ELECTROCARBOXYLATION OF CHLORINATED AROMATIC COMPOUNDS+

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Chorinated benzenes (**1**, **4**), biphenyls (**6**, **9**), dibenzofurans (**10**, **15**, **17**, **18**), 2-chlorodibenzo[1,4]dioxine (**24**) and 1-chloronaphthalene (**26**) as well as dibenzofuran (**12**) and naphthalene (**27**) themselves were transformed into carboxylic acids by galvanostatic electroreduction in the presence of carbon dioxide ("electrocarboxylation"). Dry DMF was used as solvent, zinc or stainless steel as cathode and magnesium as a sacrificial anode in an undivided cell. Hydrogenation of aromatic rings was not observed. However, reductive addition of two molecules of carbon dioxide to form dihydrodicarboxylic acids, *e.g.* **22** and **29**, occurs in the dibenzofuran and naphthalene series.

Key words: Electroreduction; Electrocarboxylation; Carboxylic acids; Chlorinated arenes; Dibenzofurans; Electrochemistry.

In the last years we have successfully used the electroreductive dehalogenation of several aromatic[1–3] and aliphatic chlorides[4,5] in methanol and methanol–water mixtures as solvents. Lead proved to be a suitable cathode material. In these electrolyses, the proton was the only electrophile present which could substitute the halogen. In the following we present our results on the electroreduction of several chlorinated as well as unsubstituted arenes and hetarenes in DMF as aprotic solvent with carbon dioxide as electrophile in an undivided cell with a sacrificial anode. The formation of carboxylic acids by this method has already been described by

+ Part 33 in the series Electroreduction of Organic Compounds; Part 32 see ref.[1]

several authors[6]. The electrochemical process can be described by the following overall equations:

Cathode: $ArCl + 2\,e + CO_2 \rightarrow ArCO_2^- + Cl^-$

Anode: $Mg - 2\,e \rightarrow Mg^{2+}$

Overall: $ArCl + CO_2 + Mg \rightarrow ArCO_2^- + Cl^- + Mg^{2+}$

The outcome of the electrolysis is thus identical with the result of a Grignard reaction. The target of these investigations was mainly to explore its preparative potential. Our studies are, however, more directed to the dehalogenation of compounds such as oligochlorobenzenes, -biphenyls, -naphthalenes and -dibenzofurans. These xenobiotics are highly toxic and persistent and, therefore, cause serious environmental problems. Microbial degradation of the most dangerous highly chlorinated substances in particular is prohibited and there is a demand for methods of lowering their chlorine content[7]. Carboxylation could, moreover, help increase the bioavailability of the products as compared with the simple hydrodechlorination.

EXPERIMENTAL

NMR spectra: Bruker WH 400 (400 MHz for ^{1}H, 100.6 MHz for ^{13}C; δ, ppm; *J*, Hz). IR spectra: ATI Mattson "Genesis"-FT-IR (ν, cm^{-1}). GC-MS: Fisons Instruments GC 8000 (equipped with a 30 m SE 54 column) an MD 800 quadrupole-MS (EI, 70 eV, *m/z* (rel.%)).

Dimethylformamide (DMF) (Merck), tetrabutylammonium bromide (Fluka), magnesium rods (Riedel de Haën), 1,2,4,5-tetrachlorobenzene (**1**) (Merck), hexachlorobenzene (**4**) (Bayer Leverkusen), 4-chlorobiphenyl (**6**) (Lancaster), 4,4′-dichlorobiphenyl (**9**) (Lancaster), dibenzofuran (**12**) (Merck), 2-chlorodibenzo[1,4]dioxine (**24**) (Promochem) and 1-chloronaphthalene (**26**) (Merck) were commercially available.

Preparation of Starting Compounds

1-(4-Chlorophenoxy)-2-nitrobenzene was prepared from 4-chlorophenol (16 g, 120 mmol) and 2-chloronitrobenzene (15.76 g, 100 mmol) by a standard procedure[8,9] in 80% yield (20.0 g); yellow crystals; m.p. 40–41 °C (95% aqueous ethanol), ref.[8] m.p. 43–43.5 °C. ^{1}H NMR ($CDCl_3$): 7.96 dd, 1 H, *J*(3,4) = 8.1, *J*(3,5) = 1.7 (H-3); 7.53 vtd, 1 H, *J*(4,5) = 7.9, *J*(3,5) = 1.7 (H-5); 7.33 AA′XX′, 2 H, *J*(AX) = *J*(A′X′) = 8.7, *J*(AA′) = *J*(XX′) = 2.8, *J*(A′X) = *J*(AX′) = 0.3 (H-3′, H-5′); 7.24 vtd, 1 H, *J*(3,4,5) = 7.9 *J*(4,6) = 1.7 (H-4); 7.03 dd, 1 H, *J*(5,6) = 8.4, *J*(4,6) = 1.3 (H-6); 6.98 AA′XX′, 2 H, *J*(AX) = *J*(A′X′) = 8.7, *J*(AA′) = *J*(XX′) = 2.8, *J*(A′X) = *J*(AX′) = 0.3 (H-2′, H-6′).

2-(4-Chlorophenoxy)aniline hydrochloride. The reduction of 1-(4-chlorophenoxy)-2-nitrobenzene was achieved with hydrazinium hydroxide and Raney nickel in boiling ethanol[10]. Precipitation of the hydrochloride was performed with concentrated HCl. Recrystallisation of the crude product from ethanol yielded 76% of grey crystals, m.p. 176–177 °C, ref.[8] m.p.

181–183 °C. IR (KBr): 2 965, 2 940, 2 925, 2 907, 2 740, 2 721, 2 649, 2 345, 1 943, 1 482, 1 093. ^{1}H NMR (CD_3OD): 7.56 dd, 1 H, *J*(3,4) = 8,0, *J*(3,5) = 1.6 (H-3); 7.49 AA′XX′, 2 H, *J*(AX) = *J*(A′X′) = 8.5, *J*(AA′) = *J*(XX′) = 2.8, *J*(A′X) = *J*(AX′) = 0.3 (H-3′, H-5′); 7.45 vtd, 1 H, *J*(4,5,6) = 7.8, *J*(3,5) = 1.3 (H-5); 7.27 vtd, 1 H, *J*(3,4,5) = 7.7, *J*(4,6) = 1.3 (H-4); 7.19 AA′XX′, 2 H, *J*(AX) = *J*(A′X′) = 8.5, *J*(AA′) = *J*(XX′) = 2.8, *J*(A′X) = *J*(AX′) = 0.3 (H-2′, H-6′); 6.99 dd, 1 H, *J*(3,4) = 8.0, *J*(4,6) = 1.3 (H-6).

2-(4-Chlorophenoxy)benzene-1-diazonium tetrafluoroborate. A solution of 2-(4-chlorophenoxy)aniline hydrochloride in water and concentrated HCl was cooled in an ice bath with vigorous stirring[8]. The hydrochloride was diazotized at 5 °C by a slow addition of $NaNO_2$ in H_2O. The product was precipitated with $NaBF_4$ from the aqueous solution of the diazonium chloride in 65% yield, m.p. 148–149 °C, ref.[8] m.p. 148–149 °C. IR (KBr): 2 274 (N≡N).

2-Chlorodibenzofuran (**10**). The 2-(4-chlorophenoxy)benzene-1-diazonium tetrafluoroborate was added to iron(II) sulfate in boiling water and the product was steam distilled to afford 62% of **10**, m.p. 98–99 °C, ref.[8] m.p. 102–103 °C, ref.[11] m.p. 102 °C. ^{1}H NMR spectrum was in agreement with ref.[11].

