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Carbon Dioxide Utilisation for the Synthesis of Unsymmetrical Dialkyl and Cyclic Carbonates Promoted by Basic Ionic Liquids

Peter Goodrich,^A H. Q. Nimal Gunaratne,^{A,D} Lili Jin,^{B,D} Yuntao Lei,^B and Kenneth R. Seddon^{A,C}

^AThe QUILL Research Centre, School of Chemistry and Chemical Engineering, The Queen's University of Belfast, Stranmillis Road, Belfast, Northern Ireland, BT9 5AG, UK.

^BDepartment of Organic Chemistry, China Pharmaceutical University,

Nanjing 210009, China.

^CDeceased.

^DCorresponding authors. Email: n.gunaratne@qub.ac.uk; jinlili@cpu.edu.cn

An efficient and greener synthesis of unsymmetrical organic carbonates mediated by Hünig's base-appended basic ionic liquids, via carbon dioxide conversion, is described here. These ionic liquids were found to be effective bases for the fixation of carbon dioxide by various alcohols and benzyl bromide, at room temperature. When the alcohol and the halide functionalities are present within the same substrate, the reaction cleanly produces a cyclic carbonate. These functionalised basic ionic liquids were fully recyclable with no loss product yields.

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The chemical conversion of carbon dioxide into value-added chemicals has been paid much attention in the past decades.^[1-3] Since the greenhouse gas CO_2 is an abundant, cheap, non-toxic, undesirable, and renewable C1 feedstock,^[4,5] it would be of interest to the scientific community and industries to utilise it to generate value-added chemicals. CO₂ is most frequently treated with alcohols^[6,7] or epoxides^[8-11] for the synthesis of symmetric, cyclic, or polycarbonates.^[11] Unsymmetrical organic carbonates are valuable chemicals in numerous applications, such as intermediates for the synthesis of pharmaceuticals^[12] and fine chemicals,^[13,14] as excellent polar aprotic solvents,^[15] and as monomers for organic glasses, synthetic lubricants or plasticisers.^[16] To produce organic carbonates, conventional synthetic methods use phosgene,^[17–19] haloformates,^[20] or carbon monoxide^[21] as starting materials. However, these chemicals are toxic and have harmful effects on environment and health. Hence, developing an alternative methodology for producing these compounds is highly desirable. Dimethyl carbonate (DMC)^[22-24] is an environmentally

Dimethyl carbonate $(DMC)^{[22-24]}$ is an environmentally friendly methylating agent which can be substituted for phosgene in some organic reactions, in particular in the preparation of organic carbonates via transesterification of DMC or DEC (diethyl carbonate) with various alcohols. The developed catalysts include 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD),^[25] MCM-41-TBD,^[26] immobilised TBD on magnetic γ -Fe₂O₃ nanoparticles,^[27] Mg-La mixed metal oxides,^[28] CsF/ α -Al₂O₃,^[29] nanocrystalline MgO,^[30] organotin-oxomolybdate coordination polymer,^[31] and 1-(3-trimethoxysilylpropyl)-3methylimidazolium chloride.^[32] However, these catalytic systems are usually operated at high temperatures (>100°C). Another method employed electrochemical synthesis starting from CO₂ and alcohols using ionic liquids (ILs)^[33] as reaction media. Unsymmetrical organic carbonates have been synthesised, recently, via a coupling reaction of alcohol, CO₂, and haloalkanes in the presence of Cs₂CO₃ or K₂CO₃,^[34–36] but these reactions need tetrabutylammonium iodide or tetrabutylammonium bromide as promoters and *N*,*N*-dimethylmethanamide as solvent.

