

# Synthesis of dialkyl ethers by decarboxylation of dialkyl carbonates

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Received 2nd June 2008, Accepted 1st August 2008

First published as an Advance Article on the web 1st October 2008

DOI: 10.1039/b809271k

The decarboxylation reaction of dialkyl carbonates to give their related ethers was investigated. The reaction was carried out at atmospheric pressure and in the presence of hydrotalcite or basic alumina as catalysts without any solvent. The influence of several reaction parameters on the selectivity was studied (*e.g.* temperature, amount of catalyst, substrate concentration, solvent). The stability of the catalyst was also investigated. The experimental data for the decarboxylation confirmed that this reaction is complicated by competitive processes, such as *dismutation* and, in one case, pyrolysis. The results obtained show that in the presence of hydrotalcite as a catalyst, symmetrical dialkyl ethers can be synthesised with yields up to 80%. Dissymmetrical ethers (*i.e.* methyl alkyl ethers) can be produced with yields up to 80% at high temperature (250 °C). The catalyst proved to be fully recyclable in all cases studied, except for the carbonate containing *n*-octyl moiety.

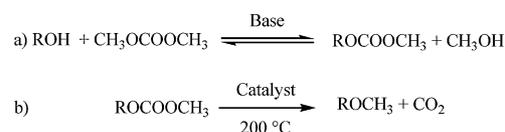
## 1. Introduction

Methylations are extremely important reactions in synthetic organic chemistry. Typically methylations are carried out using methyl halides or dimethyl sulfate. Both reagents are toxic and corrosive chemicals. Moreover the reaction requires a stoichiometric amount of a base as catalyst and produces a stoichiometric amount of inorganic salts that need to be disposed of. Dimethyl carbonate (DMC) is an environmentally benign substitute for dimethyl sulfate and methyl halides.<sup>1-4</sup> In fact, at temperatures higher than 150 °C, it acts as a methylating agent, producing CO<sub>2</sub> and methanol as the only by-products. DMC reacts in the presence of a base with nucleophiles, such as anilines,<sup>1</sup> phenols<sup>2</sup> and methylene-active compounds,<sup>3</sup> to yield, at reflux temperature, their mono-methyl derivatives, according to a B<sub>Al</sub>2 mechanism.<sup>4</sup> Under similar conditions, the reaction of alcohols with DMC gives only the transesterification product (B<sub>Ac</sub>2 attack).<sup>5</sup>

Recently we reported the synthesis of methyl ethers in high yield from the reaction of their parent alcohols with DMC by operating in the presence of catalysts (such as hydrotalcite or basic alumina) at 200 °C.<sup>6</sup>

Scheme 1 reports a possible reaction mechanism for the reaction. Presumably, under basic catalysis the carbonate derivative forms first and would then decarboxylate to the corresponding methyl ether.

This methylation procedure requires a large excess of DMC, which is used as solvent and reagent, and produces dimethyl ether as by-product. In this paper, we aim to investigate the two step synthesis of dialkyl ethers and in particular of alkyl methyl ethers, from their parent alcohols. Thus, according to



Scheme 1 Methylation of alcohols with DMC.

Scheme 1, a selection of dialkyl carbonates (Fig. 1) has been synthesised using only stoichiometric amounts of DMC. Then the decarboxylation reaction of the isolated products was investigated in the presence of catalysts and without any solvent. The influence of several reaction parameters on the selectivity was studied.

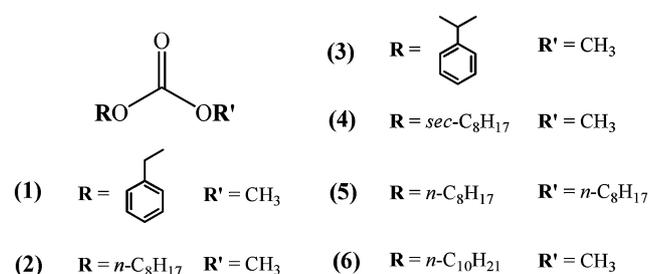


Fig. 1 Investigated dialkyl carbonates.

The advantages of this approach is that DMC is employed only in stoichiometric amounts and the catalyst of the decarboxylation reaction can be recycled.

## 2. Result and discussion

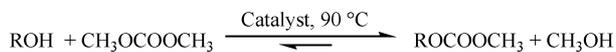
### 2.1 Decarboxylation of primary alkyl derivatives: benzyl methyl carbonate (1) and 1-octyl methyl carbonate (2)

Benzyl methyl carbonate (1) and 1-octyl methyl carbonate (2) were synthesised by transesterification with DMC from their

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parent alcohols (benzyl alcohol and 1-octanol, respectively) under reflux conditions (90 °C), in the presence of hydrotalcite KW2000 ( $\text{Mg}_{0.7}\text{Al}_{0.3}\text{O}_{1.15}$ )<sup>7</sup> or  $\text{K}_2\text{CO}_3$  as catalyst (Scheme 2), according to the procedure already reported in the literature<sup>5a</sup> or described in the Experimental.



**Scheme 2** Synthesis of alkyl methyl carbonates.

The isolated carbonates **1** and **2** were then subjected to decarboxylation. In a typical experiment the alkyl methyl carbonate was added through a funnel to the catalyst pre-heated at the given reaction temperature without any solvent present. Either basic alumina or activated hydrotalcite KW2000 was used as the catalyst.

