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Electrochemically Promoted C−N Bond Formation from Acetylenic Amines and CO_2. Synthesis of 5-Methylene-1,3-oxazolidin-2-ones

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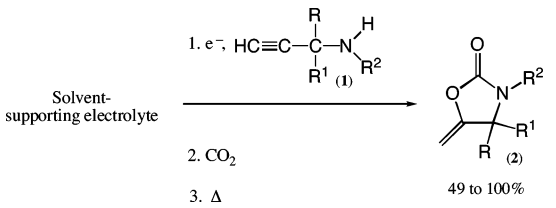

An efficient electrochemical synthesis of 5-methylene-1,3-oxazolidin-2-ones (**2a**−**h**) from acetylenic amines (**1a**−**h**) and carbon dioxide has been achieved by direct electrolysis of solution of MeCN and Et_4NPF_6 containing the amine, with subsequent CO_2 bubbling and heating. The yields vary from good to excellent, the conditions are mild, and the use of toxic and harmful chemicals and catalysts is avoided.

The direct introduction of carbon dioxide, an inexpensive, harmless, and abundant source of carbon, into organic substrates may be considered an attractive goal in organic synthesis. Therefore, in the past decades, considerable attention has been paid to any strategy suitable for the utilization of carbon dioxide as raw material.[1] Herein, we wish to report a new procedure for the synthesis of 5-methylene-1,3-oxazolidin-2-ones from carbon dioxide and acetylenic amines.

Linear and cyclic carbamates[2] are a class of compounds having a wide range of applications in agrochemical industry, pharmacology, organic synthesis (as protecting groups), and polymer chemistry.[3] In addition, a class of cyclic carbamates, chiral oxazolidin-2-ones, have gained considerable importance as chiral auxiliaries (Evans' chiral auxiliaries) in asymmetric synthesis.[4] 5-Methylene-1,3-oxazolidin-2-ones, owing to the presence of an exocyclic double bond in the structure, are especially versatile substrates in organic synthesis.[5]

The classical syntheses of linear and cyclic carbamates are based on the direct or indirect utilization of toxic and harmful reagents (phosgene, isocyanates, etc.) as a source of carbon. To overcome this drawback, significant efforts have been undertaken for the development of phosgene/isocyanate-free procedures with low environmental impact. In this context, several authors suggested the utilization of carbon dioxide as a safe substitute of phosgene.[1a,6] The thermodynamic and kinetic stability of carbon dioxide requires its preliminary activation or, alternatively, that of the substrates. The utilization of carbon dioxide in the synthesis of carbamato derivatives has been discussed in an exhaustive review by Calderazzo.[7] As far as cyclic carbamates are concerned, 5-methylene-1,3-oxazolidin-2-ones have been obtained from carbon dioxide and acetylenic amines in the presence of Ru[5a] (P_{CO_2} 50 atm, T 100°C) or Pd[5b] (P_{CO_2} 40 atm, T rt or 50 °C) catalysts or of strong organic bases (P_{CO_2} 1−10 atm, T rt to 110°C).[5c,d] 5-Methylene-1,3-oxazolidin-2-ones have also been synthesized from acetylenic amines and a tetraalkylammonium carbonate or hydrogen carbonate.[8] Recently, chiral cyclic carbamates have been obtained by us by reaction of chiral 1,2-amino alcohols and carbon dioxide in electrochemically modified MeCN−Et_4NClO_4 solutions (i.e., MeCN−Et_4NClO_4 solutions previously electrolyzed under galvanostatic control) with subsequent addition of TsCl (Scheme 1).[6b]

In this paper, we report the results of an investigation of the reaction of acetylenic amines **1a**−**h** with carbon dioxide in electrochemically reduced MeCN−Et_4NPF_6 (TEAHFP) solutions as well as in other electrochemically reduced solvents (DMSO, EtCN, DMF, and $MeNO_2$).

