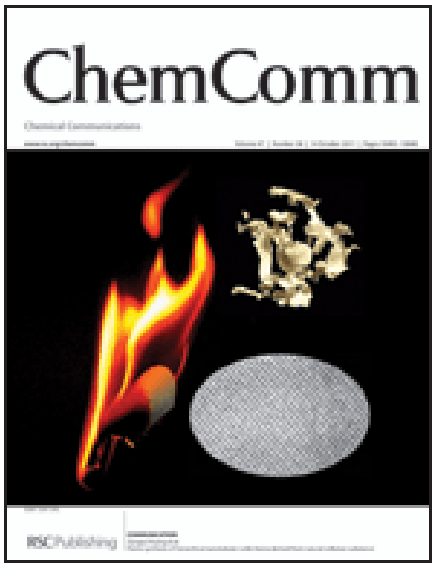

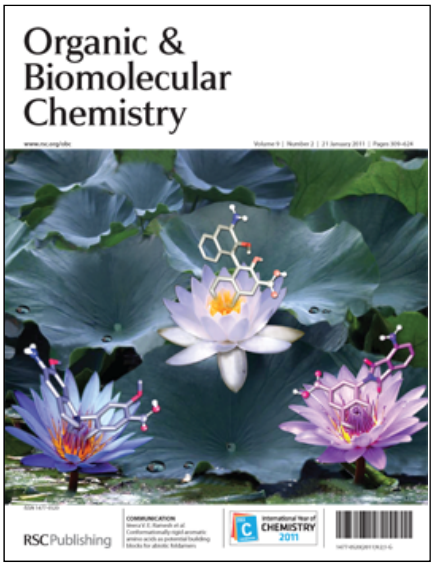

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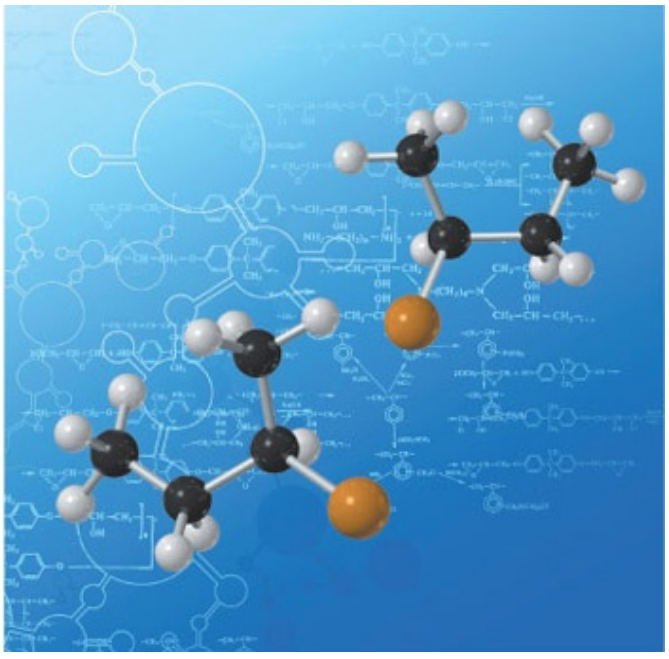

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PAPER

Carbonate, acetate and phenolate phosphonium salts as catalysts in transesterification reactions for the synthesis of non-symmetric dialkyl carbonates†‡

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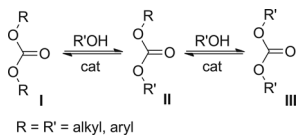
Methyl trioctylphosphonium methyl carbonate $[P_{8881}]^+[MeOCO_2]^-$ was prepared by the alkylation of trioctyl phosphine with the non-toxic dimethyl carbonate. This salt was a convenient source to synthesize different ionic liquids where the methyl trioctylphosphonium cation was coupled to weakly basic anions such as bicarbonate, acetate, and phenolate. At 90–220 °C, all these compounds $[P_{8881}]^+X^-$; X = $MeOCO_2$; $HOCO_2$; AcO; PhO were excellent organocatalysts for the transesterification of dimethyl and diethyl carbonate with primary and secondary alcohols, including benzyl alcohol, cyclopentanol, cyclohexanol, and the rather sterically hindered menthol. Conditions were optimized to operate with very low catalyst loadings up to 1 mol% and to obtain non-symmetric dialkyl carbonates ($ROCO_2R'$; R = Me, Et) with selectivity up to 99% and isolated yields >90%. The catalytic performance of the investigated ionic liquids was discussed through a cooperative mechanism of simultaneous activation of both electrophilic and nucleophilic reactants.

Introduction

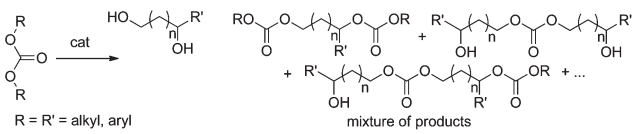
Catalytic transesterification reactions are among the most established protocols for the synthesis of both diaryl and dialkyl carbonates (Scheme 1).[1]

These transformations, however, continue to fuel extensive research activity due to the growing interest in eco-friendly carbonates as intermediates in the pharma, lubricant and polymer industries,[2] and as solvents.[1]

Both patent and open literature claim that most of the transesterification reactions of organic carbonates with alcohols (Scheme 1) use basic catalysts including phosphines and tertiary amines, alkali metal hydroxides, alkoxides, halides, and carbonates, alkali metal exchanged faujasites, and hydrotalcites.[1–3] However, acidic catalysts or co-catalysts,[4] as well as thermal (non-catalytic) procedures,[5] have also been proposed for the same reactions. All these methods show common issues: (i) reactions rarely stop at the mono-transesterification products (**II**, Scheme 1) unless at moderate conversions of the starting carbonate **I**; (ii) although (solid) catalysts can be recycled, relatively high loadings are necessary resulting in tedious and costly separations; (iii) when polyols are used, primary and secondary OH groups are not discriminated and they simultaneously react to produce mixtures of different carbonates (Scheme 2).