The results obtained at 180 °C and 200 °C are reported in Table 1 for compound **1** and in Table 2 for compound **2**.  $\text{K}_2\text{CO}_3$ -catalysed reactions were also performed for comparison. When the reaction was catalysed by alumina or hydrotalcite, the two carbonates **1** and **2** were converted into their methyl and dialkyl ethers (entries 1–4, Tables 1 and 2).

For benzyl methyl carbonate, the KW2000-catalysed reaction was complete at 180 °C after 30 minutes (entry 3, Table 1), while the alumina-catalysed reaction needed higher temperature (200 °C) to achieve an almost quantitative conversion (entry 2, Table 1). For the benzyl methyl carbonate **1**, KW2000 was more effective as a catalyst than alumina in the synthesis of symmetrical ethers. For both the substrates **1** and **2**, temperature seemed to have just a little effect on the outcome of the reactions.

As expected, no methylether products were observed for the  $\text{K}_2\text{CO}_3$ -catalysed reactions (entries 5 and 6, Tables 1 and 2).

## 2.2 Decarboxylation of secondary alkyl derivatives: 1-phenylethyl methyl carbonate (**3**) and 2-octyl methyl carbonate (**4**)

In order to study the reactivity of secondary alcohol derivatives and to investigate the related reaction mechanism, 1-phenylethyl methyl carbonate **3** and 2-octyl methyl carbonate **4** were synthesised by a transesterification reaction with DMC from their parent alcohols (1-phenylethanol and 2-octanol, respectively) and then they were decarboxylated under the same conditions employed for the compounds **1** and **2**.

The results are shown in the Tables 3 and 4, respectively.

Also in this case, when the reaction was catalysed by alumina or hydrotalcite, the two secondary carbonates were converted into the methylether products (entries 1–4, Tables 3 and 4). For 1-phenylethyl methyl carbonate **3**, the KW2000-catalysed reaction was complete at 180 °C (entries 3, Table 3), while the alumina-catalysed reaction required a higher temperature (200 °C) to achieve an almost quantitative conversion (entry 2, Table 3). However, in all the experiments a considerable amount of symmetrical ethers was also observed. Methylether products were not observed for the  $\text{K}_2\text{CO}_3$ -catalysed reactions (entries 5 and 6, Table 3 and 4).

In the decarboxylation of 1-phenylethyl methyl carbonate (Table 3) styrene was also formed as by-product. In this regard, two possible reaction pathways leading to the olefin may be envisaged: (i) the base-promoted elimination of methyl carbonate  $\text{CH}_3\text{OCOO}^-$  from the reagent carbonate, and (ii) the pyrolysis of the methyl carbonate (Tschugaev's reaction) with

**Table 1** Decarboxylation of benzyl methyl carbonate **1**; Scheme 3<sup>a</sup>

	Catalyst	<i>T</i> /°C	Conv. (%)	Product distribution (GC-MS %) R = PhCH <sub>2</sub>			
				ROME	ROR	ROCOOR	ROH
1	Al <sub>2</sub> O <sub>3</sub> (10%) <sup>b</sup>	180	71	22	38	26	10
2	Al <sub>2</sub> O <sub>3</sub> (10%) <sup>b</sup>	200	92	31	48	13	4
3	KW2000 (10%) <sup>b</sup>	180	100	31	66	—	—
4	KW2000 (10%) <sup>b</sup>	200	100	29	71	—	—
5	K <sub>2</sub> CO <sub>3</sub> (1.2 eq.)	180	47	—	—	67	26
6	K <sub>2</sub> CO <sub>3</sub> (1.2 eq.)	200	59	—	—	74	26

<sup>a</sup> Reaction conditions: Reaction time: 30 min. <sup>b</sup> **1**/catalyst 1.0 : 0.1 (w/w).

**Table 2** Decarboxylation of 1-octyl methyl carbonate **2**; Scheme 3<sup>a</sup>

	Catalyst	<i>T</i> /°C	Conv. (%)	Product distribution (%) R = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub>			
				ROME	ROR	ROCOOR	ROH
1	Al <sub>2</sub> O <sub>3</sub> (10%) <sup>b</sup>	180	80	20	3	67	11
2	Al <sub>2</sub> O <sub>3</sub> (10%) <sup>b</sup>	200	81	24	4	62	9
3	KW2000 (10%) <sup>b</sup>	180	92	21	5	63	11
4	KW2000 (10%) <sup>b</sup>	200	100	23	23	45	9
5	K <sub>2</sub> CO <sub>3</sub> (1.2 eq.)	180	14	—	—	100	—
6	K <sub>2</sub> CO <sub>3</sub> (1.2 eq.)	200	49	—	—	100	—

<sup>a</sup> Reaction conditions: Reaction time 30 min. <sup>b</sup> **2**/catalyst 1.0 : 0.1 (w/w).

