Electrogenerated Superoxide-Activated Carbon Dioxide. A New Mild and Safe Approach to Organic Carbamates

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The electrochemical reduction of O_2 ($E = -1.0$ V *vs* SCE) in dipolar aprotic solvents in the presence of CO_2 gave a carboxylating reagent ($O_2^{\bullet-}/CO_2$) able to convert amines and different types of their derivatives into carbamates. Primary and secondary aliphatic and aromatic amines were converted into the corresponding ethyl carbamates by the addition of EtI to the carbamate anions generated in the first step of the reactions. The yields were dependent on the nucleophilicity of the nitrogen atom. ω-Bromoethyl- and propylamine gave 2-oxazolidinone and tetrahydro-1,3-oxazin-2-one in moderate yields. *N*-Acyl or *N*-(alkoxycarbonyl)alkylamines bearing a leaving group at the β position of the alkyl substituent were converted into 3-substituted-2-oxazolidinones in high yields. By using chiral substrates, enantiopure 3-alkoxycarbonyl(or acyl)-4-substituted oxazolidin-2-ones (70−85% isolated yields) were obtained. This represents a new mild and safe route to these important auxiliaries for asymmetric synthesis. Some limitations of the process are also evidenced and accounted for.

Organic carbamates,[1] including 2-oxazolidinones, are valuable synthetic intermediates and biologically active compounds. Their use as protective groups for the amine function of amino acids has been known in peptide chemistry since the 30's[2] and up to the present day endless applications have been described in the literature.[3] Enantiopure 4-substituted 3-acyl-2-oxazolidinones, also known as "Evans chiral auxiliaries", were introduced in the early 80's and applied with excellent results to enantioselective aldol condensations, as well as to several other types of asymmetric reactions.[4] Chiral oxazolidinones have also been used to induce asymmetry in electroorganic synthesis.[5] On the basis of their biological activity, the most extensive use of carbamates is perhaps as pesticides,[6] although some other types of activity are also important.[1,7]

The most common syntheses of organic carbamates involve either the ammonolysis of chloroformates and carbonates or the addition of alcohols to isocyanates.[1,3] All these reagents, in turn, are generally prepared by making use of phosgene or its substitutes. To avoid the use of such toxic and harmful reagents, much effort has been devoted to the development of phosgene-free routes to carbamates, or their precursor.[8] The most obvious and convenient approach to carbamates involves the addition of a primary or secondary amine to CO_2 followed by alkylation of the intermediate carbamate anion. This route has been explored by several research groups.[9] In general, the first step has been easily accomplished *via* nonassisted (to ionic alkylammonium alkylcarbamates) or metal-assisted (to metal carbamates) addition of the amine to CO_2. By contrast, alkylation of the carbamate anion has turned out to be more difficult.[9] Ionic carbamates are converted into organic carbamates only in low to moderate yields under drastic conditions,[10a] except in the case of some particular amines.[10b] The alkylation of metal carbamates occurs sporadically and is complicated by the electrophilic attack at carbamic nitrogen to give N-alkylation products, in contrast to what is observed with acylating systems.[8a,11] Recently, the use of crown ethers has been introduced in the synthesis of carbamates *via* amine + CO_2 + alkyl halide reaction. In the presence of the macrocyclic polyether, the yields of carbamates obtained under mild conditions increase to acceptable values (typically 35−55%).[12] Finally, preliminary results from our group have shown that carbamates

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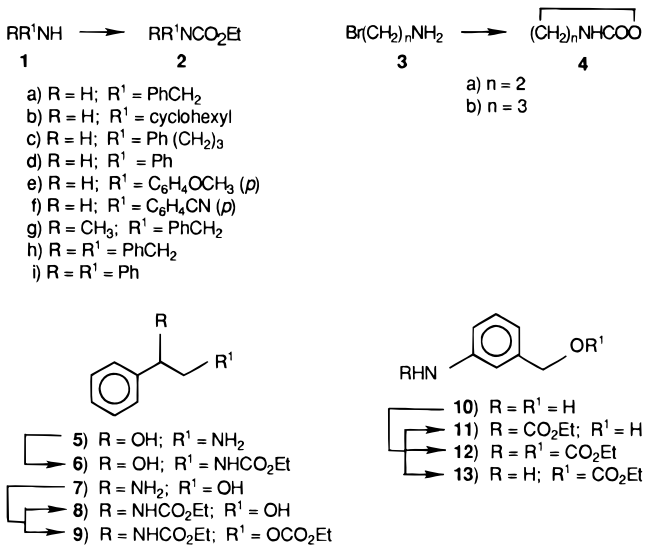
Scheme 1



are also formed in good yields by reaction of the amine with electrode-activated CO_2, followed by alkylation. However, a strongly negative working potential value ($E = -2.1$ V *vs* SCE) is required in this case.[13]

We have previously shown that the $O_2^{\bullet-}/CO_2$ system[14] is able to convert NH-protic carboxamides and alcohols, bearing a leaving group at the ω position, into oxazolidine- or 1,3-oxazine-2,4-diones[15a] and 1,3-dioxolan- or 1,3-dioxan-2-ones,[15b] respectively. The yields are high to excellent, and very mild conditions are needed. A carboxylation−cyclization process involving the formal incorporation of CO_2 into the substrate has been assumed.[15] Unsubstituted alcohols are also converted with moderate yields to the corresponding ethyl alkyl carbonates after completion of the reaction by addition of EtI.[15b]

In this note, the results obtained by reacting several amines and their derivatives (Schemes 1, 2) with the system $O_2^{\bullet-}/CO_2$ are shown, opening a new, safe, and high-yield access to both linear and cyclic organic carbamates. The reagent has been generated by electrolysis (divided cell, Hg cathode, Pt anode, room temperature) of a 0.1 M MeCN solution of TEAP where O_2 and CO_2 were continuously bubbling into the cathodic compartment. The working potential was sufficiently negative ($E = -1.0$ V *vs* SCE) to allow the selective reduction of O_2 to $O_2^{\bullet-}$ with respect to that of CO_2. The substrates were added to the solution at the end of the electrolysis. The reaction between $O_2^{\bullet-}/CO_2$ system and the nitrogen-containing substrate was considerably influenced by the reactivity of the NH group as well as by the presence of suitable leaving groups. The acidity of the CH adjacent to the nitrogen atom also played a significant role in the reaction course. The results can be summarized as follows.