Scheme 1



Scheme 2

To overcome such problems, only a few specific solutions have been described so far. For example, highly active La(III)-based catalysts have been recently reported for the selective mono-transesterification of dimethyl carbonate (DMC) to unsymmetrical alkyl methyl carbonates ($ROCO_2Me$).[6]

Another structure-specific reaction has been detailed *via* a multistep sequence involving imidazole carboxylic esters (**IV**, Scheme 3) as intermediates.[7] The combination of the leaving

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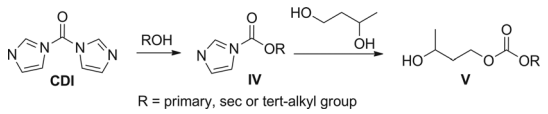
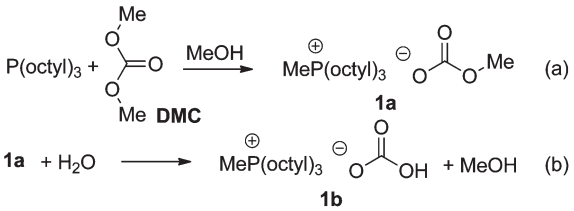
‡ Electronic supplementary information (ESI) available: NMR spectra and a synopsis of major signals observed in MS spectra are reported for all products. See DOI: 10.1039/c2ob25447f



Scheme 3



Scheme 4

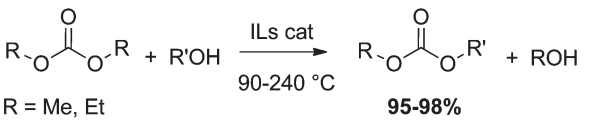
group ability and the steric bulk of imidazole allows the transesterification of esters **IV** only with primary OH functions to produce selectively unsymmetrical dialkyl carbonates **V**.

One last remarkable example concerns the use of an ionic liquid-based catalyst, namely 1-*n*-butyl-3-methylimidazolium-2-carboxylate (C_2mim-2-CO_2): this salt has been reported to be so efficient that loadings as low as 1 mol% are enough to reach quantitative yields in the synthesis of glycerol carbonate from glycerol and DMC.[8]

In this context, our long-standing interest in the use and synthesis of organic carbonates as safe reactants and solvents[2d,9] prompted us to investigate the catalytic behaviour of new ionic liquids (ILs) synthesized in our laboratories, namely methyl trioctylphosphonium methyl carbonate ($[P_{8881}][MeOCO_2]$) and methyl trioctylphosphonium bicarbonate ($[P_{8881}][HOCO_2]$) (Scheme 4: **1a** and **1b**, respectively).[10]

The use of compounds **1a–1b** offers practical advantages: their preparation method *via* the methylation of an alkyl phosphine with non-toxic dimethyl carbonate (DMC) is not only simple and green but it allows the preparation of halide-free and very pure ionic liquids that can be used straight from the reaction vessel, and are stable for months on the shelf. The most intriguing peculiarity, however, is that **1a** and **1b** exhibit an exceptionally high catalytic activity: for example, they are able to catalyze C–C bond-forming reactions including Michael and Henry additions, with performances comparable to those of the superbase DBU (1,8-diazabicyclo[5.4.0]undec-7-ene),[10,11] even though both salts possess intrinsically poorly basic anions (methyl carbonate and bicarbonate).

With the aim of further exploring their potential as organocatalysts, we decided to apply compounds **1a–1b** to the transesterification of dialkyl carbonates (DAlCs). Also, other ILs derived from **1a** were considered for this study: methyl trioctylphosphonium acetate (**1c**: $[P_{8881}][AcO]$) and methyl trioctylphosphonium phenolate (**1d**: $[P_{8881}][PhO]$) were prepared by exchange reaction of **1a** with AcOH and PhOH, respectively. The reactions of dimethyl and diethyl carbonate with model primary, secondary and tertiary alcohols, including benzyl alcohol, cyclopentanol, cyclohexanol, menthol, triphenylcarbinol and diphenyl ethanol, were explored.



R'OH = benzyl alcohol, cyclopentanol, cyclohexanol, and menthol

ILs cat: **1a**, **1b**, **1c**, and **1d**

Scheme 5

This paper reports that, in the presence of salts **1a–1d**, the investigated DAlCs reacted with primary and secondary alcohols to produce unsymmetrical dialkyl carbonates ($ROCO_2R'$; R = Me, Et) with a very high selectivity (over 99%) and complete conversion (Scheme 5).

Compounds **1c** and **1d**, particularly **1c**, showed a catalytic performance better than **1a–1b**. This indicates that excellent IL-based transesterification catalysts can be obtained by coupling alkyl phosphonium cations to weakly basic anions: not only methyl carbonate and bicarbonate, but acetate as well.

Conditions could be optimized to operate with low catalyst loadings (up to 1 mol%). Transesterification reactions were explored over a wide temperature range (90–220 °C): as expected, an increase in the temperature improves the reaction rates, but it does not appreciably affect the mono-transesterification selectivity nor does it degrade the catalysts, which proved to be highly thermally stable.

Tertiary alcohols, however, reacted mainly through alkylation and dehydration processes, yielding *O*-alkyl ethers and alkenes as major products.

Results

Transesterification of DMC with cyclohexanol: effects of catalysts and temperature

An initial screening was carried out on the reaction of dimethyl carbonate (DMC) and cyclohexanol (CyOH) in the presence of four different catalysts: the salt **1a** $[P_{8881}]^+$ $[MeOCO_2]^-$, a representative transesterification base catalyst such as K_2CO_3, and the non-ionic organic bases DMAP (*N*,*N*-dimethylaminopyridine) and DBU.[12]

In a first set of experiments, a mixture of cyclohexanol (CyOH: 1.10 g, 11.0 mmol), DMC (19.82 g, 220 mmol; the molar ratio DMC : CyOH was 20 : 1 since DMC served also as a solvent), and different amounts of the catalyst (the molar percentage of catalyst ranged from 1 to 10 mol%) was set to react at reflux (~90 °C, bp of DMC), for 3.5 h.

All reactions were followed by GC/MS: only the formation of the unsymmetrical carbonate, *i.e.* cyclohexyl methyl carbonate (CyMC: $CyOCO_2Me$), was observed. Selected mixtures of reactions catalyzed by **1a** were purified by flash column chromatography (FCC): ^1H and ^{13}C NMR of the isolated (crude) product confirmed its structure. Also, isolated and GC yields of CyMC were in substantial agreement with each other.

The results are reported in Table 1.

Among conventional catalysts, only DMAP allowed the reaction to proceed to some extent (entries 1 and 2, 5th column:

Table 1 The transesterification of DMC with cyclohexanol over different catalysts[a]

		Conversion of CyOH[c] (%, GC)				CyMC[d] (%)	
Entry	Cat (mol%)[b]	K_2CO_3	DBU	DMAP	**1a**	Sel	*Y*
1	10	1	3	65	97	>99	93
2	5	2	1	32	90		90
3	2	0	0	2	60		
4	1	0	0	0	32		
5	no cat.					no react.	

[a] All reactions were carried out at 90 °C for 3.5 h. [b] Molar percentage of catalyst relative to cyclohexanol. [c] Conversion of cyclohexanol determined by GC, using different catalysts. [d] CyMC: cyclohexyl methyl carbonate ($CyOCO_2Me$): % selectivity (Sel) and % isolated yield (*Y*, crude compound). *Y* was determined after FCC purification of the reaction catalyzed by **1a**.

