New Highly Active and Selective Heterogeneous Catalytic System for the Synthesis of Unsymmetrical Organic Carbonates: A Green Protocol

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A green, efficient, and selective synthesis of unsymmetrical organic carbonates is realised in the liquid phase by direct condensation of an alcohol and diethyl carbonate, in an eco-compatible route, in the presence of a recyclable heterogeneous solid-base CsF/α-Al_2O_3 catalyst. The catalyst displayed unprecedented activity after activation at 393 K for 4 h and produced quantitative yields with a greater rate compared with solid bases reported so far. The present process is a potential alternative to replace soluble bases in commercial synthesis.

Introduction

In recent years, increasingly demanding regulations and economic pressure have led to intense research to develop new "clean and green" methods for the minimization of toxic waste and by-products arising from the chemical processes.[1,2] Organic carbonates have been utilized ubiquitously as intermediates in fine chemicals, biological, and medicinal fields,[2,3] and have also played an important role as plasticizers, synthetic lubricants,[4] monomers for organic glass,[5] and solvents.[6] The most common procedures for the synthesis of these compounds include the reaction of phosgene with diols and the coupling of halo compounds with alcohols and phenols.[2a,7] Both methods involve the use of toxic and hazardous materials, thus creating a drive to develop alternative procedures. The modern synthesis of dimethyl carbonate (DMC)[8] attracted considerable attention, as it is an environmentally benign alternative to phosgene in several reactions, in particular for the preparation of organic carbonates as reviewed by Shaik and Sivaram.[9] The synthesis of unsymmetrical dialkyl carbonates by the transesterification of carboxylic acid diesters with an allyl alcohol in the presence of a metal base catalyst[10] (chosen from inorganic carbonates, alcoholates and hydroxides) and of a symmetrical dialkyl carbonate with an alcohol, using cesium-based salts[11] as catalyst have been demonstrated. Both the procedures utilize crown ethers or polyethylene glycols as co-catalysts in combination with the inorganic bases and produce large amounts of salts as toxic waste, which render them un-suitable for "*green technology*". Recently, a liquid-phase synthesis of alkyl carbonates by coupling of an alcohol, CO_2 and alkyl halide in the presence of Cs_2CO_3 at ambient temperatures[12] and a solid-phase reaction involving an alcohol or amine, ligated to a resin through a CO_2 linker, in the presence of Cs_2CO_3 and tetrabutyl ammonium iodide (TBAI)[13] to produce corresponding carbonates or carbamates were reported. The use of more than stoichiometric amounts of soluble bases as catalysts, long reaction times with moderate yields makes these procedures unattractive in terms of eco-friendliness and economy. Most recently, the synthesis of unsymmetrical organic carbonates as illustrated by the reaction of various alcohols with diethyl carbonate catalysed at ca. 338 K by MCM-41-TBD[14] (1,5,7-triazabicyclo[4.4.0]dec-5-ene anchored on mesoporous MCM-41 silica) required 15–24 h for high yields. The difficulty in regenerating a catalyst consisting of organics grafted on silicas and long reaction time deems this procedure unviable. Therefore, the challenge is to develop a heterogeneous catalyst for the selective synthesis of organic carbonates by an eco-economic route with high throughput and which adheres to environment protection laws.

In our continued efforts for the development of the solid base catalysts for selective organic transformations,[15,16] herein we report a fast and selective synthesis of unsymmetrical organic carbonates in the presence of a new, recyclable CsF/α-Al_2O_3 solid base catalyst by direct condensation of various alcohols and diethyl carbonate (DEC). The reaction conditions are optimised, to obtain exclusively the unsymmetrical organic carbonate in quantitative yields (Scheme 1). In the present process, the catalyst can be activated by drying at 393 K for 4 h prior to the reaction, thus avoiding the usual high activation temperatures, and DEC

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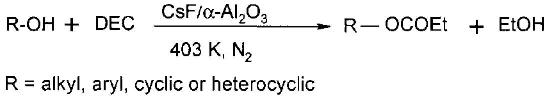
in excess is used as solvent, which can be easily separated by distillation and recycled, so that the process appears as solvent-free.



$$\text{R-OH} + \text{DEC} \xrightarrow[403\ \text{K},\ N_2]{CsF/\alpha\text{-}Al_2O_3} \text{R}-\text{OCOEt} + \text{EtOH}$$

R = alkyl, aryl, cyclic or heterocyclic

Scheme 1.

