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A New, Mild, General and Efficient Route to Aryl Ethyl Carbonates in Solvent-Free Conditions Promoted by Magnesium Perchlorate

Giuseppe Bartoli,[a] Marcella Bosco,[a] Armando Carlone,[a] Manuela Locatelli,[a] Enrico Marcantoni,[b] Paolo Melchiorre,[a] Paolo Palazzi,[a] and Letizia Sambri*[a]

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A new, general and mild method for the direct synthesis of aryl and alkyl ethyl carbonates promoted by a Lewis acid is reported. The reaction proceeds smoothly with diethyl dicarbonate in the presence of $Mg(ClO_4)_2$, a specific activator of 1,3-dicarbonyl compounds, and shows general applicability.

Introduction

For a long time, the chemical community has avoided the use of metal perchlorates out of fear that they can work as explosives.[1] However, recently Long asserted that the scarce consideration of perchlorates in commercial processes was due to "the mistaken association of perchlorate salts with the oxidizing potential of perchloric acid and the pyrotechnic performances of ammonium perchlorate".[2] Actually, perchlorate salts are only dangerous if heated over their decomposition temperature (300–500 °C)[3] in the presence of oxidizable materials or under highly acidic conditions. The National Fire Protection Association (NFPA) ranks magnesium perchlorate as barely hazardous for health and as an oxidizing product, but not as an explosive one.[4] Suppliers inform us that magnesium perchlorate is stable under ordinary conditions of use and storage, but contact with heat and reducing agents must be avoided.[5] In conclusion, the scarce use of perchlorate salts under mild conditions in organic chemistry is mainly due to a bad name rather than true chemical hazard.

On the other hand, because metal perchlorates are highly dissociated ion pairs,[6] they can act as powerful Lewis acids, exploiting their ability to activate mainly bidentate compounds. In particular, metal perchlorates can promote various acylation and esterification reactions,[7] the synthesis of β-enamino esters,[8] the protection of amines as Boc-derivatives[9] and the synthesis of aryl and alkyl *tert*-butyl ethers.[10]

[a] Università di Bologna, Dipartimento di Chimica Organica "A. Mangini",
V.le Risorgimento 4, 40136 Bologna, Italy
Fax: +39-051-2093654
E-mail: letizia.sambri@unibo.it
[b] Università di Camerino, Dipartimento di Scienze Chimiche,
Via S. Agostino 1, 62032 Camerino (Mc), Italy

Therefore, we thought to explore the efficiency of $Mg(ClO_4)_2$ to activate diethyl dicarbonate for preparing alkyl and aryl ethyl carbonates under Lewis acid catalysis.

The remarkable importance of aryl and alkyl carbonates in various chemical fields is well documented by the presence of a large number of patents[11] and papers in the literature.[12] Organic carbonates, in fact, have found employment as fuel additives, lubricating oils, herbicides, pesticides, plastics and solvents and for medicinal and biological applications. Moreover they can act as useful protecting groups of alcohols and phenols, since they are more stable than the corresponding esters under basic conditions.[13]

The traditional methods for the preparation of organic carbonates require the use of basic conditions and toxic reagents,[12a,14] such as phosgene, pyridine and carbon monoxide. Thus, much effort has been recently devoted to the development of more environmentally friendly procedures for organic carbonate synthesis.[15]

The organic carbonate interchange[12a] has probably been the most pursued approach and has given rise to the development of a large number of protocols, most of which are patented.[16] This is an equilibrium reaction, which follows thermodynamic rules; the more nucleophilic alcohol should displace the less nucleophilic one. From these considerations, phenols are expected to have difficulty in reacting with dialkyl carbonates. However, sophisticated procedures, high temperatures and appropriate catalysts allow the equilibrium to be shifted towards the desired product, even if the reactions proceed at relatively slow rates with generally low yields. Moreover, besides mixed carbonates, appreciable amounts of symmetrical carbonates are always obtained.[11f,12a]

The selective synthesis of mixed aryl or alkyl carbonates was also performed by using toxic ethyl chloroformate.[17] However, sometimes tertiary amines did not survive the re-

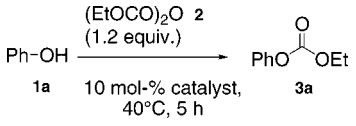
action conditions.[17e] Moreover, this reagent also requires basic conditions, and pyridine, which is the most commonly used reaction partner, can displace the reactive halide groups in an S_NAr fashion.[17f]

In conclusion, an efficient and simple protocol for the direct synthesis of mixed aryl alkyl carbonates under acidic conditions is still lacking. We wish to report herein the peculiar reactivity of diethyl dicarbonate[18] in the presence of $Mg(ClO_4)_2$, which allowed us to set up a new, simple and mild approach to aryl ethyl carbonates.

