

Cyanomethyl Anion/Carbon Dioxide System: An Electrogenerated Carboxylating Reagent. Synthesis of Carbamates under Mild and Safe Conditions

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Abstract: A new carboxylating reagent ($^-CH_2CN/CO_2$) was obtained by bubbling CO_2 in a CH_3CN -TEAP (tetraethylammonium perchlorate) solution previously electrolyzed under galvanostatic control. Organic carbamates were isolated from these solutions after addition of amines and an alkylating agent. In this paper, we describe the optimized conditions for the electrochemical synthesis of carbamates from amines and CO_2 , in mild and safe conditions, without any addition of bases, probases, or catalysts. Carbamates were isolated from primary and secondary aliphatic amines in high to excellent yields and from aromatic amines in moderate yields (dependent on the nucleophilicity of the nitrogen atom).

In the past decades, the study of organic carbamates (reactivity, synthetic methodologies, applications) received special attention, and new contributions are now available through several articles.

Organic carbamates¹ are a class of compounds of growing interest because of their multiple applications as protective groups for the amine function of amino acids in peptide chemistry.² In addition, they play a noticeable role in the synthesis of pharmaceuticals (medicinal drug), agricultural chemicals (pesticides, fungicides, herbicides) and in the chemical industry (starting materials, intermediates, solvents, etc.).³

The classical syntheses of carbamates¹ involve the direct or indirect utilization of toxic and harmful reagents

(phosgene, isocyanates, etc.) with all the drawbacks that these reagents imply. Therefore, much effort has been devoted to the development of safer alternative synthetic methods that avoid the use of these harmful chemicals.⁴

In this context, several authors suggested the utilization of carbon dioxide, a cheap and abundant reagent, as a safe substitute of phosgene.⁵

Recently, Jung et al. reported a synthesis of carbamates⁶ via a cesium base-promoted method, which allows for the efficient coupling of amines with halides in the presence of TBAI (tetrabutylammonium iodide) and CO_2 in DMF solutions.

We already described possible electrochemical routes for the synthesis of carbamates.^{7,8} At present, we are

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engaged in reviewing these procedures to seek new and simpler electrochemical synthetic methodologies.

Acetonitrile is one of the polar aprotic solvents more frequently used for the study of electrochemical reductions or oxidations. During the electrolyses of MeCN-supporting electrolyte solutions, the cathodic behavior of acetonitrile is strongly affected by the experimental conditions (cathodic material, supporting electrolyte, work potential, etc.). In the absence of a proton donor, the carbanion $^{-}\text{CH}_2\text{CN}$ may be produced.^{9,10}

In the past, Bellamy studied the reactivity of electro-generated cyanomethyl anion as nucleophile toward electrophilic centers specifically added to the cathodic material.¹¹

In addition, cyanomethyl anion (and the derived 3-aminocrotonitrile anion) shows, in MeCN-TEAP (tetraethylammonium perchlorate) solutions, i.e., in the presence of a large counterion as TEA^+ , a remarkable reactivity as base.¹²

In this paper, we report the results of an electrochemical investigation concerning the reactivity of amines versus carbon dioxide in electrolyzed MeCN-TEAP solutions, i.e., in the presence of cyanomethyl anion or other derived anions.

The purpose of this study is the development of a new methodology for the electrochemically induced synthesis of carbamates from CO_2 and amines in mild conditions, avoiding any addition of bases, probases, or catalysts and the use of toxic and dangerous material (Scheme 1).

The reactivity of amines versus carbon dioxide in electrolyzed aprotic solvents (i.e., MeCN or, for a useful comparison, DMF) has been studied using two different procedures:

Procedure A. Solutions of MeCN (DMF)-supporting electrolyte containing amines were electrolyzed, under N_2 at room temperature, in a divided cell (Pt, Cu, C, Pb, Ni, Zn cathode, and Pt anode) under galvanostatic conditions. At the end of the electrolysis, CO_2 was bubbled into the cathodic solutions for 1.0 h and an excess of alkylating agent was added.