**Table 3** Decarboxylation of 1-phenylethyl methyl carbonate **3**; Scheme 3<sup>a</sup>

Catalyst	<i>T</i> /°C	Conv. (%)	Product distribution (%) R = Ph (Me)CH				
			ROME	ROR	ROCOOR	ROH	Styrene
1 Al <sub>2</sub> O <sub>3</sub> (10%) <sup>b</sup>	180	74	37	12	3	17	29
2 Al <sub>2</sub> O <sub>3</sub> (10%) <sup>b</sup>	200	96	34	12	—	11	38
3 KW2000 (10%) <sup>b</sup>	180	98	23	25	9	19	24
4 KW2000 (10%) <sup>b</sup>	200	100	24	32	—	19	25
5 K <sub>2</sub> CO <sub>3</sub> (1.2 eq.)	200	63	—	—	80	10	10

<sup>a</sup> Reaction conditions: Reaction time 30 min. <sup>b</sup> **3**/catalyst 1.0 : 0.1 (w/w).

**Table 4** Decarboxylation of 2-octyl methyl carbonate **4**; Scheme 3<sup>a</sup>

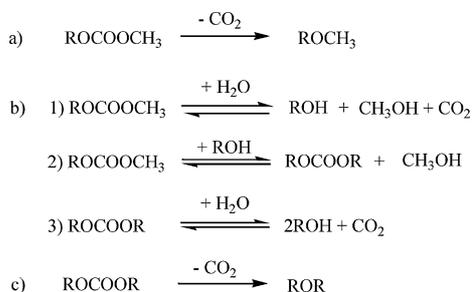
Catalyst	<i>T</i> /°C	Conv. (%)	Product distribution (%) R = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CHCH <sub>3</sub>			
			ROME	ROR	ROCOOR	ROH
1 Al <sub>2</sub> O <sub>3</sub> (10%) <sup>b</sup>	180	19	21	—	33	42
2 Al <sub>2</sub> O <sub>3</sub> (10%) <sup>b</sup>	200	24	28	—	28	39
3 KW2000 (10%) <sup>b</sup>	180	85	24	—	73	3
4 KW2000 (10%) <sup>b</sup>	200	100	35	4	53	7
5 K <sub>2</sub> CO <sub>3</sub> (1.2 eq.)	180	15	—	—	3	53
6 K <sub>2</sub> CO <sub>3</sub> (1.2 eq.)	200	10	—	—	100	—

<sup>a</sup> Reaction conditions: Reaction time 30 min. <sup>b</sup> **4**/catalyst 1.00:0.10 (w/w).

elimination of methylcarbonic acid; both rapidly decompose in CO<sub>2</sub> and methanol. However the formation of 1- or 2-octene was never observed (Table 2 and 4) in the reactions where **2** and **4** were used as substrates. The absence of any elimination by-product in these reactions demonstrates that the elimination reaction is not base-promoted, thus the styrene production is probably due only to pyrolysis reaction.

### 2.3 The reaction pathway

These preliminary results show that different and competitive processes might be involved in the decarboxylation of methylcarbonates: Scheme 3 reports a possible reaction pathway. According to the proposed mechanism, the presence of the symmetric ethers in the reaction mixture might be due to a



**Scheme 3** Competitive processes involved in the decarboxylation of alkyl methyl carbonates: (a) decarboxylation of methyl carbonates; (b) *dismutation* via transesterification (trace of methanol, due to the presence of a small amount of water, or other Brønsted acids catalyse the reaction); (c) decarboxylation of the dialkyl carbonates. Steps b1, b2 and b3 are equilibrium reactions; steps a and c are not equilibrium reactions.

*“dismutation reaction”*. In this case, the term *dismutation* is not used in the conventional redox sense; it is used instead to indicate the transformation of an alkyl methyl carbonate into dimethylcarbonate and the corresponding dialkylcarbonate.

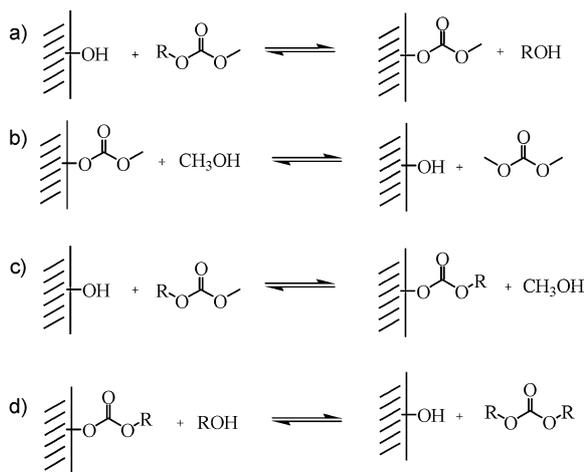
Scheme 4 describes some possible reaction pathways for the *“dismutation”* reaction catalysed by the surface hydroxyls of the catalyst. In fact, transesterification, which leads to the symmetrical carbonate, might be due to the presence of acidic hydroxyl moieties in the catalyst: hydrolysis or methanolysis of the methyl carbonates gives the alcohol, which reacts with the initial carbonate to form the symmetrical carbonates.

The acidic hydroxyl moieties of the catalyst might play a crucial role, since they are the catalysts for the transesterification reaction, too. Catalytic amounts of methanol (or water) might be sufficient to initiate these side processes since the methanol produced can react once again with the carbonate in a self-sustaining process. These acidic hydroxyls, being real catalysts, do not enter into the stoichiometry of the overall reaction.