4-Chlorodibenzofuran (**17**). A solution of **12** (5 g, 30 mmol) in dry THF under N_2-atmosphere was cooled to –60 to –70 °C. Butyllithium (25 ml, 40 mmol) was added dropwise with a syringe. The mixture was allowed to warm up to –5 to 0 °C and stirred for about 1 h. The mixture was cooled down again to –60 to –70 °C and a solution of Cl_2 in CCl_4 (25 ml, ≈36 mmol) was added dropwise. For another 2 h the mixture was stirred at –5 to 0 °C and then washed with an aqueous solution of $Na_2S_2O_5$, washed with water and dried over $MgSO_4$. The crude product was purified by column chromatography (silica gel, petroleum ether). Yield: 2.23 g (37%), m.p. 96.5 °C. ^{1}H NMR ($CDCl_3$): 7.93 dd, 1 H, *J*(8,9) = 8.1, *J*(7,9) = 1.0 (H-9); 7.83 dd, 1 H, *J*(2,3) = 8.5, *J*(1,3) = 1.0 (H-3); 7.64 dd, 1 H, *J*(6,7) = 8.1, *J*(6,8) = 1.0 (H-9); 7.49 vtd, 1 H, *J*(6,7,8) = 8.14, *J*(7,9) = 1.0 (H-7); 7.45 dd, 1 H, *J*(1,2) = 8.5, *J*(1,3) = 1.0 (H-1); 7.36 vtd, 1 H, *J*(7,8,9) = 8.1, *J*(6,8) = 1.0 (H-8); 7.26 vt, 1 H, *J*(1,2,3) = 8.5 (H-2).

2-(3,5-Dichlorophenoxy)-1-nitrobenzene was prepared from 3,5-dichlorophenol and 1-chloro-2-nitrobenzene in the same manner as 2-(4-chlorophenoxy)nitrobenzene in 75% yield. Yellow crystals, m.p. 78–79 °C (95% ethanol). ^{1}H NMR ($CDCl_3$): 7.56 dd, 1 H, *J*(3,4) = 8,0, *J*(3,5) = 1.6 (H-3); 8.02 dd, 1 H, *J*(3,4) = 7.9, *J*(3,5) = 1.8 (H-3); 7.61 ddd, 1 H, *J*(5,6) = 7.8, *J*(4,5) = 7.1, *J*(3,5) = 1.8 (H-5); 7.35 ddd, 1 H, *J*(3,4) = 7.9, *J*(4,5) = 7.4, *J*(4,6) = 1.5 (H-4); 7.15 t, 1 H, *J*(2′,4′,6′) = 1.5 J (H-4′); 7.14 dd, 1 H, *J*(4,5) = 7.1, *J*(4,6) = 1.5 (H-6); 6.90 d, 2 H, *J*(2′,6′) = *J*(4′,6′) = 1.5 (H-2′, H-6′).

2-(3,5-Dichlorophenoxy)aniline hydrochloride. The reduction of 1-(3,5-dichlorophenoxy)-2-nitrobenzene was carried out as described above. Recrystallisation of the crude product from ethanol yielded 91% of 2-(3,5-dichlorophenoxy)aniline hydrochloride as grey crystals, m.p. 167–168 °C. ^{1}H NMR (methanol-d_4): 7.59 dd, 1 H, *J*(5,6) = 7,9, *J*(4,6) = 1.6 (H-6); 7.51 ddd, 1 H, *J*(3,4) = 8.3, *J*(4,5) = 7.3, *J*(4,6) = 1.6 (H-4); 7.35 t, 1 H, *J*(2′,4′,6′) = 1.8 (H-4′); 7.3 ddd, 1 H, *J*(4,5) = 7.3, *J*(5,6) = 7.9, *J*(3,5) = 1.3 (H-5); 7.15 d, 2 H, *J*(2′,4′) = *J*(4′,6′) = 1.7 (H-2′, H-6′); 7.11 dd, 1 H, *J*(3,4) = 8.3, *J*(3,5) = 1.3 (H-3).

2-(3,5-Dichlorophenoxy)benzene-1-diazonium tetrafluoroborate. The diazotation of 2-(3,5-dichlorophenoxy)aniline hydrochloride was carried out in the same manner as described above. The precipitation of the product with an aqueous solution of $NaBF_4$ yielded 76% of diazonium tetrafluoroborate, m.p. 127–128 °C. IR (KBr): 2 263 (N≡N).

1,3-Dichlorodibenzofuran (**18**). The 2-(3,5-dichlorophenoxy)benzene-1-diazonium tetrafluoroborate was added to iron(II) sulfate in boiling water and the product was

steam-distilled to afford 65% of **18**, m.p. 118–119 °C. ^{1}H NMR ($CDCl_3$): 8.19 d, 1 H, *J*(8,9) = 7,6 (H-9); 7.56 d, 1 H, *J*(5,6) = 8.1 (H-6); 7.51 ddd, 1 H, *J*(6,7) = 8.1, *J*(7,8) = 7.1, *J*(7,9) = 1.5 (H-7); 7.48 d, 1 H, *J*(2,4) = 1.5 (H-2); 7.40 ddd, 1 H, *J*(7,8) = 7.1, *J*(8,9) = 7.6, *J*(6,8) = 1.5 (H-8); 7.33 d, 1 H, *J*(2,4) = 1.5 (H-4).

Electrolyses. General Procedure

The electrolyses were carried out at about –5 to 0 °C in an undivided cell shown in Fig. 1, with a cylindrical stainless steel gauze or a zinc-plate cathode concentrically surrounding a rod of magnesium as anode. The solvent was DMF, which was distilled just before use. A low concentration of Bu_4NBr as supporting electrolyte was required to adjust the initial conductivity since ionic species were produced during the reaction. The batch cell had to be cooled to dissipate the heat evolved during the electrolysis and to keep the temperature below 0 °C. After bubbling CO_2 for about 30 min to expel the residual air, a low overpressure (0.1 bar) of CO_2 was applied. The electrodes were connected to a power supply and a constant current of I = 0.25 A was passed through the stirred mixture. Every hour, a small sample was taken to monitor the decrease of the substrate concentration and the increase of the product concentration with respect to the charge consumption. After the electrolysis, the reaction mixture was acidified with 6 M HCl under ice-cooling. All products and residual substrate were then extracted three times with diethyl ether. The organic layer was extracted with 6 M HCl to remove residual DMF and then dried over $MgSO_4$. An aliquot part (50%) of the organic extract was treated with 2 M aqueous NaOH to separate carboxylic acids from neutral products. The aqueous layer was again acidified (pH control) and extracted with diethyl ether which, after evaporation, led to the carboxylic acid or a mixture of acids. Samples taken during the electrolysis were acidified with 6 M HCl and extracted with diethyl ether. A solution of CH_2N_2 in diethyl ether was added dropwise to the organic layer to form the methyl esters of the carboxylic acids. Identification of the products was performed by the GC-MS technique. An aliquot part of 25% of the organic extract was again derivatized with an etheral solution of CH_2N_2 and supplied with an internal standard for quantitative GC analysis.

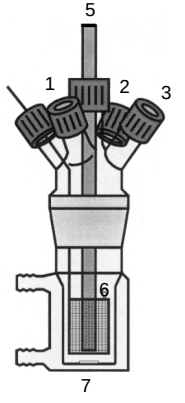


FIG. 1
Batch cell for electrocarboxylations. 1 CO_2 inlet, 2 thermometer, 3 activated carbon absorber, 4 cathode contact, 5 anode (Mg rod), 6 cathode (stainless steel net or Zn-sheet), 7 magnetic stirring bar

Electrocarboxylation of 1,2,4,5-Tetrachlorobenzene (**1**)

Starting material 1.92 g (8.9 mmol); cathode material zinc plate; charge 2.8 F; recovery 79%; current efficiency 36% (20% carboxylic acids); products (GC): 1,2,4,5-tetrachlorobenzene (**1**) 1%, 1,2,4-trichlorobenzene 8%, 1,2-dichlorobenzene 1%, 1,3-dichlorobenzene 2%, 1,4-dichlorobenzene 9%, chlorobenzene 4%, benzene 2%, 2,5-dichloroterephthalic acid (**3**) 17%, 2,4,5-trichlorobenzoic acid (**2**) 14%, 2,5-dichlorobenzoic acid 6%, 4-chlorobenzoic acid 2%, 3-chlorobenzoic acid 1%, benzoic acid 3%.

