to 100 °C and were gradually increased; GLC samples were taken periodically so that the effect of temperature on the outcome of the reaction could be determined. The results are summarized in Table 1.

Table 1. **Results of alkylation experiments using DMC and DEC at ambient pressure**[a]

substrates	alkylating agent	max. yield (%) of desired ether	temp. (°C) at max. yield
1	DMC	99	222
	DEC	94	211
2	DMC	87	221
3	DMC	90	219
	DEC	87	221
4	DMC	49	174
	DEC	41	193
5	DMC	54	177
	DEC	42	206

[a] Reaction conditions - substrate solution pumped at 0.2 mL/min (1:1 molar ratio of DMC:substrate), ambient pressure, fixed bed of γ-alumina catalyst (tubular reactor, internal volume 10 mL), temperature ramped linearly at 0.2 °C/min.

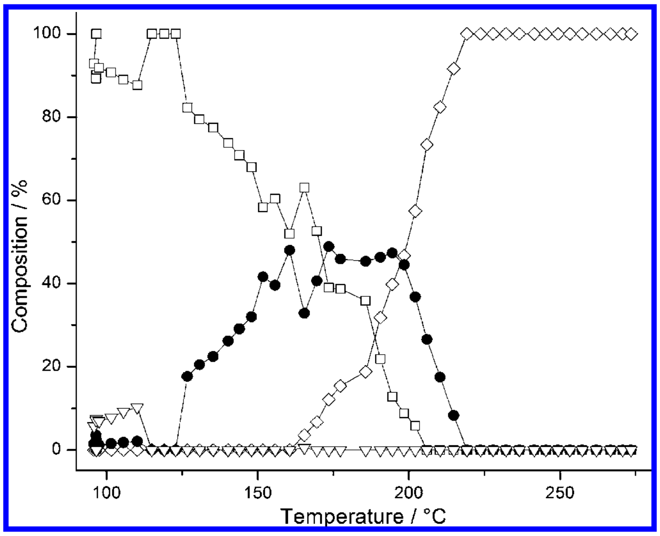


Figure 2. **Plot showing the effect of temperature on the reaction of 4 with DMC (1:1 molar ratio). Liquid reagents pumped at 0.2 mL/min, 10 cm^3 tubular reactor packed with γ-alumina catalyst, ambient pressure. Traces are labeled as follows: □ 4, ● 4b, ▽ 4c, ◇ 4e.**

Table 1 shows that high yields of methyl ethers could be obtained when the primary aliphatic alcohols, **1**, 1-pentanol (**2**), and 1-decanol (**3**) were used as substrates. The reaction of **1** with DMC has been discussed above and is shown in more detail in Figure 1. The reaction of the other primary aliphatic alcohols (**2**, **3**) with DMC proceeds in a manner similar to that of **1**; at low temperatures (<130 °C) the main product is the methyl alkyl carbonate with small amounts of methyl ether being formed. As the temperature increases, the selectivity of the reaction switches to favor the methyl ether, reaching a maximum yield of ~90% at ~220 °C. At higher temperatures (>250 °C) dehydration of the alcohol to form the corresponding alkene and its isomers becomes the dominant process, and the yield of the methyl ether decreases. The full temperature−composition plots can be found in the Supporting Information (ESI-1).

Figure 2 shows the that the secondary alcohol, 2-octanol (**4**) reacts with DMC in a manner similar to that of its primary analogue, **1**, and forms the methyl carbonate, methyl octan-2-yl carbonate (**4c**), at low temperatures (<120 °C). As the temperature is increased, the selectivity of the reaction switches to favor the methyl ether, 2-methoxyoctane (**4b**); however, the dehydration reaction to form octenes (**4e**, same as **1e**) occurs at a much lower temperature (>160 °C) compared to that for **1**. The formation of octenes at lower temperatures limits the maximum yield of the methyl ether to only ~50%. 2-Pentanol (**5**) reacts in a manner similar to that of **4** as shown in Table 1 and the temperature−composition plot in the Supporting Information (ESI-2).