The driving force for this *dismutation* reaction, which produces the symmetrical ethers as the final products, might be the formation of DMC (always present in significant amounts in the distillate, see Experimental) or methanol, both removed by evaporation from the reaction mixture at the given temperatures.

In order to understand the correlation between the acidic hydrogen of the catalyst hydrotalcite and the observed transesterification behavior which yields symmetrical ethers, IR analysis was performed on the catalyst after different heating activation methods.

The IR spectrum of untreated hydrotalcite (KBr pellet) showed the broad absorption band for the OH stretching around 3400 cm<sup>-1</sup> and the corresponding HOH bending at 1630 cm<sup>-1</sup>, along with the typical band at 1363 cm<sup>-1</sup> attributable to the



Total reaction (*dismutation*):



**Scheme 4** Dismutation of methyl alkyl carbonates. Due to the presence of acidic hydroxyls on the surface of the catalyst, transesterification reactions occur: methanol and alcohol are released which, in turn, produce, through a series of equilibria reactions, DMC and the symmetrical dialkyl carbonate. The overall reaction (addition of routes *a*, *b*, *c* and *d*) is shown.

interlayer anions  $\text{CO}_3^{2-}$ . By heating the pellet at 200 °C for two hours under vacuum, interlayer water was removed from the hydrotalcite, as shown by the lost of the band at 1630  $\text{cm}^{-1}$  and the decrease in the intensity of the band at 3400  $\text{cm}^{-1}$ . However, after a few seconds in the air, the intensity of the latter band rapidly increased.

In a separate experiment, the pellet was heated under vacuum at 450 °C for 1.5 hours in a quartz tube, equipped with a  $\text{CaF}_2$  window, which allowed recording of the IR spectrum without opening the system. The spectrum shows that this treatment completely removed not only the interlayer water and carbonate groups, but also surface hydroxyl groups. However, a very short exposure to air by opening the tube immediately restored the lost water. Such results showed that, if the decarboxylation reaction is performed under atmospheric air, heat activation may not ensure the complete absence of water on the catalyst surface. And, even when the interlayer water is completely removed, hydrolysis and transesterification reactions may also occur, due to the hydroxyl groups which are not affected by the treatment at 200 °C.

#### 2.4 Effect of the temperature and of the amount of catalyst

In order to improve the yield of the decarboxylation over the other competing pathways, the influence of some reaction parameters was investigated. In a first set of experiments, the decarboxylation of 1-octyl methyl carbonate **2** was performed using varying amounts of catalyst. In particular, the reaction was carried out using an amount of KW2000 ranging from 10% to 50% w/w. Results reported in Table 5 show that no relevant improvement was obtained increasing the catalyst/substrate ratio. On the contrary, higher ratio of catalyst increased the viscosity of the reaction, strongly impairing the stirring.

**Table 5** Decarboxylation of 1-octyl methyl carbonate **2** with different substrate/catalyst ratio

	KW2000 (%) <sup>a</sup>	Conv. (%)	Product distribution (%) R = $\text{CH}_3(\text{CH}_2)_7$			
			ROME	ROR	ROCOOR	ROH
1	10	100	23	32	34	9
2	25	100	27	63	1	6
3	50	100	33	54	2	9

<sup>a</sup> Reaction time: 30 min.  $T = 220$  °C.

In addition, the decarboxylation reactions on 1-octyl methyl carbonate **2** and 2-octyl methyl carbonate **4** were performed varying the temperature from 180 °C to 250 °C. In all cases the reaction time was 30 minutes and KW2000 was used as a catalyst.

The results, reported in Table 6, showed that performing the reaction at different temperatures did not affect the conversion, which is complete in every case, except when the reaction was carried out at 180 °C. There is, however, a little effect on the selectivity to 1-octyl methyl ether.

The yield of 1-octyl methyl ether increased at high reaction temperatures, although not significantly. The most important effect observed was the complete decarboxylation of the intermediate dioctyl carbonate into dioctyl ether.

Table 7 reports the results of the decarboxylation of 2-octyl methyl carbonate **4**. Also in this case, no major differences in the reaction outcome were observed. However, the yields of the methyl and dialkyl ether are slightly increased, whilst the yield of dialkyl carbonate decreased.

**Table 6** Decarboxylation of 1-octyl methyl carbonate **3** at different temperatures<sup>a</sup>

	$T/^\circ\text{C}$	Conv. (%)	Product distribution (%) R = $\text{CH}_3(\text{CH}_2)_7$			
			ROME	ROR	ROCOOR	ROH
1	180	92	21	5	63	11
2	200	100	23	23	45	9
3	220	100	23	32	34	9
4	240	99	27	68	0	1
5	250	100	28	70	0	2

<sup>a</sup> **3**/KW2000 1.00 : 0.10 (w/w). Reaction time: 30 min.

**Table 7** Decarboxylation of 2-octyl methyl carbonate **4** at different temperatures<sup>a</sup>

	$T/^\circ\text{C}$	Conv. (%)	Product distribution (%) R = $\text{CH}_3(\text{CH}_2)_5\text{CHCH}_3$			
			ROME	ROR	ROCOOR	ROH
1	180	85	24	0	73	3
2	200	100	35	4	53	7
3	220	100	44	13	27	13
4	240	100	53	24	0	21
5	250	100	53	31	0	14

<sup>a</sup> **4**/KW2000 1.00 : 0.10 (w/w). Reaction time: 30 min.