Table 2 Transesterification of DMC with cyclohexanol using catalyst **1a**

					CyMC[c] (%)	
Entry	*T* (°C)	*t* (h)	Cat (mol%)[a]	Conversion of CyOH[b] (%, GC)	Sel	*Y*
1	150	6	no cat.	3	>99	
2	200	6	no cat.	31	>99	
3	150	6	1	25	>99	
4	200	6	1	93	>99	90
5	150	1.2	10	62	>99	
6	200	0.5	10	93	>99	92

[a] Molar percentage of catalyst relative to cyclohexanol. [b] Conversion of cyclohexanol determined by GC. [c] % Selectivity (Sel) and % isolated yield (*Y*, crude compound) of cyclohexyl methyl carbonate (CyMC). *Y* was determined after FCC purification of the reaction catalyzed by **1a**.

conversions of 65 and 32%, respectively). The salt **1a**, however, was by far the most efficient system for the synthesis of CyMC: this was isolated in up to 93% yield. In particular, noteworthy aspects were: (i) **1a** catalyzed the reaction with a very high mono-transesterification selectivity (>99%) with substantially quantitative conversions of CyOH (entries 1 and 2, 6th column: 97 and 90%, respectively); (ii) the progress of the reaction was significant even in the presence of low amounts (1–2 mol%) of **1a** (entries 3 and 4). By contrast, under the same conditions, even DMAP was not effective (entries 3 and 4, 5th column).

Additional reactions were then carried out using a similar procedure: the same amounts and molar ratio of reactants (CyOH: 1.10 g and DMC : CyOH = 20 : 1) were used, but different temperatures (150 and 200 °C) and times (0.5 to 6 h) were considered.

In these cases, only **1a** was the catalyst. The molar ratio **1a** : CyOH was set to 1 : 1 and the molar percentage to 10 mol%. Because of the relatively high temperatures, experiments took place in autoclaves operating at (autogenic) pressures of up to 20 bar. Two control reactions were also performed without catalyst. Cyclohexyl methyl carbonate (CyMC) was the sole product observed in all experiments. Table 2 reports the results.

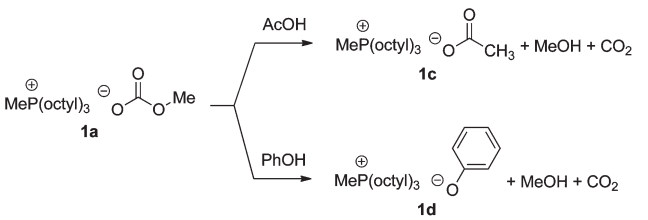
In the absence of catalyst, a thermal reaction could take place: in particular, the formation of the transesterification product (CyMC) was triggered by an increase of the temperature from 150 to 200 °C (entries 1–2: conversions of 3 and 31%, respectively, after 6 h). This matched our recent findings and other literature results for non-catalytic transesterifications of esters and organic carbonates which were reported at $T \geq 170$ °C.[5,13] Under the same conditions, however, at 200 °C, the reaction went substantially to completion when an amount as low as 1 mol% of the salt **1a** was added (entry 4: conversion of 93%). This high catalytic efficiency of **1a** was further confirmed by increasing the molar % of catalyst relative to CyOH from 1 to 10 (entries 5–6): at 200 °C, a 93% conversion was reached after only 0.5 h. The comparison of entries 4 and 6 showed a remarkable 12-fold reduction of the reaction time. In all cases, the mono-transesterification product (CyMC) was obtained with a selectivity of over 99% (by GC), and was isolated in a ≥90% yield.

An experiment was carried out by reducing the DMC : CyOH molar ratio from 20 : 1 to 5 : 1. Accordingly, a mixture of CyOH (4.41 g, 44 mmol), DMC (19.82 g, 220 mmol) and **1a** as a catalyst (54 mg, 1 mol%) was set to react at 200 °C for 4 h. At a substrate conversion of 87%, mono and bis-transesterification products ($CyOCO_2Me$: 79%; $CyOCO_2Cy$, 8%) were obtained with a 79% and 8% conversion, respectively. The reduced amount of DMC caused a modest decrease in the mono-transesterification selectivity (91%).

Transesterification of DMC with cyclohexanol in the presence of different IL catalysts

The transesterification of DMC with cyclohexanol was further investigated to compare the catalytic performance of the salt **1a** to three other phosphonium based ionic liquids. In particular, methyl trioctylphosphonium bicarbonate (**1b**: $[P_{8881}][HOCOO]$), methyl trioctylphosphonium acetate (**1c**: $[P_{8881}][AcO]$), and methyl trioctylphosphonium phenolate (**1d**: $[P_{8881}][PhO]$), were considered. Salts **1b**, **1c**, and **1d** were obtained from **1a**. The preparation of **1b** took place as described in Scheme 4 (details are in ref. 10). Compounds **1c** and **1d** were synthesized by exchange reactions of **1a** (2.00 g, 4.06 mmol) with an equimolar amount of AcOH and PhOH, respectively (AcOH: 0.244 g; PhOH: 0.382 g) (Scheme 6).

Products **1c** and **1d** were isolated in quantitative yields as viscous liquids (**1c**: 1.81 g and **1d**: 1.94 g) at rt (further details are in the Experimental section).



Scheme 6

Table 3 The transesterification of DMC with cyclohexanol using catalysts **1a**, **1b**, **1c** and **1d**[a]

Entry	Catalyst	Cat : CyOH[b] (mol : mol,%)	Conv.[c] (%, GC)	Sel[c] (%, GC)
1	**1a**: $[P_{8881}][CH_3OCOO]$	1	52	>99
2	**1b**: $[P_{8881}][HOCOO]$	1	68	
3	**1c**: $[P_{8881}][AcO]$	1	93	
4	**1d**: $[P_{8881}][PhO]$	1	78	

[a] All reactions were carried out at 200 °C for 3 h. [b] Molar percentage of catalyst relative to cyclohexanol. [c] Conv.: conversion of cyclohexanol determined by GC; Sel: the selectivity towards cyclohexyl methyl carbonate (CyMC).

In the presence of salts **1a**, **1b**, **1c**, and **1d**, the transesterification of DMC with cyclohexanol was examined under the conditions of entry 4 of Table 2 (200 °C; CyOH: 1.10 g; molar ratio DMC : CyOH = 20 : 1; molar % of catalyst relative to CyOH = 1). Experiments were carried out for 3 h. Results are reported in Table 3.

Salts **1b**, **1c** and **1d** were not only able to catalyze the selective formation of cyclohexyl methyl carbonate (CyMC), but their activity was even better than that shown by compound **1a**. At 200 °C, after 3 h, the conversion of cyclohexanol was consistently higher using **1b**, **1c**, and **1d** with respect to **1a** (compare entries 2–3 to entry 1: conversions of 68–93% and 52%, respectively). Particularly evident was the case of **1c**, which allowed a substantially complete reaction in about half the time required with **1a** (Table 2: entry 4), even with a catalyst loading of only 1 mol%.