Dimethyl 2,5-dichloroterephthalate. M.p. 134–136 °C, ref.[12] m.p. 138–140 °C. ^{1}H NMR ($CDCl_3$): 7.92 s, 2 H (H-3, H-6); 3.96 s, 6 H (OCH_3). ^{13}C NMR ($CDCl_3$): 163.8 (C=O), 133.2 (C-3, C-6), 132.9 (C-2, C-5), 131.5 (C-1, C-4), 52.5 (OCH_3). MS: 266 (1) [M^+], 264 (16) [M^+], 262 (25) [M^+], 233 (65) [$M^+ - OCH_3$], 232 (11) [$M^+ - OCH_3$], 231 (100) [$M^+ - OCH_3$], 205 (8) [$M^+ - CO_2CH_3$], 203 (12) [$M^+ - CO_2CH_3$], 190 (11) [$M^+ - CO_2CH_3$, $- CH_3$], 188 (19) [$M^+ - CO_2CH_3$, $- CH_3$], 146 (10) [$M^+ - 2\ CO_2CH_3$], 144 (13) [$M^+ - 2\ CO_2CH_3$,], 111 (15) [$C_6H_2Cl^+$], 109 (35) [$C_6H_2Cl^+$], 74 (42), 59 (39) [$CO_2CH_3^+$].

Electrocarboxylation of Hexachlorobenzene (**4**)

Starting material 1.28 g (4.5 mmol); cathode material zinc plate; charge 6.1 F; recovery 90%; current efficiency 16% (16% carboxylic acids); products (GC): hexachlorobenzene (**4**) 7%, pentachlorobenzene 1%, pentachlorobenzoic acid (**5**) 64%, tetrachloroterephthalic acid 10%, tetrachloroisophthalic acid 8%.

Methyl pentachlorobenzoate. M.p. 97–97.5 °C, ref.[13] m.p. 98–100 °C. MS: 312 (5) [M^+], 310 (16), 308 (23), 306 (14), 281(20) [$M^+ - OCH_3$], 279 (65), 277 (100), 275 (63), 251 (12), 249 (18) [$M^+ - CO_2CH_3$], 247 (12), 215 (9) [$M^+ - CO_2CH_3 - Cl$], 214 (17), 212 (13), 181 (4) [$M^+ - CO_2CH_3$, – 2 Cl], 179 (10), 177 (12), 144 (13)) [$M^+ - CO_2CH_3$, – 3 Cl], 142 (21), 107 (11) [$M^+ - CO_2CH_3 - 4$ Cl], 106 (4), 59 (8) [$CO_2CH_3^+$].

Dimethyl tetrachloroterephthalate. M.p. 157 °C, ref.[12] m.p. 156–157 °C. ^{13}C NMR ($CDCl_3$): 163.4 (C=O), 136.4 (C-1, C-4), 129.5 (C-2, C-3, C-5, C-6), 53.6 (OCH_3). MS: 334 (12) [M^+], 332 (26), 330 (18), 305 (11) [$M^+ - OCH_3$], 303 (50), 301 (100), 299 (82), 275 (2)) [$M^+ - CO_2CH_3$], 273 (4), 271 (3), 225 (5), 223 (19), 221 (18), 216 (3), 214 (6), 212 (5), 181 (4), 179 (8), 177 (8), 59 (13) [$CO_2CH_3^+$].

Dimethyl tetrachloroisophthalate. ^{13}C NMR ($CDCl_3$): 163.5 (C=O), 134.0 (C-4, C-6), 132.1 (C-5), 132.6 (C-2), 126.9 (C-1, C-3), 53.6 (OCH_3).

Electrocarboxylation of 4-Chlorobiphenyl (**6**)

A. Starting material 1.68 g (8.9 mmol); cathode material steel gauze; charge 2.5 F; recovery 99%; current efficiency 39%; products (GC): 4-chlorobiphenyl (**6**) 7%, biphenyl (**7**) 26%, biphenyl-4-carboxylic acid (**8**) 26%, dihydrobiphenylcarboxylic acids 40%.

B. Starting material 1.68 g (8.9 mmol); cathode material Pb plate; charge 1.8 F, recovery 91%; current efficiency 55%; products (GC): 4-chlorobiphenyl (**6**) 8%, biphenyl (**7**) 23%, biphenyl-4-carboxylic acid (**8**) 20%, dihydrobiphenylcarboxylic acids 41%.

Biphenyl-4-carboxylic acid (**8**). M. p. 224 °C, ref.[14] m.p. 225–226 °C. ^{1}H NMR ($(CD_3)_2CO$): 8.08 AA′XX′, 2 H, J(AX) = J(A′X′) = 8.1, J(AX′) = J(A′X) = 1.9, J(AA′) = J(XX′) = 0.5 (H-3, H-5); 7.68 AA′XX′, 2 H, J(AX) = J(A′X′) = 8.1, J(AX′) = J(A′X) = 1.9, J(AA′) = J(XX′) = 0.5 (H-2, H-6); 7.60 m, 2 H (H-2′, H-6′); 7.38 m, 2 H (H-3′, H-5′); 7.29 m, 1 H (H-4′).

Electrocarboxylation of 4,4′-Dichlorobiphenyl (**9**)

Starting material 2.0 g (8.9 mmol), cathode material steel gauze; charge, recovery and current efficiency could not be determined because the product mixture was not fully analyzed; products (GC, relative yields): 4,4′-dichlorobiphenyl (**9**) 4%, 4-chlorobiphenyl (**6**) 3%, biphenyl (**7**) 6%, biphenyl-4-carboxylic acid (**8**) 38%, other carboxylic acids 49%.

Electrocarboxylation of 2-chlorodibenzofuran (**10**)

A. Starting material 1.803 g (8.84 mmol); cathode material steel gauze; charge 36 F; recovery 75%; current efficiency 3%; products (GC): 2-chlorodibenzofuran (**10**) 49%, dibenzofuran (**12**) 3%, dibenzofuran-4-carboxylic acid (**11**) 1%, 2-chlorodibenzofurancarboxylic acid 1%, dibenzofuran-1,4-dicarboxylic acid (**13**) 7%, 2-chlorodibenzofuran-1,4-dicarboxylic acid (**14**) 13%.

B. Starting material 1.803 g (8.84 mmol); cathode material zinc plate; charge 8.1 F; recovery 76%; current efficiency 12%; products (GC): 2-chlorodibenzofuran (**10**) 6%, dibenzofuran (**12**) 1%, dibenzofuran-4-carboxylic acid (**11**) 7%, 2-chlorodibenzofurancarboxylic acid 11%, dibenzofuran-1,4-dicarboxylic acid (**13**) 30%, 2-chlorodibenzofuran-1,4-dicarboxylic acid (**14**) 20%.

Methyl dibenzofuran-4-carboxylate. M.p. 94.5 °C. ^{1}H NMR ($CDCl_3$): 8.14 dd, 1 H, *J*(2,3) = 7.6, *J*(1,3) = 1.5 (H-3); 8.11 dd, 1 H, *J*(1,2) = 7.6, *J*(1,3) = 1.5 (H-1); 7.96 dd, 1 H, *J*(8,9) = 7.6, *J*(7,9) = 1.0 (H-9); 7.71 dd, 1 H, *J*(6,7) = 7.6, *J*(6,8) = 1.0 (H-6); 7.51 vtd, 1 H, *J*(6,7,8) = 7.6, *J*(6,7) = *J*(7,8) = 1.0 (H-7); 7.41 vt, 1 H, *J*(1,2,3) = 7.6 (H-2); 7.38 vtd, 1 H, *J*(7,8) = *J*(8,9) = 7.6, *J*(6,8) = 1.0 (H-8); 4.05 s, 3 H (OCH_3). ^{13}C NMR ($CDCl_3$): 165.4 (C=O), 156.5 (C-5a), 154.9 (C-4a), 129.3 (CH), 127.8 (CH), 126.0 (C_q), 125.3 (CH), 123.2 (CH), 123.1 (C_q), 122.4 (CH), 120.6 (CH), 115.3 (C_q), 112.2 (C-6), 52.3 (OCH_3).