**Table 8** Decarboxylation of *n*-decyl methyl carbonate at different concentrations<sup>a</sup>

	Solvent	Substrate conc.	Conv. (%)	Product distribution (%) R = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>			
				ROMe	ROR	ROCOOR	ROH
1	no solvent	—	100	55	27	10	7
2	<i>n</i> -dodecane	1.2 M	100	45	42	0	13
3	<i>n</i> -dodecane	0.015 M	98	52	10	14	22

<sup>a</sup> *T* = 216 °C; KW2000 10%; reaction time: 30 minutes.

## 2.5 Effect of the substrate concentration

*n*-Dodecane was chosen as a non-polar solvent to explore the effect of the substrate concentration (if any); the decarboxylation of *n*-decyl methyl carbonate **6**, chosen as a test reaction, was carried out at the reflux temperature of the solvent, 216 °C. The results obtained for the two studied concentrations (1.2 and 0.015 M) are reported in Table 8. Entry 1 reports, for comparison, the result obtained from the reaction performed at 216 °C in the absence of solvent.

Table 8 shows that dilution does not considerably influence the yield of 1-decyl methyl ether, which is formed in about 50% yield in all cases.

## 2.6 Effect of the solvent

Because solvent polarity very often affects the reaction outcome, the decarboxylation was carried out in different solvents. In this case, a standard procedure using different solvents was used (see Experimental): the decarboxylation reaction was carried out by slow dropwise addition of the *n*-decyl methyl carbonate to the refluxing solvent. Accordingly, experiments were conducted using different solvents at their respective refluxing temperature. Table 9 reports that the selectivity to the methyl ether dramatically increased with respect to the same reaction performed by the bulk addition of the substrate (compare Table 8 to entry 2 of Table 9).

Using *n*-dodecane as the solvent at 1.2 M substrate concentration, the yield of *n*-decyl methyl ether increased from 45% (Table 8, entry 2) to 78% (Table 9, entry 2). The yield of the methyl ether was even higher (80%, entry 3, Table 9) in refluxing *n*-tetradecane (b.p. 252 °C), while slightly lower (67%, entry 1) in refluxing *trans*-decaline (b.p. 190 °C). No reaction was observed with polar aprotic solvents, such as polyethyleneglycol dimethylether (PEG 250 DME) and tri-

ethyleneglycol dimethylether (triglime). Probably, such polar solvents inhibit the absorption of the polar compounds on the catalyst, preventing the reaction from occurring. *Vice versa*, the non polar solvents, by allowing the absorption on the catalyst, promote the reaction.

Since all the non polar solvents used have a similar hydrocarbon structure, the different yields observed may be attributed to the temperature. This might indicate that the activation energy of the decarboxylation reaction is higher than that of the transesterification, since increasing the temperature (from 190 to 252 °C), increased the yield of the methyl ether (from 67 to 80%).

## 2.7 Decarboxylation of di-1-octylcarbonate (5)

Finally, in order to avoid the production of undesired by-products *via* the *dismutation* pathway, the decarboxylation of a symmetrical dialkyl carbonate was also carried out. The reaction was performed in the absence of solvent; this should give the corresponding ether only. Thus, a set of experiments was performed using di-1-octyl carbonate as the substrate at different temperatures (Table 10).

The effect of temperature on the conversion was evident. Conversion reached a plateau at 240 °C. As expected, the yield of dioctyl ether increases by increasing temperature, while the yield of 1-octanol dramatically decreases. The results support the idea that decarboxylation is highly dependent on the temperature, due to its high activation energy.

## 2.8 Catalyst stability and recycling

The stability of the catalyst is also an important parameter. Fig. 2 shows the data obtained performing the decarboxylation reaction of di-1-octyl carbonate **5** at different reaction times. After two hours the reaction shows no significant improvement

**Table 9** Decarboxylation of *n*-decyl methyl carbonate **6** by dropwise addition to refluxing solvents containing the catalyst<sup>a</sup>

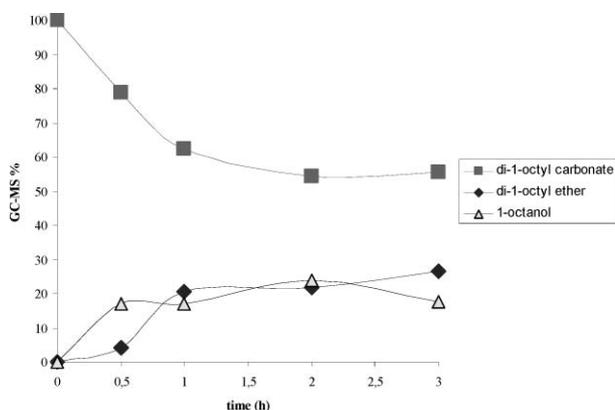
	Solvent	Reflux <i>T</i> /°C	Conv. (%)	Product distribution (%) R = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>			
				ROMe	ROR	ROCOOR	ROH
1	<i>trans</i> -decaline	190	98	67	21	—	10
2	<i>n</i> -dodecane	216	100	78	21	—	1
3	<i>n</i> -tetra decane	252	100	80	20	—	—
4	PEG 250 DME <sup>b</sup>	220	4	—	1	—	1
5	Triglime	216	9	—	—	—	9

<sup>a</sup> 1.2 M *n*-decyl methyl carbonate added dropwise; KW2000 10%; reaction time: 30 minutes after complete addition. <sup>b</sup> Poly(ethylene glycol) dimethyl ether, average *M<sub>n</sub>* ~ 250; b.p > 250 °C.