Reactivity of $O_2^{\bullet-}/CO_2$ versus Aliphatic and Aromatic Amines and Haloamines (Scheme 1). The carbamates **2a**−**h** were isolated from solutions containing the $O_2^{\bullet-}/CO_2$ system after addition of amines **1a**−**h** followed by treatment with EtI (Table 1, entries 1−8). The yields of carbamates depend *inter alia* on the amount of electricity supplied during the reduction of O_2 to $O_2^{\bullet-}$. The highest values were obtained when 3.0 F/mol of amine were consumed. In addition, the yields were strongly affected by the nucleophilicity of the amines. High values (78−97%) were obtained in the case of both primary and secondary aliphatic amines **1a**−**c,g,h** (Table 1, entries 1−3, 7, 8), whereas aniline **1d** was converted into ethyl carbanilate **2d** with only 57% yield (entry 4). The dependence of the yield values from the lone pair availability of the nitrogen atom is supported by the clear substituent effect observed in the case of 4-substituted anilines **1e**,**f** (entries 5, 6). Furthermore, diphenylamine **1i**, where steric hindrance adds to electron delocalization, is quite unreactive.

Table 1. Carboxylation of amines 1, 3, 5, 7, 10 by Electroreduction of O_2 in the Presence of CO_2 Followed by Addition of the Substrate[a]

entry	substrate	products (yield, %)[b]
1	**1a**	**2a** (85) [88]
2	**1b**	**2b** (92) [97]
3	**1c**	**2c** (75) [78]
4	**1d**	**2d** (54) [57]
5	**1e**	**2e** (83) [84]
6	**1f**	**2f** (36) [38]
7	**1g**	**2g** (91) [97]
8	**1h**	**2h** (83) [89]
9	**3a**	**4a** (60) [67]
10	**3b**	**4b** (51) [56]
11	**5**	**6** (58) [63]
12	**7**	**8** (55) [63]
		9 (19) [20]
13	**10**	**11** (35) [41]
		12 (7) [7]
		13[c]

[a] MeCN−0.1 M TEAP, Hg cathode, Pt anode, $E = -1.0$ V, 3 F/mol of substrate passed through the cell. [b] Isolated yields are given in parentheses, GC (entries 1−4, 7−10) or HPLC yields in brackets. [c] Yield not determined.

Suitable leaving groups at the ω position with respect to the nitrogen atom allow the formation of cyclic carbamates: bromoalkylamines **3a,b** were converted into 2-oxazolidinone **4a** and 1,3-oxazin-2-one **4b**, respectively (Table 1, entries 9, 10). The yields were moderate, probably because of competitive self-alkylation reaction of the substrate.

Finally, based on the previous work on the carboxylation of alcohols,[15b] the potential selectivity of NH- versus OH-carboxylation was tested by treating amino alcohols **5, 7** and **10** with $O_2^{\bullet-}/CO_2$. As a result, the amine group appeared to be preferably (Table 1, entries 12, 13) or exclusively (entry 11) carboxylated with respect to the hydroxy group. The lower reactivity of secondary alcohols favored complete selectivity. However, the yields of *N*-carboxylated products attained with such substrates were only moderate.

Reactivity of $O_2^{\bullet-}/CO_2$ versus Amine Derivatives (Scheme 2). The oxazolidin-2-ones **15a**−**c,e,f,h** were prepared in very high yields by reacting carbamates **14a**−**h** with the carboxylating reagent. The reactions were independent of the nature of the leaving group (Table 2, entries 1−8). A much better current efficiency was obtained in the synthesis of the cyclic *N*-alkoxycarbonyl carbamates: the highest yields were attained by using 1.2 F/mol of substrate. In analogy to what has been proposed in the case of ω-haloacylamines,[15a] the synthesis of **15** from **14** can be described as a deprotonation−carboxylation process involving the NH group, followed

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Scheme 2

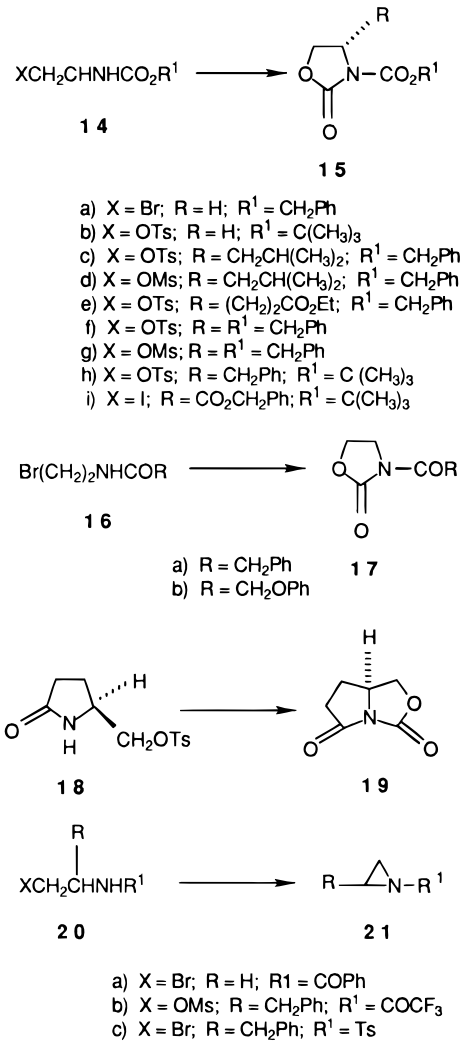

Table 2. Carboxylation of Carbamates 14 and Amides 16, 18, 20 by Electroreduction of O_2 in the Presence of CO_2 Followed by Addition of the Substrate[a]