Electrocarboxylation of 3-Chlorodibenzofuran[11] (**15**)

A. Starting material 1.80 g (8.84 mmol); cathode material zinc plate; charge 3.2 F; recovery 85%; current efficiency 31%; products (GC): 3-chlorodibenzofuran (**15**) 3%, dibenzofuran (**12**) 3%, dibenzofuran-3-carboxylic acid (**16**) 71%, dibenzofuran-1,4-dicarboxylic acid (**13**) 8%.

B. Starting material 1.80 g (8.84 mmol); cathode material steel gauze; charge 9.6 F; recovery 99%; current efficiency 13%; products (GC): 3-chlorodibenzofuran (**15**) 35%, dibenzofuran (**12**) 15%, dibenzofuran-3-carboxylic acid (**16**) 27%, dibenzofuran-1,4-dicarboxylic acid (**13**) 22%.

Methyl dibenzofuran-3-carboxylate. ^{1}H NMR ($CDCl_3$): 8.25 d, 1 H, *J*(2,4) = 1.5 (H-4); 8.06 dd, 1 H, *J*(1,2) = 8.1, *J*(2,4) = 1.5 (H-2); 8.00 d, 1 H, *J*(1,2) = 8.1 (H-1); 7.99 dd, 1 H, *J*(8,9) = 8.1, *J*(7,9) = 1.5 (H-9); 7.61 dd, 1 H, *J*(6,7) = 8.1, *J*(6,8) = 1.5 (H-6); 7.52 vtd, 1 H, *J*(6,7,8) = 8.1, *J*(7,9) = 1.5 (H-7); 7.38 vtd, 1 H, *J*(7,8,9) = 7.6, *J*(6,8) = 1.5 (H-8); 3.98 s, 3 H (OCH_3). MS: 226 (64) [M^+], 195 (76) [$M^+ - OCH_3$], 167 (30) [$M^+ - CO_2CH_3$], 139 (100), 113 (18), 98 (18), 87 (26) [$C_4H_7O_2^+$], 74 (28) [$C_3H_6O_2^+$], 63 (51), 59 (18) [$CO_2CH_3^+$], 50 (34), 39 (42).

Dimethyl dibenzofuran-1,4-dicarboxylate. M.p. 142 °C (diethyl ether). ^{1}H NMR ($CDCl_3$): 8.77 dd, 1 H, *J*(8,9) = 8.1, *J*(7,9) = 1.5 (H-9); 8.11 d, 1 H, *J*(2,3) = 8.7 (H-3); 8.01 d, 1 H, *J*(2,3) = 8.7 (H-2); 7.72 dd, 1 H, *J*(6,7) = 8.1, *J*(6,8) = 1.5 (H-6); 7.58 vtd, 1 H, *J*(6,7,8) = 8.1, *J*(7,9) = 1.5 (H-7); 7.42 vtd, 1 H, *J*(7,8,9) = 8.1, *J*(6,8) = 1.5 (H-8), 4.08 s, 6 H (OCH_3). MS: 284 (74) [M^+],

253 (81) [$M^+ - OCH_3$], 225 (9) [$M^+ - CO_2CH_3$], 194 (13) [$M^+ - CO_2CH_3$, $- OCH_3$], 166 (20) [$M^+ - 2\ CO_2CH_3$], 138 (33), 126 (22), 111 (22), 87 (23), 74 (12), 59 (100) [$CO_2CH_3^+$], 39 (25).

Electrocarboxylation of 4-Chlorodibenzofuran (**17**)

Starting material 1.616 g (8.00 mmol); cathode material zinc plate; charge 3.5 F; recovery 90%; current efficiency 29%; products (GC): 4-chlorodibenzofuran (**17**) 7%, dibenzofuran (**12**) 3%, dibenzofuran-4-carboxylic acid (**11**) 57%, dibenzofuran-1,4-dicarboxylic acid (**13**) 16%, unidentified dihydrodibenzofurandicarboxylic acids 17%.

Electrocarboxylation of 1,3-Dichlorodibenzofuran (**18**)

Starting material 1.897 g (8.00 mmol); cathode material zinc plate; charge 3.8 F; recovery 95%; current efficiency 38%; products (GC): 1,3-dichlorodibenzofuran (**18**) 5%, dibenzofuran-1-carboxylic acid (**20**) 14%, dibenzofuran-3-carboxylic acid (**16**) 11%, 1-chlorodibenzofuran-3-carboxylic acid (**19**) 46%, 3-chlorodibenzofuran-1-carboxylic acid 5%, dibenzofuran-1,3-dicarboxylic acid (**21**) 11%, dibenzofuran-1,4-dicarboxylic acid (**13**) 2%.

Methyl dibenzofuran-1-carboxylate. ^{1}H NMR ($CDCl_3$): 8.81 dd, 1 H, *J*(8,9) = 7.6, *J*(7,9) = 1.2 (H-9); 8.02 dd, 1 H, *J*(2,3) = 8.1, *J*(2,4) = 1.0 (H-2); 7.77 dd, 1 H, *J*(3,4) = 8.1, *J*(2,4) = 1.0 (H-4); 7.59 dd, 1 H, *J*(6,7) = 8.0, *J*(6,8) = 1.2 (H-6); 7.52 vtd, 1 H, *J*(6,7,8,) = 8.0, *J*(7,9) = 1.2 (H-7); 7.50 vt, 1 H, *J*(2,3,4) = 8.1 (H-3); 7.39 vtd, 1 H, *J*(7,8,9) = 7.6, *J*(6,8) = 1.2 (H-8); 4.10 s, 3 H (OCH_3). ^{13}C NMR ($CDCl_3$): 167.1 (C=O), 156.9 (C-4a), 156.7 (C-5a), 128.3 (C-7), 126.2 (C-3, C-9), 125.6 (C-2), 125.3 (C_q), 124.2 (C_q), 122.92 (C-8), 122.88 (C_q), 116.0 (C-4), 111.3 (C-6), 52.2 (OMe). MS: 226 (62) [M^+], 195 (65) [$M^+ - OCH_3$], 167 (27) [$M^+ - CO_2CH_3$], 139 (100).

Methyl 1-chlorodibenzofuran-3-carboxylate. ^{1}H NMR ($CDCl_3$): 8.76 dd, 1 H, *J*(8,9) = 8.2, *J*(7,9) = 1.5 (H-9); 7.98 d, 1 H, *J*(2,4) = 1.9 (H-2); 7.74 d, 1 H, *J*(2,4) = 1.9 (H-4); 7.57 dd, 1 H, *J*(6,7) = 8.2, *J*(6,8) = 1.5 (H-6); 7.53 vtd, 1 H, *J*(6,7,8) = 8.2, *J*(7,9) = 1.5 (H-7); 7.39 vtd, 1 H, *J*(7,8,9) = 8.2, *J*(6,8) = 1.5 (H-8); 4.05 s, 3 H (OCH_3). MS: 262 (31), 260 (100) [M^+], 231 (24), 229 (75) [$M^+ - OCH_3$], 203 (12), 201 (32) [$M^+ - CO_2CH_3$], 175 (22), 173 (65), 166, (16) [$M^+ - CO_2CH_3$, – Cl], 138 (46), 111 (24), 98 (19), 87 (46), 74 (24), 63 (32), 59 (15) [$CO_2CH_3^+$], 50 (18), 39 (25) .