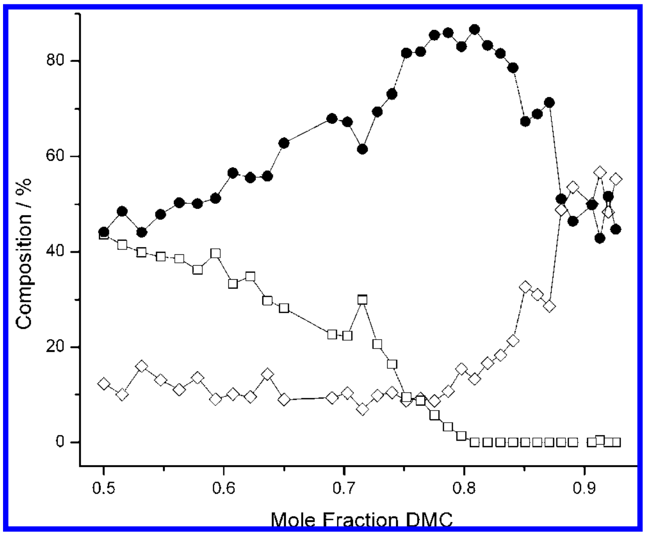


Figure 3. **Plot showing the effect of mole fraction of DMC on the composition of products from the reaction of 4 with DMC. Total organic flow rate 0.2 mL/min (composition varied by using two programmable HPLC pumps), 10 cm^3 tubular reactor packed with γ-alumina catalyst, ambient pressure, 170 °C. Traces are labeled as follows: □ 4, ● 4b, ◇ 4e.**

The effect of temperature on product composition for reactions of **1** and **3**−**5** with DEC was very similar to that observed for the reactions with DMC. The ethyl alkyl carbonate was formed at low temperatures, with the target ethyl ether formed as the temperature was increased, until a maximum yield was reached. After which the formation of alkenes dominated as the temperature was increased further, thus reducing the ether yield. DEC generally afforded a slightly lower maximum yield of the target ether than did DMC; the full temperature−composition plots for the reactions of **1** and **3**−**5** with DEC can be found in the Supporting Information (ESI-3).

Effect of DMC Concentration. To determine if higher yields of methyl ethers of secondary alcohols could be achieved by using an excess of DMC, the reaction of **4** with DMC was conducted at 170 °C and ambient pressure and the molar fraction of DMC was changed gradually. This was achieved by using two HPLC pumps, one feeding a solution of **4** and DMC (1:1 molar ratio) and the other feeding pure DMC. The pump flow rates were then programmed to change over time so that the molar ratio of DMC to **4** could be gradually decreased from 12.5:1 (0.93 mol fraction DMC) to 1:1 (0.5 mol fraction DMC) whilst maintaining the total flow of reagents at a constant 0.2 mL/min. The results are shown in Figure 3, which shows that there is a maximum in the yield of **4b** of 87% at DMC mol fraction ca. 0.8 (4.2:1 DMC to **4** molar ratio). Increasing the DMC composition beyond this point enhances the dehydration reaction to form **4e,** at the expense of the methylation reaction. To investigate this effect further, a series

Table 2. **Effect of DMC:4 molar ratios on the product composition versus temperature**[a]

DMC:**4** molar ratio	1:1	5:1	10:1
yield (%) of **4b** at 150 °C	38	52	78
yield (%) of **4b** at 175 °C	45	76	62
yield (%) of **4b** at 200 °C	34	1	<1
max. yield (%) of **4b**	60	82	94
temp. (°C) at max. yield	175	172	157

[a] Reaction conditions - substrate solution pumped at 0.2 mL/min, ambient pressure, fixed bed of alumina catalyst (tubular reactor, internal volume 10 mL), temperature ramped linearly at 0.2 °C/min.

of temperature ramp experiments similar to those conducted for Table 1 were undertaken but with various DMC:**4** molar ratios. The results are summarized in Table 2 and full temperature−composition plots can be found in the Supporting Information (ESI-4).