ILs exhibit good to excellent performance in many reactions, whether they act as catalysts or as reaction media. Their desirable properties as organic reaction media are well documented.^[33,37-40] In our previous work, we reported a new class of non-nucleophilic basic ILs (Fig. 1, except 1d),^[41,42] bearing the structure of the Hünig's base,^[43] ethyldi(isopropyl)amine (NEt^{*i*}Pr₂). This class of IL possesses a sterically hindered and non-nucleophilic tertiary amine functionality which is linked to a quaternary ammonium molecular segment. The basicity of the tertiary amine is tuned by the nature and the length of the tether, i.e. the choice of linker between the two nitrogen centres. It was hypothesised that the ILs depicted in Fig. 1 would make ideal recyclable materials for the fixation of CO₂ to form alkyl carbonates. The lack of nucleophilicity of the base unit appended to the cation of these ILs would prevent any side reactions emanating from haloalkane substrates.



Fig. 1. Set of Hünig's base-tagged basic ILs 1a-c and tetramethylguanidine-appended IL 1d used in this work, where $[NTf_2]^-$ represents bis{(trifluoromethyl)sulfonyl}amide.

ROH + R'X + CO₂
$$\xrightarrow{\text{IL, 1.0 MPa}}$$
 R \xrightarrow{O}_{O} R'

Scheme 1. The synthesis of unsymmetrical carbonates from CO_2 , alcohols, and haloalkanes.

Herein, we report a room-temperature, environmentally benign method for the synthesis of dialkyl organic carbonates from a three component reaction involving CO_2 , alcohols, and benzyl bromide, mediated by basic ILs (Scheme 1). It's worth noting that we are the first group to use a non-nucleophilic basic IL as a base catalyst to promote CO_2 chemical fixation. This method avoids the use of metal-based catalysts and co-catalysts.

The reaction was carried out in ILs 1a-d under prescribed reaction conditions ($P_{CO_2} = 1.0$ MPa, $T = 25^{\circ}$ C). The influences of different basic ILs, temperature, CO₂ pressure, and ratios of substrates were investigated. In the absence of a base, no reaction was observed (Table 1, entry 1). However, when the reaction was repeated with 1a, an IL functionalised with N'Pr₂ in the side chain, which gave only benzyl propargyl carbonate in the presence of CO₂ at 1.0 MPa and room temperature (entry 2, 47 % yield). Notably, no side products originating from direct nucleophilic attack of alcohol or base on benzyl bromide were observed. The comparative activity of the other three ILs (1b-d) was also examined, and the results showed that 1c was the most effective. As shown from our previous work,^[41] 1c is the most basic material among these ILs, as a consequence of having the longest spacer between the cationic head group and the Hünig's base unit. As expected, the higher basicity of the IL 1c, resulted in obtaining a higher yield of carbonates. Thus, 1c improved the yield to 74% (Table 1, entry 4). Furthermore, prolonging the reaction time to 60 h elevated the yield of the carbonate to 80 %(Table 1, entry 5).

The new IL **1d**, which contains the 1,1,3,3-tetramethylguanidine (TMG) group, is a strong organic base. It was designed specifically to improve the yield of the organic carbonate. Unfortunately, the desired product was not detected after the reaction, presumably due to the TMG group being insufficiently sterically hindered to prevent its nucleophilic attack on benzyl bromide, producing a quaternary salt.

The effect of the temperature on this reaction was also investigated (Table 1, entries 4, 7, 8). The yield of benzyl propargyl carbonate did not enhance significantly when the temperature increased from room temperature to 40°C, albeit shortening the reaction time. The different ratio of substrates and IL has some influence on the reaction (Table 1, entries 4, 10–12). In general, the yield of benzyl propargyl carbonate increased with increasing concentrations of propargyl alcohol. The

Table 1. Optimisation of the synthesis of benzyl propargyl carbonate

Ph Br + HC = CCH₂OH
$$\xrightarrow{CO_2}$$
 Ph \xrightarrow{O}

Entry ^A	IL	Amounts of ROH, RX, IL	$T[^{\circ}C]$	Time [h]	Yield ^B [%]
1	_	1.0, 0.5, 0	25	48	0
2	1a	1.0, 0.5, 1.2	25	48	47
3	1b	1.0, 0.5, 1.2	25	48	42
4	1c	1.0, 0.5, 1.2	25	48	74
5	1c	1.0, 0.5, 1.2	25	60	80
6	1d	1.0, 0.5, 1.2	25	48	0
7	1c	1.0, 0.5, 1.2	30	48	79
8	1c	1.0, 0.5, 1.2	40	24	76
9	1c	1.0, 0.5, 1.2	40	30	82
10	1c	1.0, 1.0, 1.2	25	48	45
11	1c	1.0, 0.25, 1.2	25	48	74
12	1c	1.0, 0.5, 0.6	25	48	76