entry	substrate	products (yield, %)[b]
1	**14a**	**15a** (79) [85]
2	**14b**	**15b** (75) [80]
3	**14c**	**15c** (72) [83]
4	**14d**	**15c** (70) [82]
5	**14e**	**15e** (85) [93]
6	**14f**	**15f** (80) [87]
7	**14g**	**15f** (85) [92]
8	**14h**	**15h** (83) [93]
9	**14i**	**22** (97) [98]
10	**16a**	**17a** (79) [90]
11	**16b**	**17b** (71) [79]
12	**18**	**19** (75) [92]
13	**20a**	**21a** (82) [92]
14	**20b**	**21b** (51) [66]
15	**20c**	**21c** (84) [98]

[a] MeCN−0.1 M TEAP, Hg cathode, Pt anode, $E = -1.0$ V, 1.2 F/mol of substrate passed through the cell. [b] Isolated yields are given in parentheses, GC (entry 2) or HPLC yields in brackets.

by a cyclization reaction. Chiral oxazolidin-2-ones **15c,e,f,h** have been obtained from chiral substrates **14c**−**h**. In order to check if racemization occurs during the carboxylation process, the enantiomeric excess of compound **15c** was determined by ^{1}H NMR spectroscopy in the presence of Eu(hfc)$_3$. Method development on the racemic product purposely prepared from (*R,S*)-**14c** showed that a *ca.* 9:1 Eu(hfc)$_3$/oxazolidinone mixture caused chemical shift nonequivalence (0.3 ppm) of one of the C_5-hydrogens. Applied to oxazolidinone **15c**, the method indicated that the ee was >98%. As evidenced in the introductory section, chiral oxazolidinones **15** are very important auxiliaries in asymmetric reactions[4,5] and the present safe, very mild route usefully adds to the known methods for their synthesis.

Furthermore, *N*-(2-bromoethyl)acetamides **16a,b** and pyrrolidone **18** underwent the carboxylation−cyclization process giving, respectively, 3-acyloxazolidin-2-ones **17** and 3,5-dioxopyrrolo[1,2-*c*]oxazole **19** in very high yields. Once again, chiral **19** was obtained from (*S*)-prolinol *p*-toluenesulfonate **18**.

It should be noted that the method suffers some limitations. In particular, if the CH adjacent to the NH group is activated by the presence of electron-withdrawing groups, the competitive deprotonation of the former can occur. As an example, *N*-Boc-3-iodoalanine benzyl ester **14i** was quantitatively converted into *N*-Boc-dehydroalanine benzyl ester **22** (Table 2, entry 9). Therefore, the β-elimination-assisted deprotonation of the methine carbon turned out to be selective in this type of substrate. Furthermore, a strong electron-withdrawing *N*-substituent hampers the carboxylation process: amides **20a**−**c** are converted into aziridines **21a**−**c** while no traces of oxazolidinones are detectable in the reaction mixture. It appears that the lower nucleophilicity of the nitrogen makes the intermolecular reaction no longer competitive with the intramolecular one, and the cyclization to the three-membered ring turns out to be a selective process.

Conclusions

The electrochemical reduction of O_2 ($E = -1.0$ V *vs* SCE), carried out in the presence of CO_2, yields an $O_2^{\bullet-}$/CO_2 system which carboxylates substrates containing NH or OH groups. By taking advantage of this peculiar reactivity, the synthesis of cyclic and linear carbamates has been achieved, under very mild conditions. The reaction of $O_2^{\bullet-}$/CO_2 with amines or their derivatives bearing a leaving group at the appropriate position of an alkyl residue affords cyclic carbamates according to a "one-pot, one-step" procedure. On the contrary, the preparation of linear carbamates, arising from unsubstituted amines, requires a further alkylation step of the first-formed carbamate anion. In any case, high to excellent yields were observed. The carboxylation−cyclization of chiral carbamates **14c**−**h** represents a selective process to prepare enantiopure 4-substituted oxazolidinones **15c,e,f,h**, useful chiral auxiliaries in asymmetric syntheses. Some limitations of the method were identified and accounted for.