Transesterification of DMC with different alcohols

The good performance of salt **1c** prompted us to explore its use as a catalyst for the reaction of DMC with other alcohols such as benzyl alcohol, cyclopentanol, menthol, 1,1-diphenylethanol and triphenylcarbinol. Experiments were carried out using the same reactant molar ratio as in Table 3 (alcohol, ROH: 11.0 mmol; molar ratio DMC : ROH = 20 : 1), though different catalyst loadings (molar % of catalyst relative to ROH was from 1 to 10), and reaction temperatures (90–240 °C) were considered. Under such conditions, primary and secondary substrates allowed highly selective mono-transesterification processes, while tertiary alcohols preferentially underwent *O*-methylation or elimination reactions. The structures of the corresponding reaction products were assigned by ^{1}H and ^{13}C NMR, MS spectra, and by comparison to authentic commercial samples. The results are reported in Scheme 7 and Table 4.

A rather clear trend emerged indicating that primary alcohols underwent more rapid transesterifications than secondary ones, which, in turn, were far more reactive than tertiary substrates. The relative reactivity of different alcohols was reflected by the conditions required for the experiments.

The reaction of DMC with benzyl alcohol took place using conventional laboratory glassware at 90 °C: after 6 h, the conversion was complete with 97% of the mono-transesterification product being generated ($PhCH_2OCO_2Me$: benzyl methyl carbonate, entry 1). When the temperature was increased to 110 °C (in an autoclave), the reaction was faster, though less selective: after 2 h, benzyl alcohol was no longer present, but a 4 : 1 mixture of benzyl methyl carbonate and dibenzyl carbonate ($PhCH_2OCO_2CH_2Ph$) was observed (result not shown in the Table). Secondary alcohols preferentially reacted at temperatures greater than 150 °C. The transesterification of DMC with cyclopentanol went to completion at 200 °C yielding cyclopentyl methyl carbonate as the sole product (entries 2–3). The reaction was remarkably quicker (2 h) than that of cyclohexanol (6 h: entry 4, Table 2): this behaviour was consistent with other comparative results reported for the same cyclic alcohols,[14] and it suggested the importance of steric hindrance as well as conformational mobility for such substrates. Even more severe conditions were required by menthol, whose transesterification proceeded efficiently only at 220 °C. After 6 h, however, the corresponding product (menthyl methyl carbonate) was isolated in 92% yield (entry 4).

Tertiary alcohols did not react at 220 °C unless the catalyst loading and the reaction times were increased considerably to 10 mol% and 20 h, respectively. Under such conditions, the transesterification was not observed. 1,1-Diphenyl ethanol was almost quantitatively converted to1,1-diphenyl ethylene (95%) by elimination of water.

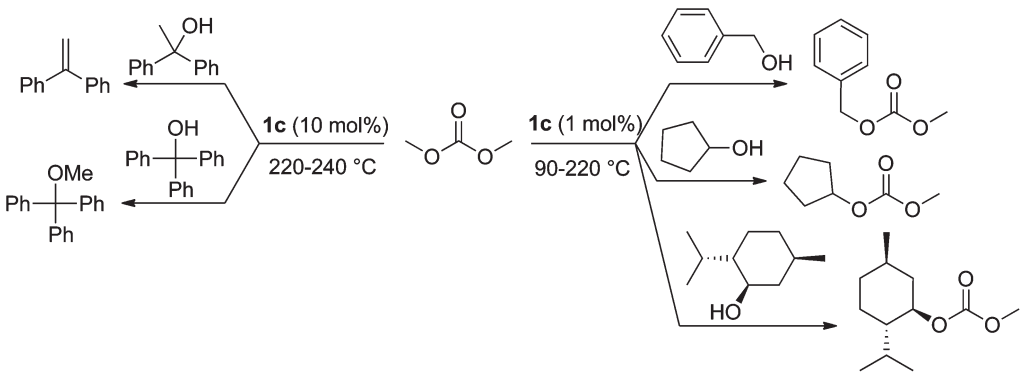
Traces of 1,1-diphenylethyl methyl ether [$Ph_2C(OMe)CH_3$, 5%)] were also detected (entry 5). The reaction of triphenylcarbinol proceeded with moderate conversions (40–54%) yielding the corresponding *O*-methyl ethers, *i.e.* methyl triphenylmethyl ether (Ph_3COCH_3, 40%) (entry 6).

To further compare the reactivity of primary and secondary alcohols, a competitive reaction was investigated. At 90 °C, an equimolar mixture of benzyl and cyclohexyl alcohols (11 mmol of each substrate) was set to react with DMC (19.82 g, 220 mmol) in a 50 mL flask, in the presence of **1c** as a catalyst (49 mg, 1 mol%). Both alcohols gave only the corresponding mono-transesterification products. Although primary and secondary OH groups were not fully differentiated, the product ratio was 3.3 : 1 with a net preference for the benzyl derivative (Scheme 8).

Transesterification of diethyl carbonate (DEC) with different alcohols

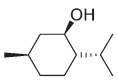
In the presence of the salt **1c**, the reactions of diethyl carbonate with secondary alcohols such as cyclohexanol, cyclopentanol and menthol were also investigated. Conditions were similar to those of Table 4. The same reactant molar ratio was used (alcohol, ROH: 11.0 mmol; molar ratio DEC : ROH = 20 : 1); though different catalyst loadings (molar % of **1c** relative to ROH was from 1 to 5), and reaction temperatures (200–240 °C) were considered. Under such conditions, all reactions proceeded with the exclusive formation of the corresponding mono-transesterification products ($ROCO_2Et$). The structures of such compounds were assigned by ^{1}H and ^{13}C NMR, and MS spectra. The results are reported in Table 5.

At 200 °C, in the presence of 1 mol% of **1c**, the transesterification of DEC with cyclohexanol was considerably slower than the corresponding reaction with DMC (compare entries 1 and 3 of Tables 5 and 3, respectively).

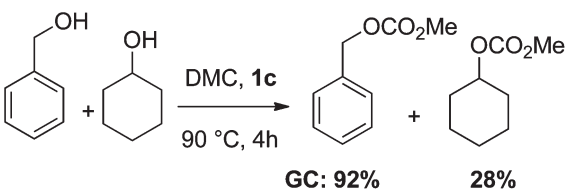


Scheme 7

Table 4 The reaction of DMC with different alcohols catalysed by salt **1c**

Entry	Alcohol (ROH)	T (°C)	t (h)	**1c** (mol%)[a]	Conv.[b] (%, GC)	Major products[c] (%, GC)			Y[d] (%)
						$ROCO_2Me$	$Ph_2C{=}CH_2$	ROMe	
1		90	6	1	100	97			95
2		150	6	1	29	29			
3		200	2	1	100	100			96
4		220	6	1	95	95			92
5		220	20	10	100		95	5	89
6		220	20	10	40			40	—

[a] Molar percentage of catalyst relative to alcohol. [b] Conv.: conversion of alcohol (ROH) determined by GC. [c] Major reaction products detected by GC. [d] Y: Isolated yield of products of transesterification ($ROCO_2Me$), O-methylation (ROMe), or elimination ($Ph_2C{=}CH_2$). Products were purified by FCC on silica-gel.