Dimethyl dibenzofuran-1,3-dicarboxylate. ^{1}H NMR ($CDCl_3$): 8.87 dd, 1 H, *J*(8,9) = 8.2, *J*(7,9) = 1.3 (H-9); 8.69 d, 1 H, *J*(2,4) = 1.3 (H-2); 8.40 d, 1 H, *J*(2,4) = 1.3 (H-4); 7.62 dd, 1 H, *J*(6,7) = 8.2, *J*(6,8) = 1.3 (H-6); 7.60 vtd, 1 H, *J*(6,7,8) = 8.2, *J*(7,9) = 1.3 (H-7); 7.42 vtd, 1 H, *J*(7,8,9) = 8.2, *J*(6,8) = 1.3 (H-8); 4.08 s, 3 H (OCH_3).

Electrocarboxylation of Dibenzofuran (**12**)

Starting material 1.50 g (8.90 mmol); cathode material zinc plate; charge, recovery and current efficiency could not be determined because the product mixture was not fully analyzed; products (GC, relative yields): dibenzofuran-1,4-dicarboxylic acid (**13**) 68%, 1,2-dihydrodibenzofuran-1,4-dicarboxylic acid (**22**) 20%, other carboxylic acids 11%.

Dimethyl 1,2,3,4-tetrahydro-3,4-methanodibenzofuran-trans-1,4-dicarboxylate (**23**). M.p. 113–113.5 °C (diethyl ether). ^{1}H NMR (C_6D_6): 7.30 dd, 1 H, *J*(8,9) = 7.7, *J*(7,9) = 1.3 (H-9); 7.23 dd, 1 H, *J*(6,7) = 8.2, *J*(6,8) = 1.0 (H-6); 6.96 vtd, 1 H, *J*(6,7,8) = 7.7, *J*(7,9) = 1.0 (H-7); 6.84 vtd, 1 H, *J*(7,8,9) = 7.7, *J*(6,8) = 1.3 (H-8); 3.34 dd, 1 H, *J*(1,2) = 7.3, *J*(1,2′) = 2.4 (H-1); 2.14 dvt, 1 H, *J*(2,2′) = 14.6, *J*(1,2′,3) = 2,4 (H-2′); 1.91 dd, 1 H, *J*(10,10′) = 4.5, *J*(3,10′) = 9.4

(H-10′); 1.74 m, 1 H (H-3); 1.49 ddd, 1 H, *J*(6,7) = 8.0, *J*(2,2′) = 14.6, *J*(1,2) = 7.3, *J*(2,3) = 4.7 (H-2); 1.03 dd, 1 H *J*(10,10′) = 4.5, *J*(3,10) = 7.3 (H-10). ^{13}C NMR ($CDCl_3$): 173.9 (C=O), 171.4 (C=O), 154.4 (C-5a), 152.5 (C-4a), 127.2 (C-9a), 123.7 (C-8), 122.7 (C-7), 119.5 (C-6), 111.3 (C-9), 107.1 (C-9b), 52.5 (OCH_3), 52.3 (OCH_3), 36.2 (C-1), 27.2 (C-3), 27.1 (C-2), 22.7 (C-10), 22.2 (C-4). MS: 300 (17) [M^+], 268 (53) [$M^+ - OCH_3$], 241 (24) [$M^+ - CO_2CH_3$], 209 (42), 181 (100), 152 (12), 139 (3), 59 (7).

Electrocarboxylation of 2-Chlorodibenzo[1,4]dioxine (**24**)

Starting material 875 mg (4.00 mmol); cathode material zinc plate; charge 5.8 F; recovery 94%; current efficiency 17%; products (GC): 2-chlorodibenzo[1,4]dioxine (**24**) 71%, dibenzo[1,4]dioxine 2%, dibenzo[1,4]dioxine-2-carboxylic acid (**25**) 21%.

Methyl dibenzo[1,4]dioxine-2-carboxylate. M.p. 104–105 °C, ref.[15] m.p. 103–107.5 °C. ^{1}H NMR ($CDCl_3$): 7.60 dd, 1 H, *J*(3,4) = 8.4, *J*(1,3) = 2.0 (H-3); 7.51 d, 1 H, *J*(1,3) = 2.0 (H-1); 6.89 m, 4 H (H-6, H-7, H-8, H-9); 6.86 d, 1 H, *J*(3,4) = 8.4 (H-4); 3.90 s, 3 H (OCH_3).

Electrocarboxylation of 1-Chloronaphthalene (**26**)

Starting material 1.30 g (8.00 mmol); cathode material zinc plate; charge 3.1 F; recovery 92%; current efficiency 32%; products (GC): 1-chloronaphthalene (**26**) 27%, naphthalene (**27**) 17%, 1-naphthoic acid (**28**) 37%, dihydronaphthalenedicarboxylic acids 10%.

Methyl 1-naphthoate. MS: 186 (56) [M^+], 155 (76) [$M^+ - OCH_3$], 127 (100) [$M^+ - CO_2CH_3$], 115 (4), 101 (9), 87 (5), 77 (26) [$C_6H_5^+$], 63 (18), 59 (3) [$CO_2CH_3^+$], 51 (13), 39 (6).

Electrocarboxylation of Naphthalene (**27**)

Starting material 1.14 g (8.90 mmol); cathode material zinc plate; charge, recovery and current efficiency could not be determined because the product mixture was not fully analyzed; products (GC, relative yields): 1,4-dihydronaphthalene-*trans*-1,4-dicarboxylic acid (**29**) 30%, 1,2-dihydronaphthalene-*trans*-1,2-dicarboxylic acid (**30**) 30%, 1-naphthoic acid (**28**) <5%, other dihydronaphthalenedicarboxylic acids 10%.

Dimethyl 1,4-dihydronaphthalene-trans-1,4-dicarboxylate. MS: 244 (2) [$M^+ - 2$ H], 215 (3) [$M^+ - OCH_3$], 214 (11) [$M^+ - CH_3OH$], 187 (22) [$M^+ - CO_2CH_3$], 186 (3) [$M^+ - 60$], 155 (30) [$M^+ - 91$], 128 (100), [$M^+ - 2\ CO_2CH_3$], 59 (14) [$CO_2CH_3^+$].

Dimethyl 1,2-dihydronaphthalene-trans-1,2-dicarboxylate. ^{1}H NMR ($CDCl_3$): 7.20–7.30 m, 3 H, 7.09 m, 1 H, 6.54 dd, 1 H, *J*(3,4) = 9.6, *J*(2,4) = 2.2 (H-4); 6.06 dd, 1 H, *J*(3,4) = 9.6, *J*(2,3) = 4.6 (H-3); 4.29 d 1 H, *J*(1,2) = 7.7 (H-1); 3.98 ddd, 1 H, *J*(1,2) = 7.7, *J*(2,3) = 4,6, *J*(2,4) = 2.2 (H-2); 3.75 s, 3 H (OCH_3); 3.70 s, 3 H (OCH_3). MS: 246 (3) [M^+], 214 (8) [$M^+ - CH_3OH$], 187 (30) [$M^+ - CO_2CH_3$], 186 (60), 155 (51) [$M^+ - 91$], 128 (100) [$M^+ - 2\ CO_2CH_3$], 59 (19).