Table 2 shows that increasing the amount of DMC also increased the overall yield of **4b** and lowered the temperature needed to achieve this yield. However increasing the amount of DMC also lowers the temperature at which formation of **4e** occurs and hence reduces the temperature window over which the reaction is selective towards methylation, reinforcing the trend shown in Figure 3. A possible reason for this trend is that the reaction temperature (170 °C) is lower than the boiling point of 2-octanol (181 °C); thus, increasing the proportion of DMC in the feed may also increase the amount of **4** which is in the gas phase which might enhance the dehydration of **4** to **4e**. Another possible explanation is that by increasing the DMC loading (i.e., reducing the concentration of **4** in the feed) one reduces the amount of time (and hence length of the catalyst bed) required in the reactor to convert **4** fully to **4b**. Thus, if **4b** is not stable under the reaction conditions, it might undergo cracking as it passes through the remainder of the catalytic bed to produce **4e**, as shown by the experiments described in the next section. This might explain why there is a sharp increase in the yield of **4e** shortly after the DMC concentration exceeds the loading required for full conversion of **4**, as shown in Figure 3.

Stability of the Ether Products. Work previously carried out at Nottingham has shown that ethers are not stable at high temperature over solid acids.[21] Gao et al.[22−24] have also observed that 1-alkenes can be produced by cracking 1-ethers over γ-alumina, including the formation of 1-octene from **1b**. Therefore, to determine whether this reaction could be occurring during the methylation of **1** and **4**, temperature ramp experiments were performed using **1**, **4**, **1b**, and **4b** as starting materials in the absence of DMC, and the variation in yield of **1e**/**4e** with temperature is shown in Figure 4.

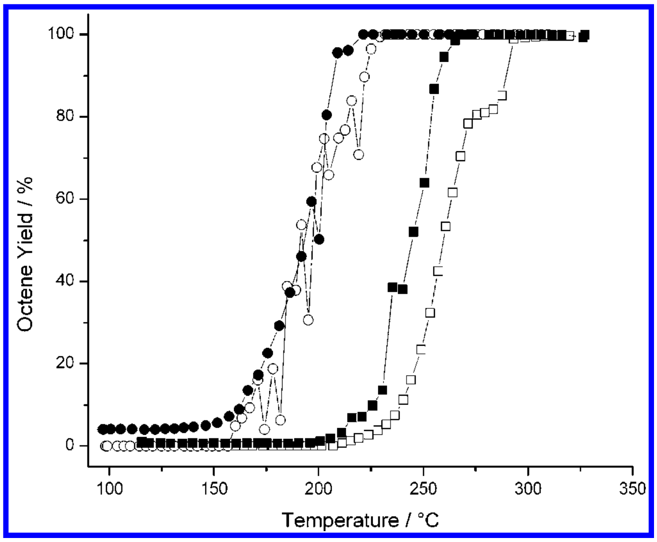


Figure 4. **Plot showing the effect of reactor temperature on the total yield of octenes (1e/4e) from different starting materials. Organic substrates pumped at 0.2 mL/min, 10 cm^3 tubular reactor packed with γ-alumina catalyst, and ambient pressure. Starting materials are as follows: □ 1, ■ 1b, ○ 4, ● 4b.**

Scheme 3. **Possible routes to alkenes during the alkylation of aliphatic alcohols with DACs**