Results and Discussion

During the course of current study, a variety of soluble and solid base catalysts have been explored on 1-phenylethanol, chosen as a model reactant in the presence of DEC. Selected solid bases were KF on different supports[15] (except KF/CaF, a commercial catalyst), CsF on α- and γ-alumina and HDT-F.[16] The catalysts $CsF/\alpha\text{-}Al_2O_3$, $KF/\alpha\text{-}Al_2O_3$, HDT-F and the homogeneous analogues KF and CsF were activated by drying at 393 K for 4 h, while the rest by calcining under nitrogen at 673 K for 3 h prior to the reaction.

Surprisingly, all the catalysts exhibited high selectivity in producing the corresponding carbonate, despite the large differences in their catalytic activity as shown in Table 1, in which the time required for complete conversion or the degree of conversion after 12 h are a measure of activity. The results obtained correlate-well with the basicity of the corresponding solids as measured by volumetric adsorption of CO_2. Complete conversion towards the corresponding product was obtained with $CsF/\alpha\text{-}Al_2O_3$, $KF/\alpha\text{-}Al_2O_3$, and HDT-F catalysts (Entry 1, 2, and 5). For the same amount of fluoride, 1 mmol/g, the turnover (TON, catalytic cycles per metal centre) reached with $CsF/\alpha\text{-}Al_2O_3$ is significantly higher (greater than 60 mol/mol of Cs) than that of $KF/\alpha\text{-}Al_2O_3$. HDT-F contains about 3 wt% F corresponding to 1.5 mmol/g and also shows a lower activity.[16] Supported KF and CsF on $\gamma\text{-}Al_2O_3$, produced moderate yields (Entry 3 and 4) in agreement with a lower basicity. This may be ascribed to a strong reaction between the fluoride moiety with the surface leading to the formation of fluoroaluminate as confirmed by powder XRD and ^{19}F MAS NMR spectroscopic studies.[16] Similar differences are observed between the two different forms of TiO_2: Rutile and anatase. The rutile form is known to be basic; the anatase form is acidic. Indeed, KF/rutile is more active than KF/anatase (Entry 6 and 7). In homogeneous reactions, equimolar amounts of homogeneous analogues of the corresponding solid bases were employed. Effectively, less than 5% product was obtained with KF even after 24 h (Entry 11), whereas, with CsF, a complete conversion towards the desired product was obtained in 12 h (Entry 12). No detectable product formation was observed with $\alpha\text{-}Al_2O_3$ (Entry 13) and a reaction performed without any catalyst (Entry 14). These results provide an evidence that the $CsF/\alpha\text{-}Al_2O_3$ is the best catalyst and that the high activity is attributed to the high dispersion of CsF on $\alpha\text{-}Al_2O_3$ support.

In an effort to understand the scope of the reaction, a variety of alcohols including, alkyl, cyclic, heterocyclic, or aryl (Table 2) and diols (Table 3) with DEC in the presence of the best evolved catalytic system were investigated. All the substrates were selectively transformed to the corresponding unsymmetrical carbonates in quantitative yields with a greater rate, compared to earlier reports. There is no significant effect of the substituent in case of 1-phenylethanol (Table 2, Entry 2 and 3). High selectivity was achieved with allylic alcohols in present liquid phase reaction (Entry 5 and 7). The inertness of the amine group has been exploited for the selective preparation of corresponding O-carbonate in case of 2-(4-aminophenyl)-ethanol (Entry 4). Chiral menthol is converted into the corresponding carbonate without any racemization or inversion (Entry 9). The steric hindrance due to the proximity of the reactive hydroxy group represents again a limiting factor (Entries 2, 3, 8, 9, and 11).