^AReaction conditions: CO_2 (1.0 MPa; carried out in a 16 mL stainless-steel autoclave). As for the selectivity of the reaction, no detectable by-products were observed in ¹H NMR spectra of isolated product (see Supplementary Material for spectra). We presumed that all the starting materials were transformed into products.

^BYield was determined by ¹H NMR spectroscopy.

product was generated in 45% yield when a stoicheiometric ratio of alcohol and benzyl bromide was used (entry 10), and in \sim 74% yield with either a 2-fold or 4-fold excess of alcohol (entries 4, 11, 12).

In order to examine the effect of pressure on the reaction, the experiment was carried out at different CO_2 pressures (Fig. 2). An effectively linear dependency of the yield upon pressure was observed, but the gradient is shallow. It is clearly advantageous to run the reaction at atmospheric pressure, rather than 10 atmospheres, as the slightly lower yield is offset against the expense and hazard of working at elevated pressures.

Further investigation on the recyclability of the IL system for these reactions, including linear and cyclic carbonation formation, proved very successful. The IL **1c** could be recovered quantitatively from the reaction system by extraction or distillation (see Supplementary Material), and used several times for the reaction, with no negative impact upon the yield.

Based on the above results, a plausible reaction mechanism (Fig. 3) was postulated. In the initial step, the basic (but non-nucleophilic) cation of the IL deprotonates the alcohol, resulting in the formation of a nucleophilic alkoxide. This then attacks the



Fig. 2. The influence of the pressure of CO_2 on the reaction with propargyl alcohol (1.0 mmol, 56 mg) and benzyl bromide (0.5 mmol, 85.5 mg) in the presence of 1c (0.6 mmol, 0.341 g) in a 16 mL stainless-steel autoclave for 24 h.



Fig. 3. Proposed mechanism for the formation of carbonate from CO₂.

weakly electrophilic carbon of CO_2 to form a carbonate anion, which subsequently reacts with the benzyl bromide (S_N2) to produce the corresponding carbonate and the protonated IL.

Having established the optimal conditions for the synthesis of benzyl propargyl carbonate, the generic nature of the reaction was investigated using a range of different alcohols and bromoalkanes (see Table 2). The unsymmetrical dialkyl carbonates were generally produced in excellent yields under mild conditions. However, no product was detected using 1-bromobutane instead of benzyl bromide, emphasising the importance of the high electrophilicity of the haloalkane for an efficient reaction (Table 2, entry 6).

Although some unsymmetrical organic carbonates are known, $^{[27,34-36,44,45]}$ these have usually been prepared by transesterification of an alcohol with DMC, thus constraining one of the substituents to be methyl. Using other common reagents such as 1,1-carbonyldiimidazole^[46] or phosgene^[19] produces only symmetric carbonates with alcohols. Thus the reaction between alcohols, haloalkanes, and CO₂ in the presence of a basic IL provides a new, green synthetic route to both known and novel unsymmetrical dialkyl carbonates.

The scope of this reaction can be extended by combining the hydroxy and halo functionalities into one molecule, such as ω -haloalkanols (see Scheme 2), which proves to be a very efficient route to cyclic carbonates.

Table 2. Formation of unsymmetrical carbonates from ROH, R'Br,and CO2 in the presence of IL 1c

Entry ^A	R	R′	Product	Time [h]	Yield ^B [%]
1	Et	Benzyl	2b ^[27]	60	82
2	Allyl	Benzyl	2c ^[44]	72	80
3	Benzyl	Benzyl	2d ^[46]	72	83
4	Phenyl	Benzyl	2e ^[45]	72	78
5	s-Butyl	Benzyl	2f	72	67
6	Benzyl	Butyl	2g ^[36b]	72	-

^AReaction conditions: ROH (1.0 mmol), R'Br (0.5 mmol), 1c (0.6 mmol, 0.3414 g), CO_2 (1.0 MPa) at 25°C. ^BIsolated yield.

