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Stereoselective electrogeneration of (*E*)-4-alkoxy-2-phenyl-5-chloro-2-oxazolines by cathodic reduction of *N*-(1-alkoxy-2,2,2-trichloroethyl)benzamides

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Abstract—The first method for the synthesis of the title compounds has been established. Quantitative reactions of benzamides with chloral hydrate provided chloralbenzamides which were efficiently converted to *N*-(1,2,2,2-tetrachloroethyl)amides by treatment with phosphorus pentachloride. These compounds reacted selectively with alcohols under mild conditions to give *N*-(1-alkoxy-2,2,2-trichloroethyl)benzamides in high yields which were stereoselectively transformed to (*E*)-4-alkoxy-2-aryl-5-chloro-2-oxazolines in fair to good yields by electrochemical reduction under constant cathodic potential in an aprotic medium.

1. Introduction

We have recently developed a new heterocyclization methodology based on the cathodic reduction of chloral derivatives. Chloral is an inexpensive, commercially available reagent whose versatile reactivity[1] allows the synthesis of a wide variety of cathodically active polychlorinated derivatives. Some of these compounds seem especially attractive for use as starting materials in electroorganic synthesis, particularly those that have a structural arrangement suitable to undergo a reductive electrochemical heterocyclization process. The key step of this type of transformation involves a migration of charge on the first electrogenerated chlorocarbanion intermediate to a remote heteroatom. In this way, the newly formed anionic intermediate contains two suitably placed centres with opposite nucleophilic–electrophilic activity capable of promoting a ring closure process by internal displacement of a chloride anion. This synthetic strategy was successfully applied for preparing previously unknown 4-amino-2-aryl-2-oxazolines[2,3] which gave access to novel 2-imidazolidinones, 1,3-oxazolidines and 1,3-thiazolidines.[4] 2-Oxazolines are in general compounds of great interest[5] since they are versatile synthetic intermediates.[5e–g] Moreover, their therapeutic potential[5c,6] and many other significant applications[5c] are also important factors in stimulating the research on the chemistry of these substances. Consequently, the synthesis of different classes of 2-oxazolines has received intense attention for many years. A recent upsurge in interest has also been observed.[7]

Given the high potentiality of this electrochemical methodology for expanding the classes of 2-oxazolines available, we attempted the synthesis of the hitherto unknown 4-alkoxy-5-chloro-2-phenyl-2-oxazolines, as is shown in Scheme 1.

2. Results and discussion

Chloralamides **2** were prepared[8] in almost quantitative yields by reaction of chloral hydrate with benzamides **1**. In order to prepare *N*-(1-alkoxy-2,2,2-trichloroethyl)benzamides **4** compounds **2** were firstly converted to *N*-(1,2,2,2-tetrachloroethyl)benzamides **3** in high yields by reaction with phosphorus pentachloride, as described previously.[8b,9] It was found that products **3** undergo selective monoalkoxylation by simple treatment with a mixture of the corresponding alcohol and triethyl amine in a 1:1 ratio to give the targeted intermediates **4** in good to quantitative yields.

Cathodic reductions of compounds **4** in an aprotic medium (acetonitrile–tetrabutylammonium perchlorate) at a mercury pool cathode were carried out under a constant

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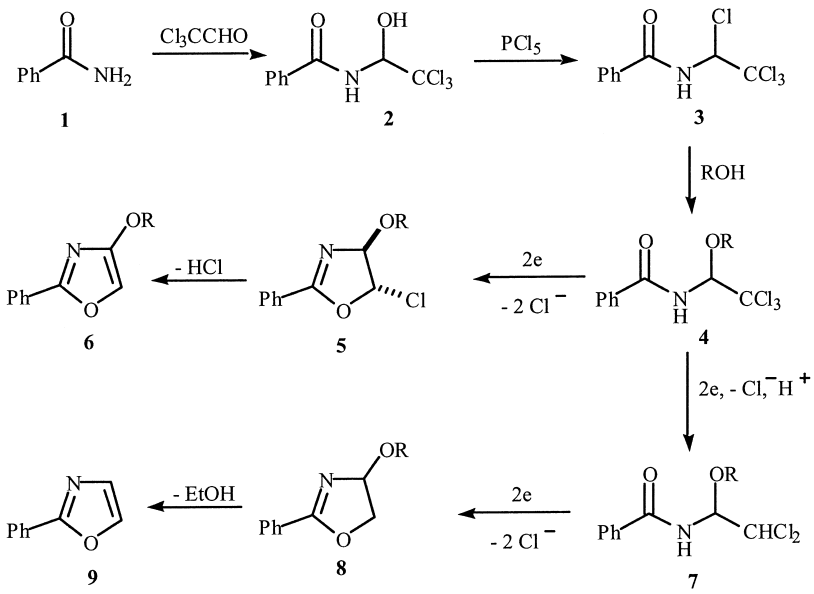


