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Synthesis and X-ray molecular structure of *N*-(1-amino-2,2-dichloroethyl)benzamides

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Abstract—Efficient procedures for the synthesis of *N*-(1-alkylamino-2,2-dichloroethyl)benzamides, *N*-(1-arylamino-2,2-dichloroethyl)benzamides and *N*-(1-amino-2,2-dichloroethyl)benzamides are reported. These compounds are of special interest as intermediates to access new heterocyclic series. *N*-(2,2-dichlorovinyl)amides react with primary or secondary alkylamines to yield the title compounds in high to quantitative yields. However, similar addition reactions with arylamines or ammonia are unsuccessful. In these cases the synthesis of the targeted products may be achieved by starting from *N*-(1,2,2,2-tetrachloroethyl)benzamides which are aminated via nucleophilic substitution yielding the corresponding *N*-(1-amino-2,2,2-trichloroethyl)benzamides. Finally, these compounds are selectively monodechlorinated by electrochemical reduction at constant cathodic potential. The crystallographic X-ray structure of *N*-(2,2-dichloro-1-isopentylaminoethyl)-4-methylbenzamide has been determined.

1. Introduction

Chloralamides **1** are inexpensive and easily available compounds that can be prepared by reaction of chloral hydrate with carboxylic amides.[1,2] As we reported, this almost quantitative reaction marks the beginning of a new synthetic route for heterocyclic compounds of significant interest. On this basis we accomplished the first synthesis of 4-alkylamino-2-aryl-2-oxazolines[3] **6** which gave access to novel 2-imidazolidinones[4] **7**. A common key step of this preparative procedure implies the electrochemical reduction of *N*-(1-amino-2,2-dichloroethyl)benzamides **4**. This process promotes a direct conversion of intermediates **4** to products **6**. In order to increase the usefulness of this heterocyclization methodology, we have given attention to the development of efficient and general procedures for preparing both types of intermediates, **3** and **4**. A convenient method to synthesize *N*-(2,2-dichlorovinyl)amides **3** was established[2] based on the treatment of chloralamides with phosphorus pentachloride to give *N*-(1,2,2,2-tetrachloroethyl)amides **2**, which can be electrochemically converted to the compounds **3** in fair to quantitative yields. We now report the results of our research on the synthesis of intermediates **4** (Scheme 1). Spectral and X-ray crystallographic structural data of this little known class of compounds are also reported.

2. Results and discussion

N-(2,2-dichlorovinyl)amides **3** were prepared according to our previously reported method,[2] and were treated in dry diethyl ether solution with 2 equiv. of the appropriate primary or secondary alkylamine. From the course of these reactions the generation at moderate rate of a single compound was clearly observed. Abundant precipitates in the majority of cases were forthcoming. Therefore, crude reaction products of a high purity could easily be isolated in high yields by simple filtration. These were crystallized and identified, after applying the usual spectroscopic techniques, elemental analysis and X-ray crystallography, as the aminated derivatives **4a**–**m**. The formation of these products involves nucleophilic addition of amino groups across the carbon–carbon double bonds of vinylidene dichorides **3**. It should be noted that many reactions between nucleophilic reagents and electronegatively substituted olefins involve substitution processes.[5–8] Addition reactions between amines and alkenes normally require either activation of the double bond via metallation or amino group activation in order to promote radical reactions.[9] Given our results, it is apparent that both geminal chlorine atoms present in compounds **3** would cause a remarkable electrophilic activity, sufficient to permit the addition of alkylamines without participation of any other factor. It was also found, however, that similar reactions of *N*-(2,2-dichlorovinyl)amides **3** with arylamines were unable to provide the corresponding *N*-(1-arylamino-2,2-dichloroethyl)benzamides **4n**,**o**. The starting materials were recovered unchanged in these cases. Such reaction failures appear clearly attributable to the remarkably lower nucleophilicity

Keywords: chloralamides; vinylidene dichlorides; vinylamides; electrosynthesis; reduction.

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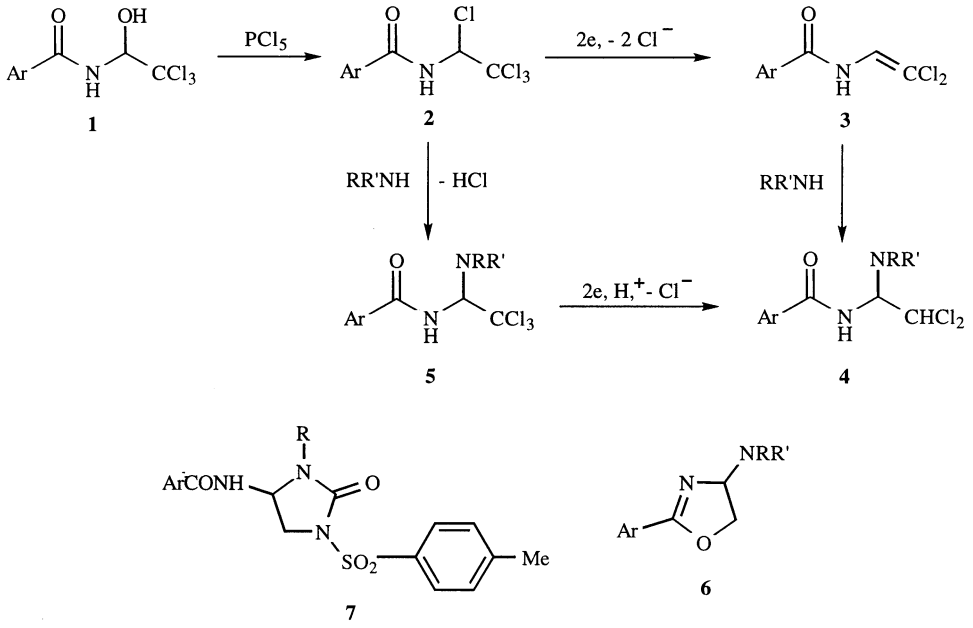