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(10) The formation of this cyanomethyl anion in anhydrous MeCN-TBAB (tetrabutylammonium bromide) or in MeCN- LiClO_4 solutions, is consistent, respectively, with the formation of an active hydride intermediate or with a direct electron transfer to the acetonitrile molecule.¹⁰ Products related to nucleophilic attack of $^{-}\text{CH}_2\text{CN}$ on the parent molecule (3-aminocrotonitrile, 3-iminobutyronitrile, 4-amino-2,6-dimethylpyrimidine, and 2,4,6-trimethyl-1,3,5-triazine) may be isolated from the cathodic solutions. Accordingly, the major product of the cathodic breakdown via in situ infrared spectroelectrochemistry is the anion of 3-aminocrotonitrile ($^{-}\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{CN} \leftrightarrow \text{HN}=\text{C}(\text{CH}_3)\text{CH}(\text{CN})^{-} \leftrightarrow \text{HN}-\text{C}(\text{CH}_3)=\text{CH}(\text{CN})$).¹⁷ Recently, Barba described the paired electrosynthesis, in MeCN-TBAB solutions, of 2,6-dimethyl-4-arylpyridine-3,5-dicarbonitrile via anodic oxidation of benzylthiocyanate and cathodic generation of 3-aminocrotonitrile anion.¹⁸

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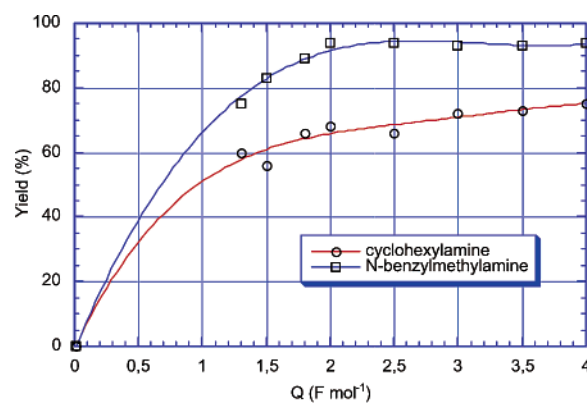
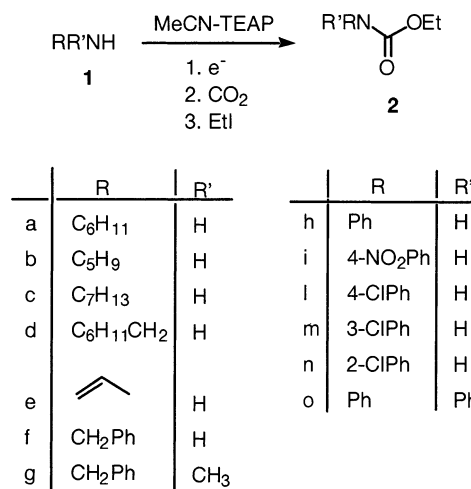


FIGURE 1. Reaction of amines **1a** and **1g** with CO_2 and EtI in MeCN-TEAP-electrolyzed solutions. Electrolyses were carried out under galvanostatic control. Divided cells, Pt cathode and anode, $I = 16 \text{ mA cm}^{-2}$. Yields (based on the starting amine) of isolated carbamates **2a** and **2g** versus Q (number of Faradays per mole of amines supplied to the electrodes) according to procedure A.

SCHEME 1



Procedure B. The electrolyses of solvent-supporting electrolyte systems were carried out in the absence of amines. At the end of the electrolyses, the substrates were added to the cathodic solutions, which were stirred under CO_2 for 1.0 h. Last, an alkylating agent was added.

The workup of the solutions provided the corresponding carbamates.

To optimize experimental conditions for the electrochemical synthesis of carbamates, several electrolyses were performed using different solvent-electrolyte systems, cathodic materials, procedures (A or B) and number (Q) of faradays per mole of amine supplied to the electrodes.

The yields of carbamates were greatly affected by the Q value (Figure 1, amines **1a** and **1g** were taken as model compounds), as well as by the solvent-supporting electrolyte system and the cathodic material (Table 1, amine **1a** was taken as model compound).

With regard to the supporting electrolyte, the nature of the anion, as well as the cation, may affect the yields in carbamates (Table 1, entries 1 and 13–16). In addition

TABLE 1. Reaction of Amine 1a with CO₂ and EtI in Electrolyzed Aprotic Solutions^a (Effect of Cathode Material, Procedure (A or B), Solvent,^b and Supporting Electrolyte versus the Yield of Isolated Carbamate 2a; Q = 2.0 F mol^{-1c})

entry	supporting electrolyte	cathode	procedure	yield of 2a ^d (%)
1	TEAP ^e	Pt	A	73
2	TEAP	Pt	B	59
3	TEAP	Pb	A	55
4	TEAP	Pb	B	60
5	TEAP	Cu	A	70
6	TEAP	Cu	B	72
7	TEAP	C	A	45
8	TEAP	C	B	46
9	TEAP	Ni	A	58
10	TEAP	Ni	B	52
11	TEAP	Zn	A	53
12	TEAP	Zn	B	57
13	TBATFB ^f	Pt	A	23
14	LiClO ₄	Pt	A	
15	TEACl ^g	Pt	A	49
16	TMAP ^h	Pt	A	57
17	TEAP	Pt	A	