Results and Discussion

When phenol (**1a**) is left to react with diethyl dicarbonate (**2**, 1.2 equiv.) in the presence of a 10 mol-% of $Mg(ClO_4)_2$ at 40 °C under solvent-free conditions (SFC), a smooth addition occurs within 5 h, giving the expected ethyl phenyl carbonate (**3a**) in almost quantitative yield (Table 1, Entry 1).[19]

Table 1. Comparison between various Lewis acid catalysts in the reaction of phenol (**1a**) with diethyl dicarbonate (**2**, 1.2 equiv.) at 40 °C.

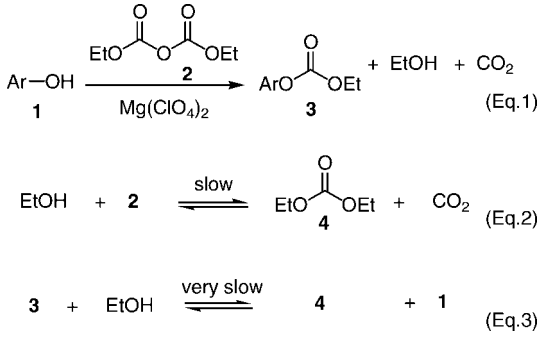


Entry	Catalyst	Yield [%]
1	$Mg(ClO_4)_2$	>99
2	$Mg(ClO_4)_2 \cdot 6H_2O$	68
3	$Mg(ClO_4)_2$[a]	90
4	$LiClO_4$	83
5	$Al(ClO_4)_3 \cdot 9H_2O$	13
6	$Zn(ClO_4)_2 \cdot 6H_2O$	90
7	$Sc(OTf)_3$	46
8	$Cu(OTf)_2$	13
9	$InCl_3$	80
10	$FeCl_3$	39
11	$Ti(OiPr)_4$	56
12	PTSA	0

[a] 1 mol-%.

A low catalyst amount (1 mol-%, Table 1, Entry 3) resulted in a lower conversion (90% instead of almost quantitative). Longer reaction times did not improve the conversion, since the competitive decomposition of diethyl dicarbonate began to be important. In order to demonstrate that $Mg(ClO_4)_2$ is the best choice, we tested other Lewis acid catalysts commonly used to activate carbonyls. Other perchlorates, though they are among the most powerful Lewis acids, are less efficient (Table 1, Entries 4–6).[6] For example, $Zn(ClO_4)_2 \cdot 6H_2O$, which was demonstrated to be more efficient than magnesium perchlorate in the acetylation of alcohols,[20] gave a lower yield. Moreover, scandium and copper triflates, which are able to convert carboxylic acids into esters by reaction with pyrocarbonates,[7a] led to very unsatisfactory results under the same experimental conditions (Table 1, Entries 7–8). In particular, with $Sc(OTf)_3$, decomposition of **2** occurs at a rate comparable with that of the addition process, while $Cu(OTf)_2$ drastically lowers the reaction rate. Other common Lewis acid catalysts, such as iron and indium chloride, gave poor results (Table 1, Entries 9–10). Finally, *p*-toluenesulfonic acid (PTSA), a protic acid, was completely unable to catalyse the reaction (Table 1, Entry 11). In conclusion, among the examined acids, our original choice was revealed as the most efficient one.

Moreover, some further comments on the advantages of this catalyst can be made. The almost quantitative yields of the recovered product demonstrate that, under the adopted experimental conditions, none of the possible side reactions occur [(Scheme 1, Equation (1)]. In fact, as will be detailed later in the text, the possible addition of the by-product ethanol to unreacted diethyl dicarbonate (**2**) [Scheme 1, Equation (2)] is slower than the addition of phenol to **2**, so that only the desired ethyl phenyl carbonate (**3a**) is successfully obtained. Moreover, the transesterification-type process depicted in Equation (3) of Scheme 1, although thermodynamically favoured, is actually very slow. On the other hand, when **3a** was added to 1 equiv. of EtOH and 10 mol-% of $Mg(ClO_4)_2$, it was recovered unaltered after 24 h of stirring at 40 °C. This experiment demonstrates that, under mild conditions, $Mg(ClO_4)_2$ is able to activate only 1,3-dicarbonyl compounds and does not catalyse the transesterification-type process generally promoted by basic catalysts.[12a]



Scheme 1.

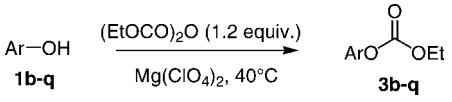
The same experimental conditions can be used to convert various phenols into aryl ethyl carbonates (Table 2). The best reaction conditions require 10 mol-% of the catalyst. The use of lower catalyst amounts (1 mol%) involves longer reaction times, except in the case of the more reactive *p*-nitro phenol (Table 2, Entry 9).