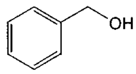
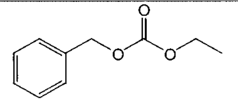
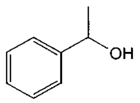
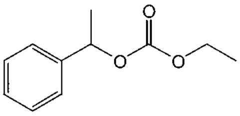
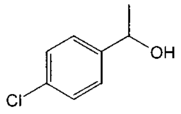
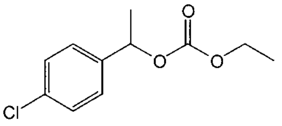
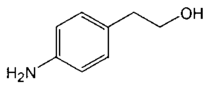
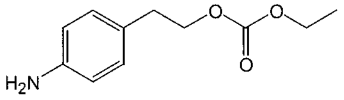
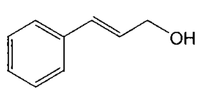
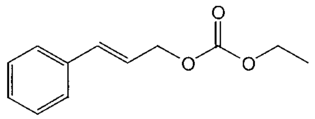
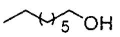
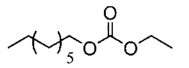
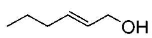
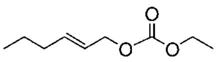
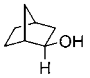
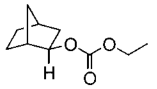
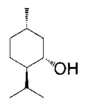
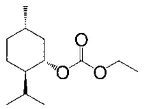
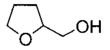
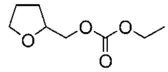
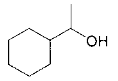
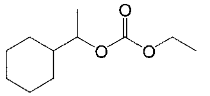
It is noteworthy that, 1,2-diols led to the formation of cyclic carbonates (Table 3, Entry 12 and 13), whereas cyclic products were not formed when the number of methylene

Table 1. Catalytic properties of various solid bases and their homogeneous analogues in direct condensation of 1-phenyl ethanol with DEC. Supported fluorides contain 1 mmol fluoride per gram of support.

Entry[a]	Catalyst	Number of basic sites (µmol/g)	Reaction time (h)	Yields (%)[b]
1	$CsF/\alpha\text{-}Al_2O_3$	11.4	0.45	100
2	$KF/\alpha\text{-}Al_2O_3$	14	5.0	100
3	$CsF/\gamma\text{-}Al_2O_3$	–	12	57[c]
4	$KF/\gamma\text{-}Al_2O_3$	98	12	36[c]
5	HDT-F	47	12	100
6	KF/TiO_2 (Rutile)	–	12	88[c]
7	KF/TiO_2 (Anatase)	–	12	8[c]
8	KF/ZrO_2	–	12	44[c]
9	KF/Al-grafted Si-MCM-41	–	12	5[c]
10	KF/CaF (20 wt.-%)	–	12	12[c]
11	KF (pure)	–	12	<5[c]
12	CsF (pure)	–	12	100
13	$\alpha\text{-}Al_2O_3$ (pure)	–	12	NR
14	Blank[d]	–	12	NR

[a] All the reactions performed on 2 mmol alcohol with 33 mmol of DEC and 0.1 g of catalyst in nitrogen atmosphere at 403 K. [b] Yields are calculated with H^1 NMR and GC. [c] Remaining is the starting material. [d] In absence of catalyst; NR represents no reaction.

Table 2. Direct condensation of various alcohols with DEC with $CsF/\alpha\text{-}Al_2O_3$ as catalyst in solvent-free system.

Entry	Alcohol[a]	Time (min)	Product	Yield (%)[b]
1		30		98
2		20 30[c] 90[d] 720[e]		99 98[c] 82[d] 14[e]
3		25 30[c] 60[c] 720[e]		98 99[c] 97[d] 21[e]
4		20		98
5		20		98
6		15		96
7		20		97
8		15		99
9		40 45[c]		99 97[c]
10		30		99
11		45		98

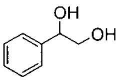
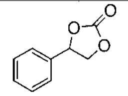
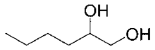
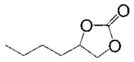
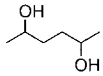
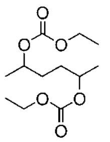
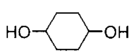
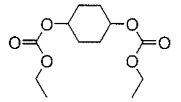
[a] All the reactions performed on 2 mmol alcohol with 33 mmol of DEC and 0.1 g of catalyst under nitrogen at 403 K. [b] Isolated yields. [c] 2nd cycle. [d] 3rd cycle. [e] 4th cycle.

groups between the alcohol functions increased. Thus, 2,5-hexanediol and 1,4-cyclohexanediol yielded the corresponding bis-carbonates as the sole reaction products (Entry 14 and 15).