Experimental Section

General. The electrochemical apparatus, the cells, and the reference electrode as well as the mp, IR, NMR, HPLC, and GC instruments were described elsewhere.[15a,16] Unless otherwise stated, column chromatography was performed on 70−230 mesh SiO_2. HPLC analyses were carried out using an RP-18 column and a CH_3CN-H_2O mixture in a linear gradient from 35:65 to absolute CH_3CN in 20 min followed by an isocratic step (5 min). The flow rate was 1 mL min^{-1}. GC analyses were carried out using a Supelco SPB-5 (30 m, 0.25 mm) column. NMR spectra were acquired on $CDCl_3$ solutions containing Me_4Si as the internal standard. The *J* values are

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reported in hertz. The enantiomeric excess was obtained by integrating the relevant peaks in ^{1}H NMR spectrum recorded in the presence of Eu(hfc)$_3$, after identification of nonoverlapping peaks of the enantiomers, carried out by using purposely prepared racemic products. $[\alpha]_D$ values were determined by a Perkin Elmer 243 polarimeter and the *c* values are given as g/100 mL. Acetonitrile (MeCN) and tetraethylammonium perchlorate (TEAP) were purified as already described.[16]

Reagents. Amines **1a**−**i**, **3a**,**b**, **5**, **7**, **10**, as well as iodoalanine **14i** were commercially available (Aldrich). **Benzyl *N*-(2-Bromoethyl)carbamate (14a)** was prepared from 2-bromoethylamine hydrobromide and benzyl chloroformate: mp 42−44 °C [lit.[17] mp 45 °C]. ***tert*-Butyl *N*-[2-(Tosyloxy)ethyl]-carbamate (14b)** was obtained from *tert*-butyl *N*-(2-hydroxyethyl)carbamate and tosyl chloride. Column chromatography of the crude reaction mixture (light petroleum−AcOEt 7:3 as eluent) gave **14b**: mp 47−49 °C (light petroleum); IR (Nujol) 3410, 1710, 1600, 1510 cm^{-1}; ^{1}H NMR δ 1.40 (s, 9H), 2.45 (s, 3H), 3.3−3.5 (m, 2H), 4.18 (t, J = 5.0, 2H), 4.7−5.1 (br s, 1H), 7.3−7.5 (m, 2H), 7.7−7.9 (m, 2H); ^{13}C NMR δ 21.82, 28.45, 39.90, 69.63, 79.97, 128.27, 130.14, 132.76, 145.23, 155.79. Anal. Calcd for $C_{14}H_{21}NO_5S$: C, 53.32; H, 6.71; N, 4.44. Found: C, 53.13; H, 6.59; N, 4.33.

Compounds **14c**−**h** were prepared according to standard procedures[3] from the corresponding *N*-protected amino alcohols. With the exception of (*S*)-2-amino-3-phenylpropan-1-ol which was purchased by Fluka, the N-protected amino alcohols were prepared from the respective *N*-protected amino acids according to the literature.[18] **Benzyl *N*-[(*S*)-4-methyl-1-(tosyloxy)pentan-2-yl]carbamate (14c)**: mp 94−95 °C (cyclohexane); $[\alpha]^{21}_D$ = −20.3 (*c* = 3.1, $CHCl_3$); IR (Nujol) 3300, 1710, 1690, 1600, 1540 cm^{-1}; ^{1}H NMR δ 0.85 (d, J = 6.5, 6H), 1.2−1.4 (m, 2H), 1.4−1.6 (m, 1H), 2.45 (s, 3H), 3.8−4.1 (m, 3H), 4.80 (br s, 1H), 5.08 (s, 2H), 7.2−7.4 (m, 2H), 7.38 (s, 5H), 7.7−7.9 (m, 2H); ^{13}C NMR δ 21.84, 22.16, 22.98, 24.67, 40.18, 48.44, 66.98, 71.91, 128.14, 128.35, 128.73, 130.12, 132.71, 136.44, 145.19, 155.83. Anal. Calcd for $C_{21}H_{27}NO_5S$: C, 62.20; H, 6.71; N, 3.45. Found: C, 61.96; H, 6.65; N, 3.27.

Benzyl *N*-[(*S*)-4-methyl-1-(mesyloxy)pentan-2-yl]carbamate (14d): mp 57−59 °C (light petroleum); $[\alpha]^{21}_D$ = −31.0 (*c* = 4.0, $CHCl_3$); IR (Nujol) 3390, 1700, 1530 cm^{-1}; ^{1}H NMR δ 0.85 (d, J = 6.5, 6H), 1.2−1.4 (m, 2H), 1.4−1.6 (m, 1H), 2.93 (s, 3H), 3.9−4.3 (m, 3H), 4.95 (br s, 1H), 5.08 (s, 2H), 7.33 (s, 5H); ^{13}C NMR δ 22.08, 23.09, 24.70, 37.33, 40.09, 48.64, 67.03, 71.49, 128.26, 128.37, 128.71, 136.43, 156.01. Anal. Calcd for $C_{15}H_{23}NO_5S$: C, 54.69; H, 7.04; N, 4.25. Found: C, 54.80; H, 6.95; N, 4.08. **Ethyl (*S*)-4-[(benzyloxycarbonyl)amino]-5-(tosyloxy)valerate (14e)**: mp 85−87 °C (cyclohexane); $[\alpha]^{21}_D$ = −15.6 (*c* = 2.8, MeOH); IR (Nujol) 3350, 1730, 1690, 1600, 1540 cm^{-1}; ^{1}H NMR δ 1.20 (t, J = 7.1, 3H), 1.83 (dt, J = 7.4, 7.0, 2H), 2.35 (t, J = 7.4, 2H), 2.40 (s, 3H), 3.9−4.2 (m, 5H), 5.10 (s, 2H), 5.0−5.2 (br s, 1H), 7.3−7.5 (m, 2H), 7.35 (s, 5H), 7.7−7.9 (m, 2H); ^{13}C NMR δ 14.33, 21.83, 26.35, 30.71, 49.92, 60.87, 67.04, 71.33, 128.13, 128.36, 128.71, 130.15, 132.51, 136.32, 145.30, 155.93, 173.04. Anal. Calcd for $C_{22}H_{27}NO_7S$: C, 58.78; H, 6.05; N, 3.12. Found: C, 58.94; H, 5.90; N, 3.02.