The nature of the substituent on the aromatic ring seems not to dramatically influence the reaction rate. In fact, complete conversion was observed in almost all cases.

All reactions were carried out under SFC in order to minimize solvent waste, since the solid alcohols dissolved in dicarbonate **2** at 40 °C. Only **1q** was not soluble in the reaction medium, making the addition of dichloromethane as solvent necessary.

The reaction is highly chemoselective. In fact, various functionalities present in the substrates are tolerated under the adopted reaction conditions, including aldehyde, ketone

Table 2. Reaction of aromatic alcohols **1** with diethyl dicarbonate (**2**, 1.2 equiv.) in the presence of $Mg(ClO_4)_2$ at 40 °C.



Entry	Ar	Catalyst amount [mol-%]	Time [h]	Product	Yield [%]
1	*o*-CH_3O–C_6H_4-	10	3	**3b**	>99
2	*m*-CH_3O–C_6H_4-	10	2	**3c**	98
3	*p*-CH_3O–C_6H_4-	10	3	**3d**	>99
4	*p*-CH_3O–C_6H_4-	1	3	**3d**	98
5	*m*-Cl–C_6H_4-	10	5	**3e**	98
6	*m*-Cl–C_6H_4-	1	5	**3e**	93
7	*p*-F–C_6H_4-	10	5	**3f**	85
8	*p*-NO_2–C_6H_4-	10	1.5	**3g**	>99
9	*p*-NO_2–C_6H_4-	1	1.5	**3g**	>99
10	*p*-CHO–C_6H_4-	10	4.5	**3h**	>99
11	*p*-CHO–C_6H_4-	1	4.5	**3h**	88
12	*m*-CH_3C=O–C_6H_4-	10	4.5	**3i**	>99
13	*m*-$N(CH_3)_2$–C_6H_4-	10	4.5	**3j**	85
14	*m*-$N(CH_3)_2$–C_6H_4-	none	6	**3j**	80
15	*p*-CN–C_6H_4-	10	4.5	**3k**	97
16	*o*-CN–C_6H_4-	10	20	**3l**	82[a]
17	4-[$HO(CH_2)_3$]–C_6H_4-	10	6	**3m**	89[b,c]
18	3-pyridyl	10	5.5	**3n**	>99
19	3-pyridyl	none	7	**3n**	98
20	1-naphthyl	10	3	**3o**	>99
21	2-naphthyl	10	3	**3p**	>99
22	8-quinolyl	10	7.5	**3q**	93[b]

[a] 15% of unreacted starting material was also recovered. [b] Reaction carried out in dichloromethane. [c] Reaction carried out with 1.05 equiv. of **2**.

and cyano substituents and heterocyclic functionalities (Table 2, Entries 10, 12, 15, 16, 18 and 22). Tertiary amines are not cleaved, in contrast to mixed carbonate formation with ethyl chloroformate.[17e]

Unlike neutral substrates, which were recovered unaltered in the absence of the catalyst, basic substrates reacted without any catalyst but in fairly lower yields (Table 2, Entries 14 and 19). These results can be rationalized by classical base catalysis or by an attack of the nitrogen on the carbonyl group followed by migration.

We also investigated the chemoselectivity of the reaction. Initially, 3-(4-hydroxyphenyl)propanol (**1m**) was allowed to react under standard reaction conditions, and a mixture of products was obtained, in which the monocarbonate **3m** was the major product, and minor products were identified as 3-{4-[(ethoxycarbonyl)oxy]phenyl}propyl ethyl dicarbonate, ethyl 3-(4-hydroxyphenyl)propyl carbonate and the starting material. Since the reaction mixture was syrupy, we thought that the medium viscosity was very likely to be responsible for the incomplete chemoselectivity. Therefore, almost equimolar amounts of **1m** and **2** were dissolved in dichloromethane (0.3 M solution of **1m**) and were allowed to react in the presence of the catalyst (Table 2, Entry 17). After 6 h, the reactants disappeared, and the regioselectivity was complete, since ethyl 4-(3-hydroxypropyl)phenyl carbonate (**3m**) was the only isolated product. Only trace amounts of the dicarbonate were detected by NMR analysis.

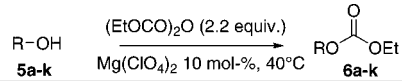
This result prompted us to extend this procedure to the synthesis of alkyl ethyl carbonates. The reaction succeeded with primary alkyl alcohols, which smoothly reacted with diethyl dicarbonate to give the corresponding mixed carbonates in good yields (Table 3, Entries 1–7). However, the reaction with aliphatic alcohols proved to be slower than that with phenols, and the ethanol by-product competed in the addition to **2** [Scheme 1, Equation (2)]. Thus, to complete the reaction, it was necessary to use 2.2 equiv. of diethyl dicarbonate. Diethyl carbonate is formed as a by-product, but it generally can be easily separated from the desired carbonate by column chromatography.

