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Electrochemical generation of *N*-(2,2-dichlorovinyl)amides

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Abstract—A convenient method for the synthesis of *N*-(2,2-dichlorovinyl)amides has been established. Treatment of chloralamides with phosphorus pentachloride provides *N*-(1,2,2,2-tetrachloroethyl)amides in high yields whose electrochemical reduction leads to the title compounds in fair to quantitative yields. This approach exhibits superior efficiency and versatility than previously reported procedures.

1. Introduction

N-(2,2-Dichlorovinyl)amides **3** have previously been prepared by direct reduction of chloralamides **1** with zinc in hot acetic acid.[1] These compounds show peculiar electrophilic activity, which allows reactions with primary and secondary alkylamines[2,3] and further nucleophilic reagents[4–6] to give the corresponding addition products **5**, which play a substantial role in developing part of our research project in electroorganic synthesis by reduction of chloral derivatives.[7,8] Thus, electrochemical reduction of aminoderivatives **5** provided the first synthesis of 4-alkylamino-2-aryl-2-oxazolines[7] which gave direct entry to novel 2-imidazolidinones.[8] It should be pointed out that reactions of amides with chloral yielding intermediates **1**, as well as addition processes of alkylamines to **3** providing products **5**, were easy and efficient. However, the transformations of **1** to **3** by reduction with zinc metal were remarkably less satisfactory. These reactions showed erratic induction periods and required a large excess of reducing reagent to give products **3** in low to moderate yields. Moreover, chloralamides **1e–g** bearing strong electron-withdrawing nitro groups attached to the aromatic ring could not be converted into the vinylamides **3e–g**. In these cases, complex mixtures of unidentified products, with the corresponding nitrobenzamides as major components, were observed. It seems reasonable to assume that nitro groups act by lowering nucleophilicity to the amido function, therefore enhancing the proclivity of chloralamides to undergo thermal reversion[9] to a chloral–amide mixture. Hence, it is apparent that non-thermally activated reductions of chloralamides merit special attention. Given both the above and the renewed interest of *N*-(2,2-dichlorovinyl)amides **3** to be used as precursors of previously unattainable heterocyclic compounds, the development of an efficient and general electrochemical entry to these compounds was attempted, as is shown in Scheme 1.

2. Results and discussion

Chloralamides **1** were prepared by reaction of chloral hydrate with aromatic and aliphatic amides.[1] Firstly a direct cathodic conversion of **1** to **3** under similar experimental conditions as those reported by using zinc was attempted. It was found, however, that reduction of **1d** yielded **4d** (70%) instead of **3d**. This adverse result suggested our exploring an alternative synthetic route based on the replacement of the hydroxyl group of chloralamides by a better leaving group, since it would circumvent the generation of products **4**. In the search for a good procedure for preparing the tetrachlorides **2**, reactions in equimolecular ratio of melt mixtures of chloralamides **1** with phosphorus pentachloride[10] were carried out. In this case, the formation of the products **2** expected was observed but accompanied by large amounts of pentachlorides **6**. Finally, a near quantitative formation of *N*-(1,2,2,2-tetrachloroethyl)amides **2** was achieved by carrying out the reactions in dry chloroform under rigorous temperature control.

Cathodic reduction of intermediates **2** was carried out in dry acetonitrile–anhydrous lithium perchlorate at a mercury pool cathode, under constant potential. The electricity consumption was 2 F/mol. Crude solid reaction products were easily isolated by evaporation of solvent and removing the electrolyte by simple washing of the residue with water. After crystallization the electrolysis products were

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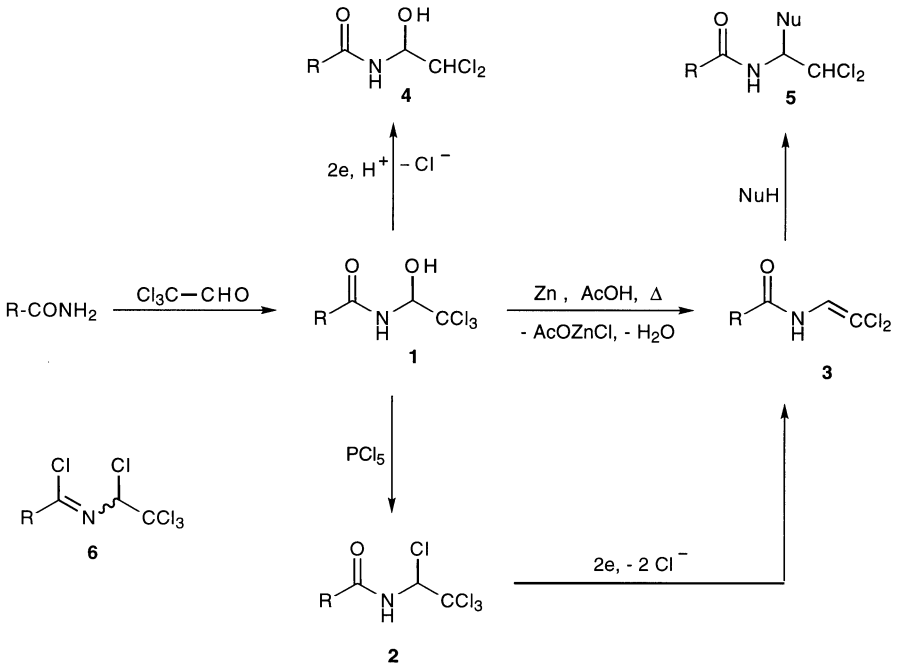

Entry	R	Entry	R
a	C_6H_5	h	4-$CH_3OC_6H_4$
b	2-ClC_6H_4	i	3,4,5-$(CH_3O)_3C_6H_2$
c	3-ClC_6H_4	j	2-$CH_3C_6H_4$
d	4-ClC_6H_4	k	4-$CH_3C_6H_4$
e	2-$NO_2C_6H_4$	l	CH_3CH_2
f	3-$NO_2C_6H_4$	m	$(CH_3)_2CH$
g	4-$NO_2C_6H_4$	n	$(CH_3)_3C$

Scheme 1.

identified by IR, MS, NMR spectroscopy and elemental analysis as the corresponding *N*-(2,2-dichlorovinyl)amides **3**. Yields ranged from high to quantitative. The products **3a,c,d,j–l** were compared with those formed by applying the earlier synthetic method[1] (yields in the range 38–57%), showing identical physical and spectroscopic properties.

In conclusion, an effective and general new procedure for preparing *N*-(2,2-dichlorovinyl)amides **3** is reported. The mildness of the reaction conditions as well as its efficiency are noteworthy features of this approach, which has substantial interest in the access to a wide range of previously unattainable heterocyclic compounds.