^a Electrolyses carried out under galvanostatic control. Divided cells, Pt anode. ^b Entries 1–16: solvent, MeCN. Entry 17: solvent, DMF. ^c Number of faradays per mole of amine supplied to the electrodes. ^d Yields of isolated carbamate **2a** based on the starting amine **1a**. ^e Tetraethylammonium perchlorate. ^f Tetrabutylammonium tetrafluoroborate. ^g Tetraethylammonium chloride. ^h Tetramethylammonium perchlorate.

no carbamates were isolated if the electrolyses were carried out using lithium salts or DMF (instead of MeCN) as solvent (Table 1, entries 14 and 17).

The highest yields were obtained when Pt or Cu cathodes (Pt anode) were used, together with MeCN–TEAP solvent-supporting electrolyte, and 2.0–3.0 F mol⁻¹ of amine were consumed (Table 1, entries 1, 2 and 5, 6). It appears to be significant that (a) the yields of carbamates are virtually unrelated to the selected procedure (A or B, Table 1, entries 1–12) and (b) no carbamate has been obtained by mere bubbling of CO₂ and addition of an alkylating agent in non-electrolyzed MeCN–TEAP solutions containing the amine.

Therefore, the electrochemical reduction of MeCN–TEAP solutions seems to be a crucial prerequisite for the synthesis of carbamates via direct reaction of amines with CO₂ without any particular addition of bases, probases, or catalysts.

Moreover, the electrochemical activation of amines versus CO₂ cannot be related to a direct electron exchange between cathodic surface and aminic substrate; in fact, carbamates have been isolated even in procedure B (i.e., addition of amine at the end of the electrolysis).

The activation of amines may be rather related to a modification of the chemical properties of the solutions as a consequence of the presence of the anion ⁻CH₂CN, electrogenerated during the electrolyses, and of the derived 3-aminocrotonitrile anion. As a confirmation, if the electrolysis was carried out in DMF instead of MeCN, no carbamate could be isolated (Table 1, entry 17).

In MeCN–TEAP solutions, cyanomethyl and 3-aminocrotonitrile anions are basic systems strong enough to deprotonate the NH group. They form the uncharged molecules MeCN and 3-aminocrotonitrile and the carbamate anion, if CO₂ is present.

TABLE 2. Electrochemical Syntheses of Carbamates by Electrolyses^a of MeCN–TEAP Solutions Containing Amines 1a–o Followed by Bubbling of CO₂ and Addition of EtI (Q = 2.0 F mol^{-1, b} Procedure A)

entry	amine	carbamates	yield ^c (%)
1	1a	2a	72
2	1b	2b	94
3	1c	2c	82
4	1d	2d	72
5	1e	2e	85
6	1f	2f	80
7	1g	2g	96
8	1h	2h	39
9	1i	2i	15
10	1l	2l	62
11	1m	2m	56
12	1n	2n	19
13	1o	2o	–

^a Electrolyses carried out under galvanostatic control. Divided cells, Pt anode. $I = 16 \text{ mA cm}^{-2}$. ^b Number of faradays per mole of amine supplied to the electrodes. ^c Yields of isolated carbamates based on starting amines.

3-Aminocrotonitrile was isolated from MeCN–TEAP solutions, electrolyzed without any addition of amines and CO₂, as well as from MeCN–TEAP solutions, electrolyzed in the presence of amines. These results suggest that the behavior of cyanomethyl anion as a base versus the aminic substrate (yielding the carbamate anion, if CO₂ is present) is always related to the behavior as a nucleophile versus the parent molecule (yielding 3-aminocrotonitrile anion).

Since the concentration of the electrogenerated cyanomethyl anion in MeCN–TEAP solutions is affected by the number *Q* of faradays supplied to the electrodes per mole of amine, the yield of carbamate increases with increasing *Q* and the optimized conditions required $Q = 2.0\text{--}3.0 \text{ F mol}^{-1}$ (Figure 1).