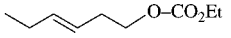
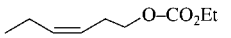
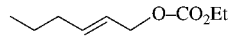
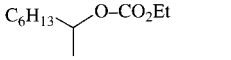
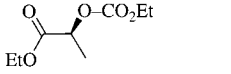
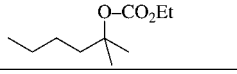
Even with aliphatic alcohols, various functional groups are tolerated, including bromide, the triisopropylsilyloxy group and carbon–carbon double bonds in various positions and geometries (Table 3, Entries 3–7).

Under the same conditions, less reactive secondary alcohols give the mixed carbonates in a maximum yield of 55% (Table 3, Entries 8–10). A complete conversion of 2-octanol into **6h** could not be obtained, even by using 4 equiv. of diethyl dicarbonate. On the other hand, tertiary alcohols are totally unreactive under the adopted reaction conditions, as demonstrated by the recovery of 2-methyl-2-hexanol (**5k**) unaltered after 15 h at 40 °C in the presence of 2.2 equiv. of **2**.

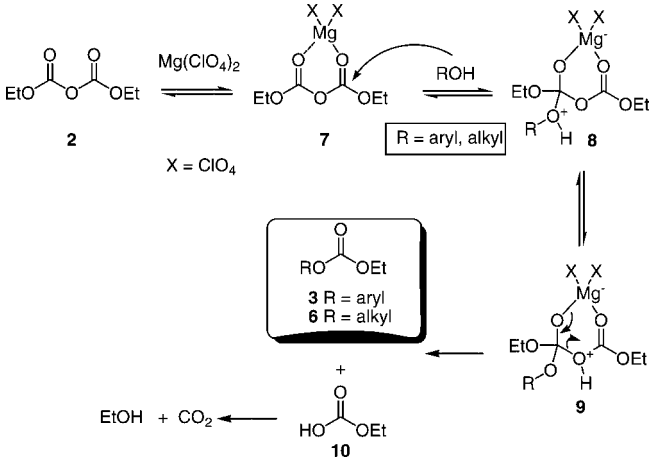
Some considerations on the reaction mechanism are necessary to explain the observed reactivity. The results obtained suggest that the reaction rate depends on the acidity

Table 3. Reaction of aliphatic alcohols (**5**) with diethyl dicarbonate (**2**, 2.2 equiv.) in the presence of 10 mol-% of $Mg(ClO_4)_2$ at 40 °C.



Entry	Product		Time [h]	Yield [%]
1	$C_8H_{17}O–CO_2Et$	**6a**	7	91
2	$PhCH_2O–CO_2Et$	**6b**	15	94
3	$Br–(CH_2)_9O–CO_2Et$	**6c**	7	92
4	$iPr_3SiO-(CH_2)_4O–CO_2Et$	**6d**	5.5	99
5		**6e**	5.5	85
6		**6f**	6.5	85
7		**6g**	10	85
8		**6h**	7.5	55
9	(*r*)-Menthyl–O–CO_2Et	**6i**	6	51
10		**6j**	7	51
11		**6k**	15	0

of the starting hydroxy compound, and not on its nucleophilicity, as in the transesterification process. In fact, the more acidic and less nucleophilic phenols react faster than aliphatic alcohols, and the *p*-nitrophenol **3g** is the most reactive among the aromatic substrates. Therefore, the release of the alcoholic proton should be involved in the rate-determining step. A similar dependence of the reaction rate on alcohol acidity was already demonstrated by Gooßen in the esterification of carboxylic acids with dicarbonates.[7a] A reasonable mechanistic hypothesis is depicted in Scheme 2.



Scheme 2. A possible mechanistic explanation.

Owing to its ability to coordinate 1,3-dicarbonyl compounds, $Mg(ClO_4)_2$ reacts with diethyl dicarbonate to form complex **7**, which can undergo the addition of the alcohol to form intermediate **8**. An internal proton shift in **8** can produce intermediate **9**, which can irreversibly decompose to the mixed carbonate **3** and to the carbonic acid monoester **10**. Owing to its high instability, **10** immediately produces EtOH and CO_2. The irreversibility of the last two steps drives the overall process towards **3**. This explanation accounts for the formation of the mixed carbonate **3** as the major product of the reaction. However, this is a speculative hypothesis, supported only by the analysis of the experimental results. Unfortunately, at the moment, all attempts to follow the reaction by NMR analysis failed to identify the presence of any intermediate, and only the starting materials and the reaction products were observed. Nevertheless, studies are in progress to find experimental evidence to elucidate the reaction mechanism.