3. Experimental

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 with direct insertion probe and 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.

3.1. Preparation of chloralamides 1

Chloralamides **1** were prepared by direct reaction of chloral hydrate with amides.[1] A solid mixture of chloral hydrate (8.2 mmol) and the corresponding amide (8.0 mmol) was heated (90–100°C) until complete melting. The reaction mixture was allowed to cool until total solidification. The product formed was washed with cold chloroform and crystallized from the appropriate solvent.

3.1.1. *N*-(2,2,2-Trichloro-1-hydroxyethyl)benzamide (1a). (96%), white needles (ethanol–water) mp 133°C. (Found: C 40.38; H 2.96; N 5.23; $C_9H_8Cl_3NO_2$ requires: C 40.26; H 3.00; N 5.22); ^{1}H NMR δ (DMSO-d_6, 300 MHz): 6.07 (m, 1H), 7.46–7.57 (m, 3H), 7.87 (s, 1H), 7.93 (d, 2H, J=7.8 Hz), 9.10 (d, 1H, J=8.8 Hz); ^{13}C NMR δ (DMSO-d_6, 75.4 MHz): 81.38 (CH), 102.66 (CCl_3), 127.91 (CH), 128.28 (CH), 131.88 (CH), 133.46 (C), 166.87 (CO); ms, *m/z* (%): 150 (23), 121 (10), 105 (100), 77 (54); IR (Nujol): 3324, 3069, 2729, 1635, 1531, 1462, 1101, 1012, 807 cm^{-1}.

3.1.2. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-2-chlorobenzamide (1b). (95%), white needles (ethanol–water) mp 130°C. (Found: C 35.70; H 2.28; N 4.67; $C_9H_7Cl_4NO_2$ requires: C 35.68; H 2.33; N 4.62); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 5.93 (dd, 1H, *J*=8.6, 4.2 Hz), 7.38–7.51 (m, 4H), 7.91 (d, 1H, *J*=4.2 Hz), 9.44 (d, 1H, *J*=8.6 Hz); ^{13}C NMR δ (DMSO-d_6, 50.4 MHz): 80.94 (CH), 102.44 (CCl_3), 127.01 (CH), 129.12 (CH), 129.74 (CH), 130.15 (C), 131.22 (CH), 135.99 (C), 166.71 (CO); ms, *m/z* (%): 184 (11), 141 (29), 139 (100), 113 (11), 111 (26), 75 (17), 50 (15); IR (Nujol): 3264, 3060, 2723, 1658, 1537, 1462, 1377, 1078, 806 cm^{-1}.

3.1.3. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-3-chlorobenzamide (1c). (95%), white needles (ethanol–water) mp 130–131°C. (Found: C 35.73; H 2.38; N 4.65; $C_9H_7Cl_4NO_2$ requires: C 35.68; H 2.33; N 4.62); ^{1}H NMR δ (DMSO-d_6, 300 MHz): 6.01–6.04 (m, 1H), 7.51 (t, 1H, *J*=7.8 Hz), 7.62 (d, 1H, *J*=7.2 Hz), 7.85–7.95 (m, 3H), 9.31 (d, 1H, *J*=8.1 Hz); ^{13}C NMR δ (DMSO-d_6, 75.4 MHz): 81.44 (CH), 102.44 (CCl_3), 126.69 (CH), 127.70 (CH), 130.27 (CH), 131.70 (CH), 133.14 (C), 135.37 (C), 165.55 (CO); ms, *m/z* (%): 184 (13), 141 (32), 139 (100), 113 (15), 111 (41), 75 (24); IR (Nujol): 3319, 3108, 1638, 1533, 1464, 1377, 1086, 1009, 833, 740 cm^{-1}.

3.1.4. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-4-chlorobenzamide (1d). (94%), white needles (ethanol–water) mp 134°C. (Found: C 35.59; H 2.32; N 4.58; $C_9H_7Cl_4NO_2$ requires: C 35.68; H 2.33; N 4.62); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 6.02–6.09 (m, 1H), 7.56 (d, 2H, *J*=7.9 Hz), 7.93–7.97 (m, 3H), 9.28 (d, 1H, *J*=8.4 Hz); ^{13}C NMR δ (DMSO-d_6, 50.4 MHz): 81.53 (CH), 102.64 (CCl_3), 128.48 (CH), 129.98 (CH), 132.29 (C), 136.88 (C), 166.03 (CO); ms, *m/z* (%): 184 (14), 141 (34), 139 (100), 113 (11), 111 (28), 75 (14); IR (Nujol): 3303, 3106, 1626, 1524, 1111, 1075, 1001, 827, 809 cm^{-1}.

3.1.5. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-2-nitrobenzamide (1e). (90%), white needles (ethanol–water) mp 130–133°C. (Found: C 34.60; H 2.29; N 8.97; $C_9H_7Cl_3N_2O_4$ requires: C 34.48; H 2.25; N 8.93); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 5.92 (dd, 1H *J*=8.7, 6.1 Hz), 7.55 (dd, 1H, *J*=7.3, 1.1 Hz), 7.72 (t, 1H, *J*=7.3 Hz), 7.82 (t, 1H, *J*=7.3 Hz), 8.04–8.12 (m, 2H), 9.68 (d, 1H, *J*=8.8 Hz); ^{13}C NMR δ (DMSO-d_6, 50.4 MHz): 81.02 (CH), 102.54 (CCl_3), 124.20 (CH), 129.46 (CH), 131.07 (CH), 132.05 (C), 133.96 (CH), 146.55 (C), 166.17 (CO); ms, *m/z* (%): 183 (6), 154 (15), 138 (100); IR (Nujol): 3266, 1657, 1532, 1348, 1087, 1072, 832, 813 cm^{-1}.

3.1.6. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-3-nitrobenzamide (1f). (93%), white needles (ethanol–water) mp 140°C. (Found: C 34.55; H 2.22; N 8.89; $C_9H_7Cl_3N_2O_4$ requires: C 34.48; H 2.25; N 8.93); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 6.07 (dd, 1H, *J*=8.0, 5.1 Hz), 7.80 (t, 1H, *J*=8.0 Hz), 8.00 (d, 1H, *J*=5.1 Hz), 8.35 (d, 1H, *J*=7.8 Hz), 8.44 (dd, 1H, *J*=8.2, 2.1 Hz), 8.75 (m, 1H), 9.67 (d, 1H, *J*=8.0 Hz); ^{13}C NMR δ (DMSO-d_6, 50.4 MHz): 79.01 (CH), 99.77 (CCl_3), 120.20 (CH), 123.90 (CH), 127.53 (CH), 131.80 (CH), 132.30 (C), 145.10 (C), 162.46 (CO); ms, *m/z* (%): 195 (12), 166 (27), 150 (100), 111 (17), 104 (43), 84 (30), 83 (25), 82 (42), 76 (50), 69 (26), 50 (32), 47 (28); IR (Nujol): 3220, 1651, 1528, 1472, 1349, 1080, 1010, 922, 829, 713 cm^{-1}.