Entry	Ar	RR'NH
a	C_6H_5	$C_6H_5CH_2NH_2$
b	C_6H_5	CH_3NH_2
c	C_6H_5	$CH_3CH_2CH_2NH_2$
d	C_6H_5	$(CH_3)_2CHNH_2$
e	C_6H_5	$(CH_3CH_2)_2NH$
f	C_6H_5	Cy-$C_6H_{11}NH_2$
g	2-ClC_6H_4	$C_6H_5CH_2NH_2$
h	3-ClC_6H_4	$C_6H_5CH_2NH_2$
i	4-ClC_6H_4	$CH_3(CH_2)_2CH_2NH_2$
j	4-$O_2NC_6H_4$	$C_6H_5CH_2NH_2$
k	3,4,5-$(CH_3O)_3C_6H_2$	$C_6H_5CH_2NH_2$
l	2-$CH_3C_6H_4$	$(CH_3)_2NH$
m	4-$CH_3C_6H_4$	$(CH_3)_2CHCH_2CH_2NH_2$
n	C_6H_5	$C_6H_5NH_2$
o	C_6H_5	4-$CH_3OC_6H_4NH_2$
p	C_6H_5	H_2NH

Scheme 1.

of arylamines than alkylamines. The reaction with ammonia also consistently failed. Attempts to promote the reactions with the assistance of catalytic amounts of the corresponding anilinium chlorides or ammonium chloride were similarly unsuccessful, whereas those reactions carried out at a relatively high temperature gave complex mixtures of products, which were not identified. Such adverse results suggested our exploring an alternative synthetic route based on performing the amination process sought, via nucleophilic substitution rather than addition. In the first place *N*-(1,2,2,2-tetrachloroethyl)benzamide **2a** (91%) was prepared by reaction of **1a** with phosphorus pentachloride. The reactions of **2a** with arylamines to yield *N*-(arylamino-2,2,2-trichloroethyl)benzamides **5n**,**o** were found to be almost quantitative. The preparation of *N*-(amino-2,2,2-trichloroethyl)benzamide **5p** (75%) by reaction of **2a** with a relatively weak nucleophilic reagent such as ammonia could also be efficiently achieved in this way. Finally, the compounds **5n**–**p** were converted to the desired *N*-(arylamino-2,2-dichloroethyl)benzamides **4n**,**o** and *N*-(amino-2,2-dichloroethyl)benzamide **4p**, respectively, in fair to high yields, by selective electrochemical monodechlorination reductions carried out under constant potential in a protic medium.

Representative structural characteristics of compounds **4** were determined by X-ray crystallography of **4m**. The molecular structure found is illustrated in Fig. 1. Selected intramolecular distances (crystallographic numbering of atoms) and selected bond angles are given in Table 1. The

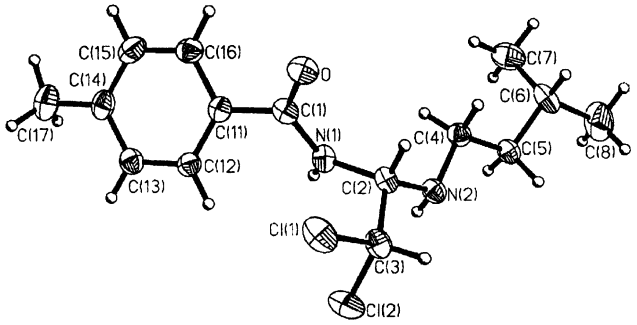

Figure 1. Molecular structure of **4m**, showing the crystallographic numbering system used.

adjacent molecules (Fig. 2) interact through one hydrogen bond. Intermolecular bond distances: N···O=2.925 Å; H···O=2.189 Å; O–H–N angle=154°.

In conclusion, it has been established in general that *N*-(2,2-dichlorovinyl)benzamides undergo efficient addition reactions with amines of relatively high nucleophilicity, such as primary and secondary alkylamines, to yield the corresponding *N*-(1-alkylamino-2,2-dichloroethyl)benzamides. The failure of similar reactions with ammonia or arylamines is attributable to their lower nucleophilicity. However, the preparation of *N*-(1-amino-2,2-dichloroethyl)benzamides and *N*-(1-arylamino-2,2-dichloroethyl)benzamides has been found to be feasible by an alternative procedure involving amination of an easily available class of tetrachlorinated derivatives followed by selective electrochemical reduction.