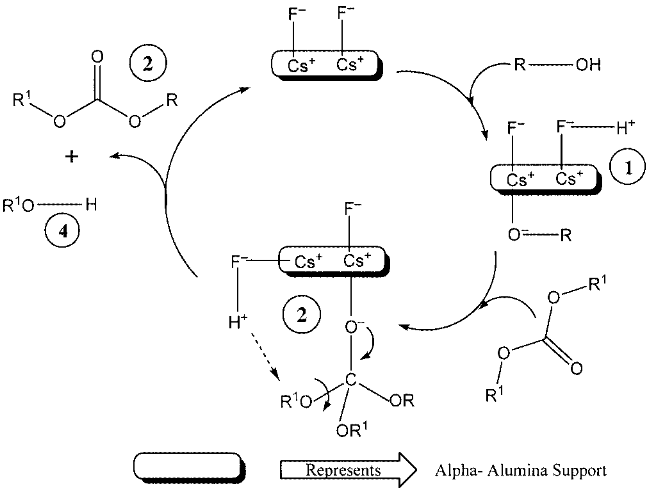
A plausible mechanism could be represented by a typical transesterification process, where the more nucleophilic reagent displaces the less nucleophilic one or when both the reagents have similar nucleophilicity, the less volatile compound displaces the more volatile one. In the present process, the nucleophilic displacement of the ethoxy group by a second molecule of the alcoholic reagent probably leads to the corresponding unsymmetrical carbonate. As shown in Scheme 2, the catalytic cycle maybe initiated by abstraction of a proton by a negatively charged fluoride moiety from an alcohol to generate an alkoxide anion stabilised at the cesium surface. Unlike other alkali equivalents, Cs-alkoxide such as **1** can react with DEC by forming an intermediate [**2**] to yield unsymmetrical alkyl carbonate **3** and producing ethanol **4** as by-product, presumably because alkoxides conjugated with cesium are considered to constitute "naked anions" exhibiting enhanced nucleophilicities.[17] Therefore, it is strongly believed that the Cs-alkoxides constitute weakly coordinated species that enhance nucleophilicity to a degree that affects the rate of nucleophilic attack on DEC, resulting in higher yields.

Recycling of the catalyst was investigated by taking out the reaction mixture after completion of the reaction, leaving the catalyst in the lowest possible amount of liquid and then adding a new feed of reactants. As reported (Table 2, Entries 2, 3 and 9) the catalyst can be recycled three times, but a longer reaction time is required for the third cycle. Interestingly, the chemical analysis of the used catalysts (af-

Table 3. Direct condensation of various diols with DEC with CsF/α-Al_2O_3 as catalyst in solvent-free system.

Entry	Alcohol[a]	Time (min)	Product	Yield (%)[b]
12		25		98
13		20		97
14		45		98
15		30		97

[a] All the reactions performed on 2 mmol alcohol with 33 mmol of DEC and 0.1 g of catalyst under nitrogen at 403 K. [b] Isolated yields.



Scheme 2. Plausible mechanism for the CsF/α-Al_2O_3 catalysed synthesis of unsymmetrical organic carbonates.

ter 4th cycle) revealed that there was no loss of Cs, K, and F. Therefore, the cause for the deactivation of the catalyst may be related to partial hydrolysis of products due to the traces of water present in the new feed of reactants which would inhibit the reaction. Indeed, basic sites are defects of the solid, which are very few (typically 30 µmol/g on CsF/α-Al_2O_3) so that traces of acid formed from water in the reactants are sufficient to kill the catalyst since they are strongly adsorbed at the surface.

In summary, we have shown that a new heterogeneous solid base CsF/α-Al_2O_3 is a highly efficient and reusable catalyst for the selective synthesis of unsymmetrical organic carbonates. The main advantages of the described procedure are (a) facile handling of the solid base, (b) greater reaction rate and quantitative yields with all the substrates tested, (c) elimination of further product purification, and (d) solvent free and direct condensation optimising the highest atom economy. The potential for commercial application is strengthened by the high throughput of the products, lower process inventories and use of an easily recyclable system.

Experimental Section

Supporting Information (see also the footnote on the first page of this article): Literature procedures for known compounds used in this work.

Catalyst: The catalyst was CsF/α-Al_2O_3 prepared by incipient wetness impregnation using an aqueous solution of fluoride. 1 mmol CsF or 1 mmol KF were loaded per gram of α-alumina (SPH, 512, 10.5 m^2/g), γ-alumina (SCP, 350, 400 m^2/g) from Rhône Poulenc. The other supports were anatase (44 m^2/g) and rutile (6 m^2/g) from Millenium Chemicals, and zirconia from MEL. The number of basic sites was measured by volumetric adsorption of CO_2.