 $X OH + CO_2 IC O$ X = Cl or Br n = 0 or 1

Scheme 2. The synthesis of cyclic carbonates from CO_2 and ω -haloalkanols in the presence of a basic IL, at room temperature.

Whereas the reactions between alcohols and CO_2 in the presence of chloroalkanes are decidedly unfavoured, an intramolecular enhancement was found for the reaction between ω -chloroalkanols and CO_2 . Thus the reactions between 3-bromopropanol or 2-chloroethanol with CO_2 in the presence of 1.2 equivalents of **1c** were compared. Remarkably, both proceeded to effective completion (> 90%) within 48 h (see Fig. 4). Possible side products such as linear chain carbonates were not found in the system: the products were exclusively cyclic.

In conclusion, we have demonstrated a simple, efficient, environmentally benign, and metal-free approach for the synthesis of unsymmetrical and cyclic organic carbonates, utilising CO_2 under ambient conditions and a range of basic ILs. The use of these ILs enabled facile product isolation, accompanied by IL recycling. This represents a green route to both novel and known unsymmetrical carbonates.

Experimental

Carbon dioxide (99.99%) was obtained from BOC. All reagents and analytical grade solvents were used as received. Propargyl alcohol, phenol, benzyl alcohol, allyl alcohol, 2-butyl alcohol, 2-bromoethanol, 2-chloroethanol, 3-bromo-1-propanol, 1,1,3,3tetramethyl guanidine (TMG), ethyl bromide, 2-[2-dimethylaminoethoxy] ethanol, and 2-diisopropylaminoethyl chloride hydrochloride, were obtained from Sigma–Aldrich or TCI.

¹H and ¹³C NMR spectra were recorded on a Bruker Ultrashield 400 plus spectrometer at 25°C using methanol (CD₃OD) or trichloromethane (CDCl₃) as solvent. Electrospray (ES)-mass spectrometry measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120°C).

ILs 1a-c were prepared according to the previously published report.^[41] The procedure for the synthesis of 1d is given in the Supplementary Material.

All the reactions were carried out in a 16 mL stainless-steel autoclave with stirring at 600 rpm and equipped with an



Fig. 4. Partial ¹H NMR (400 MHz) spectra obtained in the synthesis of cyclic carbonates by CO_2 conversion promoted by **1c**. (a) ¹H NMR spectra of a mixture of 2-chloroethanol and **1c** after treating with CO_2 (top) and 2-chloroethanol in CDCl₃ (bottom). (b) ¹H NMR spectra of a mixture of 3-bromopropanol and **1c** after treating with CO_2 (top) and 3-bromopropanol in CDCl₃ (bottom). The concentrations of haloalcohols and **1c** are 0.5 mmol and 0.6 mmol, respectively; the pressure of CO_2 is 1.0 MPa.

automatic stirrer and temperature control system. In a typical reaction procedure, IL (0.60 mmol, 1.2 equiv.), benzyl bromide (0.5 mmol, 85.5 mg, 1.0 equiv.), and alcohols (1.0 mmol, 2.0 equiv.) were added into the autoclave successively. CO_2 (1.0 MPa) was charged into the reactor at room temperature. The autoclave was stirred at 25°C for an appropriate time. After reaction, the excess of CO_2 was vented. Ethyl ether (2 mL) was added to the mixture, and the crude product was extracted into the ether layer. The pure product was obtained after evaporation of solvent and excess starting materials.

Supplementary Material

Synthetic procedures and ¹H NMR, ¹³C NMR, and HRMS data for new compounds are available on the Journal's website.

Conflicts of Interest

The authors declare no conflicts of interest.

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