The aim of this study was to achieve an electrochemically induced synthesis of 5-methylene-1,3-oxazolidin-2-ones, from acetylenic amines and carbon dioxide, under mild conditions (P_{CO_2} = 1.0 atm), avoiding the use of toxic

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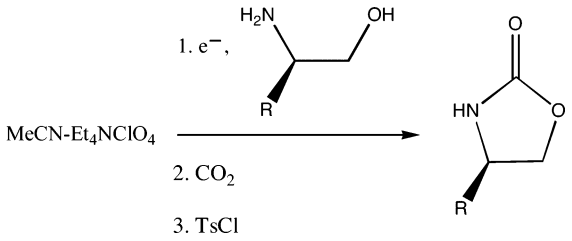
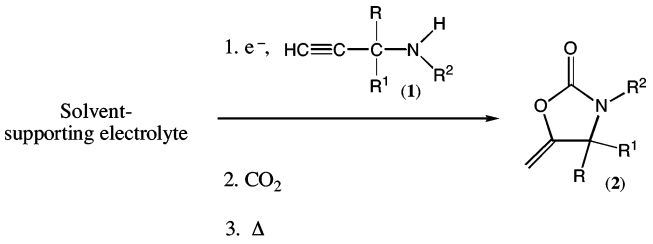
SCHEME 1



SCHEME 2



1, 2	R	R¹	R²	1, 2	R	R¹	R²
a	Me	Me	$PhCH_2$	e	Me	Et	$Ph(CH_2)_3$
b	Me	Et	$PhCH_2$	f	Me	Me	*p*-CH_3OPh
c	Me	Ph	$PhCH_2$	g	Me	Et	*p*-CH_3OPh
d	Me	Et	$Ph(CH_2)_2$	h	-$(CH_2)_5$-		*p*-CH_3OPh

and harmful chemicals, catalysts, and strong organic bases (Scheme 2).

According to a procedure previously described by us,[3] solvent−TEAHFP solutions containing the acetylenic amine **1a** (chosen as model compound), were electrochemically reduced under galvanostatic conditions in a two-compartment cell. At the end of the electrolysis, carbon dioxide was bubbled into the catholyte for 30 min at room temperature, and then the mixture was heated to reflux for 2 h.

Workup of the cathodic solution afforded 5-methylene-1,3-oxazolidin-2-one **2a**, which corresponds to a direct introduction of carbon dioxide into acetylenic amine **1a** (Table 1).

These results are consistent with a reaction pathway involving deprotonation of the acetylenic amine followed by carboxylation and then a 5-*exo-dig* cyclization[9] of the corresponding intermediate propargylic carbamate anion. Therefore, the electrochemical reduction of solutions under consideration generates bases strong enough to deprotonate the NH group of acetylenic amine **1a**. The yields of **2a** are strongly dependent on the amount of electricity supplied during the electrolyses (Q). The yields increase with Q, up to a charge of 2.00 F mol^{-1} (Table 1, entries 1−5, 7, 8, 12−18). Increasing the charge further did not improve the yield (entry 6).

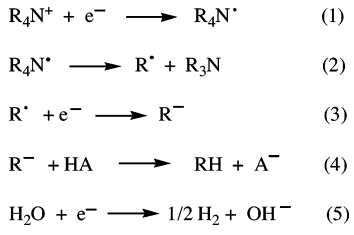
The yields also depend on the solvent. Indeed, as shown in entries 5 and 8−11, **2a** was isolated (Q = 2.00 F mol^{-1}) in 93, 85, 73, 42, and 18% yields, respectively, when the electrolysis was carried out in MeCN, DMSO, EtCN, DMF, and $MeNO_2$. Thus, the best electrogenerated bases

TABLE 1. Synthesis of 5-Methylene-1,3-oxazolidin-2-one 2a from Acetylenic Amine 1a and CO_2 in Electrolyzed[a] Solvent−TEAHFP Solutions

entry	solvent	Q[b]	yields of **2a** (%)[c]
1	MeCN[d]	0.25	9
2	MeCN[d]	0.50	15
3	MeCN[d]	0.75	26
4	MeCN[d]	1.00	81
5	MeCN[d]	2.00	93
6	MeCN[d]	3.00	93
7	MeCN[d,e]	2.00	
8	DMSO[d]	1.00	61
9	DMSO[d]	2.00	85
10	EtCN[d]	2.00	73
11	DMF[d]	2.00	42
12	$MeNO_2$[d]	2.00	18
13	MeCN[f]	0.25	8
14	MeCN[f]	0.50	13
15	MeCN[f]	0.75	23
16	MeCN[f]	1.00	44
17	MeCN[f]	2.00	57
18	DMSO[f]	1.00	45
19	DMSO[f]	2.00	74