**Table 10** Decarboxylation of di-1-octyl carbonate **5** at different temperatures<sup>a</sup>

	<i>T</i> /°C	Conv. (%)	Product distribution (%) R = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub>	
			ROR	ROH
1	180	21	20	80
2	200	57	63	35
3	220	71	79	21
4	240	98	84	14
5	250	94	82	18

<sup>a</sup> Reaction condition: **5**/KW2000 1.00 : 0.10 (w/w). For other reaction conditions see footnotes of Table 6.

**Fig. 2** Decarboxylation of dioctyl carbonate **5** with time. Reaction conditions: dioctyl carbonate/KW2000 1.00 : 0.10 (w/w). *T* = 180 °C.

on conversion; this can be attributed to possible deactivation of the catalyst.

In order to investigate the origin of such a deactivation, a few tests for the re-use of the catalyst were carried out. After the reaction, KW2000 was regenerated by washing with diethyl ether and then dehydrated in an oven at 100 °C or in a muffle oven at 500 °C; the latter treatment is the general condition used to activate the catalyst in all the experiments so far reported (see Experimental). In Table 11, the results obtained with some of the carbonates previously investigated: an aliphatic substrate **2**, an aromatic substrate **3**, and a secondary aliphatic substrate

**4**, are shown. The recovered catalyst was reused with the same carbonate for which it was originally tested.

The tests show that the catalyst is not regenerated completely when treated at 100 °C (entries 6 and 9), while it is regenerated by treatment at 500 °C (entries 7 and 10), except in the case of octyl methyl carbonate **3** (entries 2 and 4). The structure and the texture of hydrotalcite is not affected by the treatment, and its activity remains unaffected.

The results given by the C<sub>8</sub> moiety are quite interesting. In fact, after 100 °C treatment (entry 2) while the conversion is not significantly changed, the efficiency of the catalyst dramatically decreased. Visible changes (from white to dark black) were observed after treatment at 500 °C, due to carbon formation.

This behaviour might show that the cavities of hydrotalcite are particularly suited to the 1-octanol generated in the reaction, which is difficult to remove by washing and cracks during heat treatment. The affinity of 1-octanol for the catalyst cavities might also be the cause of its deactivation depicted in Fig. 2.

The only method possible for the removal of the 1-octanol from the KW2000 cavities was to wash the catalyst in diethylether using a sonicator bath.

### 3. Conclusions

The synthesis of ethers from the parent carbonates has been reported utilizing basic alumina and hydrotalcite as catalysts; the latter proved to be the best catalyst. Dimethyl carbonate was used only in a stoichiometric amount for the conversion of the alcohols to carbonates. The reaction can be carried out at atmospheric pressure and with no solvent.

In such a two step procedure, and starting from alkyl methyl carbonates, the reaction becomes complicated by the presence of symmetrical dialkyl carbonates and the corresponding dialkyl ethers as by-products.

This is due to the presence of acidic hydrogens (water, alcohols, and surface hydroxyls) which allow the organic carbonates to give transesterified compounds which produce the symmetrical ethers; this process is controlled also by the boiling points of the alkyl carbonates involved, since DMC is removed by distillation from the reaction mixture.

Dissymmetrical ethers (*i.e.* methyl alkyl ethers) can be obtained in good yield if the reactions are carried out at high

**Table 11** Recycling test. Decarboxylation of compound **2**, **3** and **4**, for each carbonate the reaction with both recycled and new catalyst<sup>a</sup>

	Substrate	Catalyst origin	Conv. (%)	Product distribution (%)				
				ROME	ROR	ROCOOR	ROH	Styrene
1	<b>2</b>	new <sup>b</sup>	92	21	5	63	11	NA
2	<b>2</b>	recycled (100 °C)	89	0	0	100	0	NA
3	<b>2</b>	new (100 °C)	77	0	0	83	17	NA
4 <sup>c</sup>	<b>2</b>	recycled (500 °C)	—	—	—	—	—	—
5	<b>3</b>	new <sup>d</sup>	98	23	25	9	19	24
6	<b>3</b>	recycled (100 °C)	54	14	4	54	21	8
7	<b>3</b>	recycled (500 °C)	96	24	18	28	16	13
8	<b>4</b>	new <sup>e</sup>	85	24	0	73	3	NA
9	<b>4</b>	recycled (100 °C)	58	14	7	71	10	NA
10	<b>4</b>	recycled (500 °C)	82	21	0	57	9	NA

<sup>a</sup> Reaction conditions: *T* = 180 °C. Reaction time: 30 min; carbonate/catalyst 1.00 : 0.10 (w/w). Data given as GC%. NA: not applicable. <sup>b</sup> Entry 3 Table 2. <sup>c</sup> The reaction was not performed due to blackening of the catalyst. <sup>d</sup> Entry 3 Table 3. <sup>e</sup> Entry 3 Table 4.

temperature. High temperature favours the decarboxylation over the “*dismutation*” reaction and methyl ethers can be obtained in high yield.