Scheme 8

Even when the temperature was increased to 220 °C, the time for complete conversion was 15 h (entry 2), approximately 5 times longer than that required for DMC. Additional experiments were then carried out with a higher catalyst loading of 5 mol%: at 220 °C, this allowed acceleration of the reactions of both cyclohexanol and cyclopentanol, which were complete in 10 and 5 h, respectively, with excellent isolated yields (>90%) of transesterification products (entries 3 and 4). Harsher conditions were necessary for menthol: after 18 h at 240 °C, a 72% conversion was observed (entry 5).

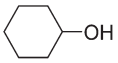
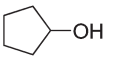
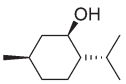
Notwithstanding the relatively high temperature and long reaction times needed for reactions of DEC, no traces of decomposition products of the catalyst **1c** were detected.

Discussion

The role of ionic liquids 1a–1d as transesterification catalysts

The experiments of Tables 1 and 3 leave few doubts about the superior catalytic activity of salts **1a–1d** (with respect to conventional organic and inorganic bases) for the model transesterification of DMC with cyclohexanol. The reaction takes place preferably at high temperatures (>150 °C). Under such conditions, the contribution of a thermally induced process cannot be ruled out, but the evidence for the catalytic role of the chosen ionic liquids is incontrovertible, especially considering that they are used in amounts as low as 1% mol (Tables 2 and 4). The comparison of compounds **1a–1d** to other base catalysts offers another remarkable aspect. At T > 180 °C, both solid bases (K_2CO_3, MgO, Al_2O_3) and zeolites efficiently activate the reactions of dialkyl carbonates with several nucleophiles;[9] these transformations, however, often proceed accompanied by extensive decarboxylations of DAlCs themselves ($ROCO_2R$; R = Me, Et, Pr, and $PhCH_2$), to produce the corresponding ethers (ROR) and CO_2.[15] By contrast, in spite of the high reaction temperature, transesterifications catalysed by compounds **1a–1d** do not generate appreciable amounts of CO_2.[16] Not only are the investigated

Table 5 The reaction of diethyl carbonate with different alcohols in the presence of catalyst **1c**

Entry	ROH	T (°C)	t (h)	1c (mol%)[a]	Conv.[b] (%, GC)	Product[c] ($ROCO_2Et$, %GC)	Y[d] (%)
1		200	3	1	6	6	
2		220	15	1	97	97	94
3		220	10	5	>99	>99	
4		220	6	5	>99	>99	92
5		240	18	5	72	72	65

[a] Molar percentage of **1c** relative to alcohol. [b] Conv.: conversion of the alcohol (ROH) determined by GC. [c] Amounts (% by GC) of the transesterification products $ROCO_2Et$. [d] Y: Isolated yield of $ROCO_2Et$ after purification by FCC on silica-gel.

ILs immune to decarboxylation side-processes, but they allow the overall reaction sustainability to be improved since unconverted dialkyl carbonates (DMC and DEC) can be fully recovered and reused.[17]

Salts **1a–1d** share the same cation structure and they are all exchanged with weakly basic anions (methyl carbonate, bicarbonate, acetate and phenolate, respectively).

The dissociation constants in water (pK_a) of the corresponding acid precursors are:[10,18]

$$4.76\ (\mathrm{AcOH}) < 5.6\ (\mathrm{CH_3OCO_2H}) < 6.4\ (\mathrm{H_2CO_3}\ ^{19}) < 9.89\ (\mathrm{PhOH})$$

If one compares such values to the activity trend observed for the transesterification of DMC with cyclohexanol (Table 3: **1a** $[P_{8881}][CH_3OCO_2]$ < **1b** $[P_{8881}][HOCO_2]$ < **1d** $[P_{8881}][$ PhO] < **1c** $[P_{8881}][CH_3CO_2]$), then no correlation can be inferred. In fact, the weakest base acetate salt (**1c**) is the most active catalyst, followed by the phenolate salt (**1d**) which possesses the strongest base anion. Then, bicarbonate and methyl carbonate follow. The catalytic performance of salts **1a–1d** does not depend only on basicity. Rather, an ambiphilic (both nucleophilic and electrophilic) catalysis appears more suitable to account for the results. This is based on a recently proved concept for ionic liquids,[20] which act as catalysts *via* ion pairs: anions and cations of ILs may activate nucleophiles (as true nucleophiles or bases) and electrophiles, respectively. According to this dual mechanism, Scheme 9 has been formulated for the investigated transesterification of dialkyl carbonates with alcohols. The model example of catalyst **1c** is considered. The strong phosphorus–oxygen affinity favours the coordination of the P centre of the catalyst (as a Lewis acid) to the basic carboxylic oxygen of the dialkyl carbonate (top, right; in analogy with Henry and *N*-alkylation reactions catalyzed by ILs[11,20b]). Another acid–base reaction between the reactant alcohol and **1c** likely accounts for the nucleophilic activation (top, left): an alkoxide exchanged IL, namely $[MeP(octyl)_3{}^{+}RO^{-}]$, forms. The existence of such salts has been recently proved.[21]

Once both the electrophile and the nucleophile are triggered by the catalyst, they may react according to the usual pattern of nucleophilic acyl substitutions ($N_{Ac}S$) to yield the transesterification product $ROCO_2R'$ and restore the initial ionic liquid **1c**. Overall, a cooperative anion/cation effect goes through a complex mix of charge-to-charge interactions. This is a plausible reason why the catalytic performance of a single IL or the activity scale among different ILs is often difficult to predict.

The reaction of different alcohols and carbonates

The cooperative catalysis effect also offers a basis to discuss the reaction selectivity. Mono-transesterification products ($ROCO_2R'$, Tables 1–5) are more hindered than DMC or DEC: therefore, they ($ROCO_2R'$) cannot undergo an efficient electrophilic activation since the corresponding acid–base adducts of Scheme 9 are disfavoured for steric reasons. The same holds true for nucleophilic activation. In our case, the progressive crowding at the OH group explains the observed reactivity of alcohols (BnOH ≫ CpOH > CyOH > menthol, Tables 4 and 5), particularly of menthol,[22] which requires more severe conditions.

