

An efficient synthesis of organic carbonates: atom economic protocol with a new catalytic system

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Selective and solvent free synthesis of unsymmetrical organic carbonates catalysed by a reusable MgLa mixed oxide is achieved for the first time *via* direct condensation of an alcohol and diethyl carbonate in economic route with excellent yields.

Organic carbonates have been utilized ubiquitously as intermediates for the synthesis of fine chemicals,^{1,2} pharmaceuticals,³ plasticizers, synthetic lubricants,⁴ monomers for organic glasses, and solvents.^{5,6} The reaction of phosgene with diols and the coupling of halo formates with isolated alcohols and phenols are the most common procedures,^{1,2,7–9} but these methods involving toxic materials are not environmentally satisfactory. The modern syntheses of dimethyl carbonate (DMC) have recently been reviewed.^{10–12} DMC is an environmentally friendly reactant which can be substituted for phosgene in several reactions, in particular the preparation of organic carbonates reviewed by Shaik and Sivaram.¹³ The preparation of alkyl carbonates from alkyl halides and alcohols has been performed using alkali metal carbonates or carbon dioxide as an environmentally benign alternative. However, these reactions produce stoichiometric amounts of salts and would not meet environmental regulations. Recent reports describe the liquid-phase synthesis of alkyl carbonates *via* coupling of an alcohol, CO₂ and alkyl halide in the presence of Cs₂CO₃ at ambient temperatures.¹⁴ A solid-phase reaction of an alcohol or amine ligated to a resin through a CO₂ linker in the presence of caesium carbonate and tetrabutylammonium iodide (TBAI) has also been described.¹⁵ The main drawbacks of these procedures are the usage of more than stoichiometric amounts of base and reagents, high reaction time and moderate yields which make them unattractive for *green technology*. Most recently, the reactions of several alcohols on diethyl carbonate catalysed at ~125 °C by MCM-41-TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene anchored on mesoporous MCM-41 silica) requires 15–24 h.¹⁶ Since organics grafted on silicas are not easily regenerated, a drive to develop alternative methods is required.

We herein report an efficient method for the selective synthesis of unsymmetrical organic carbonates in quantitative yields *via* direct condensation of various alcohols with diethyl carbonate (DEC) in the presence of a new reusable solid base MgLa mixed metal oxide. This catalytic process (Scheme 1) reported for the first time allows an eco-friendly and economic technology. MgLa mixed oxide (Mg/La atomic ratio 3) was prepared as reported earlier and calcined at 550 °C.^{17,18} It could then be regenerated at high temperature by the oxidation of organic contaminants.

We have explored a variety of solid acid and basic catalysts for the preparation of the corresponding carbonate using 1-(4-chlorophenyl)ethan-1-ol as a model reactant in presence of DEC (Table 1). The chosen solid acids were selected from catalysts which have dual Lewis and Brønsted acidic sites as described earlier: sulfated alumina,¹⁹ MCM-41 (Si/Al = 40), Cu²⁺-K10, Zn²⁺-K10^{20,21} and

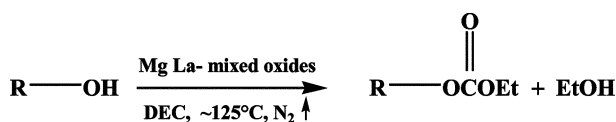
natural montmorillonite. The solid bases were Na-Laponite, KF/α-Al₂O₃,²² HDT-F²³ and MgLa mixed oxides.^{18,24} The reaction was performed at ~125 °C in a three-necked round bottomed flask equipped with a condenser. An excess of DEC (4 ml) and substrate (2 mmol) were placed in the reactor. Freshly activated catalyst (0.1 g) was added and the experiment started with stirring in a nitrogen atmosphere. Stirring was continued until the completion of the reaction, as monitored by thin-layer chromatography (TLC). After completion of the reaction, the catalyst was filtered off and the products were analysed by ¹H NMR. The structure and the purity of the products were confirmed by GC-MS analysis.

The reaction gives selectively the unsymmetrical carbonate when basic catalysis is used and a mixture of carbonate and ether/olefin when acid catalysis is involved. Solid bases gave the unsymmetrical carbonate not only with high selectivity but with a faster rate. If we compare the time required for complete reaction with the basic strength of the solids, we can conclude that the reaction is faster with stronger bases. The reaction works efficiently with a variety of alcohols including aromatic, cyclic, heterocyclic or aliphatic (Table 2). The reactivity is higher with glycols whatever their structure. In the series of substituted 1-phenylethanol, small changes in reactivity are observed with the nature of substituents and an electron withdrawing group tends to give an increase in rate (entry 3 and 4). High selectivity was achieved with allylic alcohols in the present liquid phase reaction (entries 6 and 9). Amine groups do not react under similar reaction conditions. This inertness has been exploited in the corresponding selective *O*-carbonate preparation in the case of 2-(4-aminophenyl)ethanol (entry 5). The steric hindrance in proximity to the reactive hydroxyl group represents again a limiting factor. It is noteworthy that, whereas 1,2-diols gave cyclic carbonates (Table 3 entries 1 and 3), cyclic products are not formed when the number of methylene