3.1.7. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-4-nitrobenzamide (1g). (93%), white needles (ethanol) mp 165°C. (Found: C 34.63; H 2.29; N 8.92; $C_9H_7Cl_3N_2O_4$ requires: C 34.48; H 2.25; N 8.93); ^{1}H NMR δ (DMSO-d_6, 300 MHz): 6.03 (dd, 1H, *J*=8.4, 5.7 Hz), 7.97 (d, 1H, *J*=5.7 Hz), 8.10 (d, 2H, *J*=8.7 Hz), 8.30 (d, 2H, *J*=8.7 Hz), 9.56 (d, 1H, *J*=8.4 Hz); ^{13}C NMR δ (DMSO-d_6, 75.4 MHz): 81.47 (CH), 102.31 (CCl_3), 123.40 (CH), 129.41 (CH), 139.12 (C), 149.32 (C), 165.52 (CO); ms, *m/z* (%): 195 (5), 166 (40), 150 (72), 113 (32), 111 (47), 104 (31), 92 (27), 84 (59), 82 (82), 76 (65), 50 (84), 47 (100); IR (Nujol): 3353, 3110, 1662, 1519, 1464, 1374, 1339, 1104, 801, 721 cm^{-1}.

3.1.8. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-4-methoxybenzamide (1h). (95%), white needles (acetonitrile) mp 140°C. (Found: C 39.99; H 3.43; N 4.72; $C_{10}H_{10}Cl_3NO_3$ requires: C 40.23; H 3.38; N 4.69); ^{1}H NMR δ (DMSO-d_6, 300 MHz): 3.91 (s, 3H), 6.14 (d, 1H, *J*=8.4 Hz), 7.10 (d, 2H, *J*=9.0 Hz), 7.88 (s, 1H), 8.02 (d, 2H, *J*=9.0 Hz), 8.98 (d, 1H, *J*=8.4 Hz); ^{13}C NMR δ (DMSO-d_6, 75.4 MHz): 55.52 (CH_3O), 81.46 (CH), 102.89 (CCl_3), 113.61 (CH), 125.60 (C), 130.01 (CH), 162.23 (C), 166.23 (CO); ms, *m/z* (%): 297 (M^+, 1), 180 (6), 151 (6), 135 (100), 92 (18), 77 (18), 64 (11), 63 (11); IR (Nujol): 3310, 2731, 1630, 1608, 1501, 1377, 1267, 1089, 834 cm^{-1}.

3.1.9. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-3,4,5-trimethoxybenzamide (1i). (90%), white needles (ethanol–hexane) mp 148°C. (Found: C 40.31; H 3.92; N 3.87; $C_{12}H_{14}Cl_3NO_5$ requires: C 40.19; H 3.94; N 3.91); ^{1}H NMR δ (DMSO-d_6, 300 MHz): 3.72 (s, 3H), 3.85 (s, 6H), 6.07 (d, 1H, *J*=8.1 Hz), 7.32 (s, 2H), 7.91 (s, 1H), 9.14 (d, 1H, *J*=8.1 Hz); ^{13}C NMR δ (DMSO-d_6, 75.4 MHz): 56.08 (CH_3O), 60.10 (CH_3O), 81.60 (CH), 102.74 (CCl_3), 105.51 (CH), 128.30 (C), 140.55 (C), 152.57 (C), 165.89 (CO); ms, *m/z* (%): 357 (M^+, 1), 211 (45), 196 (25), 195 (36), 140 (30), 125 (14), 117 (10), 113 (29), 111 (45), 84 (67), 82 (100), 49 (35), 47 (97); IR (Nujol): 3279, 1656, 1537, 1463, 1354, 1136, 1097, 1002, 823, 792 cm^{-1}.

3.1.10. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-2-methylbenzamide (1j). (95%), white needles (acetonitrile) mp 140°C. (Found: C 42.64; H 3.61; N 5.00; $C_{10}H_{10}Cl_3NO_2$ requires: C 42.51; H 3.57; N 4.96); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 2.37 (s, 3H), 5.98 (dd, 1H, *J*=8.7, 4.5 Hz), 7.23–7.36 (m, 4H), 7.79 (d, 1H, *J*=4.5 Hz), 9,16 (d, 1H, *J*=8.7 Hz); ^{13}C NMR δ (DMSO-d_6,50.4 MHz): 19.58 (CH_3), 80.94 (CH), 102.66 (CCl_3), 125.50 (CH), 127.47 (CH), 129.77 (CH), 130.47 (CH), 135.47 (C), 136.20 (C), 169.39 (CO); ms; *m/z* (%): 281 (M^+, 1), 146 (7), 119 (100), 91 (53), 77 (3); IR (Nujol): 3266, 3050, 2711, 1651, 1535, 1462, 1377, 1344, 1103, 1070, 1010, 886, 822, 742 cm^{-1}.

3.1.11. *N*-(2,2,2-Trichloro-1-hydroxyethyl)-4-methylbenzamide (1k). (92%), white needles (acetonitrile) mp 167–170°C. (Found: C 42.44; H 3.55; N 5.02; $C_{10}H_{10}Cl_3NO_2$ requires: C 42.51; H 3.57; N 4.96); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 2.35 (s, 3H), 6.02 (dd, 1H, *J*=8.6, 5.7 Hz), 7.27 (d, 2H, *J*=7.8 Hz), 7.80 (d, 1H,

J=5.7 Hz), 7.82 (d, 2H, J=7.8 Hz), 8.97 (d, 1H, J=8.6 Hz); ^{13}C NMR δ (DMSO-d_6, 50.4 MHz): 21.10 (CH_3), 81.41 (CH), 102.79 (CCl_3), 128.03 (CH), 128.88 (CH), 130.69 (C), 141.99 (C), 166.70 (CO); ms; *m/z* (%): 164 (10), 120 (8), 119 (100), 91 (36) 65 (20); IR (Nujol): 3324, 3089, 2735, 1633, 1537, 1503, 1463, 1377, 1346, 1276, 1111, 1081, 1009, 835 cm^{-1}.