Entry	R	**4** (%)	**5** (%)
a	CH_3CH_2	96	65
b	CH_3	98	79
c	$C_6H_5CH_2CH_2$	65	82
d	$3,4,5\text{-}(CH_3O)_3C_6H_2CH_2$	75	66
e	$4\text{-}CH_3OC_6H_4CH_2$	73	64

Scheme 1.

potential of −1.50 V vs SCE. The electricity consumption was 2 F/mol of **4** in all cases. After electrolyses, the catholyte solutions were checked by TLC and GC, showing a total transformation of starting materials to single products, which were easily isolated and purified. These were oily compounds that were identified by IR, MS, NMR spectroscopy and elemental analysis as (*E*)-4-alkoxy-2-aryl-5-chloro-2-oxazolines **5** which pertain to a new family of 2-oxazoline compounds. Yields ranged from fair to good.

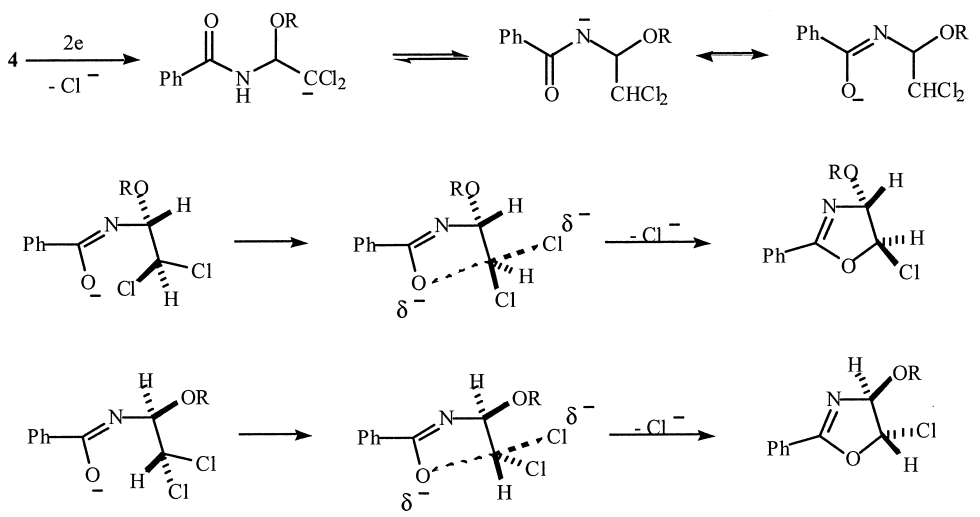
Spectroscopic analyses of products **5** were corroborated by treatment of **5b** with potassium *tert*-butoxide. It caused a total conversion to 2-phenyl-4-methoxyoxazol **6b**, which was conclusively identified by comparison with an authentic sample.[10]

On the other hand, it was found that electrogeneration of products **5** occurs with stereoselectivity towards the formation of (*E*)-isomers. This configurational assignment is firmly supported by categorical ^{1}H NMR studies[11,12] on stereochemistry of substituted five-membered cyclic compounds from which it has been established as a general rule that the arrangement of vicinal protons corresponds to a (*E*)-configuration when they show spin coupling constants of $J<5$ Hz, whereas a (*Z*)-configuration always shows coupling constants with $J>5$ Hz, and ~8 Hz is the value most frequently found. This method leads to the conclusion that the stereochemistry of products **5** corresponds to a (*E*)-configuration since the coupling constants between H-4 and H-5 protons are remarkably small, with *J* values ranging from 1.5 to 1.6 Hz in all cases.