Table 1. Selected bond lengths and bond angles in crystal structure of **4m**

Bond lengths (Å)			
Cl(1)–C(3)	1.782(2)	N(2)–C(4)	1.470(3)
O–C(1)	1.235(2)	C(1)–C(11)	1.494(3)
N(1)–C(1)	1.349(3)	C(2)–C(3)	1.531(3)
N(1)–C(2)	1.453(3)	C(14)–C(17)	1.504(3)
N(2)–C(2)	1.443(3)		
Bond angles (°)			
C(1)–N(1)–C(2)	125.7(2)	N(2)–C(2)–C(3)	107.5(2)
C(2)–N(2)–C(4)	114.2(2)	N(1)–C(2)–C(3)	110.5(2)
O–C(1)–N(1)	123.7(2)	C(2)–C(3)–Cl(1)	111.1(2)
O–C(1)–C(11)	122.1(2)	Cl(2)–C(3)–Cl(1)	108.65(11)
O–C(1)–C(11)	122.1(2)	N(2)–C(4)–C(5)	110.2(2)
N(1)–C(1)–C(11)	114.2(2)	C(7)–C(6)–C(8)	110.5(2)
N(2)–C(2)–N(1)	114.6(2)		

3. Experimental

3.1. General

NMR spectra were determined on Bruker AC-200 or Varian 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.

Chloralamides **1**, *N*-(1,2,2,2-tetrachloroethyl)benzamide **2**, and *N*-(2,2-dichlorovinyl)benzamides **3** were prepared as previously described.[1,2]

3.2. Preparation of *N*-(1-alkylamino-2,2-dichloroethyl)-benzamides 4a–m

To a solution of the appropriate dichlorovinylamide **3** (3 mmol) in dry ether (10 mL) a solution of the corresponding alkylamine (6 mmol) in dry ether (10 mL) was added dropwise and the reaction mixture was stirred at room temperature for 24 h. The solid precipitated was filtered off and was crystallized from the appropriate solvent. In those cases where a precipitate was not formed the solvent was evaporated under reduced pressure, leaving a solid residue that was crystallized as above. Owing to the high volatility of methylamine the reaction with this reagent was carried out at −5°C.

3.3. Electrochemical generation of products 4n–p

Preparative electrolyses were carried out under a constant

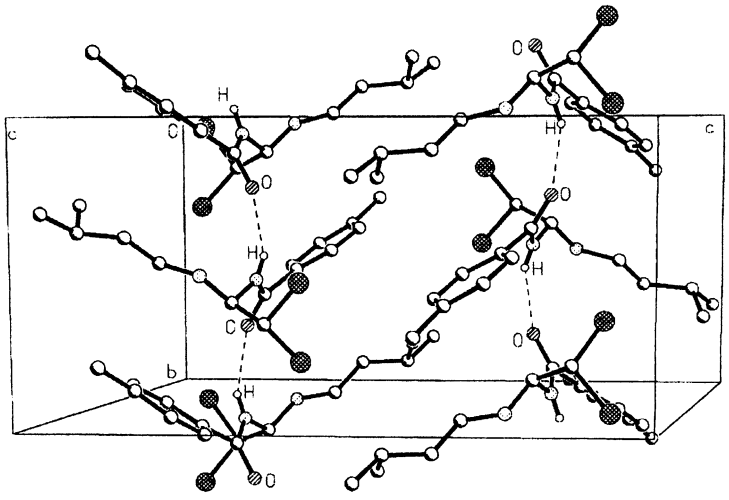

Figure 2. A perspective of the crystal packing of **4m**, showing the hydrogen interactions.

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 MeCN–$LiClO_4$, 0.5 M of which 35 mL and 15 mL, approximately, were placed, respectively, in the cathodic and the anodic compartments. Acetic acid (5 mmol) was added to the cathodic compartment. Solutions of compounds **5** (5 mmol) were electrolyzed under the following cathodic potentials: **5n** (−1.30); **5o** (−1.70); **5p** (−1.20 V vs SCE). The electricity consumption was 2 F/mol in all cases. The duration of the electrolyses ranged from 1.6 to 1.8 h. The average current intensity was 240 mA at the beginning and 15 mA at the end. All electrolysis products were isolated by removing the solvent in vacuo.[10] The residue was then shaken with water, leaving a white solid that was collected by filtration, was air-dried and crystallized from the appropriate solvent. The product **4p** was purified by column chromatography (silica gel, hexane–ethyl acetate; 1:1).

3.3.1. *N*-(1-Benzylamino-2,2-dichloroethyl)benzamide (4a). (70%), white needles (pet ether–dichloromethane) mp 136°C. (Found: C 59.38; H 5.02; N 8.53; $C_{16}H_{16}Cl_2N_2O$ requires: C 59.46; H 4.99; N 8.67); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 2.18 (s br, 1H), 3.96 (s, 2H), 5.37 (dd, 1H, J=8.3, 2.5 Hz), 6.03 (d, 1H, J=2.5 Hz), 6.52 (d, 1H, J=8.3 Hz), 7.25–7.55 (m, 8H), 7.75 (d, 2H, J=8.1 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 50.55 (CH_2), 68.81 (CH), 74.47 ($CHCl_2$), 127.15 (CH), 127.47 (CH), 128.21 (CH), 128.66 (CH), 128.78 (CH), 132.21 (CH), 133.47 (C), 139.25 (C), 167.66 (CO); FAB$^+$: 323 (M^++1); IR (Nujol): 3359, 3305, 1623, 1510, 1487, 1328, 1276, 1008, 804, 796, 725, 700 cm^{-1}.