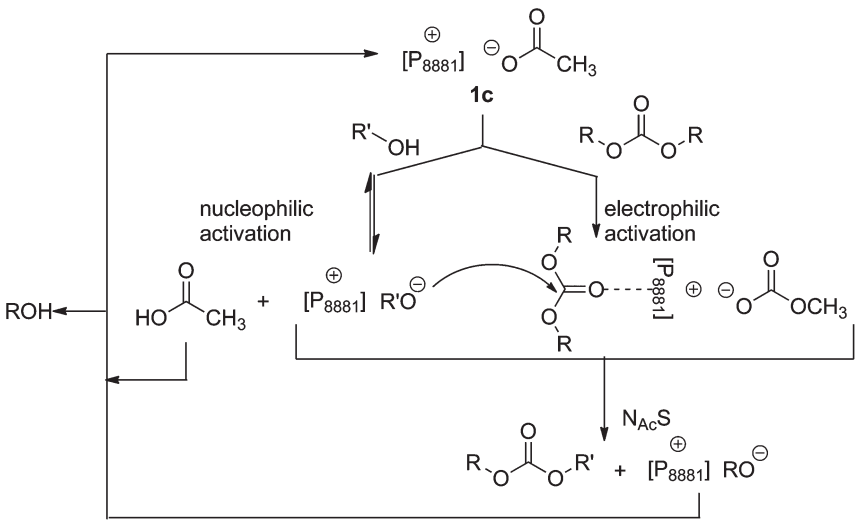
The effect of neighbouring groups becomes so relevant for tertiary alcohols that the transesterification reactions is no longer observed. In its place, other less sterically demanding transformations take place: 1,1-diphenyl ethanol produces a highly conjugated alkene, 1,1-diphenyl ethylene, while triphenylcarbinol preferentially attacks the methyl group of DMC. The same reactions have been already observed at high temperature in the presence of faujasite catalysts;[23] under such conditions, they have been discussed according to the modes of interactions of alcohols and DMC on the solid catalytic surface.

However, the lack of reactivity of tertiary alcohols towards transesterification is so common that *t*-BuOH, for example, is often used as a co-solvent during the transesterification of biodiesel precursors.[24]

The analysis of Tables 4 and 5 also shows that, regardless of the alcohol used, the reactions of DMC are always favoured over those of DEC. This difference reflects the trend of relative reactivity of DMC and DEC which has been observed in many comparative tests of the two dialkyl carbonates.[1,2,9,15,25]

Conclusions

Ionic liquids **1a–1d** based on carbonate, acetate and phenolate exchanged phosphonium salts prove to be excellent organocatalysts for the transesterification of dimethyl and diethyl carbonate with primary and secondary alcohols, to produce non-symmetrical dialkyl carbonate with very good yields (>90%) and



Scheme 9

selectivity (>99%). Reactions, especially for more hindered secondary substrates, are rather energy intensive and they are conveniently carried out using a rather large excess (up to 20 mol) of dialkyl carbonate.

However, at 150–220 °C, appreciable reaction rates are observed even operating with catalyst loadings as low as 1–5 mol%, and the surplus of light reactants (both DMC and DEC) can be easily separated and recycled.

The steric bulk of tertiary alcohols makes these compounds not suitable for the transesterifications examined; however, they follow other intriguing and selective pathways including *O*-methylation reactions. Under the conditions investigated, two aspects should be considered: (i) no trace of thermal degradation of IL-catalysts was detected; (ii) in contrast to the behaviour shown by several inorganic (solid) catalysts, neither the reactant nor the product dialkyl carbonates were activated by ILs towards decarboxylation side-processes. Overall, the investigated ILs allow not only a robust and selective protocol, but also the complete recycling of unconverted DMC or DEC.

The catalytic performance of compounds **1a–1d** is not due to a superbase nature; rather, thanks to their ionic structures, both salts may display ambiphilic properties which operate synchronously without interfering with each other. Accordingly, both electrophilic and nucleophilic activation of the reactants can be invoked under a cooperative catalysis mechanism.

Experimental

Materials

Dimethyl carbonate (DMC), cyclohexanol (CyOH), cyclopentanol, benzyl alcohol, menthol, diphenylethanol, triphenylcarbinol, phenol and acetic acid were ACS grade and were employed without further purification. **1a** and **1b** were prepared accordingly to a method recently reported by us.[10,20*b*]

GC/MS (EI, 70 eV) analyses were run using a HP5-MS capillary column (30 m). Electrospray ionization mass spectra (ESI-MS) were recorded on a quadrupole ion trap instrument using an acetonitrile flow of 0.050 mL min^{-1} (nebulizer 15.0 psi; dry gas 5.0 L min^{-1}; dry temp 325 °C).

^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra at 101 MHz, ^{31}P NMR spectra at 162 MHz. Chemical shifts were reported in δ values downfield from TMS; $CDCl_3$ and DMSO-d_6 were used as solvents. IR spectra were run on a Perkin Elmer Spectrum-One FT-IR spectrophotometer.

Reaction procedures

Transesterification of DMC with cyclohexanol in the presence of different catalysts at reflux. In a round bottomed flask equipped with a reflux condenser, a mixture of cyclohexanol (CyOH: 1.10 g, 11.0 mmol), DMC (19.82 g, 220 mmol) and the appropriate amount of the selected catalyst (K_2CO_3, 15–152 mg; DBU, 16.9–169 mg; DMAP, 13–133 mg; **1a**, 54–542 mg; see Table 1 for details) was set to react at reflux (~90 °C, bp of DMC) for 3.5 h.

Transesterification of DMC with cyclohexanol catalysed by different phosphonium salts at high temperatures. A typical procedure is described with the most active catalyst, compound **1c**, and the substrates most used in this work, cyclohexanol and DMC (Conditions of entry 3 in Table 3). A 120 mL stainless-steel autoclave fitted with a pressure gauge and a thermocouple for temperature control was charged with cyclohexanol (CyOH: 1.10 g, 11.0 mmol), DMC (19.82 g, 220 mmol) and methyl trioctylphosphonium acetate (**1c**: 49 mg, 0,11 mmol, 1 mol% with respect to CyOH). The autoclave was flushed with nitrogen, closed, and then heated at 200 °C for 3 h with magnetic stirring. The reactor was subsequently cooled to rt and vented. The excess of DMC was removed by rotary evaporation. The GC/MS analysis of the residual oily mixture (1.79 g) showed the presence of cyclohexyl methyl carbonate (93%) along with unreacted cyclohexanol (7%). This mixture was purified by FCC on silica gel (100 g) using a solution of ethyl acetate (EA) and petroleum ether (PE) (EA–PE = 1 : 3 *v*/*v*; 400 mL). R_f of the reagent and the product were 0.25 and 0.82, respectively. Cyclohexyl methyl carbonate was obtained as a colourless liquid (1.56 g, 90%) with

a GC-purity of 98%. (Further details on the product characterization are given later in this section, and in the ESI‡).