X-Ray Structure Analyses

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-143347 (methyl ester of **11**), CCDC-138250 (dimethyl ester of **13**) and CCDC-138251 (**23**). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk; *cf*. also the ORTEP plots (Fig. 2) and Table I. The structures were

TABLE I
X-Ray structural data of **11**-methyl ester, **13**-dimethyl ester and **23**

	11-Methyl ester	**13**-Dimethyl ester	**23**
Chemical formula	$C_{14}H_{10}O_3$	$C_{16}H_{12}O_5$	$C_{17}H_{16}O_5$
Formula weight	226.22	284.26	300.30
Crystal system	monoclinic	triclinic	triclinic
Space group	P_21/c	$P_{\bar{1}}$	$P_{\bar{1}}$
Crystal color	white	white	white
Lattice parameters, pm, °	a = 1 633.9(2)	a = 1 028.3(1)	a = 826.2(1)
	b = 1 694.8(2)	b = 1 060.2(1)	b = 910.4(1)
	c = 1 700.1(2)	c = 1 301.9(1)	c = 1 125.1(1)
	α = 90.00	α = 80.62(1)	α = 108.08(1)
	β = 166.800(10)	β = 73.27(1)	β = 91.19(1)
	γ = 90.00	γ = 76.24(1)	α = 115.12(1)
Volume of cell, pm^3	1 075.0(2)·10^6	1 313.4(2)·10^6	716.87(13)·10^6
Z value	4	4	2
R factor	0.0774	0.0539	0.0744
Rw factor	0.1734	0.1480	0.1645
Goodness-of-fit-value	1.189	0.905	2.750

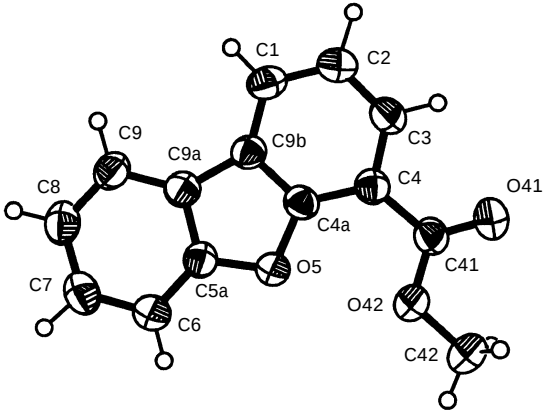


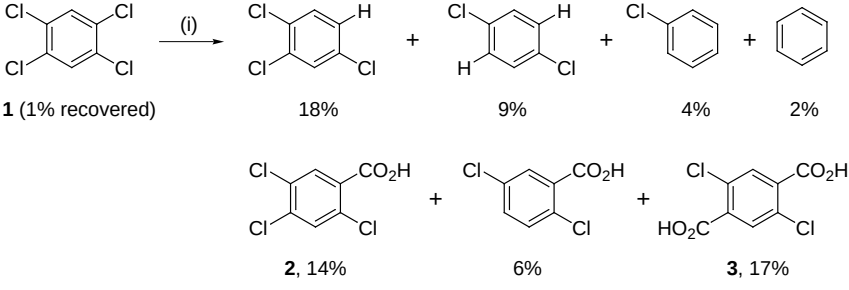
FIG. 2
ORTEP plot of the X-ray structure of **11**-methyl ester. Thermal ellipsoids are drawn on the 50% probability level

solved by direct methods using the SIR97 program[16] and refined by full-matrix-block least-squares on F^2 using all data and the SHELXL97 program[17].

RESULTS AND DISCUSSION

Electrocarboxylation in the Benzene Series

Electrocarboxylation of benzenes with up to three chloro substituents has been described by Perichon *et al.*[6]. They have shown that halogenated benzenes can well be transformed into monocarboxylic acids with good to excellent yields. Our aim was to test the electrocarboxylation of higher chlorinated benzenes because these are the notorious xenobiotics. We used 1,2,4,5-tetrachlorobenzene (**1**) and hexachlorobenzene (**4**) as starting material. One interesting question was whether di- or oligocarboxylic acids would be formed, which does not occur in the case of trichlorobenzene[6]. Moreover, the total extent of dehalogenation, either by hydrodechlorination or carboxylation, was important. The result of the electrocarboxylation of **1** is shown in Scheme 1.



(i) e, CO_2, DMF; Mg anode, Zn cathode

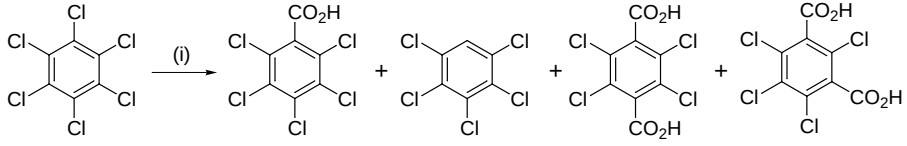
SCHEME 1

The selectivity of the reaction is low. In addition to a mixture of neutral reduction products (33% overall yield) including benzene, three carboxylic acids (37% in total) were formed. The same neutral compounds are formed if **1** is electrolyzed in methanol in the absence of carbon dioxide[2]. Unexpectedly, 2,5-dichloroterephthalic acid (**3**) was the main acid formed. Obviously, the primary product 2,4,5-trichlorobenzoic acid (**2**) is selectively carboxylated in position 4 but **3** is not further reduced. No isophthalic acid derivatives were found.

Since we used an aprotic solvent-supporting electrolyte (dry DMF), the formation of hydrodechlorinated products needs a comment. We can ex-

clude traces of water and even tetrabutylammonium ions, which can undergo Hofmann elimination, as the source of protons because their amount is too small to account for the considerable yields of protonated products. Therefore, only DMF itself comes into question as a source of protons.

The electrocarboxylation of hexachlorobenzene (**4**) is shown in Scheme 2. The dehalogenation almost stops after the replacement of only one chlorine atom. Only small amounts of tetrachlorocarboxylic acids are found – a result quite similar to the electrocarboxylation of **1**. Pentachlorobenzoic acid (**5**) is the main product of this reaction. Pentachlorobenzene, the product of hydrodechlorination, is only produced in trace amounts.



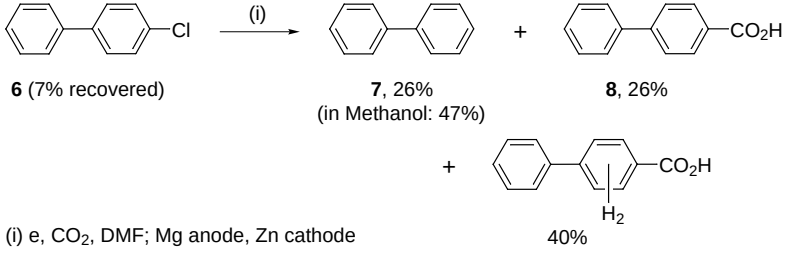
4 (7% recovered) **5**, 64% 1% 10% 8%

(i) e, CO_2, DMF; Mg anode, Zn cathode

SCHEME 2

Electrocarboxylation in the Biphenyl Series

We have shown earlier that the electroreduction of halogenated biphenyls (PCB) in methanol yields biphenyl (**7**) as expected, but also, in addition, hydrogenated products[2]. The interesting question was now, whether the electrocarboxylation could suppress this side reaction or not. Our experiments were performed with 4-chlorobiphenyl (**6**) and 4,4′-dichlorobiphenyl (**9**) as substrates. The products found after the electrocarboxylation of **6** are shown in Scheme 3. As expected, biphenyl-4-carboxylic acid (**8**) was formed but in a yield of only 26%, whereas 40% of a mixture of three dihydrocarboxylic acids was also obtained. In addition, hydro-



6 (7% recovered) **7**, 26% (in Methanol: 47%) **8**, 26%

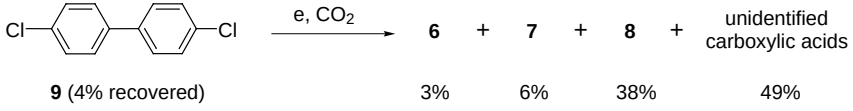
40%

(i) e, CO_2, DMF; Mg anode, Zn cathode

SCHEME 3

dechlorination to **7** took place, which was, however, not further hydrogenated. The acid **8** was clearly identified after isolation. Its dihydroderivatives could not be fully characterized. But from their mass spectra one could conclude that all the three should be isomeric 4-phenylcyclohexadiene-1-carboxylic acids, *i.e.* hydrogenation occurs in the benzene ring of **8** carrying the carboxylic group.

