

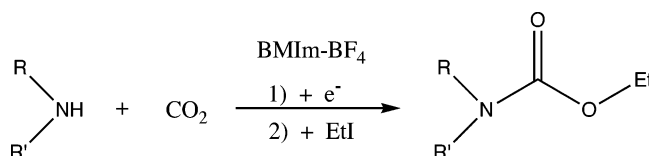
Electrochemically Promoted C–N Bond Formation from Amines and CO₂ in Ionic Liquid BMIm–BF₄: Synthesis of Carbamates

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A new electrochemical procedure for the synthesis of organic carbamates from amines and carbon dioxide has been developed using selective cathodic reduction of carbon dioxide in CO₂-saturated room-temperature ionic liquid BMIm-BF₄ solutions containing amines 1a–j, followed by addition of EtI as an alkylating agent. The synthesis was carried out under mild ($P_{\text{CO}_2} = 1.0$ atm, $t = 55$ °C) and safe conditions, and the use of volatile and toxic solvents and catalysts (according to the growing demand for ecofriendly synthetic methodologies), as well as of any supporting electrolyte (for a very easy workup of the reaction mixture), was avoided. Carbamates 2a–j were isolated in good to high yields.

Introduction

The chemistry of organic carbamates¹ arouses a continuous and strong interest in many researchers, concerning both new synthetic pathways and practical applications (synthesis of pharmaceuticals, agricultural chemistry, protective groups for the amine function, etc.).² In recent years, efforts have been directed toward the use of carbon dioxide, a safe and abundant source of carbon,³ as a possible raw material in the synthesis of linear and cyclic carbamates⁴ in place of toxic and harmful classical reagents (phosgene and its derivatives). Consequently, alternative ecofriendly routes carried out by direct incorporation of CO₂ into amines, yielding the carbamate anion, and alkylation (via alkyl halides) of this intermediate anion have been established.⁵

Nevertheless, the reactivity of carbamate anion versus the alkylating reagent (O-alkylation or N-alkylation) is strongly affected by the nature of the ion pair, i.e., carbamate anion–metal cation or carbamate anion–nonmetal cation. Metal carbamates give predominantly nitrogen-derived products (N-alkylation with elimination of carbon dioxide)⁶ and are converted into organic carbamates (O-alkylation) in low to moderate yields only under drastic conditions;⁷ to obtain acceptable values of carbamate yield, the use of crown ethers is necessary.⁸

Consequently, to establish an efficient procedure of the synthesis of carbamates via reaction of amines + CO₂ + alkyl halides, one of the key problems is identification of the conditions suitable to promote O-alkylation versus N-alkylation.

Some electrochemical procedures for the synthesis of organic carbamates from amines and CO₂ (in the organic solvents CH₃CN and DMF, containing tetraalkylammonium salts as supporting electrolytes) have been reported. These syntheses were carried out by cathodic reduction of CO₂,^{9a} of a mixture O₂ and CO₂,^{9b} of a suitable probase,^{9c} or of the supporting

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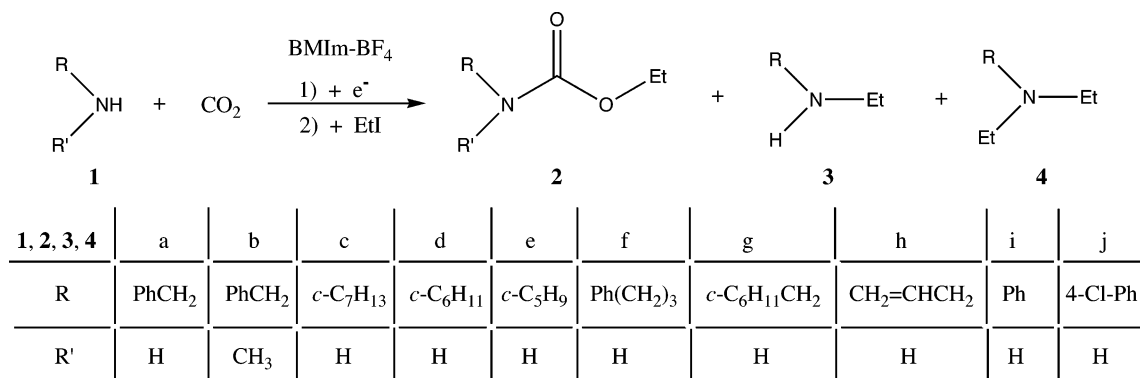
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SCHEME 1



electrolyte–solvent system.² In any case, after addition of EtI as an alkylating agent, the carbamates were isolated from the cathodic solutions in good or high yields. Therefore, under the above-indicated experimental conditions (i.e., in organic solvents containing large nonmetal cations such as tetraalkylammonium ions), the O-alkylation reaction of the carbamate anions (yielding organic carbamates) is strongly competitive with the N-alkylation reaction (yielding *N*-ethylamines).