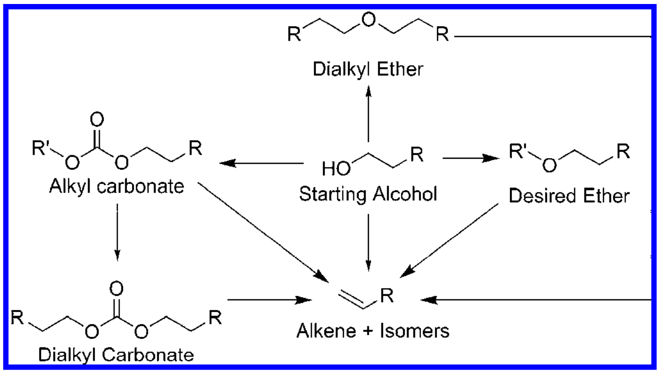


Figure 4 shows that **1e** is formed from both **1** and **1b** at around the same temperature (200 °C); this is also the case for **4** and **4b** although the temperature is lower (160 °C). These temperatures are similar to those observed for octene formation during the methylation reactions of **1** and **4**, supporting the suggestion that the reason why **4e** yield increases with DMC composition as shown in Figure 3 is due to the cracking of the ether product **4b**.

The reason for the large offset in yield of **1e** from **1** and **1b** at temperatures between 225 and 275 °C is the formation of **1f** *via* bimolecular dehydration of **1**. The yield of **1f** during the dehydration of **1** reaches a maximum of around 40% at 250 °C, whereas the yield of the branched dioctyl ether (**4f**) never exceeded 1% during the dehydration of **4**. This is presumably due to the secondary centre in **4f** being less stable than the primary centre in **1f**, and **4f** itself undergoes cracking to **4e**. This formation of linear ethers also contributes to the upper temperature limit for selective methylation with DMC. Thus, the upper temperature for effective alkylation with DACs is probably determined by three effects; the dehydration of the starting materials, the cracking of the ether products, and the decomposition of the DAC. In addition, alkenes may possibly be formed from the decomposition of methyl (or ethyl) alkyl carbonates and DACs *via* pyrolysis,[19,25,26] as illustrated in Scheme 3.

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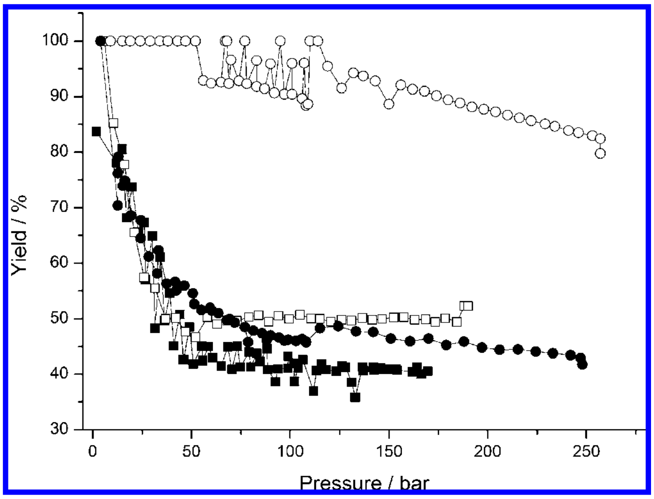

Figure 5. **Plot showing the effect of pressure on the yield of 1b. Solutions of DMC and 1 (2:1 molar ratio) pumped at 0.2 mL/min, 10 cm^3 tubular reactor packed with γ-alumina catalyst, temperature set to 220 °C. Additional solvent key: ○CO_2 pumped at 1.0 mL/min (pump head at −10 °C, 56 bar), □ *n*-heptane pumped at 1.0 mL/min, ■ *n*-pentane pumped at 1.0 mL/min, ● no additional solvent.**

Effect of Pressure and Solvent Medium. Our previous process[20] used high pressure (100 bar) with $scCO_2$ as the solvent, and we obtained similar yields of methyl ethers at very similar temperatures, suggesting that pressure has little effect on the outcome of the reaction. To determine whether this was the case in the absence of CO_2, a solution of **1** and DMC (1:2 molar ratio) was pumped at 0.2 mL/min over a fixed bed of γ-alumina catalyst at 220 °C, and the pressure was gradually increased from 5 to 250 bar.