3.1.12. *N*-(2,2,2-Trichloro-1-hydroxyethyl)propionamide (1l). (98%), white needles (acetonitrile) mp 125°C. (Found: C 27.31; H 3.65; N 6.41; $C_5H_8Cl_3NO_2$ requires: C 27.24; H 3.66; N 6.35); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 1.00 (t, 3H, J=7.6 Hz) 2.22 (q, 2H, J=7.6 Hz), 5.74 (dd, 1H, J=9.0, 5.7 Hz), 7.63 (d, 1H, J=5.7 Hz), 8.65 (d, 1H, J=9.0 Hz); ^{13}C NMR δ (DMSO-d_6, 50.4 MHz): 9.70 (CH_3), 28.40 (CH_2), 80.48 (CH), 102.71 (CCl_3), 173.56 (CO); ms, *m/z* (%): 204 (1), 202 (1), 186 (1), 184 (1), 149 (2), 147 (2), 113 (2), 111 (4), 103 (2), 84 (5), 82 (7), 57 (100); IR (Nujol): 3294, 3110, 1660, 1540, 1460, 1383, 1245, 1095, 1026, 915, 833 cm^{-1}.

3.1.13. *N*-(2,2,2-Trichloro-1-hydroxyethyl)isobutyramide (1m). (94%), white needles (acetonitrile) mp 128°C. (Found: C 30.66; H 4.37; N 6.14; $C_6H_{10}Cl_3NO_2$ requires: C 30.73; H 4.30; N 5.97); ^{1}H NMR δ (DMSO-d_6, 300 MHz): 1.00 (d, 6H, J=6.9 Hz), 2.59 (sept, 1H, J=6.9 Hz), 5.74 (dd, 1H, J=9.1, 5.7 Hz), 7.59 (d, 1H, J=5.7 Hz), 8.57 (d, 1H, J=9.0 Hz); ^{13}C NMR δ (DMSO-d_6, 75.4 MHz): 16.13 (CH_3), 17.13 (CH_3), 30.87 (CH), 77.70 (CH), 100.10 (CCl_3), 173.92 (CO); ms, *m/z* (%): 199 (1), 197 (1), 148 (5), 146 (6), 116 (27), 110 (50), 83 (62), 81 (82), 71 (100); IR (Nujol): 3289, 3070, 1658, 1544, 1463, 1378, 1091, 1010, 833, 811 cm^{-1}.

3.1.14. *N*-(2,2,2-Trichloro-1-hydroxyethyl)trimethylacetamide (1n). (90%), white needles (acetonitrile) mp 108°C. (Found: C 33.79; H 4.93; N 5.61; $C_7H_{12}Cl_3NO_2$ requires: C 33.83; H 4.87; N 5.64); ^{1}H NMR δ (DMSO-d_6, 300 MHz): 1.12 (s, 9H), 5.78 (dd, 1H, J=9.0, 6.0 Hz), 7.58 (d, 1H, J=6.0 Hz), 7.80 (d, 1H, J=9.0 Hz); ^{13}C NMR δ (DMSO-d_6, 75.4 MHz): 24.25 (CH_3), 35.75 (C), 78.15 (CH), 100.25 (CCl_3), 174.75 (CO); ms, *m/z* (%): 211 (1), 174 (1), 147 (1), 130 (7), 112 (4), 111 (4), 85 (18), 57 (100); IR (Nujol): 3343, 3153, 1640, 1515, 1464, 1374, 1116, 1003, 838, 816 cm^{-1}.

3.2. Preparation of *N*-(1,2,2,2-tetrachloroethyl)amides 2

To a stirred suspension of chloralamide (7 mmol) in dry chloroform (30 mL) a suspension of phosphorus pentachloride (7 mmol) in dry chloroform (30 mL) was slowly added (10 min) under a careful temperature (25°C) control. The mixture was stirred at room temperature for 30 min; during this time the evolution of hydrogen chloride and a progressive loss of turbidness of the reaction mixture was perceptible until the mixture became totally transparent. Then, chloroform was removed under reduced pressure and the residue washed with cold petroleum ether and crystallized from the appropriate solvent.

3.2.1. *N*-(1,2,2,2-Tetrachloroethyl)benzamide (2a). (91%), white needles (acetonitrile) mp 123–124°C. (Found: C 37.79; H 2.38; N 4.93; $C_9H_7Cl_4NO$ requires: C 37.67; H 2.46; N 4.88); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 6.75 (d, 1H, J=10.5 Hz), 7.15 (d, 1H, J=10.5 Hz), 7.44–7.63 (m, 3H), 7.79–7.85 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 74.28 (CH), 99.67 (CCl_3), 127.50 (CH), 129.00 (CH), 132.24 (C), 133.05 (CH), 166.12 (CO); ms, *m/z* (%): 168 (4), 105 (100), 77 (28), 51 (10); IR (Nujol): 3270, 1651, 1509, 1459, 1380, 1319, 1152, 793, 735 cm^{-1}.

3.2.2. *N*-(1,2,2,2-Tetrachloroethyl)-2-chlorobenzamide (2b). (85%), white needles (acetonitrile) mp 150°C (dec). (Found: C 33.79; H 1.79; N 4.40; $C_9H_6Cl_5NO$ requires: C 33.63; H 1.88; N 4.36); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 6.74 (d, 1H, J=10.8 Hz), 7.35–7.46 (m, 4H), 7.77 (d, 1H, J=7.2 Hz) ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 74.06 (CH), 99.36 (CCl_3), 127.49 (CH), 130.81 (CH), 131.19 (CH), 132.37 (C), 132.86 (CH), 164.97 (CO); ms, *m/z* (%): 319 (M^+, 1), 141 (38), 139 (100), 111 (26), 75 (15); IR (Nujol): 3220, 3192, 1666, 1528, 1464, 1379, 1328, 1170, 1054, 804, 760 cm^{-1}.

3.2.3. *N*-(1,2,2,2-Tetrachloroethyl)-3-chlorobenzamide (2c). (87%), white needles (acetonitrile) mp 135–136°C. (Found: C 33.77; H 1.79; N 4.23; $C_9H_6Cl_5NO$ requires: C 33.63; H 1.88; N 4.36); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 6.71 (d, 1H, J=10.6 Hz), 7.19 (d, 1H, J=10.6 Hz), 7.38–7.45 (t, 1H, J=7.7 Hz), 7.55 (d, 1H, J=8.2 Hz), 7.68 (d, 1H, J=7.6 Hz), 7.78 (t, 1H, J=1.8 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 74.06 (CH), 99.49 (CCl_3), 125.51 (CH), 127.89 (CH), 130.28 (CH), 133.07 (CH), 133.94 (C), 135.24 (C), 165.02 (CO); ms, *m/z* (%): 319 (M^+, 1), 141 (30), 139 (100), 113 (12), 111 (33), 75 (19); IR (Nujol): 3272, 1656, 1519, 1462, 1323, 1263, 1161, 774, 678 cm^{-1}.