Catalytic Reactions: The reactants (purum quality) were purchased from Aldrich and used without any further purification. In a typical reaction, an excess of DEC (33 mmol) and 1-phenylethanol (2 mmol), were placed in a three-neck round-bottomed flask equipped with a condenser. Freshly activated catalyst (100 mg) was added and the experiment started with stirring under nitrogen at ca. 403 K. Stirring was continued until the completion of the reaction, as monitored by thin-layer chromatography (TLC) (ethyl acetate/hexane, 1:10). After completion of the reaction, reaction mixture was filtered and the catalyst washed with DEC (2 × 2.5 mL) to wash off the product adhered on the surface of the catalyst. The combined filtrate fractions were concentrated by distillation under reduced pressure to obtain almost clean product. The excess DEC that is removed from the reaction mixture can be reused in subsequent reaction without further purification. The products were analysed by ^1H NMR and the structure and purity of the products were confirmed by GC-MS analysis. For the recycling experiments, the products and the starting materials were separated by the column chromatography in order to purify them. Silica gel (60–120 mesh) was used for the column and the mobile phase was 5 to 20% ethylacetate in hexane system.

^1H and ^{13}C NMR spectra were recorded with a Bruker AM 250 spectrometer (250 and 62.5 MHz, respectively). The chemical shifts are reported in ppm (δ scale) relative to internal TMS and coupling constants are reported in Hertz (Hz). The elemental analysis and mass spectrometry were carried out at Service Central d'Analyse (CNRS), Echangeur de Solaize, BP 22 – Vernaison, France. Elemental analysis (percentage of the C and H were determined with infrared analysis of the gases produced upon combustion of the product at 1000 °C and for the N: the NO_x produced was reduced to N_2 gas and measured by GLC using catharometric detection). Mass spectrometry was performed using LCT (Micromass – Waters) electrospray positive mode (ESI) technique to determine the molecular ion peak (single mass) for all the new compounds; except compound **7**, for which EI mass was performed at 70 eV.

Characterizations data for the new compounds

Ethyl 1-(4-Chloro)phenethyl Carbonate (3): Colourless oil. ^1H NMR (250 MHz, $CDCl_3$): δ [ppm] = 7.32 (s, 4 H, aromatic), 5.7 [q, J = 6.6 Hz, 1 H, $CH(CH_3)$], 4.38–4.15 (m, 2 H, $CH_3CH_2OCO_2$), 1.58 (d, J = 6.6 Hz, 3 H, $\mathrm{OCH}\mathit{CH}_3$), 1.29 (t, J = 7.1 Hz, 3 H, $\mathrm{OCO_2CH_2}\mathit{CH}_3$). ^{13}C NMR (63 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 154.43 ($\mathrm{OCO_2}$), 139.67 (Cl–C), 133.9 [$\mathit{C}\mathrm{CH(CH_3)}$], 128.76–127.49 (CH, aromatic), 75.43 ($\mathrm{CH_3}\mathit{C}\mathrm{HOCO_2}$), 64.03 ($\mathrm{OCO_2}\mathit{C}\mathrm{H_2CH_3}$), 22.28 [$\mathrm{CH(}\mathit{CH}_3\mathrm{)}$], 14.23 ($\mathrm{OCO_2CH_2}\mathit{CH}_3$). MS (ES+): m/z = [$\mathrm{MNa^+}$] 251. $\mathrm{C_{11}H_{13}O_3}$: calcd. C 57.78, H 5.73; found C 58.10, H 5.75.

Ethyl 2-(4-Amino)phenethyl Carbonate (4): Pale yellow oil. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 7.02 (d, J = 8.5 Hz, 2 H, aromatic), 6.65 (d, J = 8.3 Hz, 2 H, aromatic), 4.26 (t, J = 7.2 Hz, 2 H, $\mathrm{OCO_2}\mathit{CH}_2\mathrm{CH_3}$), 4.18 (q, J = 7.1 Hz, 2 H, $\mathrm{CH_2}\mathit{CH}_2\mathrm{OCO_2}$), 3.6 (br., 2 H, $\mathrm{N}\mathit{H}_2$), 2.85 (t, J = 7.3 Hz, 2 H, $\mathit{CH}_2\mathrm{CH_2OCO_2}$), 1.3 (t, J = 7.1 Hz, 3 H, $\mathrm{OCO_2CH_2}\mathit{CH}_3$). ^{13}C NMR (63 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 155.15 ($\mathrm{OCO_2}$), 145.09 ($\mathrm{CNH_2}$), 129.75 (CH, aromatic), 126.94 ($\mathit{C}\mathrm{CH_2}$), 115.27 (CH, aromatic), 68.60 ($\mathrm{CH_2CH_2OCO_2}$), 63.86 ($\mathrm{OCO_2}\mathit{C}\mathrm{H_2CH_3}$), 34.28 ($\mathit{C}\mathrm{H_2CH_2OCO_2}$), 14.27 ($\mathrm{OCO_2CH_2}\mathit{C}\mathrm{H_3}$). MS (ES+): m/z = [$\mathrm{MNa^+}$] 232. $\mathrm{C_{11}H_{15}O_3N}$: calcd. C 63.14, H 7.23, N 6.69; found C 63.39, H 7.37, N 6.63.