3.3.2. *N*-(2,2-Dichloro-1-methylaminoethyl)benzamide (4b). (86%), white needles (pet ether–dichloromethane) mp 125–126°C. (Found: C 48.38; H 4.96; N 11.23; $C_{10}H_{12}Cl_2N_2O$ requires: C 48.60; H 4.89; N 11.34); ^{1}H NMR δ (DMSO-d_6, 200 MHz): 2.14 (s br, 1H), 2.37 (s, 3H), 5.00 (s br, 1H), 6.26 (d, 1H, J=4.0 Hz), 7.46–7.62 (m, 3H), 7.91 (d, 2H, J=8.1 Hz), 8.58 (d, 1H, J=7.8 Hz); ^{13}C NMR δ (DMSO-d_6, 50.4 MHz): 30.00 (CH_3), 68.54 (CH), 72.25 ($CHCl_2$), 124.72 (CH), 125.71 (CH), 128.97 (CH), 131.05 (C), 164.14 (CO); FAB$^+$: 247 (M^++1); IR (Nujol): 3332, 3310, 1647, 1524, 1464, 1378, 1108, 973, 765, 710 cm^{-1}.

3.3.3. *N*-(2,2-Dichloro-1-propylaminoethyl)benzamide (4c). (68%), white needles (ether) mp 101–103°C. (Found: C 52.51; H 5.93; N 10.23; $C_{12}H_{16}Cl_2N_2O$ requires: C 52.38; H 5.86; N 10.18); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 0.91 (t, 3H, J=7.3 Hz), 1.45–1.57 (m, 2H), 1.90 (s br, 1H), 2.69–2.73 (m, 2H), 5.31 (dd, 1H, J=8.0, 2.5 Hz), 6.02 (d, 1H, J=2.5 Hz), 6.75 (d, 1H, J=8.0 Hz), 7.43–7.53 (m, 3H), 7.81 (dd, 2H, J=8.0, 1.6 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 11.61 (CH_3), 23.05 (CH_2), 48.26 (CH_2), 69.05 (CH), 74.46 ($CHCl_2$), 127.11 (CH), 128.69 (CH), 132.08 (CH), 133.48 (C), 167.73 (CO); FAB$^+$: 275 (M^++1); IR (Nujol): 3280, 1665, 1644, 1538, 1469, 1380, 1342, 1123, 780, 718 cm^{-1}.

3.3.4. *N*-(2,2-Dichloro-1-isopropylaminoethyl)benzamide (4d). (76%), white needles (pet ether) mp 80°C dec. (Found: C 52.60; H 5.71; N 10.13; $C_{12}H_{16}Cl_2N_2O$ requires: C 52.38; H 5.86; N 10.18); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 1.11 (d, 3H, J=6.4 Hz), 1.13 (d, 3H, J=6.2 Hz), 2.12 (s br, 1H), 3.05 (sept., 1H, J=6.2 Hz), 5.38 (dd, 1H, J=8.2, 2.5 Hz), 6.02 (d, 1H, J=2.5 Hz), 6.67 (d, 1H, J=8.2 Hz), 7.39–7.53 (m, 3H), 7.81 (d, 1H, J=7.5 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 22.39 (CH_3), 23.85 (CH_3), 45.98 (CH), 67.18 (CH), 74.82 ($CHCl_2$), 127.10 (CH), 128.69 (CH), 132.07 (CH), 133.51 (C), 167.50 (CO); FAB$^+$: 275 (M^++1); IR (Nujol): 3314, 1642, 1536, 1465, 1378, 1346, 1276, 1078, 1001, 758 cm^{-1}.

3.3.5. *N*-(2,2-Dichloro-1-diethylaminoethyl)benzamide (4e). (99%), white needles (pet ether) mp 91–92°C. (Found: C 54.00; H 6.52; N 9.49; $C_{13}H_{19}Cl_2N_2O$ requires: C 53.80; H 6.60; N 9.65); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 1.10 (t, 6H, J=7.1 Hz), 2.57–2.85 (m, 4H), 5.44 (dd, 1H, J=9.2, 4.7 Hz), 5.91 (d, 1H, J=4.6 Hz), 6.94 (d, 1H, J=9.1 Hz), 7.39–7.56 (m, 3H), 7.81 (d, 2H, J=6.8 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 13.50 (CH_3), 43.81 (CH_2), 71.33 (CH), 74.28 ($CHCl_2$), 127.14 (CH), 128.74 (CH), 132.02 (CH), 133.83 (C), 167.95 (CO); FAB$^+$: 289 (M^++1); IR (Nujol): 3233, 1633, 1529, 1464, 1376, 1335, 1209, 1076, 771, 744, 706 cm^{-1}.