Benzyl *N*-[(*S*)-1-benzyl-2-(tosyloxy)ethyl]carbamate (14f): mp 94−96 °C (AcOEt−cyclohexane); [lit.[19] mp 96−97 °C].

Benzyl *N*-[(*S*)-1-benzyl-2-(mesyloxy)ethyl)]carbamate (14g):[20] mp 108−109 °C (benzene−cyclohexane); IR (Nujol) 3350, 1690, 1540 cm^{-1}; ^{1}H NMR δ 2.8−3.0 (m, 2H), 2.94 (s, 3H), 4.05−4.30 (m, 3H), 5.0−5.2 (br s, 1H), 5.07 (s, 2H), 7.1−7.3 (m, 10H); ^{13}C NMR δ 37.25, 37.38, 51.56, 67.11, 69.73, 127.25, 128.30, 128.44, 128.76, 129.01, 129.42, 136.37, 136.53, 155.87. Anal. Calcd for $C_{18}H_{21}NO_5S$: C, 59.49; H, 5.82; N, 3.85. Found: C, 59.25; H, 5.65; N, 3.72.

***tert*-Butyl *N*-[(*S*)-1-benzyl-2-(tosyloxy)ethyl]carbamate (14h):**[21] mp 111−115 °C dec (cyclohexane).

N-(2-Bromoethyl)amides were prepared from 2-bromoethylamine hydrobromide and the opportune acyl chloride.

***N*-(2-Bromoethyl)phenylacetamide (16a)**: mp 84−85 °C (benzene) [lit.[22] mp 84−85 °C]. ***N*-(2-Bromoethyl)phenoxyacetamide (16b)**: mp 76−77 °C (cyclohexane); IR (Nujol) 3340, 1660, 1530 cm^{-1}; ^{1}H NMR δ 3.50 (t, J = 6.0, 2H), 3.75 (q, J = 6.0, 2H), 4.51 (s, 2H), 6.9−7.2 (m, 4H), 7.2−7.4 (m, 2H); ^{13}C NMR δ 31.89, 40.73, 67.42, 114.85, 122.38, 129.97, 157.22, 168.64. Anal. Calcd for $C_{10}H_{12}BrNO_2$: C, 46.53; H, 4.69; N, 5.43. Found: C, 46.35; H, 4.54; N, 5.30.

***N*-(2-Bromoethyl)benzamide (20a)**: mp 101−103 °C (benzene) [lit.[23] mp 104−105 °C]. **(*S*)-5-[(Tosyloxy)methyl]-2-pyrrolidinone (18)** was prepared as reported in the literature:[24] mp 127−128 °C (EtOH) [lit.[25] mp 130 °C].

(*S*)-2-(Trifluoroacetamido)-3-phenylpropyl mesylate (20b) was prepared by standard procedure from the corresponding hydroxy derivative obtained as described.[26]

20b: mp 150−152 °C (benzene); $[\alpha]^{21}_D$ = −13.3 (*c* = 2.3, MeOH); IR (Nujol) 3310, 1700, 1560 cm^{-1}; ^{1}H NMR δ 2.95 (dd, J = 14.0, 8.0, 1H), 3.01 (dd, J = 14.0, 7.0, 1H), 3.03 (s, 3H), 4.20 (dd, J = 11.0, 5.0, 1H), 4.34 (dd, J = 11.0, 4.0, 1H), 4.38−4.48 (m, 1H), 6.69 (br s, 1H), 7.1−7.4 (m, 5H); ^{13}C NMR δ 36.48, 37.63, 50.77, 68.27, 114.68, 127.54, 129.08, 129.14, 135.40, 157.14. Anal. Calcd for $C_{12}H_{14}F_3NO_4S$: C, 44.31; H, 4.34; N, 4.31. Found: C, 44.45; H, 4.41; N, 4.20.

***N*-(*S*)-(1-Bromo-3-phenylprop-2-yl)-4-toluenesulfonamide (20c)** was prepared according to the literature:[27] mp 118−120 °C (cyclohexane−acetone) [lit.[27] mp 120−122 °C).

Electrochemistry. The electrolyses were carried out at −1.0 V *vs* SCE in 0.1 M MeCN solution of TEAP (40 mL), where O_2 and CO_2 were simultaneously bubbling. At the end of the electrolysis, N_2 was flowing through the solution for 5 min, and the substrate (2 mmol) was added. In the case of linear carbamates, a fivefold molar excess of EtI was added 60 min after the current was switched off. The solution was stirred overnight at rt, a sample (2 mL) was taken off for HPLC or GC analyses, and the solvent was removed under reduced pressure from the remaining solution. The residue was extracted with Et_2O (5 × 30 mL); H_2O (100 mL) was added to the insoluble portion in ether, and the mixture was extracted with $CHCl_3$ (AcOEt for the mixture from **18**) (3 × 50 mL). The extracts were dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. The residues were analyzed by IR, ^{1}H NMR, and TLC and combined if they had the same composition. Column chromatography of the mixtures and/or crystallization of the residues allowed the isolation of the single components that were identified by comparison with authentic samples or fully characterized.

The isolated and HPLC or GC yields are reported in Tables 1 and 2.

Electrocarboxylation of 1. 3 F/mol of amine was employed. Carbamates **2** were isolated after column chromatography (eluent given in parentheses) of the residue of the ethereal extracts.

Ethyl benzylcarbamate (2a) (Al_2O_3; hexane−Et_2O 3:2; 265 mg, 85%): mp 43−44 °C [lit.[28] mp 44 °C].

Ethyl cyclohexylcarbamate (2b) (Al_2O_3; hexane−Et_2O 3:2; 275 mg, 92%): mp 49−51 °C [lit.[29] mp 52 °C].