Ethyl *trans*-2-Hexenyl Carbonate (7): Colourless oil. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 5.9–5.75 (m, 1 H, olefinic), 5.52–5.67 (m, 1 H, olefinic), 4.55 (d, J = 6.5 Hz, 2 H, $\mathrm{CH}\mathit{CH}_2\mathrm{OCO_2}$), 4.18 (q, J = 7.1 Hz, 2 H, $\mathrm{OCO_2}\mathit{CH}_2\mathrm{CH_3}$), 2.04 (q, J = 7.1 Hz, 2 H, $\mathrm{CH_2}\mathit{CH}_2\mathrm{CH}$), 1.41 (sext, J = 7.5 Hz, 2 H, $\mathrm{CH_3}\mathit{CH}_2\mathrm{CH_2}$), 1.3 (t, J = 7.1 Hz, 3 H, $\mathrm{OCO_2CH_2}\mathit{CH}_3$), 1.9 (t, J = 7.2 Hz, 3 H, $\mathit{CH}_3\mathrm{CH_2CH_2}$). ^{13}C NMR (63 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 155.12 ($\mathrm{OCO_2}$), 137.16–123.5 (CH), 68.48 ($\mathrm{CH}\mathit{C}\mathrm{H_2OCO_2}$), 63.87 ($\mathrm{OCO_2}\mathit{C}\mathrm{H_2CH_3}$), 34.34–22.02 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH}$), 14.31–13.65 ($\mathit{C}\mathrm{H_3}$). MS (EI): m/z = [$\mathrm{M^+}$] 172 (2), 57 (100), 67 (83), 82 (63). $\mathrm{C_9H_{16}O_3}$: calcd. C 62.77, H 9.36; found C 63.04, H 9.45.

Ethyl Tetrahydrofurfuryl Carbonate (10): Colourless oil. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 4.25–4.05 (m, 5 H, $\mathrm{CH_3}\mathit{CH}_2\mathrm{OCO_2}$, $\mathrm{CHO}\mathit{CH}_2\mathrm{OCO_2}$, $\mathrm{C}\mathit{H}\mathrm{OCH_2OCO_2}$), 3.95–3.75 (m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{OCH_2}$), 2.1–1.85 (m, 3 H, furfuryl), 1.75–1.55 (m, 1 H, furfuryl), 1.3 (t, J = 7.1 Hz, 3 H, $\mathit{CH}_3\mathrm{CH_2OCO_2}$). ^{13}C NMR (63 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 155.12 ($\mathrm{OCO_2}$), 76.24 (OCH), 69.43–68.43–64.05 ($\mathrm{O}\mathit{C}\mathrm{H_2}$), 27.87–25.64 ($\mathrm{CH_2}$), 14.26 ($\mathit{C}\mathrm{H_3CH_2OCO_2}$). MS (ES+): m/z = [$\mathrm{MNa^+}$] 197. $\mathrm{C_8H_{14}O_4}$: calcd. C 55.17, H 8.1; found C 55.6, H 7.98.