[a] Electrolyses carried out according to the general procedure. [b] Number of faradays per mole of added acetylenic amine **1a** supplied to the electrode. [c] Isolated yields, based on the starting acetylenic amine **1a**. [d] Solvent-supporting electrolyte solutions, containing **1a**, were electrolyzed under galvanostatic conditions. [e] $LiClO_4$ was used as supporting electrolyte. From the cathodic solution 95% of starting material was recovered. [f] The acetylenic amine **1a** was added to the cathodic solutions at the end of the electrolysis carried out under galvanostatic conditions.

SCHEME 3



for this reaction are the ones obtained in acetonitrile. The use of propionitrile allows to isolate **2a** in 73% yield (compared to 93% in MeCN). The yield is lower with propionitrile probably because of the larger steric bulk of its conjugate base. The low yield in **2a** obtained using nitromethane as solvent is most probably due to the weakness of its conjugate base (pK_a = 17.2).[10]

In regard to the formation of these electrogenerated bases, a further mechanistic hypothesis,[3] on the basis of published work on the reduction of tetraalkylammoniun salts,[11] has been proposed (described in Scheme 3, steps 1−4). Electrochemical reduction of tetraethylammonium cations at the cathode generates a carbanion, a strong base (steps 1−3).[11] The latter would then abstract a proton from the solvent, present in large excess, the conjugate base of which would then abstract a proton from the acetylenic amine yielding the solvent itself and avoiding the presence of a byproduct in the cathodic solution. According to this peculiarity, the use of the

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conjugate base of the solvent as EGB may be considered more profitable with respect to other EGBs and to strong organic bases.

This hypothesis is supported by the observation of gas evolution at the electrode during the electrolysis (Scheme 3, step 4, RH is ethane). In addition, if a lithium salt (instead of a R_4N^+ salt) was used as supporting electrolyte, no 5-methylene-1,3-oxazolidin-2-one was isolated from the cathodic solution (Table 1, entry 7). Although Simonet[12] reported that the cathodic reduction of tetraalkylammonium salts at platinum electrodes generates a very reactive species (as a base and reductant: [Pt_n^-, R_4N^+, R_4NX]) at the surface of the electrode, he specifically mentions that tetraalkylammonium hexafluorophosphate salts ($X^- = PF_6^-$) are not reactive in this cathodic reaction. The concomitant cathodic reduction of residual water (Scheme 3, step 5) cannot be excluded.

Alternatively, the procedure was modified by carrying out the electrochemical reduction of the solvent-supporting electrolyte solution and adding the acetylenic amine **1a** at the end of the electrolysis. According to this new methodology, the cyclic carbamate **2a** was isolated in yields comparable to or lower than with those obtained using to the previous procedure (compare entries 12−18 of Table 1 with entries 1−8, respectively). These results are consistent with the proposed hypothesis, involving deprotonation of the NH group by an electrogenerated base obtained by the cathodic reduction of the solvent−supporting electrolyte system. Direct cathodic reduction of the acetylenic amines is far less probable.