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Ethyl (3-phenylpropyl)carbamate (2c) (hexane−Et_2O 7:3; 275 mg, 75%): IR (film) 3330, 1700, 1600, 1530 cm^{-1}; ^1H NMR δ 1.22 (t, J = 7.1, 3H), 1.7−1.9 (m, 2H), 2.63 (t, J = 7.3, 2H), 3.1−3.3 (m, 2H), 4.11 (q, J = 7.1, 2H), 4.7−4.9 (br s, 1H), 7.1−7.4 (m, 5H); ^{13}C NMR δ 14.56, 31.53, 32.96, 40.46, 60.59, 125.85, 128.24, 128.32, 141.36, 156.65. Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.46; H, 8.21; N, 6.70.

Ethyl phenylcarbamate (2d)[30] (hexane−Et_2O 4:1; 155 mg, 54%).

Ethyl (4-methoxyphenyl)carbamate (2e) (hexane−AcOEt 7:3, 285 mg; 83%): mp 54−56 °C [lit.[29] mp 56 °C].

Ethyl (4-cyanophenyl)carbamate (2f)[31] (hexane−AcOEt; 7:3; 120 mg, 36%): mp 114−116 °C; IR (Nujol) 3300, 2220, 1730, 1590, 1530 cm^{-1}; ^1H NMR δ 1.27 (t, J = 7.2, 3H), 4.22 (q, J = 7.2, 2H), 7.22 (br s, 1H), 7.5−7.6 (m, 4H); ^{13}C NMR δ 14.35, 61.72, 105.88, 118.23, 118.93, 133.21, 142.34, 153.03. Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.99; H, 5.24; N, 14.66.

Ethyl *N*-benzyl-*N*-methylcarbamate (2g)[32] (hexane−Et_2O 4:1; 310 mg, 91%).

Ethyl *N*,*N*-dibenzylcarbamate (2h)[33] (hexane−Et_2O 9:1; 400 mg, 83%).

IR and ^1H NMR spectra of the residue of the ethereal extract from **1i** showed the presence of starting material as the only compound.

Electrocarboxylation of 3. 3 F/mol of bromoamine was employed. The residue of the combined extracts from the reaction of **3a** was 2-oxazolidinone **4a** (100 mg, 60%), as stated by comparison with an authentic sample (Aldrich).

The residue of the combined extracts from the reaction of **3b** was **3,4,5,6-tetrahydro-2*H*-1,3-oxazin-2-one (4b)** (98 mg, 51%): mp 80−82 °C (AcOEt) [lit.[34] mp 82−83 °C].

Electrocarboxylation of 5, 7 and 10. 3 F/mol of amino alcohol was employed. Column chromatography of the residue of the combined extracts from **5** (light petroleum−AcOEt 3:2 as eluent) gave **ethyl *N*-(2-hydroxy-2-phenylethyl)carbamate (6)** (230 mg, 58%): mp 85−87 °C (cyclohexane) [lit.[35] mp 86−87 °C] and starting **5** (65 mg, 25%). Column chromatography of the residue of the combined extracts from **7** (light petroleum−AcOEt 7:3 as eluent) gave **ethyl 2-[(ethoxycarbonyl)amino]-2-phenylethyl carbonate (9)** (100 mg, 19%) and **ethyl (2-hydroxy-1-phenylethyl)carbamate (8)** (218 mg, 55%).

8: mp 79−81 °C (cyclohexane); IR (Nujol) 3380, 3330, 1690, 1550 cm^{-1}; ^1H NMR δ 1.21 (t, J = 7.0, 3H), 2.0−2.4 (br s, 1H), 3.6−3.9 (m, 2H), 4.11 (q, J = 7.0, 2H), 4.7−4.9 (m, 1H), 5.3−5.6 (br s, 1H), 7.1−7.5 (m, 5H); ^{13}C NMR δ 14.53, 57.10, 61.20, 66.61, 126.57, 127.85, 128.83, 139.28, 156.71. Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.01; H, 7.16; N, 6.58.

9: mp 61−63 °C (light petroleum); IR (Nujol) 3330, 1740, 1690, 1540 cm^{-1}; ^1H NMR δ 1.15 (t, J = 7.0, 3H), 1.22 (t, J = 7.1, 3H), 3.9−4.1 (m, 4H), 4.30 (d, J = 5.5, 2H), 4.9−5.1 (m, 1H), 5.2−5.4 (br s, 1H), 7.27 (s, 5H); ^{13}C NMR δ 14.46, 14.79, 54.70, 61.71, 64.96, 70.11, 127.59, 129.00, 129.78, 139.45, 156.25, 157.14. Anal. Calcd for $C_{14}H_{19}NO_5$: C, 59.78; H, 6.81; N, 4.98. Found: C, 59.91; H, 6.73; N, 4.82. Column chromatography of the residue of the combined extracts from **10** (light petroleum−AcOEt 1:1 as eluent) gave **ethyl 3-[(ethoxycarbonyl)amino]benzyl carbonate (12)** (35 mg, 7%), **ethyl *N*-[3-(hydroxymethyl)phenyl]carbamate (11)** (130 mg, 35%), starting **10** (35 mg, 15%), and an unresolved fraction whose ^1H NMR spectrum showed the presence of **ethyl 3-aminobenzyl carbonate (13)**.