From Figure 5 it can be seen that when no additional solvent was used, pressure did in fact significantly influence the outcome of the reaction. At 5 bar the yield of **1b** is close to 100% but it rapidly decreased with increasing pressure to be only 50% at 50 bar; and only 40% at 240 bar. Additionally this decrease in yield was found to be due to a decrease in the conversion of **1** and not due to the formation of byproducts. Interestingly the conversion of DMC is unaffected by changing the pressure, but instead of reacting with **1**, it undergoes a thermal catalytic reaction to form DME. The decrease in conversion of **1** with increasing pressure is unexpected because increasing the pressure also increases the overall density of the mixture in the reactor, increasing concentration and residence time which could be expected to increase conversion.

Figure 5 shows that the use of $scCO_2$ in our earlier work[20] enhanced the yield of the methyl ether with ~86% yield at 100 bar with $scCO_2$ compared with only 46% at 100 bar with no solvent. In order to investigate this effect further the pressure ramp experiment was repeated but with an additional stream of CO_2 pumped into the reactor at 1 mL/min, all other conditions were the same as those for the experiment without solvent, and these results are also included in Figure 5. As the pressure was increased from 5 to 125 bar, the yield of **1b** remained around 100% apart from a "noisy" region between 55 and 100 bar which is probably due to the way in which the sample loop withdraws random samples from a multiphasic mixture.[27] As the pressure was increased above 125 bar, there was a gradual decrease in the yield of **1b** from 100 to 85%, and again it was observed that the decrease in yield with increasing pressure was due to a decrease in conversion of **1** rather than to a change in selectivity of the reaction. Thus, the addition of CO_2 clearly has a marked effect on the outcome of the reaction when performed at high pressure and increases the useful pressure range over which effective methylation can be conducted by ~120 bar.

To determine whether this effect was simply due to dilution of the reactants by a solvent, the experiment was repeated with *n*-heptane as the solvent instead of CO_2. From Figure 5, it can be seen that the yield versus pressure trend for *n*-heptane was very similar to that of the experiment with no solvent. This clearly shows that the role of CO_2 is not simply that of a diluent. To determine whether this large decrease in yield with pressure was due to the phase change from vapour to liquid, which occurs at around 13.6 bar at 220 °C for pure *n*-heptane,[28] a similar experiment was conducted but using *n*-pentane. At 220 °C *n*-pentane is above its critical temperature,[28] and so it should not cross through a vapor−liquid phase transition as the pressure is increased in this experiment. Figure 5 shows that the results were very similar to those observed for *n*-heptane. Thus, the effect of CO_2 is probably unconnected with phase changes.

As these experiments are designed to have only a small excess of DMC, if some of the DMC decomposes to form DME instead of reacting with the alcohol, it then becomes impossible for the alcohol to form the methyl ether as there is insufficient methylating agent remaining for 100% conversion. Therefore, any process that accelerates the rate at which DMC is decomposed to DME will reduce the amount of DMC available to react with the alcohol, and hence, the conversion of the alcohol and the yield of the methyl ether will also be reduced. Thus, to explain why the yield of **1b** is reduced at high pressure without the use of CO_2, we propose two possible scenarios either of which could explain why the rate of decomposition of DMC is affected compared to the rate of reaction between substrate and DMC. First, it might be the case that, CO_2 could be reducing the rate at which DMC is decomposing to DME, possibly by blocking the catalytic sites which are responsible for this reaction. This would result in a higher proportion of DMC remaining to react with the alcohol to form the methyl ether in higher yield when CO_2 was the solvent. As the other solvents used may not be able to block or hinder access of DMC to the catalyst surface, they would have little effect on the rate at which DMC decomposes to DME; hence, this could explain why, when the other solvents are used at high pressure, the yield of the ether is lower.

Alternatively if, at high pressure, the rate at which the alcohol or methyl ether adsorbs or desorbs from the catalyst surface is slow, then there will be a lower proportion of the alcohol at the surface for DMC to react with and hence DMC will instead decompose to DME. Therefore it is also possible that CO_2 may

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also affect the rate at which the alcohol/methyl ether adsorbs/desorbs from the catalyst surface and hence increase the rate at which DMC reacts with the alcohol and thus increases the yield of methyl ether.