The experiment was extended to substrates **1b–o**, under optimized conditions, to study the reactivity of aliphatic as well as aromatic amines versus CO₂ in MeCN–TEAP electrolyzed solutions (i.e., in the presence of cyanomethyl anion) (Table 2).

As we previously observed in O₂/CO₂–amine systems,^{7a} the yield of isolated carbamates is affected by the nucleophilicity of the amines. In fact, primary and secondary amines were converted in carbamates in good to high yields (72–96%, Table 2, entries 1–7), while aniline was converted in low yield (Table 2, entry 8). In this last case, there was a considerable substituent effect, depending on the availability of the lone pair and its role (Table 2, entries 9–12). In fact, when the lone pair is widely delocalized, the yields in carbamate are considerably lowered (*p*-NO₂-aniline **1i**) or even put at zero (diphenylamine **1o**). Besides, the introduction of a chlorine atom enhances the yields (except in the 2-position, ortho effect).

In conclusion, electrolyses of MeCN–TEAP solutions, under galvanostatic control, yield a basic system (cyanomethyl and 3-aminocrotonitrile anions) which enables, when CO₂ is present, the carboxylation of primary and secondary amines, added to the solutions at the beginning or at the end of the electrolyses.

Therefore, a new electrochemical methodology for the synthesis of carbamates from amines and CO₂ has been

set up. This synthesis is carried out under mild conditions, without any addition of bases, probases, or catalysts and avoiding the use of toxic, dangerous, or polluting chemicals.

Carbamates have been isolated in high to excellent yields.

Experimental Section

General Methods. The electrochemical apparatus, the cell, the NMR instrument, and the melting point apparatus have been previously described.¹³ Acetonitrile (MeCN), *N,N*-dimethylformamide (DMF), and tetraethylammonium perchlorate (TEAP) were purified as previously described.¹⁴ Lithium perchlorate, tetramethylammonium perchlorate (TMAP), tetrabutylammonium tetrafluoroborate (TBATFB), and tetraethylammonium chloride were dried at 40 °C in a vacuum for 24 h.

Reagents. All reagents were commercially available and used as received.

General Procedure. The electrolysis was carried out under galvanostatic conditions ($I = 16 \text{ mA cm}^{-2}$) at the Pt cathode and anode (divided cell), at rt, in MeCN–TEAP (20 mL, 0.1 mol L⁻¹) containing 1.0 mmol of amine (procedure A) or not (procedure

B) with continuous N₂ bubbling. At the end of the electrolysis (2.0 F mol⁻¹ of amine), carbon dioxide was bubbled (and the amine was added in the case of procedure B) into the cathodic solution for 1 h, EtI (a 3-fold excess) was added, and the mixture was stirred at rt overnight. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography to afford the corresponding carbamate.

Isolated Products. All the isolated products gave spectral data in accordance with those reported in the literature.¹⁵

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(15) Carbamates **2e** and **2i–n** are commercial products. Carbamates **2a** and **2f–h**, see ref 7a. Carbamate **2b**: Barluenga, J.; Jimenez, C.; Najera, C.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 3, 591–593. Carbamate **2c**: Barco, A.; Benetti, S.; De Risi, C.; Marchetti, P.; Pollini, G. P.; Zanirato, V. *Tetrahedron* **1999**, 55, 5923–5930. Carbamate **2d**. ¹H NMR δ (CDCl₃): 4.67 (s, 1H, NH); 4.07 (q, 2H, $J = 7.14 \text{ Hz}$, CH₂-CH₃); 2.98 (t, 2H, $J = 6.4 \text{ Hz}$, CH₂NH); 1.71–1.33 (m, 9H, CHCH₂-CH₂); 1.21 (t, 3H, $J = 7.14 \text{ Hz}$, CH₂CH₃); 0.95–0.79 (m, 2H, CH₂). ¹³C NMR δ (CDCl₃): 156.78, 60.43, 47.07, 38.12, 30.49, 26.25, 25.65, 14.45. GC–MS m/z : 185 (M⁺, 6), 156 (M⁺ – Et, 3), 97 (C₆H₁₁ – CH₂⁺, 12), 83 (C₆H₁₁⁺, 13).

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(14) Casadei, M. A.; Cesa, S.; Feroci, M.; Inesi, A.; Rossi, L.; Micheletti-Moracci, F. *Tetrahedron* **1997**, 53, 167–176. CAUTION! Anhydrous tetraethylammonium perchlorate, TEAP, is potentially explosive. Unfortunately the use of other supporting electrolytes causes a sensible decrease in the yields.