The results of the cathodic reductions of *N*-(1-alkoxy-2,2,2-trichloroethyl)benzamides **4**, along with our previous reports[2,3] on studying electroreductions of *N*-(1-amino-2,2-dichloroethyl)benzamides, provide important insights into the high potential of this heterocyclization methodology, which appears specially suitable to accomplish the synthesis of complex 2-oxazolines.

The formation of oxazolines **5** (Scheme 2) can be reasonably explained on the basis of a two-electron selective cathodic cleavage of one carbon–chlorine bond with generation of a dichlorocarbanionic intermediate which would generate an amide anion. Therefore, the cyclization to yield racemic products **5** would occur by nucleophilic displacement of one of the remaining chlorine atoms. A transition state involving minimal steric interactions between the stationary chlorine atom and a vicinal alkoxyl group would participate.

Given the success in preparing the oxazolines **5**, we also attempted the synthesis of 4-alkoxy-2-phenyl-2-oxazolines **8** by applying a similar methodology. *N*-(1-Ethoxy-2,2-trichloroethyl)benzamide **7a** was used as model compound for this study. It was prepared by cathodic reduction of **4a** in a protic medium. The electrochemical reduction of **7a** was carried out under a similar experimental conditions to those used in the electrolyses of compounds **4**. A considerably more negative potential (−1.90 V versus SCE), however, must be applied in this case. In contrast to that observed with compounds **4**, the passing current did not decrease spontaneously when the charge consumption reached 2 F/mol.



Scheme 2.

At values close to 3 F/mol, the catholyte showed a high basicity; the electrolysis was then stopped and the reaction products present in the catholyte were analyzed by GC/MS. A complex mixture of compounds with 2-phenyloxazol **9** (24%) and 4-ethoxy-2-penyl-2-oxazoline **8a** (17%) as main components was detected. The identity of **9** was corroborated by comparison with an authentic specimen.[13] The progressive conversion of **8a** to **9** in the basic catholyte medium was observed, and even occurred without electricity passing. In the case of shorter electrolyses (1.9 F/mol), a remarkable variety of reaction products was also observed. These adverse results are attributable to the highly negative cathodic potential operating, which causes indiscrimination in electrode process and basicity in the solvent–electrolyte system.

To conclude, a convenient method for the synthesis of (*E*)-4-alkoxy-2-aryl-5-chloro-2-oxazolines, a previously unattainable class of compounds, is reported. Versatility, good yields, easy availability of starting materials, mildness and simple experimental procedure are noteworthy advantages of this approach. However, this method has been found to be of no use in the synthesis of 4-alkoxy-2-aryl-2-oxazolines.

3. Experimental

3.1. General

NMR spectra were determined on Bruker AC-200 or Varian Unity 300 Unity instruments with tetramethylsilane as internal reference. Electron-impact mass spectra were obtained on Hewlett–Packard 5995 and Autospect 5000 VG spectrometers under an ionizing voltage of 70 eV. IR spectra (nujol emulsions) were recorded on a Nicolet Impact 400 spectrophotometer. Microanalyses were performed on a Carlo Erba EA-1108 analyzer. Melting points were determined on a Kofler hot-plate melting point apparatus, and are uncorrected. Electrochemical experiments were performed with an Amel 557 potentiostat coupled to an Amel 558 integrator. Chloralamides **2** and *N*-(1,2,2,2-tetrachloroethyl)benzamides **3** were prepared as described previously.[8b,9]

3.2. Preparation of *N*-(1-alkoxy-2,2,2-trichloroethyl)-benzamides (4)

General procedure. A solution of the corresponding alcohol (5.25 mmol) and triethylamine (5.25 mmol) in dry acetone (6 mL) was added dropwise at room temperature to a stirred solution of the appropriate *N*-(1,2,2,2-tetrachloroethyl)-amide **3** (5.25 mmol) in dry acetone (9 mL) and the stirring was continued for 10 h. The white solid precipitate formed was removed by filtration and the solvent was evaporated under reduced pressure leaving a residue which was washed with cold petroleum ether. The resulting solid product was crystallized in the appropriate solvent.