Ethyl 1-Cyclohexylethyl Carbonate (11): Colourless oil. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 4.64–4.52 (quintet, J = 6.3 Hz, 1 H, $\mathrm{C}\mathit{H}\mathrm{O(CH_3)}$), 4.24–4.12 (q, J = 7.1 Hz, 2 H, $\mathrm{CH_3}\mathit{CH}_2\mathrm{OCO_2}$), 1.85–1.6 (m, 4 H, cyclic), 1.59–1.42 (m, 1 H, cyclic $\mathrm{C}\mathit{H}$), 1.31 (t, J = 7.1 Hz, 3 H, $\mathit{CH}_3\mathrm{CH_2OCO_2}$), 1.23 [d, J = 6.4 Hz, 3 $\mathrm{HCHO(}\mathit{CH}_3\mathrm{)}$], 1.3–0.9 (m, 6 H, cyclic). ^{13}C NMR (63 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 155.08 ($\mathrm{OCO_2}$), 78.91 ($\mathrm{O}\mathit{C}\mathrm{HCH_3}$), 63.60 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2OCO_2}$), 42.61 ($\mathit{C}\mathrm{H}$, cyclic), 28.48–28.35–26.35–26.03–25.97 ($\mathit{C}\mathrm{H_2}$, cyclic), 17.00 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)}$], 14.31 ($\mathit{C}\mathrm{H_3CH_2OCO_2}$). MS (ES+): m/z = [$\mathrm{MNa^+}$] 223; $\mathrm{C_{11}H_{20}O_3}$: calcd. C 65.99, H 10.07; found C 66.58, H 10.14.

2,5-Bis(ethoxycarbonyloxy)hexane (14): Colourless oil. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 4.85–4.7 (m, 2 H, 2 $\mathrm{C}\mathit{H}\mathrm{OCH_3}$), 4.2 (q, J = 7.1 Hz, 4 H, 2 $\mathrm{OCO_2}\mathit{CH}_2$), 1.78–1.55 (m, 4 H, $\mathit{CH}_2\mathit{CH}_2$), 1.31 (t, J = 7.2 Hz, 6 H, $\mathrm{2OCO_2CH_2}\mathit{CH}_3$), 1.29 (d, J = 6.2 Hz, 6 H, $\mathrm{2CHOC}\mathit{H}_3$). ^{13}C NMR (63 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 154.78 ($\mathrm{OCO_2}$), 74.81–74.48 ($\mathit{C}\mathrm{HOCO_2}$), 63.74 ($\mathrm{OCO_2}\mathit{C}\mathrm{H_2CH_3}$), 31.82–31.39 ($\mathrm{CH}\mathit{C}\mathrm{H_2}$), 19.98–19.86 ($\mathrm{CH}\mathit{C}\mathrm{H_3}$), 14.27 ($\mathrm{OCO_2CH_2}\mathit{C}\mathrm{H_3}$). MS (ES+): m/z = [$\mathrm{MNa^+}$] 285; $\mathrm{C_{12}H_{22}O_6}$: calcd. C 55.95, H 8.45; found C 55.94, H 8.60.

1,4-Bis(ethoxycarbonyloxy)cyclohexane (15): White crystalline solid, m.p. 46 °C (uncorrected). ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 4.78–4.65 (br., 2 H, 2 $\mathrm{C}\mathit{H}\mathrm{OCO_2}$), 4.2 (q, J = 7.1 Hz, 4 H, 2 $\mathrm{OCO_2C}\mathit{H}_2$), 2.1–1.55 (m, 8 H, cyclic), 1.32 (t, J = 7.1 Hz, 6 H, 2 $\mathrm{OCO_2CH_2}\mathit{CH}_3$). ^{13}C NMR (63 MHz, $\mathrm{CDCl_3}$): δ [ppm] = 154.59 ($\mathrm{OCO_2}$), 74.33–73.58 ($\mathit{C}\mathrm{HO}$), 63.82–63.77 ($\mathrm{OCO_2}\mathit{C}\mathrm{H_2CH_3}$), 27.51–27.18 ($\mathrm{CH_2}$, cyclic), 14.28 ($\mathrm{OCO_2CH_2}\mathit{C}\mathrm{H_3}$). MS (ES+): m/z = [$\mathrm{MH^+}$] 261. $\mathrm{C_{12}H_{20}O_6}$: calcd. C 55.37, H 7.74; found C 55.33, H 7.67.

[1] a) P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press: New York, **1998**; pp. 160; b) P. T. Anastas, L. B. Bartlett, M. M. Kirchhoff, T. C. Williamson, *Catal. Today* **2000**, *55*, 11–22; c) W. F. Holderich, *Stud. Surf. Sci. Catal.* **1993**, *75*, 127–163.

[2] a) A. F. Hegarty, in: *Comprehensive Organic Chemistry* (Ed.: I. O. Sutherland), Pergamon: London, **1979**, vol. 2, p. 1067; b) R. A. Sheldon, *Chemistry & Industry (London)*, **1997**, 12–15; c) J. M. Thomas, R. Raja, G. Sankar, B. F. Johnson, D. W. Lewis, *Chem. Eur. J.* **2001**, *7*, 2973–2978.