However, since the release of the alcoholic proton in **8** seems to be the key step of the process, an easy shift of the proton will accelerate the overall reaction. In other words, a higher acidity of the starting alcohol will result in a faster formation of **3**. Aryl alcohols are therefore more reactive than aliphatic ones. Among alkyl alcohols, steric hindrance, together with the relative acidity, probably influences the reactivity, primary alcohols being more reactive than secondary ones and tertiary alcohols being completely unreactive.

Conclusions

In conclusion, we have developed a new, mild and general method for the direct synthesis of ethyl aryl carbonates catalysed by a Lewis acid. Mixed carbonates are generally prepared under basic catalysis, but side reactions often occur. With the aim of avoiding the formation of by-products, we explored the efficiency of Lewis acid catalysis. Our original idea was to activate diethyl dicarbonate with $Mg(ClO_4)_2$, a specific coordinating agent for dicarbonyl compounds. This approach proved to be effective in focusing the reaction exclusively towards the desired product.

In addition, the reaction proceeds under mild conditions at 40 °C with a slight excess of dicarbonate under SFC. Various functional groups are tolerated, and the protocol can be successfully applied to primary alcohols, allowing for a new, simple approach to alkyl ethyl carbonates. Finally, an easy tuning of the reaction conditions allows a simple and chemoselective formation of alkyl aryl carbonates in the presence of aliphatic hydroxyl groups.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were recorded at 400 or 300 MHz and 100 or 75 MHz, respectively. The chemical shifts (δ) are given in ppm relative to the signals of the solvent ($CHCl_3$) or TMS. Coupling constants are given in Hz. Carbon types were determined by DEPT ^{13}C NMR experiments. The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and bs (broad signal). The purification of the reaction products was carried out by flash chromatography on silica gel (230–400 mesh).

Materials: Commercial grade reagents and solvents were used without further purification. All starting alcohols, anhydrous $Mg(ClO_4)_2$ and diethyl dicarbonate were purchased from Aldrich and used as received.

General Procedure for the Synthesis of Aryl Ethyl Carbonates (3): In a two-necked flask equipped with a magnetic stirring bar, $Mg(ClO_4)_2$ (0.10 mmol), the phenol **1** (1.0 mmol) and diethyl dicarbonate **2** (1.2 mmol) were added. The mixture was stirred at 40 °C until the GM-MS analysis revealed the presence of **1**. The crude reaction mixture was diluted with water and extracted with Et_2O. The organic layer was separated, dried with $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The aryl ethyl carbonate **3** was purified by flash chromatography on silica gel with a mixture of petroleum ether/Et_2O = 95:5. Ethyl phenyl carbonate (**3a**) and ethyl 4-nitrophenyl carbonate (**3g**) are commercial products. Ethyl 2-methoxyphenyl carbonate (**3b**),[21] ethyl 4-methoxyphenyl carbonate (**3d**)[22] and ethyl 4-formylphenyl carbonate (**3h**)[23] are completely characterized known compounds. Ethyl 3-methoxyphenyl carbonate (**3c**),[24] ethyl 3-chlorophenyl carbonate (**3e**),[25] ethyl 4-fluorophenyl carbonate (**3f**),[26] ethyl 3-(dimethylamino)phenyl carbonate (**3j**)[27] ethyl 4-cyanophenyl carbonate (**3k**),[28] ethyl 2-cyanophenyl carbonate (**3l**)[29] ethyl pyrid-3-yl carbonate (**3n**),[30] ethyl naphth-1-yl carbonate (**3o**),[31] ethyl naphth-2-yl carbonate (**3p**)[24] and ethyl quinol-8-yl carbonate (**3q**)[32] are known compounds.

^1H and ^{13}C NMR spectroscopic data for uncharacterized compounds follow.

Ethyl 3-Acetylphenyl Carbonate (3i): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.40 (t, J_{HH} = 7.4 Hz, 3 H), 2.60 (s, 3 H), 4.33 (q, J_{HH} = 7.4 Hz, 2 H), 7.35–7.40 (m, 1 H), 7.45–7.55 (m, 1 H), 7.75–7.80 (m, 1 H), 7.80–7.85 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 26.6 (CH_3), 64.9 (CH_2), 120.8 (CH), 125.7 (CH), 125.8 (CH), 129.6 (CH), 138.5 (C), 151.4 (C), 153.3 (C), 196.7 (C) ppm. IR: $\tilde{\nu}$ = 1759 (s), 1686 (s), 1234 (vs) cm^{-1}. EI–MS: *m/z* (%) = 208 (3), 164 (4),149 (19), 136 (32), 121 (100), 93 (19), 65 (10), 43 (24). HRMS: calcd. for $C_{11}H_{12}O_4$ 208.07356; found 208.07312.