Preparation of **4a**. *N*-(1,2,2,2-Tetrachloroethyl)benzamide **3a** (7 mmol) was added to dry ethanol (30 mL) and the stirred solution was heated at 40 °C for 1 h. After cooling the crystalline product was isolated by filtration.

3.2.1. *N*-(2,2,2-Trichloro-1-ethoxyethyl)benzamide (4a). 96%. Colourless needles, mp 148 °C (ethanol). (Found: C, 44.64; H, 4.14; N, 4.77. $C_{11}H_{12}Cl_3NO_2$ requires: C, 44.55; H, 4.08; N, 4.72); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 1.31 (t, 3H, J=7.2 Hz), 3.79–3.94 (m, 2H), 5.90 (d, 1H, J=9.8 Hz), 6.75 (d, 1H, J=9.8 Hz), 7.26–7.58 (m, 3H), 7.81–7.86 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 14.91 (CH_3), 66.54 (CH_2), 86.39 (CH), 99.66 (CCl_3), 127.28 (CH), 128.94 (CH), 132.61 (CH), 133.05 (C), 167.46 (CO); MS, *m/z* (%): 216 (29), 178 (17), 105 (100), 77 (91), 51 (36); IR (Nujol): 3306, 1645, 1516, 1462, 1340, 1272, 1108, 915, 821, 791, 720 cm^{-1}.

3.2.2. *N*-(2,2,2-Trichloro-1-methoxyethyl)benzamide (4b). 98%. Colourless needles, mp 99–102 °C (pet ether). (Found: C, 42.48; H, 3.62; N, 5.01. $C_{10}H_{10}Cl_3NO_2$ requires: C, 42.51; H, 3.57; N, 4.96); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.63 (s, 3H), 5.82 (d, 1H, J=10.0 Hz), 6.75 (d, 1H, J=10.0 Hz), 7.45–7.59 (m, 3H), 7.82–7.87 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 58.01 (CH_3), 87.89 (CH), 99.22 (CCl_3), 127.29 (CH), 128.95 (CH), 132.69 (CH), 132.85 (C), 167.71 (CO); MS, *m/z* (%): 283 (M^++2, 4), 281 (M^+, 5), 246 (11), 215 (51), 164 (82), 126 (21), 105 (100), 77 (89); IR (Nujol): 3266, 1648, 1523, 1461, 1377, 1103, 796 cm^{-1}.

3.2.3. *N*-[2,2,2-Trichloro-1-(2-phenylethoxy)ethyl]benzamide (4c). 65%. Colourless needles, mp 97 °C (pet ether). (Found: C, 54.89; H, 4.29; N, 3.71. $C_{17}H_{16}Cl_3NO_2$ requires: C, 54.79; H, 4.33; N, 3.76); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 2.96 (t, 2H, J=6.9 Hz), 3.95–4.05 (m, 2H), 5.90 (d, 1H, J=9.8 Hz), 6.53 (d, 1H, J=9.8 Hz), 7.23–7.25 (m, 5H), 7.42–7.57 (m, 3H), 7.68–7.73 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 35.97 (CH_2), 71.33 (CH_2), 86.53 (CH), 99.45 (CCl_3), 126.51 (CH), 127.28 (CH), 128.44 (CH), 128.87 (CH), 129.18 (CH), 132.61 (C), 132.89 (CH), 138.12 (C), 167.49 (CO); MS, *m/z* (%): 371 (M^+0.2), 336 (0.4), 250 (2), 216 (8), 105 (100), 91 (25), 77 (93); IR (Nujol): 3285, 1648, 1528, 1464, 1379, 1277, 1098, 1081, 813, 699 cm^{-1}.