3.3.6. *N*-(1-Cyclohexylamino-2,2-dichloroethyl)benzamide (4f). (66%), white needles (pet ether) mp 121–122°C. (Found: C 40.31; H 2.96; N 5.27; $C_{15}H_{20}Cl_2N_2O$ requires: C 40.26; H 3.00; N 5.22); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 1.20–2.04 (m, 11H), 2.67 (s br, 1H), 5.40 (dd, 1H, J=8.1, 2.4 Hz), 6.03 (d, 1H, J=2.4 Hz), 6.52 (d, 1H, J=8.1 Hz), 7.45–7.54 (m, 3H), 7.78 (d, 2H, J=7.4 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 24.57 (CH_2), 24.86 (CH_2), 25.91 (CH_2), 32.92 (CH_2), 34.39 (CH_2), 53.86 (CH), 66.95 (CH), 74.88 ($CHCl_2$), 127.13 (CH), 128.77 (CH), 132.11 (CH), 133.58 (C), 167.33 (CO); FAB$^+$: 315 (M^++1); IR (Nujol): 3331, 1629, 1513, 1464, 1377, 1140, 794, 695 cm^{-1}.

3.3.7. *N*-(1-Benzylamino-2,2-dichloroethyl)-2-chlorobenzamide (4g). (90%), white needles (pet ether) mp 121–123°C. (Found: C 56.99; H 6.45; N 8.93; $C_{16}H_{15}Cl_3N_2O$ requires: C 57.15; H 6.39; N 8.89); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.08 (s br, 1H), 3.09 (d, 1H, J=12.2 Hz), 4.05 (d, 1H, J=12.2 Hz), 5.39 (dd, 1H, J=8.7, 2.7 Hz), 6.03 (d, 1H, J=2.7 Hz), 6.63 (d, 1H, J=8.4 Hz), 7.26–7.46 (m, 8H), 7.66 (d, 1H, J=7.2 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 50.41 (CH_2), 68.75 (CH), 74.28 ($CHCl_2$), 127.33 (CH), 127.53 (CH), 128.36 (CH), 128.66 (CH), 130.47 (CH), 130.50 (CH), 130.77 (C), 131.91 (CH), 134.24 (C), 139.09 (C), 166.76 (CO); MS m/z (%): 286 (1), 273 (M^+−$CHCl_2$, 2), 201 (1), 166 (4), 139 (49), 111 (20), 106 (30), 91 (100), 75 (19); IR (Nujol): 3307, 1657, 1532, 1464, 1378, 1344, 1159, 1135, 1081, 974, 779, 754 cm^{-1}.

3.3.8. *N*-(1-Benzylamino-2,2-dichloroethyl)-3-chlorobenzamide (4h). (98%), white needles (pet ether–dichloromethane) mp 128°C. (Found: C 53.88; H 4.28; N 7.77; $C_{16}H_{15}Cl_3N_2O$ requires: C 53.73; H 4.23; N 7.83); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.20 (s br, 1H), 3.95 (s, 2H), 5.35 (dd, 1H, J=8.4, 2.4 Hz), 6.02 (d, 1H, J=2.7 Hz), 6.46 (d, 1H, J=8.1 Hz), 7.26–7.68 (m, 9H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 50.71 (CH_2), 69.13 (CH), 74.31 ($CHCl_2$),

125.20 (CH), 127.49 (CH), 127.57 (CH), 128.18 (CH), 128.72 (CH), 130.08 (CH), 132.20 (CH), 135.00 (C), 135.23 (C), 139.26 (C), 166.32 (CO); MS *m/z* (%): 328 (1), 285 (2), 273 (6), 166 (11), 156 (5), 141 (28), 111 (43), 106 (87), 91 (100), 75 (16); IR (Nujol): 3293, 1634, 1523, 1465, 1378, 1037, 1009, 794, 732 cm^{-1}.

3.3.9. *N*-(1-Butylamino-2,2-dichloroethyl)-4-chlorobenzamide (4i). (98%), white needles (pet ether) mp 89–92°C. (Found: C 48.04; H 5.16; N 8.50; $C_{13}H_{17}Cl_3N_2O$ requires: C 48.24; H 5.29; N 8.66); ^1H NMR δ ($CDCl_3$, 300 MHz): 0.90 (t, 3H, *J*=7.2 Hz), 1.31–1.49 (m, 4H), 2.70–2.79 (m, 2H), 5.29 (dd, 1H, *J*=8.5, 2.1 Hz), 6.02 (d, 1H, *J*=2.4 Hz), 6.60 (d, 1H, *J*=8.1 Hz), 7.41 (d, 2H, *J*=8.4 Hz), 7.74 (d, 2H, *J*=8.4 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 13.90 (CH_3), 20.24 (CH_2), 32.05 (CH_2), 46.26 (CH_2), 69.27 (CH), 74.41 ($CHCl_2$), 128.58 (CH), 129.00 (CH), 131.95 (C), 138.42 (C), 166.66 (CO); MS *m/z* (%): 286 (M^+-HCl, 1), 239 (M^+-CHCl_2, 6), 156 (7), 139 (100), 111 (53), 90 (10), 84 (20), 77 (5); IR (Nujol): 3279, 1640, 1536, 1464, 1376, 1340, 1127, 1012, 845, 773, 755 cm^{-1}.