Table 1 Catalytic properties of various solids in direct condensation of 1-(4-chlorophenyl)ethan-1-ol with DEC: a model reaction for catalyst screening

Entry	Catalyst	Reaction time/h	Yield ^a (%)	
			I	II
1	MgLa mixed oxides	3.5	100	—
2	KF/α-Al ₂ O ₃	5	100	—
3	HDT-F	15	46 ^b	—
4	Laponite	2	95	5 ^c
5	Al ₂ O ₃ ·SO ₄ (<i>h</i> = 1)	0.5	31	69 ^d
6	MCM-41 (Si/Al = 40)	0.5	—	100 ^e
7	Cu ²⁺ -K10 mont	0.3	—	100 ^e
8	Zn ²⁺ -K10 mont	0.4	—	100 ^e
9	Natural mont	15	No reaction	

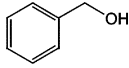
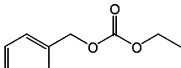
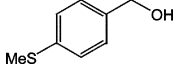
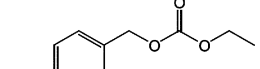
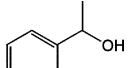
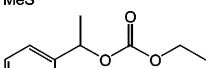
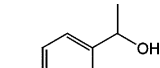
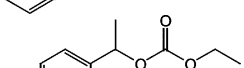
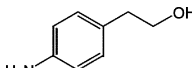
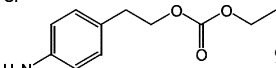
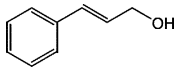
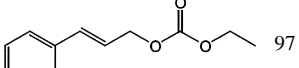
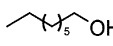
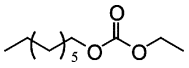
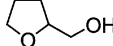
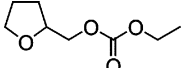
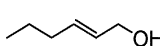
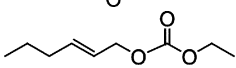

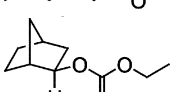

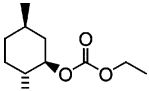
^a Yield from ¹H NMR. ^b Remainder is the starting material. ^c *p*-Chlorostyrene. ^d Olefin and corresponding di-ether. ^e Olefin, ether and unidentified polymeric product.



R = Aliphatic, aromatic, cyclic and heterocyclic

Scheme 1

Table 2 Direct condensation of various alcohols with DEC in the presence of MgLa mixed oxides as catalyst at ~125 °C in solvent free system

Entry	Alcohol ^a	Time/h	Product	Yield (%) ^b
1		6		98
2		5		97
3		4		99
4		3.5 4 ^c 7 ^d		98 97 ^c 98 ^d
5		2.5		98
6		8		97
7		0.5		98
8		4		99
9		2		96
10		0.75 1		99 98 ^d
11		0.75		99

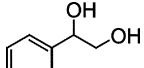
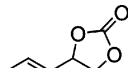
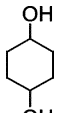
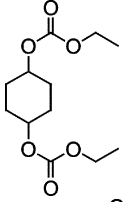
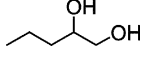
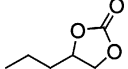
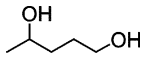
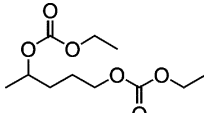
^a Alcohol and DEC molar ratio (1 : excess). ^b Isolated yields. ^c 2nd Cycle. ^d 5th Recycle.

groups between the alcohol functions increases. Thus, 1,4-cyclohexanediol and 1,4-pentanediol yielded the corresponding bis-carbonates as a sole reaction products (Table 3, entries 2 and 4). The $[\alpha]_D$ value of the carbonate obtained from L-(–)-menthol found to be (–52) [where $c = 1$, ethanol], therefore it can be concluded that menthol is not racemized nor inverted. An investigation towards the synthesis of industrially useful chiral auxiliaries is under progress.

Recycling of the catalyst was investigated by taking out the total reaction mixture after completion of the reaction by leaving the catalyst in the lowest possible amount of liquid, then adding a new feed of reactants. As reported (Table 2, entry 4 and 10) the catalyst is still active after 5 re-cycles, but longer reaction times show that some deactivation or loss of catalyst may have occurred.

In conclusion, the present process represents the first example of the synthesis of organic carbonates wherein MgLa mixed oxides are used. The yields of the products are quantitative with the highest atom economy. The potential for its commercial application is

Table 3 Direct condensation of various diols with DEC in the presence of MgLa mixed oxides as catalyst at ~125 °C in solvent free system

Entry	Alcohol ^a	Time/h	Product	Yield (%) ^b
1		2		98
2		0.75		97
3		1		97
4		0.75		98

^a Alcohol and DEC molar ratio (1 : excess). ^b Isolated yields.

strengthened by the high throughput of the products, lower process inventories and use of an easily recyclable system.

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