A possible reason for this temperature effect is that entropic factors facilitate the elimination of CO<sub>2</sub> at high temperatures, as a consequence of the higher activation energy of the decarboxylation process. The catalyst proved to be fully recyclable in all cases, except with the compound containing the *n*-octyl moiety.

## 4. Experimental

### 4.1 General information

All compounds used were ACS grade and were used without further purification. Al<sub>2</sub>O<sub>3</sub> was from Merck, type 5016A basic standard grade, 150 mesh, no activation. KW2000 was from Kyowa Chemical Industry Co. Tokyo, Mg<sub>0.7</sub>Al<sub>0.3</sub>O<sub>1.15</sub>, specific surface area 202 m<sup>2</sup> g<sup>-1</sup>, activated at 500 °C for 4 hours.

GC-MS analyses were performed at 70 eV (MS) with a 30 m HP 5 capillary GC column.

Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (<sup>1</sup>H, <sup>13</sup>C) were obtained on AVANCE 300 Bruker spectrometers at 25 °C and referred to internal tetramethylsilane.

Basic alumina type 5016A basic standard grade, 150 mesh, was purchased from Merck, and hydrotalcite was a kind gift from Cognis Company.

If not otherwise specified, all the reactions were performed in batch conditions and at atmospheric pressure.

### 4.2 Preparation of methyl carbonates: general procedure, Scheme 2

In a three-necked flask equipped with a dephlegmator, alcohol (30 g), DMC (100 g) and KW2000 (Mg<sub>0.7</sub>Al<sub>0.3</sub>O<sub>1.15</sub>) (30 g) were heated at refluxing conditions (90 °C) under magnetic stirring. Continuous removal of methanol as an azeotropic mixture with DMC (3 : 1 w/w) boiling at 64 °C pushed the equilibrium toward the carbonate. The reaction was followed by GC-MS analysis of the reaction mixture. At complete conversion of the substrate (usually after 24 hours), the mixture was filtered over Gooch no. 4 to remove the solid catalyst, and the solid was washed three times with 100 ml of diethylether. After removal of diethylether, methanol and unreacted DMC by evaporation under vacuum, alkyl methyl carbonate was obtained as a colourless oil.

**1:** 39 g obtained; yield: 85%; b.p.: 68–70 °C/7 torr (lit.<sup>8</sup> 125–127 °C/20 torr); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, lit.<sup>8</sup>): δ 3.81 (s, 3H); δ 5.19 (s, 2H); δ 7.37–7.41 (m, 5H)

**2:** 33 g obtained; yield: 75%; b.p.: 238 °C/760 torr (lit.<sup>9</sup> 73 °C/1 torr); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, lit.<sup>10a</sup>): δ 1.62–1.64 (d, 3H); δ 3.77 (s, 3H); δ 5.73–5.80 (m, 1H); δ 7.32–7.40 (m, 5H)

**3:** 38 g obtained; yield: 88%; b.p. 70 °C/7 torr; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, lit.<sup>10b</sup>): δ 0.86–0.90 (t, 3H); δ 1.27 (m, 10H); δ 1.62–1.70 (m, 2H); δ 3.78 (s, 3H); δ 4.11–4.16 (t, 2H)

**4:** 39 g obtained; yield: 90%; b.p. 45 °C/7 torr; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.89 (t, 3H), δ 1.27–1.29 (m, 8H), δ 1.46–1.55 (m, 2H), δ 1.60–1.65 (m, 2H), δ 3.77 (s, 3H) δ 4.71–4.81 (m, 1H)

**6:** 36 g obtained; yield: 89%; b.p. 75 °C/7 torr; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.86–0.90 (t, 3H); δ 1.27 (m, 14H); δ 1.62–1.70 (m, 2H); δ 3.78 (s, 3H); δ 4.11–4.16 (t, 2H)

### 4.3 Preparation of di-1-octyl carbonate (5)

In a three-necked flask equipped with a dephlegmator, 1-octanol (85 g), 1-octyl methyl carbonate (30 g) and KW2000 (30 g) were heated at 110 °C with magnetic stirrer. The reaction was followed by GC-MS analysis of the reaction mixture. At complete conversion of the substrate, which took place after 5 hours, the mixture was filtered over Gooch no. 4 to remove the catalyst and the solid was washed three times with 100 ml of diethylether. After removal of diethylether and unreacted 1-octanol by distillation under vacuum, the symmetrical carbonate was obtained as colourless oil.

**5:** 37 g obtained; yield: 82%; b.p. 165 °C/7 torr (lit.<sup>11</sup> 168–170 °C/5 torr); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, lit.<sup>12</sup>): δ 0.87–0.91 (t, 6H); δ 1.28 (m, 20H); δ 1.62–1.72 (m, 4H); δ 4.10–4.15 (t, 4H)

### 4.4 Decarboxylation reactions (Tables 1–7 and Tables 9 and 10)

All the decarboxylation reactions were carried out in a three neck round bottom flask at atmospheric pressure. The flask was equipped with a condenser and a dropping funnel. The reactor was heated using a heating jacket and the temperature was controlled by a thermocouple dipped in the reaction mixture through the side neck.