11: mp 44−46 °C; IR (Nujol) 3440, 3280, 1700, 1610, 1540 cm^{-1}; ^1H NMR δ 1.29 (t, J = 7.1, 3H), 2.5−3.0 (br s, 1H), 4.16 (q, J = 7.1, 2H), 4.55 (s, 2H), 6.9−7.4 (m, 5H); ^{13}C NMR δ 14.44, 61.19, 64.78, 117.27, 117.88, 121.76, 129.05, 138.15, 142.00, 153.84. Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.17. Found: C, 61.37; H, 6.64; N, 7.09.

12: mp 50−52 °C; IR (Nujol) 3350, 1730, 1720, 1620, 1560 cm^{-1}; ^1H NMR δ 1.21 (t, J = 7.0, 3H), 1.22 (t, J = 7.2, 3H), 4.11 (q, J = 7.2, 2H), 4.12 (q, J = 7.0, 2H),5.05 (s, 2H), 6.7−6.9 (br s, 1H), 6.9−7.4 (m, 4H); ^{13}C NMR δ 14.38, 14.67, 61.40, 64.32, 69.30, 118.43, 118.80, 123.09, 129.43, 136.41, 138.49, 153.76, 155.24. Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.30; H, 6.34; N, 5.15.

13: ^1H NMR δ 1.27 (t, J = 7.1, 3H), 3.4−3.9 (br s, 2H), 4.21 (q, J = 7.1, 2H), 5.07 (s, 2H), 6.6−7.3 (m, 4H). ^{13}C NMR δ 14.47, 64.29, 69.63, 114.84, 115.32, 118.49, 129.73, 136.68, 146.82, 155.33.

Electrocarboxylation of 14. 1.2 F/mol of carbamate was employed. Column chromatography (light petroleum−AcOEt 1:1 as eluent) of the residue of the combined extracts from **14a** gave **3-(benzyloxycarbonyl)-2-oxazolidinone (15a)** (330 mg, 79%): mp 99−100 °C (EtOH) [lit.[36] mp 101−102 °C].

IR and ^1H NMR spectra of the residue of the ethereal extracts from **14b** showed the presence as the only compound of **3-(*tert*-butyloxycarbonyl)-2-oxazolidinone (15b)** (265 mg, 75%): mp 83−85 °C (cyclohexane) [lit.[37] mp 85 °C].

Column chromatography (light petroleum−AcOEt 1:1 as eluent) of the residue of the combined extracts from **14c** gave **(*S*)-3-(benzyloxycarbonyl)-4-(2-methylpropyl)-2-oxazolidinone (15c)** (380 mg, 72%): mp 55−57 °C (light petroleum); $[\alpha]^{21}_D$ = +49.2 (c = 1.4, $CHCl_3$); IR (Nujol) 1820, 1790, 1730 cm^{-1}; ^1H NMR δ 0.89 (d, J = 6.0, 3H), 0.93 (d, J = 6.0, 3H), 1.50−1.80 (m, 3H), 4.06 (dd, J = 8.0, 2.5, 1H), 4.31 (tdd, J = 8.0, 3.0, 2.0, 1H), 4.37 (t, J = 8.0, 1H), 5.27 (d, J = 12.5, 1H), 5.34 (d, J = 12.5, 1H), 7.35−7.45 (m, 5H); ^{13}C NMR δ 21.48, 23.37, 24.58, 41.88, 53.84, 67.21, 68.56, 128.26, 128.56, 128.60, 134.81, 150.71, 151.83. Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 65.10; H, 7.00; N, 4.96.

Column chromatography of the residue of the combined extracts from **14d** gave **15c** (370 mg, 70%).

Column chromatography ($CHCl_3$−AcOEt 9:1 as eluent) of the combined extracts from **14e** gave **(*S*)-3-(benzyloxycarbonyl)-4-[2-(ethoxycarbonyl)ethyl]-2-oxazolidinone (15e)** (510 mg, 85%): mp 66−68 °C (cyclohexane); $[\alpha]^{21}_D$ = +37.7 (c = 1.9, $CHCl_3$); IR (Nujol) 1810, 1800, 1730 cm^{-1}; ^1H NMR δ 1.25 (t, J = 7.0, 3H), 2.07 (dtd, J = 14.0, 8.0, 2.5, 1H), 2.10 (dtd, J = 14.0, 8.0, 4.5, 1H), 2.36 (t, J = 8.0, 2H), 4.10 (q, J = 7.0, 2H), 4.12 (dd, J = 8.0, 2.5, 1H), 4.40 (t, J = 8.0, 1H), 4.44 (tdd, J = 8.0, 4.5, 2.5, 1H), 5.32 (s, 2H), 7.30−7.45 (m, 5H); ^{13}C NMR δ 14.14, 28.29, 29.23, 54.26, 60.70, 66.77, 68.77, 128.27, 128.60, 128.66, 134.76, 150.80, 151.59, 172.09. Anal. Calcd for $C_{16}H_{19}NO_6$: C, 59.81; H, 5.96; N, 4.36. Found: C, 59.64; H, 5.84; N, 4.25.

Column chromatography (light petroleum−AcOEt 3:2 as eluent) of the residue of the ethereal extracts from **14f** gave **(*S*)-3-(benzyloxycarbonyl)-4-benzyl-2-oxazolidinone (15f)** (470 mg, 80%): mp 70−71 °C (cyclohexane); $[\alpha]^{21}_D$ = +28.5 (c = 2.0, $CHCl_3$); IR (Nujol) 1820, 1800, 1720 cm^{-1}; ^1H NMR δ 2.84 (dd, J = 13.5, 9.5, 1H), 3.30 (dd, J = 13.5, 3.5, 1H), 4.14 (dd, J = 9.0, 3.5, 1H), 4.21 (dd, J = 9.0, 7.5, 1H), 4.54 (ddt, J = 9.5, 7.5, 3.5, 1H), 5.35 (s, 2H), 7.10−7.40 (m, 10H); ^{13}C NMR δ 38.58, 56.17, 65.93, 68.90, 127.52, 128.51, 128.85, 129.12, 129.50, 134.97, 135.06, 150.90, 151.81. Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 65.09; H, 6.99; N, 4.92. The residue of the ethereal extracts from **14g** (500 mg, 85%) was identified as **15f** on the basis of its IR and ^1H NMR spectra.