[3] a) J. P. Parrish, R. N. Salvatore, K. W. Jung, *Tetrahedron* **2000**, *56*, 8207–8237; b) C. Ghiron, T. Rossi, R. J. Thomas, *Tetrahedron Lett.* **1997**, *38*, 3569–3572; c) H. K. Kole, M. Akamatsu, B. Ye, X. Yan, D. Barford, P. P. Roller, T. R. Burke, Jr., *Biochem. Biophys. Res. Commun.* **1995**, *209*, 817–822; d) M. Acemoglu, S. Bantle, T. Mindt, F. Nimmerfall, *Macromolecules* **1995**, *28*, 3030–3037.

[4] a) D. L. Cottle, F. Knoth, Jr., D. W. Young (Esso Research and Engineering Co.), US Pat. 2758975, **1956**; b) S. Gryglewicz, F. A. Oko, G. Gryglewicz, *Ind. Eng. Chem. Res.* **2003**, *42*, 5007–5010.

[5] J. L. R. Williams, K. R. Dunham (Eastman Kodak Co.), US Pat. 2843567, **1958**.

[6] F. Mizia, F. Rivetti (ENICHEM), US Pat. Appl. No. 20020056468, **2002**.

[7] a) R. M. Burk, M. B. Roof, *Tetrahedron Lett.* **1993**, *34*, 395–398; b) G. Bertolini, G. Pavich, B. Vergani, *J. Org. Chem.* **1998**, *63*, 6031–6034; c) A. R. Choppin, J. W. Rogers, *J. Am. Chem. Soc.* **1948**, *70*, 2967; d) Y. Ono, *Appl. Catal. A: General* **1997**, *155*, 133–166.

[8] a) Y. Ono, *Catal. Today* **1997**, *35*, 15–25; b) P. Tundo, M. Selva, *Acc. Chem. Res.* **2002**, *35*, 706–716; c) D. Delledonne, F. Rivetti, U. Romano, *Appl. Catal. A: General* **2001**, *221*, 241–251.

[9] A.-A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951–976.

[10] a) Y. Proux, M. Pellegrina, (Societe Francaise d'Organo Synthese, Fr.). Fr 2608812, **1988**; b) P. Tundo, F. Trotta, G. Moraglio, F. Ligorati, *Ind. Eng. Chem. Res.* **1988**, *27*, 1565–1571; c) P. Tundo, F. Trotta, G. Moraglio, F. Ligorati, *Ind. Eng. Chem. Res.* **1989**, *28*, 881–890.

[11] F. J. Liotta, Jr. (Arco Chemical Technology, L. P., USA). US Pat. 5206408, **1993**.

[12] S.-I. Kim, F. Chu, E. E. Dueno, K. W. Jung, *J. Org. Chem.* **1999**, *64*, 4578–4579.

[13] R. N. Salvatore, V. L. Flanders, D. Ha, K. W. Jung, *Org. Lett.* **2000**, *2*, 2797–2800.

[14] S. Carloni, D. E. De Vos, P. A. Jacobs, R. Maggi, G. Sartori, R. Sartorio, *J. Catal.* **2002**, *205*, 199–204.

[15] a) J.-M. Clacens, D. Genuit, L. Delmotte, A. Garcia-Ruiz, G. Bergeret, R. Montiel, J. Lopez, F. Figueras, *J. Catal.* **2004**, *221*, 483–490; b) F. Figueras, J. Lopez, J. Sanchez-Valente, T. T. H. Vu, J.-M. Clacens, J. Palomeque, *J. Catal.* **2003**, *211*, 144–149; c) J. Barrault, J.-M. Clacens, Y. Pouilloux, *Topics in Catalysis* **2004**, *27*, 137–142.

[16] B. M. Choudary, M. Lakshmi Kantam, V. Neeraja, K. Koteswara Rao, F. Figueras, L. Delmotte, *Green Chem.* **2001**, *3*, 257–260.

[17] a) C. Galli, *Org. Prep. Proced. Int.* **1992**, *24*, 285–307 .and references cited therein; b) F. Chu, E. E. Dueno, K. W. Jung, *Tetrahedron Lett.* **1999**, *40*, 1847–1850.

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