3.2.4. *N*-(1,2,2,2-Tetrachloroethyl)-4-chlorobenzamide (2d). (90%), white needles (acetonitrile) mp 135–136°C. (Found: C 33.74; H 1.82; N 4.20; $C_9H_6Cl_5NO$ requires: C 33.63; H 1.88; N 4.36); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 6.71 (d, 1H, J=10.8 Hz), 7.18 (d, 1H, J=10.8 Hz), 7.43–7.47 (m, 2H), 7.73–7.77 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 74.16 (CH), 99.55 (CCl_3), 128.94 (CH), 129.26 (CH), 130.56 (C), 139.48 (C), 165.24 (CO); ms, *m/z* (%): 319 (M^+, 1), 141 (34), 139 (100), 113 (10), 111 (30), 75 (20); IR (Nujol): 3279, 1671, 1652, 1524, 1462, 1377, 1321, 794, 762 cm^{-1}.

3.2.5. *N*-(1,2,2,2-Tetrachloroethyl)-2-nitrobenzamide (2e). (85%), white needles (acetonitrile) mp 107°C (dec). (Found: C 32.69; H 1.81; N 8.41; $C_9H_6Cl_4N_2O_3$ requires: C 32.56; H 1.82; N 8.44); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 6.67 (d, 1H, J=10.5 Hz), 6.87 (d, 1H, J=9.9 Hz), 7.53 (dd, 1H, J=7.5, 1.8 Hz), 7.67 (td, 1H, J=8.1, 1.5 Hz), 7.76 (td, 1H, J=7.3, 1.5 Hz), 8.14 (dd, 1H, J=9.0, 1.5 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 73.43 (CH), 99.26 (CCl_3), 125.01 (CH), 128.55 (CH), 130.95 (C), 131.70 (CH), 134.21 (CH), 146.23 (C), 165.22 (CO); ms, *m/z* (%): 213 (2), 150 (100), 76 (59), 51 (72), 50 (57); IR (Nujol): 3243, 1668, 1529, 1345, 1325, 1258, 1159, 1029, 744 cm^{-1}.

3.2.6. *N*-(1,2,2,2-Tetrachloroethyl)-3-nitrobenzamide (2f). (80%), white needles (pet ether–chloroform) mp 125°C (dec). (Found: C 32.74; H 1.75; N 8.41; $C_9H_6Cl_4N_2O_3$ requires: C 32.56; H 1.82; N 8.44); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 6.75 (d, 1H, J=10.5 Hz), 7.25 (d, 1H, J=

9.9 Hz), 7.74 (t, 1H, J=7.9 Hz), 8.20 (d, 1H, J=7.8 Hz), 8.46 (d, 1H, J=8.0 Hz), 8.66 (t, 1H, J=1.9 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 73.95 (CH), 99.34 (CCl_3), 122.54 (CH), 127.50 (CH), 130.42 (CH), 133.44 (CH), 133.86 (C), 148.43 (C), 163.99 (CO); ms, *m/z* (%): 295 (1), 213 (3), 150 (100), 104 (27), 76 (22), 50 (11); IR (Nujol): 3335, 1669, 1515, 1352, 1311, 1263, 1163, 1085, 1027, 797, 757, 704 cm^{-1}.

3.2.7. *N*-(1,2,2,2-Tetrachloroethyl)-4-nitrobenzamide (2g). (86%), yellow needles (pet ether) mp 122–126°C. (Found: C 32.69; H 1.79;N 8.31; $C_9H_6Cl_4N_2O_3$ requires: C 32.56; H 1.82; N 8.44); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 6.71 (d, 1H, J=10.5 Hz), 7.30 (s br, 1H), 8.01 (d, 2H, J=8.6 Hz), 8.33 (d, 2H, J=8.7 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 73.84 (CH), 99.31 (CCl_3), 124.18 (CH), 128.80 (CH), 137.63 (C), 150.40 (C), 164.35 (CO); ms, *m/z* (%): 330 (M^+, 3), 282 (5), 182 (13), 138 (100); IR (Nujol): 3328, 1667, 1530, 1488, 1333, 1318, 1151, 798, 736 cm^{-1}.

3.2.8. *N*-(1,2,2,2-Tetrachloroethyl)-4-methoxybenzamide (2h). (95%), white needles (pet ether) mp 114–116°C. (Found: C 38.03; H 2.78; N 4.35; $C_{10}H_9Cl_4NO_2$ requires: C 37.89; H 2.86; N 4.42); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.86 (s, 3H), 6.76 (d, 1H, J=10.7 Hz), 6.96 (d, 2H, J= 8.9 Hz), 7.03 (d, 1H, J=10.7 Hz), 7.80 (d, 2H, J=8.9 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 55.59 (CH_3O), 74.49 (CH), 99.76 (CCl_3), 114.19 (CH), 124.30 (C), 129.55 (CH), 163.42 (C), 165.52 (CO); ms, *m/z* (%): 315 (M^+, 1), 152 (5), 135 (100), 107 (8), 92 (13), 77 (13); IR (Nujol): 3262, 1668, 1657, 1603, 1503, 1456, 1326, 1253, 1181, 1037, 847, 803, 727 cm^{-1}.

3.2.9. *N*-(1,2,2,2-Tetrachloroethyl)-3,4,5-trimethoxybenzamide (2i). (92%), white needles (pet ether) mp 128–132°C. (Found: C 38.09; H 3.55; N 3.64; $C_{12}H_{13}Cl_4NO_4$ requires: C 38.23; H 3.48; N 3.71); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.90 (s, 3H), 3.91 (s, 6H), 6.73 (d, 1H, J= 10.6 Hz), 7.01–7.08 (m, 3H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 56.46 (CH_3O), 61.00 (CH_3O), 74.31 (CH), 99.67 (CCl_3), 104.97 (CH), 127.46 (C), 142.28 (C), 153.42 (C), 165.90 (CO); ms, *m/z* (%): 375 (M^+, 2), 195 (100), 152 (11), 137 (9), 81 (11); IR (Nujol): 3284, 1652, 1584, 1492, 1461, 1350, 1238, 1129, 992 cm^{-1}.