Nevertheless, the use of volatile and toxic solvents (CH₃CN, DMF, etc.) and of large amounts of supporting electrolytes makes more complex the workup of the reaction mixture targeted at the isolation of the products and the recovery of the solvents. In addition, with the growing demand of environmental friendly technologies, any effort should be devoted to avoid the use of volatile and damaging solvents.

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Room-temperature ionic liquids [RTILs; e.g., salts of quaternary ammonium, phosphonium, imidazolium, or pyridinium cations with inorganic counterions (BF₄)[−], (PF₆)[−], (CF₃SO₃)[−], etc.] are molten salts with melting points close to room temperature.¹⁰ In recent years, RTILs, because of their low vapor pressure, chemical and thermal stability, solvating ability, nonflammability, and ability to act as catalysts, have been frequently used as “green” reaction media in clean organic synthetic processes as substitutes for conventional toxic and volatile solvents.

Recently, chemical fixation of carbon dioxide with epoxides in RTILs to form cyclic carbonates has been described (temperature, 110 °C; CO₂ pressure, 1.5 MPa; catalyst, ZnCl₂; time, 1.0 h).¹¹ In addition, 5-methylene-1,3-oxazolidin-2-ones were isolated via reaction of propargyl alcohols, aliphatic primary amines, and CO₂ in ionic liquids under relatively mild conditions (temperature, 100 °C; CO₂ pressure, 2.5 MPa; catalyst, CuCl; time, 10 h).¹²

In addition to the above-reported properties, RTILs show a high ionic conductivity and a wide electrochemical potential window.¹³ Accordingly, ionic liquids have been frequently used as electrolytes for studies related to organic electrosynthesis and to the evaluation of the redox behavior of electroactive substrates,¹⁴ as well as metal deposition, batteries, photovoltaic devices, fuel cells, and solar cells.^{13b,c} As concerns electro-

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chemically promoted CO₂ fixation, the synthesis of cyclic carbonates from epoxides in ionic liquids has been reported by Deng et al.^{14a}

Conversely, as far as we know, investigations concerning chemical fixation of carbon dioxide with amines in ionic liquids (to form linear carbamates) have not been reported. With this in mind, we began studying the reactivity of aliphatic and aromatic amines in electrolyzed CO₂-saturated RTIL solutions. The aim of this investigation was to set up an alternative methodology for the synthesis of linear carbamates via electrochemically induced C–N bond formation from amines and carbon dioxide. The synthesis was carried out in an RTIL (i.e., in the absence of the conventional solvent–supporting electrolyte system) by cathodic activation of CO₂, under mild conditions (temperature, 55 °C; CO₂ pressure, 1.0 atm) and without catalysts.

Results and Discussion

The reactivity of amines versus electrochemically activated CO₂ in an RTIL was analyzed according to the following procedure. A solution of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF₄) containing amine **1**, with continuous bubbling of CO₂, was electrolyzed under potentiostatic control in a divided cell ($E = -2.4$ V vs Ag electrode; $t = 55$ °C). At the end of electrolysis, after N₂ bubbling for 1.0 h to eliminate residual CO₂, an excess of EtI, as an alkylating agent, was added. Workup of the cathodic solution (see Experimental Section) provided the corresponding carbamate **2** (O-alkylation product) and alkylated amines **3** and **4** (N-alkylation products) (Scheme 1).

To optimize the experimental conditions for the electrochemical synthesis of carbamates (i.e., high yields of carbamates **2**, absence of alkylamines **3** and **4** as possible byproducts and high current yields), the influence of various parameters was checked using amine **1a** as a model compound (Table 1). Accordingly, several electrolyses were carried out using different numbers of faradays per mole of amine supplied to the electrodes (Q), different cathode materials, different workups of the cathodic solutions, and different procedures (see below). The yields of isolated products depend, inter alia, on the amount of electricity supplied to the electrodes during the reduction of CO₂ to CO₂^{•-}.