The same procedure was used to investigate the performance of different ILs as catalysts. Accordingly, the above described autoclave was charged with a mixture of cyclohexanol (CyOH: 1.10 g, 11.0 mmol), DMC (19.82 g, 220 mmol), and the desired amount of phosphonium salt **1a** (54 and 542 mg), or **1b** (49 mg), or **1d** (53 mg). The mixture was set to react at different temperatures (in the range of 150–200 °C) and times (0.5–6 h) (see Tables 2 and 3 for details).

Transesterification of DMC with different alcohols catalysed by 1c. The above described procedure for high temperature reactions was also used for the transesterification of different alcohols with DMC. Accordingly, a 120 mL stainless-steel autoclave was charged with a mixture of the selected alcohol (11.0 mmol: cyclopentanol, 0.95 g; benzyl alcohol, 1.19 g; menthol, 1.72 g; 1,1-diphenylethanol, 2.18 g; triphenylmethanol, 2.86 g), dimethyl carbonate (19.82 g, 220 mmol) and **1c** (54 mg, 0.11 mmol). The mixture was set to react at different temperatures (in the range of 150–220 °C) and times (2–20 h) (see Table 4 for details).

The transesterification of DMC with benzyl alcohol was also carried out at reflux (entry 1, Table 4). In this case, a mixture of benzyl alcohol (11.0 mmol, 1.19 g), dimethyl carbonate (19.82 g, 220 mmol) and **1c** (54 mg, 0.11 mmol) was set to react in a 50 mL round bottomed flask equipped with a reflux condenser and a magnetic stirrer. The experiment was performed at 90 °C for 6 h. Further details on the purification and characterization of the product (benzyl methyl carbonate) are given later in this section.

Transesterification of DEC with different alcohols catalysed by 1c. The above described procedure for high temperature reactions was used also for the transesterification of alcohols with diethyl carbonate. Accordingly, a 120 mL stainless-steel autoclave was charged with a mixture of the selected alcohol (11.0 mmol: cyclohexanol: 1.10 g; cyclopentanol, 0.95 g; menthol, 1.72 g), diethyl carbonate (DEC, 25.99 g, 220 mmol), and **1c** (0.55 mmol; 5 mol%). The mixture was set to react at different temperatures (in the range of 200–240 °C) and times (3–18 h) (see Table 5). Further details on the purification and characterization of the products (alkyl ethyl carbonates, $ROCO_2Et$) are given later on this section.

Synthesis of anion exchanged phosphonium salts

Methyl trioctylphosphonium acetate [P_{8881}][AcO] **1c** and methyl trioctylphosphonium phenate [P_{8881}][PhO] **1d** were prepared by anion exchange reactions of methyl trioctylphosphonium methyl carbonate **1a**. Both salts **1c** and **1d** were new compounds and they were characterized by ^{1}H-, ^{13}C-, ^{31}P-NMR, ESI-MS, and elemental analysis (further details are in the ESI section‡).

Methyl trioctylphosphonium acetate [P_{8881}][AcO] 1c. A 50 mL round bottomed flask was charged with an equimolar mixture of methyl trioctylphosphonium methyl carbonate (**1a**; 2.00 g, 4.06 mmol) and acetic acid (0.244 g). The mixture was kept under magnetic stirring for 2 h at 40 °C. Then, volatile materials were removed by rotary evaporation yielding the desired product **1c** in the form of a viscous clear colourless liquid (1.81 g, 100%). ESI-MS (CH_3CN), positive ion 385 [$C_{25}H_{54}P$]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45–2.31 (m, 6H), 2.06 (d, J = 13.6 Hz, 3H), 1.95 (s, 3H), 1.57–1.40 (m, 12H), 1.36–1.17 (m, 24H), 0.87 (t, J = 6.7 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5 (1C), 31.6 (3C), 30.6 (d, J = 14.9 Hz, 3C), 28.9 (6C), 25.1 (1C), 22.5 (d, J(P,H) = 1.1 Hz, 3C), 21.7 (d, J(P,H) = 4.6 Hz, 3C), 20.0 (d, J(P,H) = 48.7 Hz, 3C), 14.0 (s, 3C), 4.2 (d, J(P,H) = 52.3 Hz, 1C); ^{31}P NMR (162 MHz, DMSO-d_6) δ 30.0. Anal. Calcd for $C_{27}H_{57}O_2P$: C, 72.92; H, 12.92. Found: C, 72.89; H, 12.90%.

Methyl trioctylphosphonium phenate [P_{8881}][PhO] 1d. A 50 mL round bottomed flask was charged with methyl trioctylphosphonium methyl carbonate (**1a**; 2.00 g, 4.06 mmol). An equimolar amount of phenol (0.382 g) was then added and the resulting mixture was kept under magnetic stirring for 2 h at 50 °C. During this time forming methanol was continuously removed by reduced pressure (150 mbar). Product **1d** was obtained as a brown oil (1.94 g, 100%). ESI-MS (CH_3CN), positive ion 385 [$C_{25}H_{54}P$]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.94 (dd, J = 8.5, 7.2 Hz, 2H), 6.58 (dd, J = 8.5, 1.1 Hz, 2H), 6.38 (tt, J = 7.3, 1.1 Hz, 1H), 2.21–2.07 (m, 6H), 1.77 (d, J = 14.0 Hz, 3H), 1.53–1.12 (m, 36H), 0.93–0.79 (m, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.3 (1C), 128.7 (2C), 116.7 (2C), 114.0 (1C), 31.2 (3C), 30.03 (d, J = 15.4 Hz, 3C), 28.4 (3C), 28.2 (3C), 22.1 (3C), 20.5 (d, J (P,H) = 4.3 Hz, 3C), 19.0 (d, J (P,H) = 48.9 Hz, 3C), 13.9 (3C), 3.08 (d, J (P,H) = 51.3 Hz, 1C); ^{31}P NMR (162 MHz, DMSO-d_6) δ 33.1. Anal. Calcd for $C_{31}H_{59}OP$: C, 77.77; H, 12.42. Found: C, 77.81; H, 12.48%.