According to Baldwin's rules for ring closure,[9] two products could have been obtained in this reaction: the one from a 5-*exo-dig* closure (5-methylene-1,3-oxazolidin-2-one) and the one from a 6-*endo-dig* closure (3,4-dihydro-1,3-oxazin-2-one). However, the reaction is 100% regioselective, giving only the five-membered ring resulting from a 5-*exo-dig* cyclization (as in the majority of the chemical syntheses).[5b,c,8]

To ascertain whether this method of synthesis of cyclic carbamates from acetylenic amines and carbon dioxide could be generalized, the reactivity of acetylenic amines **1b**−**h** versus carbon dioxide in electrochemically reduced solvents has been studied. The investigation was carried out under the reaction conditions of entry 5 of Table 1 (which gave the highest yield): MeCN as solvent, Q = 2.00 F mol^{-1}, electrolysis carried out in the presence of the acetylenic amine. As seen in Table 2, entries 2−8, 5-methylene-1,3-oxazolidin-2-ones **2b**−**h** have been synthesized in good to excellent yields, depending on the substituents, the best yields being obtained when R, R^1, and R^2 are alkyl substituents (entries 1, 2, 4, and 5).

In conclusion, the study of the reactivity of acetylenic amines **1a**−**h** versus carbon dioxide in electrochemically reduced solutions (MeCN, DMSO, EtCN, DMF, and $MeNO_2$ as solvents and tetraethylammonium hexafluorophosphate as supporting electrolyte) allowed us to establish a new procedure for the direct introduction of carbon dioxide into acetylenic amines. 5-Methylene-1,3-oxazolidin-2-ones **2a**−**h** have been synthesized under mild conditions, in good to excellent yields, the highest yields being obtained in MeCN as solvent, TEAHFP as supporting electrolyte, and by adding the acetylenic amine to the cathodic solution prior to the electrolysis. Using MeCN as solvent also allows a very easy workup of the reaction mixture. The use of transition-metal catalysts, strong bases, and toxic and harmful chemicals can thus be eliminated.

TABLE 2. Synthesis of 5-Methylene-1,3-oxazolidin-2-ones 2a−h from Acetyleic Amines 1a−h and CO_2 in Electrolyzed[a] MeCN−TEAHFP Solutions (Q^b = 2.00)

entry	acetylenic amine	5-methylene-1,3-oxazolidin-2-ones	yields[c] (%)
1	**1a**	**2a**	93
2	**1b**	**2b**	93
3	**1c**	**2c**	64
4	**1d**	**2d**	100
5	**1e**	**2e**	91
6	**1f**	**2f**	77
7	**1g**	**2g**	73
8	**1h**	**2h**	49

[a] MeCN−TEAHFP solutions, containing the acetylenic amine **1a**−**h**, were electrolyzed under galvanostatic control (I = 16 mA cm^{-2}), divided cell, Pt cathode and anode, rt. [b] Number of faradays mol^{-1} of added acetylenic amine **1a**−**h** supplied to the electrode. [c] Isolated yields, based on the starting acetylenic amines **1a**−**h**.

Experimental Section

General Procedures. Amines **1a**−**h** were synthesized following the methods reported in the literature.[13] Constant current electrolyses were performed in a divided glass cell (Pt spiral cathode, apparent area 4.5 cm^2, volume of the catholite: 20 mL) using an Amel model 552 potentiostat equipped with an Amel model 572 integrator. The counter electrode was a cylindrical platinum gauze, apparent area 1.3 cm^2, 3.0 cm high, volume of the anolite: 10 mL; it was separated from the catholyte through a porous glass plug filled with an agar gel (i.e., methyl cellulose 0.5% volume dissolved in DMF−Et_4NClO_4 1.0 mol L^{-1}). The electrolyses were carried out, under nitrogen atmosphere at room temperature, under galvanostatic control (J = 16 mA cm^{-2}) on solutions of the amine in solvent, 0.1 mol L^{-1} TEAHFP. At the end of the electrolysis, CO_2 was bubbled into the catholite and the solution was heated to reflux for 2 h. Usual workup (ether extraction and, when necessary, flash chromatography: *n*-hexane/ethyl acetate 8/2) gave oxazolidinones **2a**−**h** in the reported yields. All of the known isolated products gave spectral data in accordance with those reported in the literature.[14]

3-Benzyl-4-methyl-5-methylene-4-phenyl-1,3-oxazolidin-2-one (2c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34−7.16 (m, 10H), 4.67 (d, 1H, J = 3.4 Hz), 4.64 (d,1H, J = 15.5 Hz), 4.02 (d, 1H,

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(14) For spectral data of known 5-methylene-1,3-oxazolidin-2-ones: **2a**: see ref 4b. **2b**: see ref 7. **2f**: Ohe, K.; Matsuda, H.; Ishihara, T.; Ogoshi, S.; Chatani, N.; Murai, S. *J. Org. Chem.* **1993**, *58*, 1173−1177.