The result of the electrocarboxylation of **9** is shown in Scheme 4. The acid **8** is formed as the main product whereas hydrodechlorination to **6** and **7** is only a minor side-reaction. Again a considerable amount of hydrogenated carboxylic acids of the same type as in the case of Scheme 3 is formed as found by GC-MS analysis. Neither hydrobiphenyls nor biphenyl-4,4′-dicarboxylic acid were detectable.



SCHEME 4

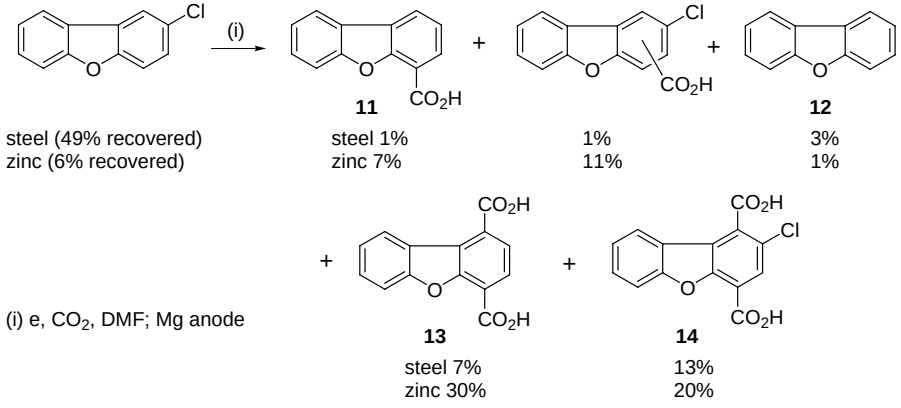
Electrocarboxylation in the Dibenzofuran Series

Direct electrolysis of halogenated dibenzofurans in protic solvents produces, besides dibenzofuran (**12**) as the main product, also a relatively large amount of dihydrodibenzofurans[11,18]. This is a crucial drawback of this procedure because of the toxicity of these products for most microorganisms. To face this disadvantage, we have developed new procedures to avoid the formation of dihydrodibenzofurans. The indirect electrolysis with mediators (*e.g.* Ni) has turned out to be a suitable method. It can be carried out in methanol as protic solvent and leads to dibenzofuran (**12**) in a very good yield without formation of any hydrogenated dibenzofuran species[1]. Electrocarboxylation could provide an alternative because carboxylic acids should not be as toxic and, in addition, should also exhibit an increased bioavailability.

The direct electroreduction of 2-chlorodibenzofuran (**10**) is a slow process because the cleavage of the Cl–C bond requires the highest activation energy in the monochlorodibenzofuran series. As a result, the current efficiency is very low and the main product of the direct electrolysis in protic solvents is 1,4-dihydrodibenzofuran, instead of dibenzofuran[11] (**12**). Better results are again achieved by use of a Ni mediator[1].

Electrocarboxylation of **10** at a zinc cathode produces a multitude of carboxylic acids. Stainless steel as cathode material is disadvantageous since

the turnover and the current efficiency are low and the complexity of the product mixture is even more marked (Scheme 5). Surprisingly, the expected dibenzofuran-2-carboxylic acid is not at all formed. Instead, its isomer, dibenzofuran-4-carboxylic acid (**11**) can be isolated as methyl ester



SCHEME 5

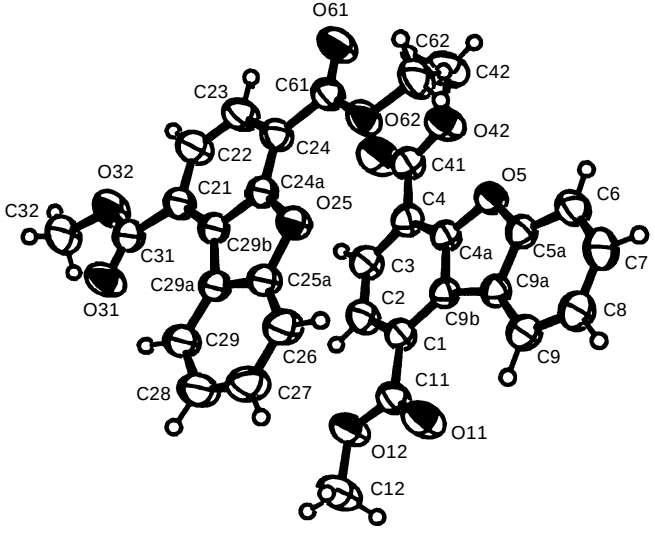


FIG. 3

ORTEP plot of the X-ray structure of **13**-dimethyl ester. Two independent molecules with slightly but not significantly different geometrical parameters are located in the asymmetric unit. Thermal ellipsoids are drawn on the 50% probability level

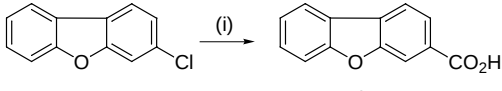
from the mixture (7%). Its structure was elucidated by analysis of the ^{1}H and ^{13}C NMR spectra including correlation techniques and eventually by an X-ray structural analysis (Fig. 2, Table I). Furthermore, it turned out to be identical with the electrocarboxylation product of 4-chlorodibenzofuran **17** (see below).

Dibenzofuran-1,4-dicarboxylic acid (**13**) was produced as the main product (30%). Also 2-chlorodibenzofuran-1,4-dicarboxylic acid (**14**) and 2-chlorodibenzofuranmonocarboxylic acids were found in considerable amounts.

We have proved the structure of **13** by NMR spectroscopy and, unequivocally, by an X-ray diffraction analysis of its dimethyl ester (Fig. 3, Table I).

The formation of **11**, **13**, and **14** needs an explanation. Obviously, **10** and the dechlorinated **12** can be directly substituted with carboxyl groups during electrolysis in an overall carboxydeprotonation process. Reductive addition of two carbon dioxide molecules to arenes under formation of dihydrodicarboxylic acids – though without rearomatization – is known from the literature[6,19]. In order to prove this possibility, we have performed the direct electrocarboxylation of **12** and confirmed our results (see below).

The electrocarboxylation of 3-chlorodibenzofuran (**15**) leads to dibenzofuran-3-carboxylic acid (**16**) as the main product (Scheme 6), as expected. Especially at a zinc cathode **16** is formed with high yield and selectivity. The by-products **12** and **13** are formed in only small amounts. The application of stainless steel as cathode leads to a considerably smaller overall yield of only 65%. Furthermore, the product selectivity is not satisfactory (*cf.* Fig. 4).



15	**16**	+ **12**	+ **13**
steel (36% recovered)	27%	15%	22%
zinc (3% recovered)	71%	3%	8%

(i) e, CO_2, DMF; Mg anode

SCHEME 6

As mentioned above, **13** is formed by direct electrocarboxylation of **12**. This reaction occurs as a follow-up reaction and is the reason for the formation of **13** during the electrolysis of **15** and of any other chlorinated dibenzofuran in the presence of carbon dioxide. This is demonstrated in Fig. 5.

Dibenzofuran-4-carboxylic acid **11** was the main product obtained by electrocarboxylation of 4-chlorodibenzofuran **17**. The selectivity was rather high (yield of **11**: 57%). Dibenzofuran **12** and the dicarboxylic acid **13** as well as several unidentified dihydrodibenzofurandicarboxylic acids were found as by-products (Scheme 7).