In fact, using a Cu cathode as well as a Pt cathode, the chemical yield of isolated **2a** increases with increasing Q ; the yields of isolated **3a** and **4a** move in the opposite direction, i.e., decrease with increasing Q (Table 1, entries 2–6 and 9–13). The yield of **2a** remains almost unchanged above 3.0 F mol⁻¹, in accordance with a notable decrease of the current efficiency (Table 1, entries 6–8 and 13–15). The maximum chemical yield of **2a** (80%, in the absence of byproducts **3a** and **4a**) is obtained (using a Pt cathode) at 3.0 F per mole of **2a** (Table 1, entry 13). Further changes of the cathode material (Ni instead of Cu or Pt) do not increase the chemical yields of isolated **2a** (Table 1, entry 16).

To evaluate the nature of the carboxylating agent, it should be considered that carbamates were isolated only from CO₂-saturated BMIm-BF₄ electrolyzed solutions containing **1a** and not from nonelectrolyzed solutions (Table 1, entries 2–6 vs entry 1). The cathode potential ($E = -2.4$ V vs Ag electrode) is negative enough to induce the selective reduction of CO₂ to CO₂^{•-}.^{14a} In aprotic solvents, the radical anion CO₂^{•-} yields, via CO₂^{•-}–CO₂ and CO₂^{•-}–CO₂^{•-} coupling reactions, the

TABLE 1. Reactivity of Amine **1a** versus Electrochemically Activated CO₂ in BMIm-BF₄.^a Effect of Q^b and Cathode Material on the Nature and Yield of Products

entry	Q	cathode	products (yield, %) ^c		
			2a	3a	4a
1	0.0	–	–	13	62
2	1.0	Cu	5	14	54
3	1.5	Cu	28	–	45
4	2.0	Cu	36	–	38
5	2.5	Cu	55	5	18
6	3.0	Cu	61	–	15
7	3.5	Cu	61	–	13
8	4.0	Cu	63	–	10
9	1.0	Pt	10	13	54
10	1.5	Pt	23	21	48
11	2.0	Pt	38	11	44
12	2.5	Pt	57	–	32
13	3.0	Pt	80	–	–
14	3.5	Pt	82	–	–
15	4.0	Pt	82	–	–
16	3.0	Ni ^d	60	–	26
17	2.0	Pt ^e	27	19	59
18	2.0	Pt ^f	32	–	14

^a Number of faradays per mole of amine supplied to the electrodes.

^b Electrolyses carried out under potentiostatic control ($E = -2.4$ V, vs Ag), divided cell, Pt anode, 55 °C, in the presence of **1a**, with continuous CO₂ bubbling. EtI added at the end of the electrolyses. ^c Yields of isolated products, based on starting **1a**. ^d $E = -2.7$ V vs Ag. ^e Amine **1a** added to the cathodic solution after the end of the electrolysis. ^f Cathodic solution extracted only with diethyl ether.

derived carbonate (with loss of CO) and oxalate anions.¹⁵ Consequently, the carboxylation of amines to carbamate anions might be related to the presence, in BMIm-BF₄, of the CO₃²⁻ system.

To ascertain the specific roles of CO₃²⁻ anion and of neutral CO₂, an alternative procedure was set up. The electrolysis of a CO₂-saturated BMIm-BF₄ solution was carried out in the absence of **1a**. At the end of the electrolysis, and after a prolonged bubbling of N₂ (until complete CO₂ elimination), **1a** was added to the cathodic solution. The usual workup, after addition of EtI, provided carbamate **2a**. The yield of isolated **2a** by this alternative procedure ($Q = 2.0$ F mol⁻¹; **1a** added at the end of the electrolysis, after the elimination of CO₂) is comparable to that obtained by the previous procedure ($Q = 2.0$; **1a** added in the presence of CO₂, Table 1, entry 11 vs entry 17). Consequently, the carboxylating power in BMIm-BF₄ solutions of CO₃²⁻ anion versus amines is unrelated to the presence of neutral CO₂.

Last, when the alkylating agent EtI was added to the cathodic solution after a high supply of current ($Q > 3.0$ F mol⁻¹), i.e. in the presence of an excess of CO₃²⁻ anions, carbamate **2a** was isolated in high yields, and alkylated amines **3a** and **4a** were completely absent (Table 1, entries 13–15). Therefore, BMIm-BF₄ enhances the nucleophilic nature of the oxygen center of the carbamate anion and promotes O-alkylation with respect to N-alkylation. (O-alkylation is a completely selective reaction versus EtI.) As previously reported, in BMIm-BF₄, the interaction between the carbamate anion and the BMIm⁺ cation (a