Isolation and characterization of the products

All mono-transesterification products ($ROCO_2Me$ and $ROCO_2Et$, respectively), and 1,1-diphenylethene were isolated by FCC, and fully characterized by GC/MS, ^{1}H and ^{13}C NMR. New compounds such as cyclopentyl methyl carbonate and methyl menthyl carbonate were characterized also by IR and elemental analysis (see below and ESI‡ section). In particular:

Cyclohexyl methyl carbonate.[26] The product was isolated at the end of five different reactions of cyclohexanol (1.10 g, 11.0 mmol) and DMC (19.82 g, 220 mmol) catalyzed by both **1a** (entries 1, 2 of Tables 1 and 4, 6 of Table 2) and **1c** (entry 3 of Table 3). In all cases, the final reaction mixtures were purified by FCC: according to the above described method (see typical procedure), silica gel and an eluent solution of ethyl acetate (EA) and petroleum ether (PE), EA–PE = 1 : 3 *v*/*v*) were used. The title compound was a colourless liquid (Y: 93, 90, 90, 92, and 90% respectively, Tables 1–3; GC-purity > 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67–4.54 (m, 1H), 3.76 (s, 3H), 1.97–1.85 (m, 2H), 1.80–1.67 (m, 2H), 1.60–1.18 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 76.8, 54.5, 54.5, 31.6, 25.3, 23.7.

Benzyl methyl carbonate.[27] The product was isolated from the reaction of benzyl alcohol (1.19 g, 11 mmol) and DMC (19.82 g, 220 mmol) carried out under the conditions of entry 1 of Table 4. The final mixture was purified by FCC: according to the above described method (see typical procedure), silica gel

and an eluent solution of ethyl acetate (EA) and petroleum ether (PE) (EA–PE = 1 : 3 *v*/*v*) were used. The title compound was isolated as a pale yellow liquid (*Y*: 1.73 g, 95%; GC-purity 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.31 (m, 5H), 5.17 (s, J = 3.3 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 135.4, 128.72, 128.66, 128.4, 69.8, 55.0.

Cyclopentyl methyl carbonate. The product was isolated from the reaction of cyclopentanol (0.95 g, 11 mmol) and DMC (21.2 mL, 220 mmol) carried out under the conditions of entry 3 of Table 4. The final mixture was purified by FCC: according to the above described method (see typical procedure), silica gel and an eluent solution of ethyl acetate (EA) and petroleum ether (PE) (EA–PE = 1 : 3 *v*/*v*) were used. The title compound was isolated as a colourless liquid (*Y*: 1.52 g, 96%; GC-purity 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10–5.03 (m, 1H), 3.74 (s, 3H), 1.92–1.66 (m, 6H), 1.65–1.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCL_3$) δ 155.5, 81.1, 54.4, 32.6, 23.5. IR (Neat): ν = 2961, 2875, 1747 cm^{-1}. Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.38; H, 8.45%.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl methyl carbonate (methyl menthyl carbonate).[28] The product was isolated from the reaction of menthol (1.71 g, 11 mmol) and DMC (19.82 g, 220 mmol) carried out under the conditions of entry 4 of Table 4. The final mixture was purified by FCC: according to the above described method (see typical procedure), silica gel and an eluent solution of ethyl acetate (EA) and petroleum ether (PE) (EA–PE = 1 : 3 *v*/*v*) were used. The title compound was isolated as a white low melting (mp < 30 °C) solid (*Y*: 2.17 g, 92%, GC-purity 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (td, J = 10.9, 4.4 Hz, 1H), 3.77 (s, 3H), 2.11–2.04 (m, 1H), 1.96 (dtd, J = 13.8, 6.9, 2.5 Hz, 1H), 1.72–1.63 (m, 2H), 1.56–1.34 (m, 2H), 1.12–0.98 (m, 2H), 0.91 (d, J = 6.9 Hz, 3H), 0.90 (d, J = 7.3 Hz, 3H), 0.79 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 78.6, 54.6, 47.2, 40.9, 34.3, 31.5, 26.2, 23.5, 22.1, 20.8, 16.4. IR (Neat): ν = 2958, 2872, 1747 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C, 67.30; H, 10.42%.

1,1-Diphenylethene.[29] The product was isolated from the reaction of 1,1-diphenylethanol (2.18 g, 11 mmol) DMC (19.82 g, 220 mmol) carried out under the conditions of entry 5 of Table 4. The final mixture was purified by FCC: according to the above described method (see typical procedure), silica gel and an eluent solution of petroleum ether (PE) were used. The title compound was isolated as a colourless oil (*Y*: 1.76 g, 89%; GC-purity 99%) that turned to a white solid once refrigerated at +4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.33 (m, 10H), 5.64 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.6, 128.4, 128.3, 127.8, 114.3.

Cyclohexyl ethyl carbonate.[30] The product was isolated from the reaction of cyclohexanol (1.1 g, 11 mmol) and DEC (25.99 g, 220 mmol) carried out under the conditions of entry 2 of Table 5. The final mixtures were purified by FCC: according to the above described method (see typical procedure), silica gel and an eluent solution of ethyl acetate (EA) and petroleum ether (PE) (EA–PE = 1 : 3 *v*/*v*) were used. The title compound was a colourless oil (Y: 1.78 g, 94%; GC-purity 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64–4.55 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.96–1.87 (m, 2H), 1.80–1.69 (m, 2H), 1.60–1.17 (m, 6H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 77.3, 76.6, 63.6, 31.7, 25.4, 23.8, 14.4.

Cyclopentyl ethyl carbonate.[31] The product was isolated from the reaction of cyclopentanol (0.95 g, 11 mmol) and DEC (26.0 g, 220 mmol) carried out under the conditions of entry 4 of Table 5. The final mixture was purified by FCC: according to the above described method (see typical procedure), silica gel and an eluent solution of ethyl acetate (EA) and petroleum ether (PE) (EA–PE = 1 : 3 *v*/*v*) were used. The title compound was isolated as a pale yellow liquid (*Y*: 1.60 g, 92%; GC-purity 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08–5.01 (m, 1H), 4.16 (t, J = 7.1 Hz, 2H), 1.89–1.48 (m, 8H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 80.9, 63.7, 32.7, 23.6, 14.4.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl ethyl carbonate.[26] **(ethyl menthyl carbonate).**[32] The product was isolated from the reaction menthol (1.71 g, 11 mmol) and DEC (26.0 g, 220 mmol) carried out under the conditions of entry 5 of Table 5. The final mixture was purified by FCC: according to the above described method (see typical procedure), silica gel and an eluent solution of ethyl acetate (EA) and petroleum ether (PE) (EA–PE = 1 : 3 *v*/*v*) were used. The title compound was isolated as a yellow liquid (*Y*: 1.63 g, 65%; GC-purity 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (td, J = 10.9, 4.4 Hz, 1H), δ 4.24–4.08 (m, 2H), 2.11–2.02 (m, 1H), 2.01–1.90 (m, 1H), 1.71–1.62 (m, 2H), 1.60–1.44 (m, 2H), 1.40–1.33 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.11–0.96 (m, 2H), 0.90 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 7.2 Hz, 3H), 0.78 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 78.2, 63.7, 47.2, 40.9, 34.3, 31.5, 26.2, 23.4, 22.1, 20.9, 16.4, 14.4.

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