It should be stressed that neither of these scenarios has yet been tested experimentally and there is no clear evidence to support or refute either. Thus, it is possible that there is an entirely different reason for the trends observed in Figure 5 and we are currently conducting further work to determine the exact role of CO_2. However, the fact remains that our results are consistent with any process that accelerates the rate of decomposition of DMC relative to its rate of reaction with the alcohol.

Conclusion

We have reported a high-yielding, greener route to the continuous synthesis of ethers *via* the reaction of aliphatic alcohols with DACs over a solid acid catalyst. The reaction can be conducted at ambient pressure with no solvent, giving high yields of several primary methyl and ethyl aliphatic ethers whilst requiring only stoichiometric amounts of DMC or DEC. This methodology improves upon previous routes to alkylation of aliphatic alcohols with DACs, which have often been conducted in batch mode with large excesses of the alkylating agent.

Good yields of secondary ethers were also formed using stoichiometric amounts of DACs and were increased further by using a slight excess of DAC. The upper temperature for effective alkylation was restricted by the formation of dehydrated products; these are produced by both the dehydration of the starting alcohols and by the cracking of the ether products.

The use of pressures above 5 bar has negative impact upon conversion of aliphatic alcohols when no solvent was used or when *n*-heptane or *n*-pentane was used as solvent. However, when CO_2 was used as the solvent, high yields of the methyl ether could be obtained at pressures up to 125 bar and reasonable yields even at 250 bar. This means that, by using CO_2, this reaction procedure has the flexibility to be integrated more easily into an existing process which requires the use of high pressure.

Experimental Section

CAUTION! The experiments described in this paper involve the use of relatively high pressures and require equipment with the appropriate pressure rating.

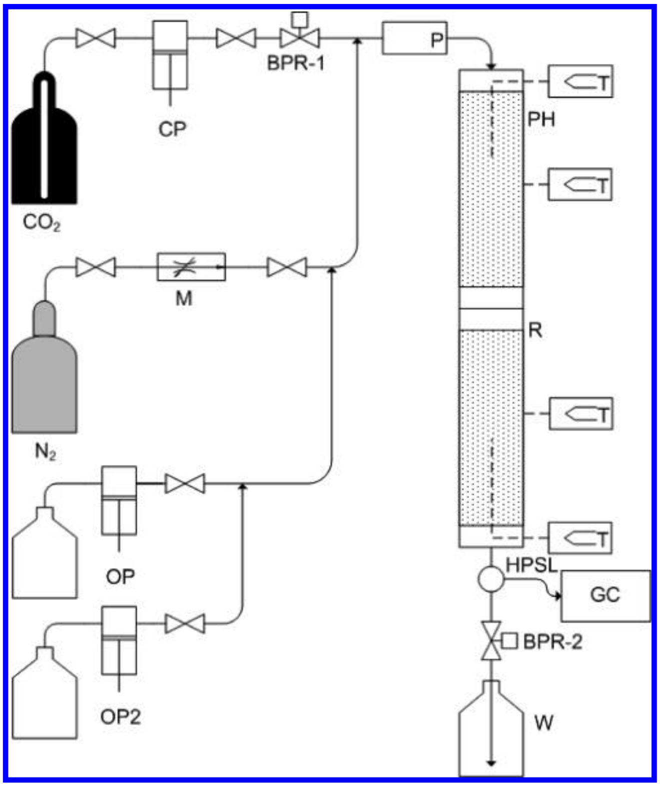

Figure 6. **Schematic of the automated supercritical flow reactor developed at the University of Nottingham. The reactant solutions are pumped by two HPLC pumps (OP and OP2), and CO_2 is pumped by a chilled CO_2 pump (CP), which is connected to a back pressure regulator (BPR) which allows pressures below that of the cylinder to be investigated. The N_2 flow is regulated by a mass flow controller (M), the streams are then mixed in a heated mixing unit (PH) and passed over a heated fixed catalyst bed (R). The system pressure is controlled by another back pressure regulator (BPR-2), and the products are collected once the pressure is released in a collection vessel (W). Whilst the product stream is flowing from the exit of R to the BPR, the high pressure sample loop (HPSL) can remove aliquots of the product mixture and introduce them directly into the carrier gas stream of the gas liquid chromatograph (GC) for analysis.**