Ethyl 4-(3-Hydroxypropyl)phenyl Carbonate (3m): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.37 (t, J_{HH} = 7.3 Hz, 3 H), 1.79–1.81 (m, 2 H), 2.02 (bs, 1 H, OH, exchange with D_2O), 2.67 (t, J_{HH} = 7.3 Hz, 2 H), 3.62 (t, J_{HH} = 6.3 Hz, 2 H), 4.29 (q, J_{HH} = 7.3 Hz, 2 H), 7.07 (d, J_{HH} = 8.2 Hz, 2 H), 7.18 (d, J_{HH} = 8.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 31.3 (CH_2), 34.0 (CH_2), 61.8 (CH_2), 64.7 (CH_2), 120.8 (CH), 129.2 (CH), 133.5 (C), 149.1 (C), 153.7 (C) ppm. IR: $\tilde{\nu}$ = 3379 (vs), 2937 (s), 1758 (vs), 1255 (vs) cm^{-1}. EI–MS: *m/z* (%) = 224 (3), 206 (17), 135 (23), 134 (100), 133 (52), 107 (49), 91 (11), 77 (10). HRMS: calcd. for $C_{12}H_{16}O_4$ 224.10486; found 224.10474.

General Procedure for the Synthesis of Alkyl Ethyl Carbonates (6): In a two-necked flask equipped with a magnetic stirring bar, $Mg(ClO_4)_2$ (0.10 mmol), the alcohol **5** (1.0 mmol) and diethyl dicarbonate (**2**) (2.2 mmol) were added. The mixture was stirred at 40 °C until the GM-MS analysis revealed the presence of **1**. The crude reaction mixture was diluted with water and extracted with Et_2O. The organic layer was separated, dried with $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The alkyl ethyl carbonate **6** was separated from the residual alcohol by flash chromatography on silica gel with a mixture of petroleum ether/Et_2O = 95:5. Ethyl octyl carbonate (**6a**),[33] benzyl ethyl carbonate (**6b**),[34] (*E*)-ethyl hex-2-enyl carbonate (**6g**),[35] ethyl octan-2-yl carbonate (**6h**),[36] ethyl (*R*)-menthyl carbonate (**6i**)[27] and (*S*)-ethyl 2-(ethoxycarbonyloxy) propanoate (**6j**)[37] are completely characterized known compounds. (*E*)-ethyl hex-3-enyl carbonate (**6e**)[38] and (*Z*)-ethyl hex-3-enyl carbonate (**6f**)[31] are known compounds.

^1H and ^{13}C NMR spectroscopic data for uncharacterized compounds follow.

9-Bromononyl Ethyl Carbonate (6c): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.20–1.50 (m, 13 H), 1.60–1.75 (m, 2 H), 1.80–1.90 (m, 2 H), 3.41 (t, J_{HH} = 6.9 Hz, 2 H), 4.12 (t, J_{HH} = 6.2 Hz, 2 H), 4.19 (t, J_{HH} = 7.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (CH_3), 26.0 (CH_2), 28.4 (CH_2), 29.0 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 33.0 (CH_2), 34.4 (CH_2), 64.2 (CH_2), 68.3 (CH_2), 155.7 (C) ppm. IR: $\tilde{\nu}$ = 2929 (s), 2855 (s), 1747 (vs), 1258 (vs) cm^{-1}. ESI-MS: (*m/z*) = 319–317 $[M+Na]^+$, 295–297 $[M+H]^+$. $C_{12}H_{23}BrO_3$ (295.21): calcd. C 48.82, H 7.85, Br 27.07, O 16.26; found C 48.90, H 7.85.

Ethyl 4-(Triisopropylsilyloxy)butyl Carbonate (6d): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00–1.10 (m, 21 H), 1.31 (t, J_{HH} = 7.3 Hz, 3 H), 1.55–1.70 (m, 2 H), 1.70–1.85 (m, 2 H), 3.73 (t, J_{HH} = 6.2 Hz, 2 H), 4.15–4.25 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9 (CH), 14.2 (CH_3), 18.0 (CH_3), 25.2 (CH_2), 29.2 (CH_2), 62.3 (CH_2), 63.6 (CH_2), 67.8 (CH_2), 155.3 (C) ppm. IR: $\tilde{\nu}$ = 2942 (s), 2866 (s), 1747 (vs), 1258 (vs), 1105 (s), 1012 (s) cm^{-1}. ESI-MS: (*m/z*) = 341 $[M+Na]^+$, 319 $[M+H]^+$. $C_{16}H_{34}O_4Si$ (318.52): calcd. C 60.33, H 10.76, O 20.09, Si 8.82; found C 60.30, H 10.75.