3.2.4. *N*-[2,2,2-Trichloro-1-(3,4,5-trimethoxybenzyloxy)ethyl]benzamide (4d). 75%. Colourless needles, mp 102–103 °C (dichloromethane–hexane). (Found: C, 50.66; H, 5.08; N, 3.26. $C_{19}H_{20}Cl_3NO_5$ requires: C, 50.86; H, 4.49; N, 3.12); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 3.79 (s, 3H), 3.81 (s, 6H), 4.75 (s, 2H), 6.00 (d, 1H, J=9.6 Hz), 6.64 (s, 2H), 6.75 (d, 1H, J=9.6 Hz), 7.44–7.58 (m, 3H), 7.77 (d, 2H, J=6.0 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 56.02 (CH_3O), 60.75 (CH_3O), 72.31 (CH_2), 85.80 (CH), 99.38 (CCl_3), 105.36 (CH), 127.15 (CH), 128.83 (CH), 131.69 (C), 132.61 (CH), 132.74 (C), 137.83 (C), 153.20 (C), 167.37 (CO); MS, *m/z* (%): 447 (M^+, 27), 216 (100), 196 (36), 181 (34), 169 (30), 148 (18), 138 (21), 105 (34), 77 (75); IR (Nujol): 3276, 1681, 1597, 1530, 1465, 1379, 1332, 1270, 1239, 1133, 1085, 1011, 815, 697 cm^{-1}.

3.2.5. *N*-[2,2,2-Trichloro-1-(4-methoxybenzyloxy)ethyl]benzamide (4e). 73%. Colourless needles, mp 105–107 °C (hexane). (Found: C, 52.60; H, 4.09; N, 3.52. $C_{17}H_{16}Cl_3NO_3$ requires: C, 52.53; H, 4.15; N, 3.60); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.78 (s, 3H), 4.76 (d, 2H, J=6.4 Hz), 5.95 (d, 1H, J=9.8 Hz), 6.73 (d, 1H, J=9.8 Hz), 6.87 (d, 2H, J=8.6 Hz), 7.34 (d, 2H, J=8.6 Hz), 7.44–7.58 (m, 3H), 7.80 (dd, 2H, J=6.7, 1.2 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 55.30 (CH_3O), 71.93 (CH_2), 85.57 (CH), 99.54 (CCl_3), 113.98 (CH), 127.27 (CH), 128.17 (C), 128.90 (CH), 130.20 (CH), 132.60 (CH), 133.01 (C), 159.78 (C), 167.46 (CO); MS, *m/z* (%): 387 (M^+, 2), 252 (2), 233 (3), 216 (74), 180 (10), 137 (58), 121 (78), 105 (100), 77 (62); IR (Nujol): 3328, 1657, 1520, 1461, 1349, 1258, 1097, 1056, 1034, 998, 808, 716 cm^{-1}.

3.3. Preparation of (*E*)-4-alkoxy-5-chloro-2-phenyl-2-oxazolines (5)

Preparative electrolyses were carried out under a constant cathodic potential in a concentric cylindrical cell with two compartments separated by a circular glass frit (medium) diaphragm. A mercury pool (diameter 5 cm) was used as the cathode and a platinum plate as the anode. The catholyte was magnetically stirred. The temperature was kept at approximately 18 °C by external cooling. The reductions were performed in anhydrous MeCN–Bu_4NClO_4, 0.4 M, of which approximately 35 mL and 15 mL were placed, respectively, in the cathodic and the anodic compartments. Anhydrous sodium carbonate (3 g) was placed in the anode compartment to prevent accumulation of electrogenerated acid. Solutions of compounds **4** (5 mmol) were electrolyzed under a cathodic potential of −1.50 V vs SCE. All electrolysis products were isolated by removing the solvent in vacuo. The residue was then shaken with ether (3×50 mL) over a period of 30 min. The ethereal solutions were combined and concentrated leaving oily crude products that were purified by column chromatography on silica gel (entries a, b, d, e: ethyl acetate or ethyl acetate–hexane 1:3; entry c: petroleum ether–diethyl ether 4:1). The isolated products were viscous oils that gave satisfactory elemental and spectroscopic analyses.