Figure 6 shows a simplified schematic of the automated supercritical flow reactor. This system is a modified version of the one described previously,[20,21] and only a brief overview of the equipment will be provided here. A programmable HPLC CO_2 pump (Jasco PU-1580-CO2), two programmable liquid HPLC pumps (Jasco PU-980) and a nitrogen mass flow controller (Brooks Instrument 5850TR) were connected to a 10 mL 316 stainless steel tube (156 mm ×12 mm OD) packed with sand. This first tube acts as both mixer and preheater and directly feeds the fixed bed reactor, which consists of a 10 mL 316 stainless steel tube (156 mm ×12 mm OD) packed with catalyst. The preheater and reactor tubes are heated by cartridge heaters within an aluminium heating block and the temperature controlled *via* a programmable heating controller (Eurotherm 2216). There were two programmable BPRs (Jasco BP-1580−81) present in the system the first was placed in between the outlet of the CO_2 pump and the inlet of the preheater and was permanently set to 70 bar, allowing pressures below that of the CO_2 cylinder to be investigated. The second BPR was placed at the outlet of the system to control the system pressure. The setup uses an online sample loop (VICI EPCI4W.06, 0.06 mL, micro-electronically actuated, 250 ms switching time) which is positioned upstream of the expansion system to allow direct sampling of the product stream *via* GLC analysis using a Shimadzu GC-14B equipped with a CP-Sil 8 CB column (Varian, 30 m, 0.25 mm I.D., 0.25 μm F.T.) using H_2 carrier gas and a flame ionisation detector. This sampling provides a method to obtain an instantaneous ‘snapshot’ of the reaction products at the current reactor conditions. The identity of compounds was confirmed by injection of authentic samples and by GLC-MS using a Thermo-Finnigan Polaris-Q instrument fitted with a RTX-1MS column (30 m, 0.25 mm ID, 0.25 μm FT). Reaction conditions are monitored using a PicoLog TC-08 connected to thermocouples positioned internally and externally on the reactor and to the pressure transducers located within the HPLC pumps and the BPRs.

In a typical experiment, the catalyst was loaded in the reactor and sealed into the apparatus. The initial conditions for the experiment were set at the pumps, BPR, and temperature controllers, and the system was allowed to equilibrate over at least 30 min. The experimental parameters were then programmed into pumps, BPR, temperature controllers, and GLC such that samples are injected into the GLC periodically as one or more reaction parameters (e.g., temperature and pressure) were varied.

For all the reactions conducted at ambient pressure, BPR-2 was removed from the system and the outlet from HPSL directly fed into W. The back pressure required to pump the reagents through the pipe work was measured at the pumps and never exceeded 2 bar.

A commercially available acidic PURALOX NWa-155 γ-alumina (Supplied by Sasol; powder, 150 m^2/g surface area and containing trace impurities of SiO_2, Fe_2O_3, and Na_2O) was used as a catalyst in all experiments. Dimethyl carbonate 99% (Acros Organics), diethyl carbonate 99% (Acros Organics), 1-pentanol 99% (Acros Organics), 2-pentanol 99% (Alfa Aesar), 1-octanol 99% (Sigma-Aldrich), 2-octanol 97% (Acros Organics), 1-decanol 99% (Acros Organics), N_2 99.998% (BOC), and CO_2 99.9% (Cryoservice) were used without further purification. 1-Methoxyoctane 96% and 2-methoxyoctane 92% were obtained by fractional distillation at reduced pressure of the products collected at the end of methylation experiments of 1-octanol and 2-octanol, respectively; the ethers were obtained as a colourless liquid, and the purity was analysed by GLC.

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Supporting Information Available

This material is available free of charge via the Internet at http://pubs.acs.org.

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