3.3.10. *N*-(1-Benzylamino-2,2-dichloroethyl)-4-nitrobenzamide (4j). (72%), yellow powder (ethyl acetate–hexane) mp 136°C. (Found: C 51.97; H 4.04; N 11.23; $C_{16}H_{15}Cl_2N_3O_3$ requires: C 52.19; H 4.11; N 11.41); ^1H NMR δ ($CDCl_3$, 300 MHz): 2.04 (br s, 1H), 3.94 (d, 1H, *J*=15.8 Hz), 4.00 (d, 1H, *J*=15.8 Hz), 5.38 (dd, 1H, *J*=8.4, 2.4 Hz), 6.03 (d, 1H, *J*=2.5 Hz), 6.47 (d, 1H, *J*=8.3 Hz), 7.23–7.37 (m, 5H), 7.83 (d, 2H, *J*=8.7 Hz), 8.27 (d, 2H, *J*=8.7 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 50.72 (CH_2), 69.27 (CH), 74.05 ($CHCl_2$), 123.87 (CH), 127.52 (CH), 128.05 (CH), 128.27 (CH), 128.70 (CH), 138.93 (C), 139.15 (C), 149.89 (C), 165.55 (CO); MS *m/z* (%): 368 (M^++1, 1), 209 (2), 195 (4), 166 (31), 150 (87), 120 (14), 106 (21), 91 (100), 77 (14); IR (Nujol): 3288, 1639, 1599, 1524, 1464, 1377, 1344, 1318, 870, 846, 796 cm^{-1}.

3.3.11. *N*-(1-Benzylamino-2,2-dichloroethyl)-3,4,5-trimethoxybenzamide (4k). (74%), white needles (pet ether–dichloromethane) mp 145–148°C. (Found: C 55.48; H 5.43; N 6.58; $C_{19}H_{22}Cl_2N_2O_4$ requires: C 55.22; H 5.37; N 6.78); ^1H NMR δ ($CDCl_3$, 200 MHz): 2.31 (s, 1H), 3.89 (s, 2H), 3.90 (s, 6H), 3.96 (s, 3H), 5.35 (dd, 1H, *J*=9.0, 2.5 Hz), 6.03 (d, 1H, *J*=2.7 Hz), 6.54 (d, 1H, *J*=8.4 Hz), 6.99 (s, 2H), 7.27–7.35 (m, 5H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 50.62 (CH_2), 56.46 (CH_3O), 60.98 (CH_3O), 69.04 (CH), 74.43 ($CHCl_2$), 104.71 (CH), 127.51 (CH), 128.18 (CH), 128.66 (CH), 128.78 (C), 139.17 (C), 153.36 (C), 167.31 (CO); MS *m/z* (%): 211 (4), 196 (3), 140 (4), 118 (8), 91 (100), 77 (5); IR (Nujol): 3290, 1631, 1582, 1497, 1471, 1356, 1237, 1132, 998, 847 cm^{-1}.

3.3.12. *N*-(2,2-Dichloro-1-dimethylaminoethyl)-2-methylbenzamide (4l). (80%), white needles (hexane) mp 112°C. (Found: C 52.44; H 5.92; N 9.98; $C_{12}H_{16}Cl_2N_2O$ requires: C 52.38; H 5.86; N 10.18); ^1H NMR δ ($CDCl_3$, 200 MHz): 2.45 (s, 6H), 2.49 (s, 3H), 5.20 (dd, 1H, *J*=9.6 Hz, *J*=3.6 Hz), 5.99 (d, 1H, *J*=3.7 Hz), 6.38 (d, 1H, *J*=8.5 Hz), 7.21–7.48 (m, 4H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 20.09 (CH_3), 41.56 (CH_3), 73.14 (CH), 73.68 ($CHCl_2$), 125.98 (CH), 126.74 (CH), 130.51 (CH), 131.30 (CH), 135.66 (C), 136.39 (C), 170.49 (CO); MS *m/z* (%): 191 (M^+-CHCl_2, 6), 119 (100), 91 (54), 77 (2), 65 (27); IR (Nujol): 3244, 1645, 1538, 1463, 1377, 1338, 1271, 1082, 1031, 777 cm^{-1}.

3.3.13. *N*-(2,2-Dichloro-1-isopentylaminoethyl)-4-methylbenzamide (4m). (73%), white needles (pet ether) mp 89–90°C. (Found: C 56.58; H 7.03; N 8.74; $C_{15}H_{22}Cl_2N_2O$ requires: C 56.79; H 6.99; N 8.83); ^1H NMR δ ($CDCl_3$, 300 MHz): 0.87 (d, 3H, *J*=6.6 Hz), 0.88 (d, 3H, *J*=6.6 Hz), 1.34–1.45 (m, 2H), 1.61–1.66 (m, 1H), 1.72 (br s, 1H), 2.40 (s, 3H), 2.73–2.82 (m, 2H), 5.30 (dd, 1H, *J*=8.2, 2.7 Hz), 6.02 (d, 1H, *J*=2.4 Hz), 6.49 (d, 1H, *J*=8.2 Hz), 7.25 (d, 2H, *J*=7.5 Hz), 7.70 (d, 2H, *J*=8.4 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.43 (CH_3), 22.47 (CH_3), 22.56 (CH_3), 25.83 (CH), 38.90 (CH_2), 44.63 (CH_2), 69.05 (CH), 74.47 ($CHCl_2$), 127.05 (CH), 129.32 (CH), 131.16 (C), 142.56 (C), 167.45 (CO); MS *m/z* (%): 280 (M^+-HCl, 1), 233 (M^+-CHCl_2, 3), 224 (2), 189 (3), 146 (3), 136 (7), 119 (100), 91 (48), 65 (21); IR (Nujol): 3323, 1644, 1536, 1468, 1377, 1121, 965, 840, 770 cm^{-1}.