3.2.10. *N*-(1,2,2,2-Tretrachloroethyl)-2-methylbenzamide (2j). (98%), white needles (hexane) mp 130°C (dec). (Found: C 39.70; H 3.09; N 4.60; $C_{10}H_9Cl_4NO$ requires: C 39.90; H 3.01; N 4.65); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 2.48 (s, 3H), 6.72 (s br, 1H), 7.25–7.44 (m, 5H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 20.02 (CH_3), 73.85 (CH), 99.61 (CCl_3), 126.14 (CH), 126.94 (CH), 131.35 (CH), 131.57 (CH), 133.75 (C), 137.11 (C), 168.22 (CO); ms; *m/z* (%): 299 (M^+, 1), 146 (2), 119 (100), 91 (51), 77 (2); IR(Nujol): 3228, 1664, 1515, 1461, 1377, 1323, 1272, 1157, 1032, 813, 788 cm^{-1}.

3.2.11. *N*-(1,2,2,2-Tretrachloroethyl)-4-methylbenzamide (2k). (98%), white needles (hexane) mp 100°C (dec). (Found: C 39.69; H 2.97; N 4.60; $C_{10}H_9Cl_4NO$ requires: C 39.90; H 3.01; N 4.65); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 2.43 (s, 3H), 6.76 (d, 1H, J=10.7 Hz), 6.96 (d, 1H, J=10.7 Hz), 7.30 (d, 2H, J=8.0 Hz), 7.72 (d, 2H, J=8.2 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 21.68 (CH_3), 74.36 (CH), 99.75 (CCl_3), 129.39 (C), 129.69 (CH), 143.91 (C), 165.88 (CO); ms; *m/z* (%): 299 (M^+, 1), 182 (2), 119 (100), 91 (34), 77 (1); IR (Nujol): 3269, 1653, 1525, 1502, 1462, 1376, 1318, 1267, 1161, 753 cm^{-1}.

3.2.12. *N*-(1,2,2,2-Tetrachloroethyl)propionamide (2l). (80%), white needles (hexane) mp 87°C (dec). (Found: C 25.03; H 2.91; N 5.90; $C_5H_7Cl_4NO$ requires: C 25.14; H 2.95; N 5.86); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 1.22 (t, 3H, J=7.5 Hz), 2.38 (q, 2H, J=7.5 Hz) 6.59 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 9.20 (CH_3), 29.61 (CH_2), 73.72 (CH), 99.53 (CCl_3), 173.01 (CO); ms, *m/z* (%): 202 (2), 148 (5), 120 (13), 57 (100); IR (Nujol): 3290, 1682, 1673, 1526, 1462, 1376, 1212, 1072, 1028, 810, 751 cm^{-1}.

3.2.13. *N*-(1,2,2,2-Tetrachloroethyl)isobutyramide (2m). (87%), white needles (hexane) mp 137°C (dec). (Found: C 28.21; H 3.63; N 5.47; $C_6H_9Cl_4NO$ requires: C 28.49; H 3.59; N 5.54); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 1.22 (d, 6H, J=6.9 Hz), 2.51 (sept, 1H, J=6.9 Hz), 6.54–6.60 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 18.82 (CH_3), 19.32 (CH_3), 35.61 (CH), 73.73 (CH), 99.67 (CCl_3), 175.87 (CO); ms, *m/z* (%): 251 (M^+, 3), 218 (16), 216 (18), 134 (37), 71 (100); IR (Nujol): 3270, 1681, 1519, 1463, 1384, 1211, 1095, 1025, 798, 734 cm^{-1}.

3.2.14. *N*-(1,2,2,2-Tetrachloroethyl)trimethylacetamide (2n). (83%), white needles (hexane) mp 98°C (dec). (Found: C 31.33; H 4.09; N 5.12; $C_7H_{11}Cl_4NO$ requires: C 31.49; H 4.15; N 5.25); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 1.26 (s, 9H), 6.56 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 27.07 (CH_3), 39.20, (C) 73.91 (CH), 99.77 (CCl_3), 177.08 (CO); ms, *m/z* (%): 265 (M^+, 1), 148 (5), 85 (19), 57 (100); IR (Nujol): 3350, 1674, 1499, 1460, 1377, 1167, 818, 785, 727 cm^{-1}.

3.3. Electrochemical generation of *N*-(2,2-dichlorovinyl)-amides 3

Reductive electrolyses of **2** were carried out under nitrogen atmosphere at 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 15°C by external cooling. The reduction was performed in dry MeCN–anhydrous $LiClO_4$ 0.5 M; 35 and 15 mL were placed in the cathodic and the anodic compartments, respectively. To prevent accumulation of electrogenerated acid in the anodic compartment, anhydrous sodium carbonate (3 g) was placed in this compartment. Solutions of **2** (5 mmol) were electrolyzed under the following cathodic potentials (V vs SCE): **2a** (0.98); **2b** (0.60); **2c** (0.75), **2d** (0.45); **2e** (0.69); **2f** (0.80); **2g** (0.61); **2h** (0.60); **2i** (1.20); **2j** (1.10); **2k** (1.10); **2l** (1.19); **2m** (0.85); **2n** (1.10). The electricity consumption was 2 F/mol. Isolation of products **3** was carried out by removing the solvent under reduced pressure, then the solid residue was washed with cold water, collected and dried under vacuum filtration. The isolated high purity crude products were crystallized from the appropriate

solvent. Products **3e–g,n** were purified by column chromatography (silica gel petroleum ether–ethyl acetate; 1:1)

3.3.1. *N*-(2,2-Dichlorovinyl)benzamide (3a). (90%), white needles (pet ether) mp 64°C. (Found: C 49.78; H 3.10; N 6.43; $C_9H_7Cl_2NO$ requires: C 50.03; H 3.27; N 6.48); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 6.75 (d, 1H, J=10.6 Hz), 7.21 (d, 1H, J=10.6 Hz), 7.42–7.62 (m, 3H), 7.79–7.84 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 107.27 (CCl_2), 121.85 (CH), 127.30 (CH), 129.00 (CH), 132.41 (C), 132.79 (CH), 163.58 (CO); ms, *m/z* (%): 215 (M^+, 3), 105 (100), 77 (68), 51 (54); IR (Nujol): 3347, 1666, 1649, 1505, 1471, 1380, 1296, 1199, 945, 719 cm^{-1}.

3.3.2. *N*-(2,2-Dichlorovinyl)-2-chlorobenzamide (3b). (71%), white needles (pet ether) mp 49–51°C. (Found: C 42.95; H 2.44; N 5.33; $C_9H_6Cl_3NO$ requires: C 43.15; H 2.41; N 5.59); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 7.35–7.49 (m, 4H), 7.83 (d, 1H, J=8.4 Hz), 8.30 (d, 1H, J=8.3 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 108.25 (CCl_2), 121.50 (CH), 127.49 (CH), 130.73 (CH), 130.92 (C), 131.47 (CH), 132.16 (C), 132.70 (CH), 162.35 (CO); ms, *m/z* (%): 251 (M^++2, 1), 249 (M^+, 1), 141 (28), 139 (100), 113 (16), 111 (44), 75 (42), 50 (21); IR (Nujol): 3291, 3084, 1663, 1648, 1501, 1467, 1297, 1197, 951, 750 cm^{-1}.