Column chromatography (light petroleum−AcOEt 1:1 as eluent) of the residue of the combined extracts from **14h** gave **(*S*)-3-(*tert*-butyloxycarbonyl)-4-benzyl-2-oxazolidinone (15h)** (435 mg, 83%): mp 101−103 °C (cyclohexane); $[\alpha]^{21}_D$ = +20.8 (c = 1.2, $CHCl_3$); IR (Nujol) 1800, 1710 cm^{-1}; ^1H NMR

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δ 1.60 (s, 9H), 2.80 (dd, J = 13.5, 9.5, 1H), 3.30 (dd, J = 13.5, 3.5, 1H), 4.10 (dd, J = 9.0, 3.5, 1H) 4.16 (t, J = 9.0, 1H), 4.46 (tt, J = 9.5, 3.5 1H), 7.15−7.35 (m, 5H). ^{13}C NMR δ 28.20, 38.90, 56.30, 65.65, 84.23, 127.53, 129.20, 129.53, 135.41, 149.39, 152.28. Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.32; H, 5.41; N, 4.40.

IR and ^{1}H NMR spectra of the residue of the combined extracts from **14i** showed the presence of ***N*-Boc dehydroalanine benzyl ester (22)** as the only compound (510 mg, 97%): IR (film) 3420, 1740, 1720, 1630, 1510 cm^{-1}; ^{1}H NMR δ 1.40 (s, 9H), 5.18 (s, 2H), 5.71 (d, J = 1.5, 1H), 6.11 (s, 1H), 6.98 (br s, 1H), 7.30 (s, 5H); ^{13}C NMR δ 28.44, 67.83, 80.92, 105.65, 128.41, 128.74, 128.85, 131.52, 135.36, 152.76, 164.09. Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 64.82; H, 6.84; N, 4.96.

Electrocarboxylation of 16. 1.2 F/mol of bromoamide was employed. Column chromatography (light petroleum−AcOEt 1:1 as eluent) of the residue of the combined extracts from **16a** gave **3-(phenylacetyl)-2-oxazolidinone (17a)** (285 mg, 79%): mp 56−58 °C [lit.[38] mp 55−56 °C].

Column chromatography (light petroleum−AcOEt 3:2 as eluent) of the residue of the combined extracts from **16b** gave **3-(phenoxyacetyl)-2-oxazolidinone (17b)** (280 mg, 71%): mp 93−95 °C [lit.[38] mp 95.5−96.5 °C].

Electrocarboxylation of 18. 1.2 F/mol of pyrrolidone was employed. The residue of the combined extracts from **18** was **(*S*)-1*H*,3*H*-5,6,7,7*a*-tetrahydro-3,5-dioxopyrrolo[1,2-*c*]oxazole (19)** (200 mg, 75%): mp 136−138 °C (benzene); $[\alpha]^{21}_D$ = +12.2 (c = 9.0, $CHCl_3$); IR (Nujol) 1850, 1800, 1730, 1710 cm^{-1}; ^{1}H NMR δ 2.06 (tt, J = 13.0, 8.5, 1H), 2.44 (br ddd, J = 13.0, 8.0, 6.0, 1H), 2.72 (br dd, J = 17.0, 8.0, 1H), 2.84 (ddd, J = 17.0, 13.0, 8.0, 1H), 4.15 (t, J = 8.5, 1H), 4.64 (t, J = 8.5, 1H), 4.72 (qd, J = 8.5, 6.0, 1H); ^{13}C NMR δ 27.61, 35.71, 56.61, 71.01, 149.68, 171.54. Anal. Calcd for $C_6H_7NO_3$: C, 51.06; H, 5.00; N, 9.92. Found: C, 50.94; H, 4.90; N, 9.85.

Cyclization of 20. 1.2 F/mol of amide was employed. Aziridines **21** were isolated after column chromatography (eluent given in parentheses) of the residue from the combined extracts.

1-Benzoylaziridine (21a)[39] (light petroleum−AcOEt 1:1; 230 mg, 82%).

(*S*)-1-(Trifluoroacetyl)-2-benzylaziridine (21b) ($CHCl_3$−propan-2-ol 95:5; 220 mg, 51%): $[\alpha]^{21}_D$ = −50.3 (c = 2.3, $CHCl_3$); IR (film) 1690, 1610 cm^{-1}; ^{1}H NMR δ 2.77 (dd, J = 14.0, 8.0, 1H), 3.17 (dd, J = 14.0, 5.0, 1H), 4.23 (dd, J = 9.0, 8.0, 1H), 4.44 (t, J = 9.0, 1H), 4.56−4.66 (m, 1H), 7.20−7.32 (m, 5H); ^{13}C NMR δ 40.64, 67.56, 73.74, 116.33, 126.96, 128.71, 129.21, 136.37, 155.20. Anal. Calcd for $C_{11}H_{10}F_3NO$: C, 57.64; H, 4.40; N, 6.11. Found: C, 57.46; H, 4.29; N, 5.99.

1-Tosyl-2-benzylaziridine (21c) (light petroleum−AcOEt 4:1; 460 mg, 84%): mp 90−91 °C [lit.[40] mp 92−94 °C].

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