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[1] J. C. Schumacher, *Perchlorates – Their Properties, Manufacture and Uses*, ACS Monograph Series, Reinhold, New York, **1960**.
[2] J. Long, *Chem. Health Saf.* **2002**, *9*(3), 12–18.
[3] A. M. El-Awad, R. M. Gabr, M. M. Girgis, *Thermochim. Acta* **1991**, *184*, 205–212.
[4] http://en.wikipedia.org/wiki/List_of_NFPA_704_ratings#M.
[5] http://www.jtbaker.com/msds/englishhtml/a6648.htm.
[6] In the Hard/Soft Acid/Base (HSAB) theory, bond dissociation energy is low with soft anions, and perchlorates are classified as "soft", since they can easily delocalize a negative charge. See also G. Wulfsberg, *Principles of Descriptive Inorganic Chemistry*, Wadsworth, Monterey, **1987**, ch. 2.
[7] a) L. Gooßen, A. Döhring, *Adv. Synth. Catal.* **2003**, *345*, 943–947; b) G. Bartoli, J. Boeglin, M. Bosco, M. Locatelli, M. Massaccesi, P. Melchiorre, L. Sambri, *Adv. Synth. Catal.* **2005**, *347*, 33–38.
[8] G. Bartoli, M. Bosco, M. Locatelli, E. Marcantoni, P. Melchiorre, L. Sambri, *Synlett* **2004**, 239–242.
[9] G. Bartoli, M. Bosco, M. Locatelli, E. Marcantoni, M. Massaccesi, P. Melchiorre, L. Sambri, *Synlett* **2004**, 1794–1798.
[10] G. Bartoli, M. Bosco, M. Locatelli, E. Marcantoni, P. Melchiorre, L. Sambri, *Org. Lett.* **2005**, *7*, 427–430.
[11] Some examples of patents that appeared recently follow: a) H. Buchold, J. Eberhadt, U. Wagner, H.-J. Woelk, (Lurgi Ag, Germany) PCT Int. Appl. WO 2005028415 (**2005**); b) M. Miyamoto, T. Tayama, JP 2005126496 (**2005**); c) N. Miyake, T. Watanabe, K. Onishi, A. Sato, PCT Int. Appl. WO 2005000783 (**2005**); d) Y. Sasaki, M. Takehara, M. Ue, (Mitsubishi Chemical Corp., Japan) JP 2004010491 (**2004**); e) H. Kawanami, K. Sasaki, Y. Ikushima, (National Institute of Advanced Industrial Science and Technology, Japan). JP 2004107241 (**2004**); f) T. Kanamaru, (Mitsubishi Chemical Corporation, Japan). PCT Int. Appl. WO 2004016577 (**2004**).
[12] a) A.-A. G. Shaikh, S. Siviram, *Chem. Rev.* **1996**, *96*, 951 and references cited therein; b) J. P. Parrish, R. N. Salvatore, K. W. Jung, *Tetrahedron* **2000**, *56*, 8207.