3.3.1. (*E*)-5-Chloro-4-ethoxy-2-phenyl-2-oxazoline (5a). 65%. Pale yellow oil. (Found: C 58.40; H 5.41; N 6.18; $C_{11}H_{12}ClNO_2$ requires C 58.55; H 5.36; N 6.21); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 1.27 (t, 3H, J=7.2 Hz), 3.71–3.77 (m, 1H), 3.93–3.98 (m, 1H), 5.61 (d, 1H, J=1.5 Hz), 6.16 (d, 1H, J=1.5 Hz), 7.44–7.60 (m, 3H), 8.06–8.08 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 15.23 (CH_3), 64.91 (CH_2), 92.44 (CH), 104.91 (CH), 125.77 (C), 128.71 (CH), 129.33 (CH), 133.17 (CH), 165.92 (C=N); MS, *m/z* (%): 225 (M^+, 3), 190 (4), 180 (8), 161 (58), 152 (10), 132 (10), 117 (25), 104 (100), 90 (14), 77 (51), 51 (30); IR (film): 2982, 2933, 1656, 1449, 1337, 1252, 1103, 1032, 979, 895, 749, 693 cm^{-1}.

3.3.2. (*E*)-5-Chloro-2-phenyl-4-methoxy-2-oxazoline (5b). 79%. Pale yellow oil. (Found: C 56.80; H 4.70; N 6.56; $C_{10}H_{10}ClNO_2$ requires C 56.75; H 4.76; N 6.62); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.55 (s, 3H), 5.52 (d, 1H, J=1.6 Hz), 6.14 (d, 1H, J=1.6 Hz), 7.40–7.55 (m, 3H), 8.00–8.06 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 56.19 (CH_3O), 91.96 (CH), 106.51 (CH), 126.01 (C), 128.57 (CH), 129.06 (CH), 132.83 (CH), 165.67 (C=N); MS, *m/z* (%): 211 (M^+, 4), 176 (8), 147 (75), 117 (11), 104 (100), 90 (10), 77 (39); IR (film): 2942, 2836, 1659, 1651, 1452, 1337, 1105, 1063, 1033, 981, 968, 849, 746 cm^{-1}.

3.3.3. (*E*)-5-Chloro-2-phenyl-4-(2-phenylethoxy)-2-oxazoline (5c). 82%. Pale yellow oil. (Found: C 67.77; H 5.35; N 4.60; $C_{17}H_{16}ClNO_2$ requires C 67.66; H 5.34; N 4.64); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.95 (t, 2H, J=7.2 Hz), 3.85–3.90 (m, 1H), 4.05–4.10 (m, 1H), 5.59 (d, 1H, J=1.5 Hz), 6.08 (d, 1H, J=1.5 Hz), 7.21–7.47 (m, 8H), 8.00–8.04 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 36.34 (CH_2), 69.80 (CH_2), 92.25 (CH), 105.82 (CH), 126.48 (CH), 128.52 (CH), 128.65 (CH), 129.00 (CH), 129.11 (CH), 132.81 (CH), 165.57 (C=N); MS, *m/z* (%): 301 (M^+, 6), 266 (7), 197 (4), 180 (14), 152 (21), 104 (100), 91 (24), 77 (32); IR (film): 3029, 2925, 2870, 1725, 1660, 1498, 1453, 1253, 1099, 1031, 972, 750, 701 cm^{-1}.

3.3.4. (*E*)-5-Chloro-2-phenyl-4-(3,4,5-trimethoxybenzyloxy)-2-oxazoline (5d). 66%. Pale yellow oil. (Found: C 60.29; H 5.40; N 3.63; $C_{19}H_{20}ClNO_5$ requires C 60.40; H 5.34; N 3.71); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 3.64 (s, 3H), 3.66 (s, 6H), 4.46 (d, 1H, J=11.7 Hz), 4.65 (d, 1H, J=11.7 Hz), 5.50 (d, 1H, J=1.5 Hz), 5.99 (d, 1H, J=1.5 Hz), 6.42 (s, 2H), 7.23–7.36 (m, 3H), 7.85 (d, 2H, J=7.2 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 56.08 (CH_3O), 60.81 (CH_3O), 70.97 (CH_2), 92.21 (CH), 105.13 (CH), 126.14 (CH), 128.60 (CH), 129.02 (CH), 130.37 (C), 132.57 (C), 132.83 (CH), 137.76 (C), 153.36 (C), 165.77 (C=N); MS, *m/z* (%): 379 (M^++2, 23), 377 (M^+, 35), 342 (7), 196 (40), 181 (100), 167 (14), 146 (42), 104 (34), 77 (29); IR

(film): 2946, 1738, 1650, 1594, 1506, 1463, 1423, 1336, 1239, 1130, 1083, 1008, 848 cm^{-1}.