The reactions were carried out in the absence of solvent. The methylcarbonate (2 g) was added dropwise over a 1 minute period through the funnel to the catalyst pre-heated at the reaction temperature (typically at 180 or 200 °C). Basic alumina (0.2 g) or hydrotalcite KW2000 (0.2 g) or K<sub>2</sub>CO<sub>3</sub> (1.2 eq) were used as the catalysts.

Addition of the methylcarbonate substrates to the catalyst produced, in every case, vigorous foaming, due to the rapid evolution of CO<sub>2</sub>. The results obtained performing the decarboxylation reaction on the carbonates **1–6** at 180 °C and 200 °C are reported in Tables 1–7 and Tables 9 and 10, leaving out the value for DMC; however, it was always present in the chromatograms as 15% of total compounds.

### 4.5 Substrate concentration analysis (Table 8)

A round bottom flask was equipped with condenser and two dropping funnels. After heating the catalyst (1.8 g or 0.02 g) at 220 °C, *n*-dodecane (75 mL) was added from the first funnel. When the refluxing temperature of *n*-dodecane was reached (*T* = 216 °C), *n*-decyl methyl carbonate, according to the chosen concentration (18 g or 0.24 g), was quickly added from the second funnel.

### 4.6 Catalyst recycling (Table 11)

After a typical decarboxylation reaction, KW2000 was separated by a paper filter, washed with diethyl ether and submitted to 2 different treatments: dehydration in an oven at 100 °C (entries 2, 5 and 9, Table 11) and reactivation in a muffle oven up to 500 °C (entries 3, 7 and 10, Table 11). The so-treated catalyst

was then re-used performing a reaction exactly as the one from which the catalyst was taken.

## Acknowledgements

This work was supported by the Interuniversity Consortium “La Chimica per l’Ambiente” (Chemistry for the Environment) INCA, and Università “Ca’ Foscari” di Venezia.

## Notes and references

- 1 M. Selva, A. Bomben and P. Tundo, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1041.
- 2 A. Bomben, M. Selva and P. Tundo, *Ind. Eng. Chem. Res.*, 1999, **38**, 2075.
- 3 (a) P. Tundo, G. Moraglio and F. Trotta, *Ind. Eng. Chem. Res.*, 1989, **28**, 881; (b) A. Bomben, C. A. Marques, M. Selva and P. Tundo, *Tetrahedron*, 1995, **51**, 11573; (c) A. Bomben, M. Selva and P. Tundo, *J. Chem. Res. (S)*, 1997, 448.
- 4 (a) P. Tundo, M. Selva, A. Perosa and S. Memoli, *J. Org. Chem.*, 2002, **67**, 1071; (b) S. Memoli, M. Selva and P. Tundo, *Chemosphere*, 2001, **43**, 115; (c) P. Tundo, L. Rossi and A. Loris, *J. Org. Chem.*, 2005, **70**(6), 2219–2224.
- 5 (a) P. Tundo, F. Trotta, G. Moraglio and F. Ligorati, *Ind. Eng. Chem. Res.*, 1988, **27**, 1565; (b) P. Tundo, S. Bassanello, A. Loris and G. Sathicq, *Pure Appl. Chem.*, 2005, **77**(10), 1719.
- 6 P. Tundo, S. Memoli, D. Hérault and K. Hill, *Green Chem.*, 2004, **6**, 609.
- 7 As is well known, hydrotalcite is a synthetic aluminium-magnesium-hydroxycarbonate. Hydrotalcite-like anionic clays are a family of interesting materials with many practical applications as catalysts, catalyst supports, ion exchangers, and composite materials. Natural hydrotalcite,  $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ , structurally similar to brucite,  $Mg(OH)_2$ , is composed of sheets of edge-sharing  $Mg(OH)_6$  and  $Al(OH)_6$  octahedra. Due to isomorphous substitution of  $Al^{3+}$  for  $Mg^{2+}$ , the sheets are positively charged and stacked on top of each other and held together by charge-balancing anions, normally  $CO_3^{2-}$ , and/or hydrogen bonding. The  $Mg^{2+}$  and  $Al^{3+}$  in the sheets can also be isomorphously substituted by other metal ions having two or three positive charges and the  $CO_3^{2-}$  in the interlayer space by other inorganic and organic anions, forming new hydrotalcite-like materials. The general formula can be described as  $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{+}A_{x/n}^{n-} \cdot mH_2O$ , where M denotes metal ions, A denotes exchangeable anions with valence  $n$ , and  $x$  is within 0.17–0.33.
- 8 M. Selva, F. Trotta and P. Tundo, *J. Chem. Soc., Perkin Trans. 1*, 1992, **2**(4), 519.
- 9 Taylor, *J. Chem. Soc. B*, 1971, 622.
- 10 (a) M. Verdecchia, M. Feroci, L. Palombi and L. Rossi, *J. Org. Chem.*, 2002, **67**(23), 828; (b) C. Yu, B. Zhou, W. Su and Z. Xu, *Synth. Commun.*, 2007, **37**(4), 647.
- 11 Fukui *et al.*, *Chem. Abstr.*, 1963, **58**, 2366.
- 12 S. Sakai, Y. Kobayashi and Y. Ishii, *J. Org. Chem.*, 1971, **36**, 1176.