J = 3.4 Hz), 3.73 (d, 1H, J = 15.5 Hz), 1.60 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 160.8, 155.1, 140.5, 137.3, 128.8, 128.6, 128.5, 128.0, 127.7, 126.3, 86.2, 66.6, 44.9, 25.4; EIMS (*m/z*) 279 ($M^{+\bullet}$, 2), 264 (11), 91 (100), 77 (32).

4-Ethyl-4-methyl-5-methylene-3-(2-phenylethyl)-1,3-oxazolidin-2-one (2d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33−7.17 (m, 5H), 4.69 (d, 1H, J = 3.1 Hz), 4.14 (d, 1H, J = 3.5 Hz), 3.51−3.40 (m, 1H), 3.11−2.91 (m, 3H), 1.77−1.57 (m, 1H), 1.54−1.43 (m, 1H), 1.23 (s, 3H), 0.77 (t, 3H, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.7, 154.7, 138.3, 128.7, 128.5, 126.5, 84.2, 65.1, 42.1, 34.9, 32.3, 26.4, 7.6; EIMS (*m/z*) 245 ($M^{+\bullet}$, 1), 216 (30), 105 (100), 77 (16).

4-Ethyl-4-methyl-5-methylene-3-(3-phenylpropyl)-1,3-oxazolidin-2-one (2e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31−7.15 (m, 5H), 4.68 (d, 1H, J = 3.2 Hz), 4.14 (d, 1H, J = 3.2 Hz), 3.35−3.20 (m, 1H), 3.10−2.88 (m, 1H), 2.68−2.61 (m, 2H), 2.06−1.86 (m, 2H), 1.75−1.61 (m, 1H), 1.61−1.38 (m, 1H), 1.35 (s, 3H), 0.78 (t, 3H, J = 7.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.8, 154.9, 141.0, 128.4, 128.3, 128.2, 126.0, 125.7, 84.2, 65.1, 40.0, 33.7, 33.3, 32.3, 30.7, 27.0, 7.7; EIMS (*m/z*) 259 ($M^{+\bullet}$, 2), 230 (57), 91 (100), 77 (12).

4-Ethyl-3-(4-methoxyphenyl)-4-methyl-5-methylene-1,3-oxazolidin-2-one (2g): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.18−7.12 (m, 2H), 6.95−6.89 (m, 2H), 4.78 (d, 1H, J = 3.4 Hz), 4.23 (d, 1H, J = 3.1 Hz), 3.80 (s, 3H), 1.76−1.46 (m, 2H), 1.38 (s, 3H), 1.00 (t, 3H, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.5, 158.6, 129.9, 126.5, 114.7, 84.9, 66.9, 55.5, 32. 6, 27.3, 8.0. EIMS (*m/z*) 247 ($M^{+\bullet}$, 16), 232 (3), 219 (13), 218 (100).

1-(4-Methoxyphenyl)-4-methylene-3-oxa-1-azaspiro[4.5]-decan-2-one (2h): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.11−7.07 (m, 2H), 6.94−6.89 (m, 2H), 4.79 (d, 1H, J = 3.1 Hz), 4.55 (d, 1H, J = 3.1 Hz), 3.80 (s, 3H), 1.90−1.50 (m, 9H), 1.20−0.90 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 159.9, 158.8, 154.2, 131.9, 125.8, 114,6, 88.1, 64.7, 55.5, 34.8, 23.8, 21.4; EIMS (*m/z*,) 273 ($M^{+\bullet}$, 54), 245 (18), 149 (100), 107 (7).

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Supporting Information Available: General procedures and NMR spectra of amines **1d** and **1e** and of oxazolidinones **2c**,**d**,**e**,**g**,**h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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