3.3.3. *N*-(2,2-Dichlorovinyl)-3-chlorobenzamide (3c). (91%), white needles (pet ether) mp 84–85°C. (Found: C 42.90; H 2.38; N 5.42; $C_9H_6Cl_3NO$ requires: C 43.15; H 2.41; N 5.59); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 7.41 (t, 1H, J=7.8 Hz), 7.43 (d, 1H, J=10.8 Hz), 7.53 (ddd, 1H, J=8.1, 2.0, 0.9 Hz), 7.66 (dt, 1H, J=7.8, 1.5 Hz), 7.78 (t, 1H, J=1.8 Hz), 7.82 (d, 1H, J=10.8 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 108.04 (CCl_2), 121.58 (CH), 125.22 (CH), 127.86 (CH), 130.12 (CH), 132.78 (CH), 134.14 (C), 135.26 (C), 162.33 (CO); ms, *m/z* (%): 249 (M^+, 2), 141 (29), 139 (100), 113 (15), 111 (47), 75 (24); IR (Nujol): 3279, 3072, 1655, 1643, 1505, 1376, 1303, 954, 761, 742 cm^{-1}.

3.3.4. *N*-(2,2-Dichlorovinyl)-4-chlorobenzamide (3d). (75%), white needles (pet ether) mp 96–97°C. (Found: C 43.23; H 2.44; N 5.55; $C_9H_6Cl_3NO$ requires: C 43.15; H 2.41; N 5.59; ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.42–7.48 (m, 3H), 7.71–7.78 (m, 3H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 107.75 (CCl_2), 121.67 (CH), 128.72 (CH), 129.26 (CH), 130.75 (C), 139.19 (C), 162.59 (CO); ms, *m/z* (%): 249 (M^+, 1), 141 (34), 139 (100), 113 (19), 111 (61), 75 (44); IR (Nujol): 3281, 3098, 1665, 1644, 1502, 1470, 1291, 1188, 755 cm^{-1}.

3.3.5. *N*-(2,2-Dichlorovinyl)-2-nitrobenzamide (3e). (82%), white powder (pet ether–ethyl acetate) mp 131–133°C. (Found: C 41.19; H 2.23; N 10.68; $C_9H_6Cl_2N_2O_3$ requires: C 41.41; H 2.32; N 10.73); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 7.36 (d, 1H, J=10.8 Hz), 7.53 (dd, 1H, J=7.5, 1.5 Hz), 7.62–7.76 (m, 3H), 8.08 (dd, 1H, J=8.3, 1.2 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 108.72 (CCl_2), 121.14 (CH), 124.80 (CH), 128.65 (CH), 130.89 (C), 131.45 (CH), 134.09 (CH), 146.34 (C), 163.08 (CO); ms, *m/z* (%): 260 (M^+, 2), 150 (100), 104 (13), 76 (32), 51 (36), 50 (25); IR (Nujol): 3243, 1670, 1648, 1530, 1344, 954, 854, 794, 756 cm^{-1}.

3.3.6. *N*-(2,2-Dichlorovinyl)-3-nitrobenzamide (3f). (98%), white powder (pet ether–ethyl acetate) mp 150–152°C. (Found: C 41.37; H 2.24; N 10.69; $C_9H_6Cl_2N_2O_3$ requires: C 41.41; H 2.32; N 10.73); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 7.43 (s, 1H), 8.81 (t, 1H, J=8.0 Hz), 8.32 (d, 1H, J=8.0 Hz), 8.45 (d, 1H, J=8.0 Hz), 8.71 (s, 1H), 10.52 (s, 1H); ^{13}C NMR δ (DMSO-d_6, 50.3 MHz): 104.82 (CCl_2), 120.51 (CH), 120.90 (CH), 124.14 (CH), 127.47 (CH), 131.40 (C), 132.20 (CH), 145.00 (C), 160.47 (CO); ms, *m/z* (%): 260 (M^+, 3), 225 (5), 150 (100), 104 (44), 76 (31); IR (Nujol): 3280, 1654, 1644, 1512, 1465, 1377, 1351, 907, 720 cm^{-1}.

3.3.7. *N*-(2,2-Dichlorovinyl)-4-nitrobenzamide (3g). (88%), white powder (pet ether–ethyl acetate) mp 150–153°C. (Found: C 41.65; H 2.26; N 10.70; $C_9H_6Cl_2N_2O_3$ requires: C 41.41; H 2.32; N 10.73); ^{1}H NMR δ (DMSO-d_6, 300 MHz): 7.43 (d, 1H, J=9.3 Hz), 8.12 (d, 2H, J=8.8 Hz), 8.34 (d, 2H, J=8.8 Hz), 10.47 (d, 1H, J=9.3 Hz); ^{13}C NMR δ (DMSO-d_6, 75.4 MHz): 107.57 (CCl_2), 123.37 (CH), 129.81 (CH), 138.26 (C), 149.47 (C), 163.73 (CO); ms, *m/z* (%): 260 (M^+, 3), 225 (4), 150 (100), 104 (37), 92 (19), 76 (30), 50 (19); IR (Nujol): 3404, 3079, 1699, 1518, 1342, 1287, 865, 713 cm^{-1}.

3.3.8. *N*-(2,2-Dichlorovinyl)-4-methoxybenzamide (3h). (98%), white needles (pet ether) mp 102–104°C. (Found: C 49.03; H 3.67; N 5.62; $C_{10}H_9Cl_2NO_2$ requires: C 48.81; H 3.69; N 5.69); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 3.86 (s, 3H), 6.96 (d, 2H, J=8.7 Hz), 7.47 (d, 1H, J=10.5 Hz), 7.72 (d, 1H, J=10.5 Hz), 7.78 (d, 2H, J=8.7 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 55.53 (CH_3O), 106.50 (CCl_2), 114.16 (CH), 122.01 (CH), 124.46 (C), 129.27 (CH), 162.99 (C), 163.18 (CO); ms, *m/z* (%): 245 (M^+, 10), 210 (22), 136 (33), 135 (100), 107 (32), 92 (60), 77 (69), 64 (37), 63 (31); IR (Nujol): 3383, 3083, 1669, 1649, 1609, 1264, 1179, 1028, 953, 839, 760 cm^{-1}.