3.3.14. *N*-(2,2-Dichloro-1-phenylaminoethyl)benzamide (4n). (87%), white needles (pet ether–dichloromethane) mp 146–149°C. (Found: C 57.97; H 4.78; N 8.98; $C_{15}H_{15}Cl_2N_2O$ requires: C 58.08; H 4.87; N 9.03); ^1H NMR δ ($CDCl_3$, 300 MHz): 4.56 (br s, 1H), 6.05 (dd, 1H, *J*=7.2, 2.7 Hz), 6.16 (d, 1H, *J*=2.4 Hz), 6.57 (d, 1H, *J*=7.5 Hz), 6.76–6.86 (m, 3H), 7.19–7.25 (m, 2H), 7.38–7.54 (m, 3H), 7.73–7.77 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 65.22 (CH), 73.65 ($CHCl_2$), 114.05 (CH), 119.94 (CH), 127.19, (CH), 128.81 (CH), 129.71 (CH), 132.35 (CH), 133.14 (C), 144.15 (C), 167.54 (CO); MS *m/z* (%): 308 (M^+, 1), 272 (1), 137 (2), 225 (15), 187 (2), 152 (2), 122 (18), 105 (100), 93 (31), 77 (98); IR (Nujol): 3416, 3312, 1629, 1607, 1504, 1484, 1311, 1134, 1080, 1063, 792, 753 cm^{-1}.

3.3.15. *N*-[2,2-Dichloro-1-(4-methoxyphenylamino)ethyl]-benzamide (4o). (80%), white needles (pet ether–dichloromethane) mp 120–121°C. (Found: C 56.71; H 4.80; N 8.30; $C_{16}H_{16}Cl_2N_2O_2$ requires: C 56.65; H 4.75; N 8.26); ^1H NMR δ ($CDCl_3$, 200 MHz): 3.71 (s, 3H), 4.31 (d, 1H, *J*=8.8 Hz), 5.96 (td, 1H, *J*=8.4, 2.4 Hz), 6.14 (d, 1H, *J*=2.4 Hz), 6.60 (d, 1H, *J*=7.6 Hz), 6.76 (d, 4H, *J*=3.3 Hz), 7.36–7.51 (m, 3H), 7.72–7.76 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 55.72 (CH_3O), 66.12 (CH), 73.81 ($CHCl_2$), 115.15 (CH), 115.66 (CH), 127.17 (CH), 128.79 (CH), 132.30 (CH), 133.20 (C), 137.95 (C), 153.75 (C), 167.58 (CO); MS *m/z* (%): 338 (M^+, 5), 256 (6), 181 (5), 147 (4), 134 (40), 123 (58), 108 (46), 105 (100), 77 (80); IR (Nujol): 3339, 1634, 1506, 1484, 1379, 1251, 1041, 829, 790, 722 cm^{-1}.

3.3.16. *N*-(1-Amino-2,2-dichloroethyl)benzamide (4p). (67%), white needles (ethyl acetate–hexane) mp 82–85°C. (Found: C 45.97; H 4.77; N 12.02; $C_9H_{11}Cl_2N_2O$ requires: C 46.18; H 4.74; N 11.97); ^1H NMR δ ($CDCl_3$, 200 MHz): 2.13 (br s, 2H), 5.33 (dd, 1H, *J*=7.0, 1.8 Hz), 6.10 (d, 1H, *J*=1.8 Hz), 6.78 (d, 1H, *J*=5.5 Hz), 7.41–7.54 (m, 3H), 7.78 (d, 2H, *J*=7.7 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 64.80 (CH), 75.31 ($CHCl_2$), 127.12 (CH), 128.78 (CH), 132.22 (CH), 133.42 (C), 167.20 (CO); MS *m/z* (%): 217 (2), 215 (3), 180 (2), 121 (2), 105 (100), 77 (58); IR (Nujol): 3407,

3315, 1633, 1522, 1489, 1460, 1380, 1307, 1076, 1045, 933, 789, 720 cm^{-1}.

3.4. Preparation of *N*-(arylamino-2,2,2-trichloroethyl)-benzamides 5n,o and *N*-(amino-2,2,2-trichloroethyl)-benzamide 5p

Products **5n**,**o** were prepared by reaction of **2a** with the corresponding amines: To a well-stirred solution of **2a** (7 mmol) in dry acetone (5 mL) at room temperature, a solution of the arylamine (7 mmol) and triethylamine (7 mmol) in dry acetone (10 mL) was added dropwise. An almost instantaneous formation of a precipitate of triethylamine hydrochloride was observed upon addition of the first drops. This solid was removed by filtering and the solvent was removed under reduced pressure, leaving an oily residue, which was shaken with petroleum ether. The white solid formed was collected by filtration and crystallized from the appropriate solvent.