[13] T. W. Greene, P. G. M. Wuts in *Protective Groups in Organic Synthesis*, Wiley, New York, 3rd ed., **1999**.
[14] A. F. Hegarty in *Comprehensive Organic Chemistry* (Ed.: I. O. Sutherland), Pergamon, London, **1979**, vol. 2, p. 1067.
[15] Some selected references follow: a) P. Tundo, M. Selva, *Acc. Chem. Res.* **2002**, *35*, 706–716; b) B. Veldurthy, J. M. Clacens, F. Figueras, *Eur. J. Org. Chem.* **2005**, 1972–1976; c) S. Carloni, D. E. De Vos, P. A. Jacobs, R. Maggi, G. Sartori, R. Sartorio, *J. Catal.* **2002**, *205*, 199–204; d) P. Tundo, L. Rossi, A. Loris, *J. Org. Chem.* **2005**, *70*, 2219–2224; e) B. Veldurthy, F. Figueras, *Chem. Commun.* **2004**, 734–735; f) M. Verdecchia, M. Feroci, L. Palombi, L. Rossi, *J. Org. Chem.* **2002**, *67*, 8287–8289; g) M. O. Bratt, P. C. Taylor, *J. Org. Chem.* **2003**, *68*, 5439–5444; h) R. N. Salvatore, F. Chu, A. S. Nagle, E. A. Kapxhiu, R. M. Cross, K. W. Jung, *Tetrahedron* **2002**, *58*, 3329–3347; i) R. Srivastava, D. Srinivas, P. Ratnasamy, *Appl. Catal., A* **2005**, *289*, 128–134.
[16] For instance see: a) S. Fukuoka, M. Tojo, M. Kawamura (Asahi Chemical Industry Co.) WO 9109832 (**1991**); b) H. Krimm H. J. Buysch, H. Rudolph, (Bayer A. G.) DE 2736062, (**1979**).
[17] See, among others: a) J. W. Faller, J. C. Wilt, *Organometallics* **2005**, *24*, 5076–5083; b) N. Shobana, M. Amirthavalli, V. Deepa, P. Shanmugan, *Indian J. Chem. Ser. B* **1988**, *27*, 965–966; c) W. Toshimitsu, N. Yoshio, M. Shinichi, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3081–3082; d) S. Ogosh, S. Nishiguchi, K. Tsutsumi, H. Kurosawa, *J. Org. Chem.* **1995**, *60*, 4650–4652; e) S. M. Rahmathullah, J. E. Hall, B. C. Bender, D. R. McCurdy, R. R. Tidwell, D. W. Boykin, *J. Med. Chem.* **1999**, *42*, 3994–4000; f) D. K. Kim, N. Lee, D. H. Ryu, Y. W. Kim, K. Chang, G. J. Im, W. S. Choi, Y. B. Cho, K. H. Kim, D. Colledge, S. Locarini, *Bioorg. Med. Chem.* **1999**, *7*, 1715–1725.
[18] Diethyl dicarbonate has been used to ultimately obtain diaryl carbonates in the presence of Ti^{IV} butoxide at high temperature: K. Shigematsu, F. Togawa: (Idemitsu Kosan Co.) JP04187661, (**1992**).
[19] The anhydrous form worked better than the hydrated one (Table 1, entries 1–2). However, the presence of small amounts of water did not lower the reaction efficiency, and hence $Mg(ClO_4)_2$ can be used as supplied.
[20] G. Bartoli, M. Bosco, R. Dalpozzo, E. Marcantoni, M. Massaccesi, L. Sambri, *Eur. J. Org. Chem.* **2003**, 4611–4617.
[21] N. Bensel, V. Pevere, J. R. Desmurs, A. Wagner, C. Mioskowsi, *Tetrahedron Lett.* **2002**, *43*, 4281–4283.
[22] H. J. Koh, J. W. Lee, H. W. Lee, I. Lee, *Can. J. Chem.* **1998**, *76*, 710–716.
[23] Sadtler Standard Carbon-13 NMR Spectra.
[24] E. A. Caress, I. E. Rosenberg, *J. Org. Chem.* **1972**, *37*, 3160–3163.
[25] E. A. Caress, I. E. Rosenberg, *J. Org. Chem.* **1971**, *36*, 769–772.
[26] G. Gill, D. A. K. Jones, R. Taylor, *J. Org. Chem.* **1963**, *28*, 3547–3550.
[27] W. R. Brown, F. A. Mason, *J. Chem. Soc.* **1934**, 651–653.
[28] T. H. Fife, J. E. C. Hutchins, *J. Am. Chem. Soc.* **1981**, *103*, 4194–4199.
[29] A. Einhorn, G. Haas, *Ber. Dtsch. Chem. Ges.* **1905**, 3627–3632.
[30] J. Larrouquere, *Bull. Soc. Chim. Fr.* **1968**, 329–335.
[31] P. M. Kraemer, M. P. Marco, B. D. Hammock, *J. Agric. Food Chem.* **1994**, *42*, 934–943.
[32] R. E. Stenseth, R. M. Schisla, W. Baker, *J. Chem. Eng. Data* **1960**, *5*, 390–397.
[33] S. Carloni, D. E. De Vos, P. A. Jacobs, R. Maggi, G. Sartori, R. Sartorio, *J. Catal.* **2002**, *205*, 199–204.
[34] C. Bakhtiar, E. H. Smith, *J. Chem. Soc., Perkin Trans. 1* **1994**, 239–243.
[35] D. W. Knight, A. L. Redfern, J. Gilmore, *J. Chem. Soc., Perkin Trans. 1* **2001**, 2874–2883.
[36] I. I. Khatuntsev, S. S. Zlotskii, E. V. Pastushenko, A. B. Terent′ev, D. L. Rakhmankulov, *J. Appl. Chem. USSR (Engl. Transl.)* **1985**, *58*, 1077–1079.
[37] A. Cipollone, M. A. Loreto, L. Pellacani, P. A. Tardella, *J. Org. Chem.* **1987**, *52*, 2584–2586.
[38] S. Okamoto, A. Kasatkin, P. K. Zubaidha, F. Sato, *J. Am. Chem. Soc.* **1996**, *118*, 2208–2216.

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