3.3.5. (*E*)-5-Chloro-2-phenyl-4-(4-methoxybenzyloxy)-2-oxazoline (5e). 64%. Pale yellow oil. (Found: C 64.13; H 5.11; N 4.34; $C_{17}H_{16}ClNO_3$ requires C 64.26; H 5.08; N 4.41); ^1H NMR δ ($CDCl_3$, 200 MHz): 3.78 (s, 3H), 4.63 (d, 1H, J=11.2 Hz), 4.84 (d, 1H, J=11.2 Hz), 5.66 (d, 1H, J=1.5 Hz), 6.13 (d, 1H, J=1.5 Hz), 6.88 (d, 2H, J=8.6 Hz), 7.31 (d, 2H, J=8.6 Hz), 7.44–7.55 (m, 3H), 8.03 (dd, 2H, J=8.0, 1.2 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 55.33 (CH_3O), 70.49 (CH_2), 92.38 (CH), 104.76 (CH), 114.02 (CH), 126.31 (C), 128.61 (CH), 129.09 (CH), 129.92 (CH), 132.77 (CH), 159.62 (C), 165.67 (C=N); MS, *m/z* (%): 318 (M^++1, 2), 152 (8), 146 (100), 121 (67), 104 (31), 91 (15), 77 (35), 63 (9); IR (film): 2939, 1719, 1651, 1612, 1513, 1451, 1339, 1253, 1178, 1084, 1033, 971, 823, 750 cm^{-1}.

3.3.6. Preparation of *N*-(2,2-dichloro-1-ethoxyethyl)benzamide (7a). Product **7a** was electrochemically prepared by cathodic reduction by using a divided cell as described above. The electrolysis of compound **4a** (3 mmol) was carried out under a constant cathodic potential of −1.60 V vs SCE in DMF–$LiClO_4$ 0.4 M. Acetic acid (3 mmol) was used as proton donor. The electricity consumption was 2 F/mol. The electrolysis product was isolated by dropping the catholyte solution onto ice–water (200 mL). The white solid precipitated was air-dried and crystallized from petroleum ether.

80%. White needles, mp 98–99 °C (pet ether). (Found: C, 50.58; H, 4.93; N, 5.28. $C_{11}H_{13}Cl_2NO_2$ requires: C, 50.40; H, 5.00; N, 5.34); ^1H NMR δ ($CDCl_3$, 200 MHz): 1.26 (t, 3H, J=7.0 Hz), 3.71–3.82 (m, 2H), 5.78 (dd, 1H, J=9.5, 2.4 Hz), 5.89 (d, 1H, J=2.4 Hz), 6.85 (d, 1H, J=9.5 Hz), 7.44–7.57 (m, 3H), 7.84 (d, 2H, J=6.8 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 14.95 (CH_3), 65.23 (CH_2), 72.67 ($CHCl_2$), 81.54 (CH), 127.24 (CH), 128.83 (CH), 132.42 (CH), 133.16 (C), 167.59 (CO); MS, *m/z* (%): 224 (4), 218 (14), 216 (22), 178 (11), 105 (100), 77 (58), 51 (18); IR (Nujol): 3211, 1635, 1524, 1466, 1379, 1085, 791, 696 cm^{-1}.

3.3.7. Reductive electrolysis of *N*-(2,2-dichloro-1-ethoxyethyl)benzamide (7a). Cathodic reductions of **7a** were performed in a divided cell as described above and were carried out under a constant cathodic potential of −1.90 V vs SCE in acetonitrile–tetrabutylammonium perchlorate 0.5 M. The electrolysis products were isolated by removing the solvent in vacuo. The residue was then shaken with ether (3×50 mL) over a period of 30 min. The ethereal solutions were combined and concentrated. These experiments revealed no synthetic utility since the formation of complex mixtures of products was detected by GC/MS. For a 3 F/mol electrolysis, 2-phenyloxazol **9** (24%) and 4-ethoxy-2-penyl-2-oxazoline **8a** (17%) could be identified among other non characterised products.

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