Product **5p** was prepared by reaction of **2a** with ammonia in a two-phase system (Et_2O–NH_3 aq). A solution of **2a** (10 mmol) in ether (30 mL) was added dropwise at room temperature to a vigorously stirred solution of ammonium hydroxide (30%) in water (25 mL), stirring was continued for 10 min. Then the organic layer was dried on anhydrous magnesium sulphate. Evaporation of ether gave a white solid residue which was crystallized from hexane/dichloromethane.

3.4.1. *N*-(2,2,2-Trichloro-1-phenylaminoethyl)benzamide (5n). (96%), white needles (hexane–dichloromethane) mp 172–174°C. (Found: C 52.58; H 3.79; N 8.22; $C_{15}H_{13}Cl_3N_2O$ requires: C 52.43; H 3.81; N 8.15); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 4.57 (br s, 1H), 6.41 (d, 1H, J=9.2 Hz), 6.74 (d, 1H, J=9.1 Hz), 6.80–6.87 (m, 3H), 7.17–7.26 (m, 2H), 7.37–7.57 (m, 3H), 7.75–7.80 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 70.94 (CH), 101.43 (CCl_3), 114.46 (CH), 120.11 (CH), 127.28 (CH), 128.84 (CH), 129.72 (CH), 132.42 (CH), 133.24 (C), 144.02 (C), 167.44 (CO); MS *m*/*z* (%): 344 (1), 342 (M^+, 1), 271 (1), 225 (18), 167 (1), 151 (1), 122 (21), 105 (100), 93 (17), 77 (80); IR (Nujol): 3367, 3280, 1646, 1603, 1530, 1504, 1344, 1300, 1078, 1032, 885, 776, 745 cm^{-1}.

3.4.2. *N*-[2,2,2-Trichloro-1-(4-methoxyphenylamino)-ethyl]benzamide (5o). (97%), white needles (hexane–dichloromethane) mp 170–171°C. (Found: C 51.46; H 3.98; N 7.46; $C_{16}H_{15}Cl_3N_2O_2$ requires: C 51.43; H 4.05; N 7.50); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.71 (s, 3H), 6.29 (d, 1H, J=9.5 Hz), 6.77 (br s, 5H), 7.38–7.50 (m, 3H), 7.73–7.77 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 55.69 (CH_3O), 71.98 (CH), 102.00 (CCl_3), 115.12 (CH), 115.91 (CH), 127.24 (CH), 128.81 (CH), 132.36 (CH), 133.27 (C), 137.86 (C), 153.84 (C), 167.55 (CO); MS *m*/*z* (%):372 (M^+, 1), 255 (10), 216 (1), 181 (2), 166 (2), 152 (6), 134 (35), 122 (24), 105 (100), 77 (67); IR (Nujol): 3373, 3218, 1643, 1547, 1512, 1375, 1286, 1236, 1149, 1037, 814, 796, 720 cm^{-1}.

3.4.3. *N*-(1-Amino-2,2,2-trichloroethyl)benzamide (5p). (75%), white needles (hexane–dichloromethane) mp 96–99°C. (Found: C 40.29; H 3.43; N 10.41; $C_9H_9Cl_3N_2O$ requires: C 40.40; H 3.39; N 10.47); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.29 (s, 2H), 5.76 (d, 1H, J=9.3 Hz), 6.71 (d, 1H, J=8.7 Hz), 7.43–7.55 (m, 3H), 7.78–7.81 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 70.60 (CH), 103.38 (CCl_3), 127.26 (CH), 128.85 (CH), 132.37 (CH), 133.49 (C), 166.96 (CO); MS *m*/*z* (%): 230 (M^+−HCl, 1), 195 (2), 149 (21), 105 (100), 77 (52); i.r.: 3370, 3290, 1651, 1553, 1377, 1334, 827, 794, 710 cm^{-1}.

3.5. X-Ray crystallographic analysis of *N*-(2,2-dichloro-1-isopentylaminoethyl)-4-methylbenzamide (4m)

Crystal data: $C_{15}H_{22}Cl_2N_2O$, M_r=317.25, monoclinic, $P2(1)/c$, a=10.7446(7), b=9.0414(5), c=17.8914(10) Å, β=106.440 (10)°, V=1667.0(2) $Å^3$, Z=4, λ (Mo Kα)= 0.71073 Å, T=−100°C. *Data collection*: colorless block 0.60×0.34×0.32 mm^3, Siemmens P4 diffractometer, 4361 intensities (2932 unique), $2\theta_{max}$ 50°. *Structure solution and refinement*: direct methods, refined on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen), H atoms with riding model except H01 and H02 free, *wR* (F^2) 0.0996, *R* (F) 0.036, 189 parameters, S=1.099, max. $\Delta\rho$ 0.335 e $Å^{-3}$.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the reference numbers CCDC 178736. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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10. Caution must be exercised when handling perchlorates in order to exclude explosion risk. Evaporation of organic solutions containing perchlorates requires to be carried out in vacuo and at moderate temperature. The contact with strong acids must be avoided.