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TABLE 2. Synthesis of Carbamates **2** via Reaction of Amine **1** with Electrochemically Activated CO₂ in BMIm-BF₄,^a Followed by Addition of EtI ($Q = 3.0 \text{ F mol}^{-1}$,^b Pt Cathode)

entry	amine	carbamate	yield ^c (%)
1	1a	2a	80
2	1b	2b	87
3	1c	2c	85
4	1d	2d	76
5	1e	2e	78
6	1f	2f	83
7	1g	2g	74
8	1h	2h	73
9	1i	2i	38
10	1j	2j	76

^a Experimental conditions described in Table 1, footnote b. ^b Number of faradays per mole of amine supplied to the electrodes. ^c Yields of isolated carbamates based on starting amines.

highly polarizable organic counterion) is not significant enough to depress the oxygen nucleophilicity and the carbamate anion can be considered as a “naked” anion with a strong oxygen nucleophilicity versus EtI.^{5h} As concerns this problem, it must be considered that, although carbamate **2a** was not obtained at all from nonelectrolyzed CO₂-saturated BMIm-BF₄ solutions containing amine **1a**, the alkylated amines **3a** and **4a** were isolated in good yields (Table 1, entry 1). In addition, **3a** (22% yield) and **4a** (32%) were also obtained by us via simple addition of EtI to BMIm-BF₄ solutions containing **1a** in the absence of CO₂.¹⁶ Consequently, the formation of **3a** and **4a**, via addition of EtI to electrolyzed CO₂-saturated RTIL solutions containing **1a**, might be related to the direct alkylation of unreacted **1a**, unrelated to the N-alkylation of the carbamate anion (which is not competitive).

To test the effectiveness and generality of this methodology, we extended the investigation to amines **1b–j**, carrying out the reactions under optimized conditions (see Table 1, entry 13). With all amines, carbamates were obtained. Moreover, the yields were strongly affected by the nucleophilicity of the amine, as previously reported.⁹

In fact, carbamates **2a–h** were obtained in good to high yields (76–87%) from primary (**1a,c–h**) and secondary (**1b**) aliphatic amines (Table 2, entries 1–8), whereas aniline **1i** was converted

into ethyl carbanilate **2i** in only moderate yield (38%, Table 2, entry 9). Last, in accordance with a considerable substituent effect, *p*-chloroaniline **1j** was converted into ethyl carbamate **2j** in good yield (76%, Table 2, entry 10).

Conclusions

In conclusion, a new electrochemical procedure for the synthesis of organic carbamates from amines and carbon dioxide has been established by selective cathodic reduction of carbon dioxide in CO₂-saturated BMIm-BF₄ solutions containing amines **1a–j**, followed by addition of EtI as an alkylating agent. The use of volatile and toxic solvents and catalysts (according to the growing demand of ecofriendly synthetic methodologies), as well as of any supporting electrolyte (for a very easy workup of the reaction mixture), has been avoided. The synthesis was carried out under mild conditions ($P_{\text{CO}_2} = 1.0 \text{ atm}$, $t = 55 \text{ }^\circ\text{C}$), and carbamates **2a–j** were isolated in good to high yields. Further investigations using different classes of RTILs and alkylating agents, to establish the scope and the generality of this procedure, are in progress.

Experimental Section

Typical Experiment. The potentiostatic electrolysis was performed in a divided glass cell (Pt spiral cathode and anode; apparent area, 0.8 cm²; volume of catholyte and anolyte, 1 mL) using an Amel model 552 potentiostat equipped with an Amel model 572 integrator. The third electrode was an Ag wire, and it was used as a quasireference electrode.¹⁷ (All potentials are given with respect to this reference electrode.) Anolyte and catholyte were separated through a G-5 glass septum. The electrolysis was carried out under carbon dioxide atmosphere at 55 °C, at a constant potential of $E = -2.4 \text{ V}$, on a solution of amine **1a** (1 mmol) in 1 mL of BMIm-BF₄. At the end of the electrolysis, EtI was added in 3-fold molar excess, and the catholyte was allowed to stand at room temperature, under stirring, for 2 h. The reaction mixture was washed with aqueous NaHCO₃ (10 mL) and extracted with diethyl ether (3 × 5 mL), and the combined organic layers were dried over anhydrous Na₂SO₄. After the solvent had been removed under reduced pressure, product **2a** was purified using flash chromatography (*n*-hexane/ethyl acetate 8/2). The product spectral data were in accordance with those reported in the literature.¹⁸

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Supporting Information Available: General procedures and ¹H NMR and ¹³C NMR spectra of compounds **2a–j**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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