3.3.9. *N*-(2,2-Dichlorovinyl)-3,4,5-trimethoxybenzamide (3i). (92%), white needles (pet ether) mp 122°C. (Found: C 46.94; H 4.19; N 4.55; $C_{12}H_{13}Cl_2NO_4$ requires: C 47.08; H 4.28; N 4.58); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 3.90 (s, 3H), 3.91 (s, 6H), 7.01 (s, 2H), 7.46 (d, 1H, J=10.5 Hz), 7.73 (d, 1H, J=10.5 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 56.42 (CH_3O), 60.96 (CH_3O), 104.81 (CH), 107.16 (CCl_2), 121.88 (CH), 127.71 (C), 142.08 (C), 153.40 (C), 163.39 (CO); ms, *m/z* (%): 305 (M^+, 1), 195 (100), 152 (14), 137 (11), 122 (11), 109 (13), 83 (12), 81 (14), 77 (12), 66 (22), 53 (14); IR (Nujol): 3326, 3067, 1670, 1655, 1584, 1487, 1335, 1228, 1122, 1006, 910 cm^{-1}.

3.3.10. *N*-(2,2-Dichlorovinyl)-2-methylbenzamide (3j). (70%), white needles (water) mp 57–59°C. (Found: C 52.10; H 3.90; N 6.05; $C_{10}H_9Cl_2NO$ requires: C 52.20; H 3.94; N 6.09); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 2.41 (s, 3H), 7.15–7.38 (m, 6H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 20.14 (CH_3), 107.25 (CCl_2), 121.70 (CH), 126.13 (CH), 126.96 (CH), 131.22 (CH), 131.67 (CH), 133.83 (C), 137.32 (C), 165.82 (CO); ms; *m/z* (%): 229 (M^+, 1), 119 (100), 91 (65), 77 (1), 65 (25); IR (Nujol): 3276, 1659, 1636, 1504, 1377, 1305, 1259, 1192, 950, 889, 835, 735 cm^{-1}.

3.3.11. *N*-(2,2-Dichlorovinyl)-4-methylbenzamide (3k).

(72%), white needles (pet ether) mp 104°C. (Found: C 52.30; H 3.89; N 6.03; $C_{10}H_9Cl_2NO$ requires: C 52.20; H 3.94; N 6.09); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 2.41 (s, 3H), 7.26 (d, 2H, J=8.0 Hz), 7.46 (d, 1H, J=10.7 Hz), 7.70 (d, 2H, J=8.2 Hz), 7.79 (d, 1H, J=10.7 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 21.58 (CH_3), 106.86 (CCl_2), 121.91 (CH), 127.29 (CH), 129.31 (C), 129.60 (CH), 143.52 (C), 163.50 (CO); ms; *m/z* (%): 229 (M^+, 1), 119 (100), 91 (56), 65 (30); IR (Nujol): 3292, 1661, 1644, 1611, 1522, 1487, 1464, 1377, 1286, 1200, 947, 880 cm^{-1}.

3.3.12. *N*-(2,2-Dichlorovinyl)propionamide (3l). (73%), white needles (pet ether) mp 59°C (dec). (Found: C 35.70; H 4.17; N 8.27; $C_5H_7Cl_2NO$ requires: C 35.74; H 4.20; N 8.34); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 1.21 (t, 3H, J= 7.6 Hz), 2.36 (q, 2H, J=7.6 Hz), 7.25–7.33 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 9.30 (CH_3), 29.51 (CH_2), 106.22 (CCl_2), 121.49 (CH), 170.52 (CO); ms, *m/z* (%): 167 (M^+, 1) 149 (2), 102 (21), 57 (100), 46 (59); IR (Nujol): 3274, 3094, 1682, 1653, 1506, 1463, 1378, 1217, 1030, 961, 884, 868, 704 cm^{-1}.

3.3.13. *N*-(2,2-Dichlorovinyl)isobutyramide (3m). (81%), white needles (hexane) mp 76–78°C. (Found: C 39.48; H 5.02; N 7.62; $C_6H_9Cl_2NO$ requires: C 39.59; H 4.98; N 7.69); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 1.21 (d, 6H, J= 6.9 Hz), 2.51 (sept, 1H, J=6.9 Hz), 7.27 (br s, 2H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 19.29 (CH_3), 35.46 (CH), 106.30 (CCl_2), 121.57 (CH), 173.75 (CO); ms, *m/z* (%): 183 (M^++2, 10), 181 (M^+,16), 113 (70), 111 (100), 85 (21), 83 (34), 71 (79); IR (Nujol): 3232, 3089, 1670, 1653, 1508, 1466, 1378, 1219, 986, 901, 871, 850 cm^{-1}.

3.3.14. *N*-(2,2-Dichlorovinyl)trimethylacetamide (3n). (65%), oil. (Found: C 42.66; H 5.67; N 7.07; $C_7H_{11}Cl_2NO$ requires: C 42.88; H 5.65; N 7.14); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 1.25 (s, 9H), 7.29 (s br, 2H); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 27.24 (CH_3), 39.02 (C), 106.38 (CCl_2), 121.75 (CH), 174.96 (CO); ms, *m/z* (%): 195 (M^+, 2), 113 (8), 111 (13), 85 (10), 57 (100); IR: 3447, 3342, 3087, 2965, 1695, 1652, 1486, 1212, 1138, 978, 885 cm^{-1}.

3.4. Electrochemical generation of *N*-(2,2-dichloro-1-hydroxyethyl)-4-chlorobenzamide 4d

Chloralamide **1d** was electrolyzed in acetonitrile (30 mL)–acetic acid (20 mL)–Li ClO_4 (0.4 M) at −1.10 V. vs. SCE following a procedure as that described above.

3.4.1. *N*-(2,2-Dichloro-1-hydroxyethyl)-4-chlorobenzamide (4d). (70%), white needles (chloroform) mp 117°C. (Found: C 40.03; H 3.02; N 5.19; $C_9H_8Cl_3NO_2$ (requires: C 40.26; H 3.00; N 5.22); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 5.58 (s, 1H), 5.88–5.98 (m, 2H), 7.22 (d, 1H, J=8.7 Hz), 7.39 (d, 2H, J=8.4 Hz), 7.69 (d, 2H, J=8.4 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 73.29 (CH), 76.74 ($CHCl_2$), 128.77 (CH), 129.16 (CH), 131.20 (C), 139.10 (C), 167.23 (CO); ms, *m/z* (%): 184 (9), 155 (11), 141 (30), 139 (100), 111 (35), 75 (23); IR (Nujol): 3281, 3222, 1660, 1537, 1483, 1102, 1015, 851, 777, 764 cm^{-1}.

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