The electrocarboxylation of 1,3-dichlorodibenzofuran (**18**) leads to a multitude of products (Scheme 8). Nevertheless, the reaction shows a certain se-

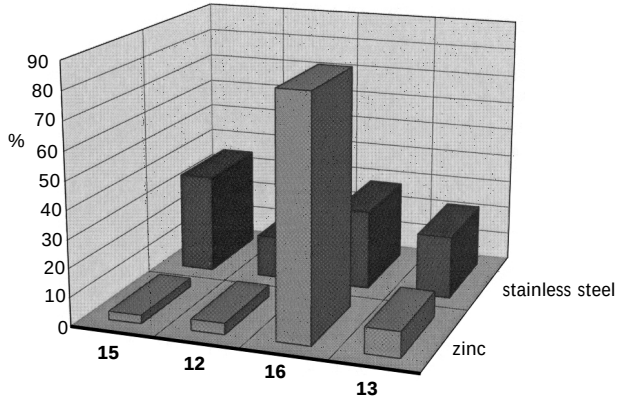


FIG. 4
Product distribution after electrocarboxylation of **15** at zinc or stainless steel cathodes (*cf.* Scheme 6)

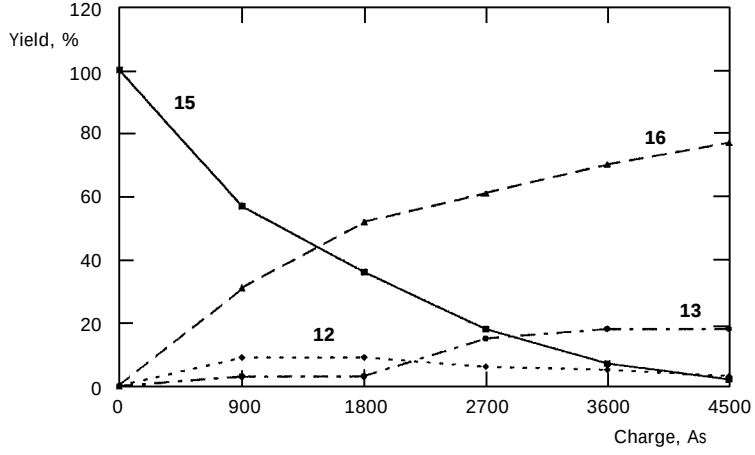
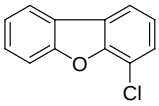


FIG. 5
Course of electrocarboxylation of **15** at a Zn cathode



(i)

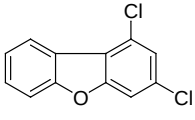
11 + **12** + **13** + dihydrodibenzofuran-dicarboxylic acids

17 (7% recovered) 57% 3% 16% 17%

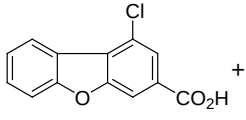
(i) e, CO_2, DMF; Mg anode, Zn cathode

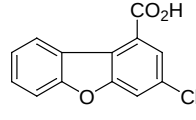
SCHEME 7

lectivity. Reaction temperatures below 0 °C favour the formation of 1-chlorodibenzofuran-3-carboxylic acid (**19**) as the main product. However, there is only a relatively low level of dehalogenation (*cf.* Scheme 8). An increase of the temperature above 0 °C leads to a lower selectivity but causes a higher level of dehalogenation, *i.e.*, the formation of more dibenzofuran-1-carboxylic (**20**)[20], -3-carboxylic (**16**) and -1,3-dicarboxylic acids (**21**).



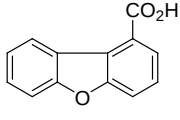
e, CO_2

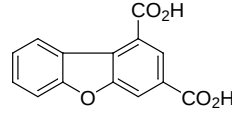


+ 

+ **16**

18 (5% recovered) **19**, 46% 5% 11%

+ 

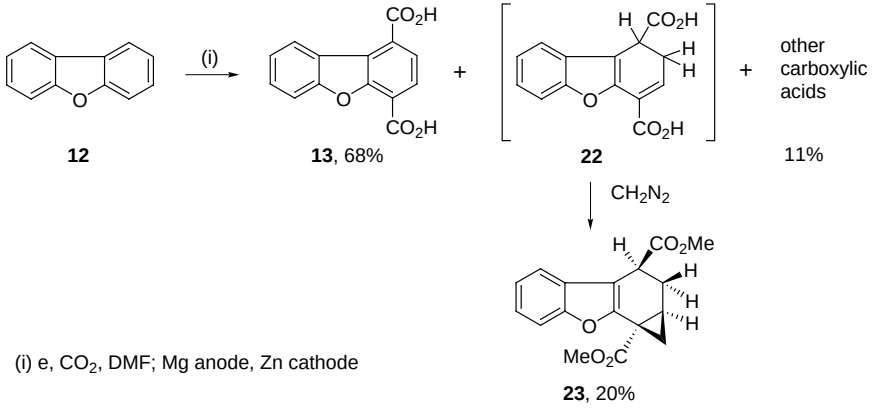
+ 

+ **13**

20, 14% **21**, 11% 2%

SCHEME 8

Dibenzofuran (**12**) itself was studied because we wanted to verify the formation of **13** from any chlorodibenzofuran *via* **12** as an intermediate. Scheme 9 shows that the electrocarboxylation of **12** leads indeed to **13** with good selectivity and a yield of 68%. In addition, other carboxylic acids are formed. One crystalline component could be isolated in 20% yield from the mixture of methyl esters, which were prepared by use of diazomethane. According to its NMR spectra, we assigned a cyclopropano structure (**23**) to this ester and could confirm it by X-ray structural analysis of a single crystal. Figure 6 shows an ORTEP plot of **23**, which also demonstrates the *trans* configuration of the two ester groups (*cf.* also Table I). Obviously, **23** is formed from the dihydrodicarboxylic acid **22** in the reaction with diazomethane. Dihydro derivatives such as **22** should also be precursors of **13**. Their rearomatization occurs at the anode since the electrolyses are run in an undivided cell.



SCHEME 9

Chlorinated dibenzo[1,4]dioxines ("dioxine") are perhaps the most notorious environmental pollutants. Although we have shown that monochloro-, dichloro- and oligochlorodibenzo[1,4]dioxines can be dechlorinated by direct electroreduction in methanol[3], we were interested in their electrocarboxylation. We chose 2-chlorodibenzo[1,4]dioxine (**24**) as an example. However, a first preliminary experiment was disappointing. Only a 21% yield of dibenzo[1,4]dioxine-2-carboxylic acid (**25**) was achieved besides traces of dibenzo[1,4]dioxine (Scheme 10). Further investigations to improve this result are under way.

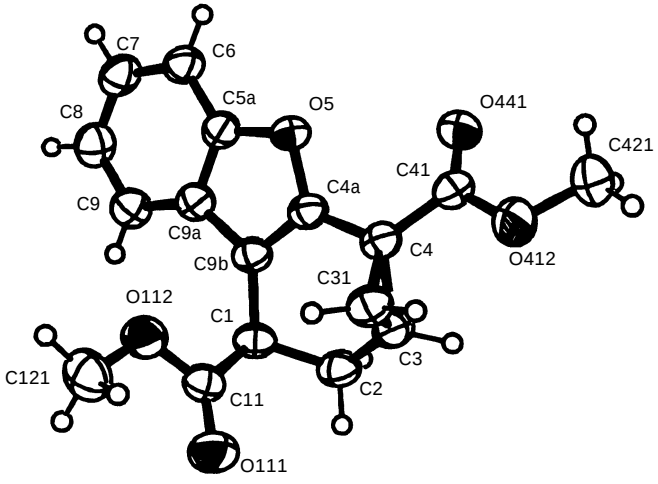
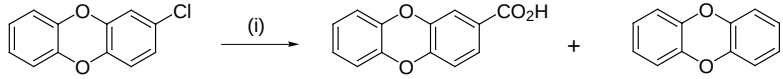


FIG. 6
ORTEP plot of the X-ray structure of **23**. Thermal elllipsoids are drawn on the 50% probability level



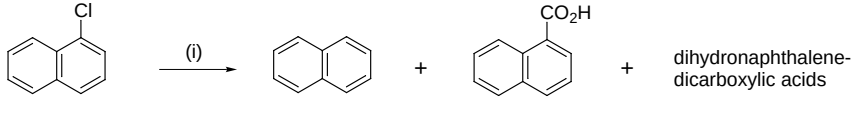
24 (71% recovered) **25**, 21% 2%

(i) e, CO_2, DMF; Mg anode, Zn cathode

SCHEME 10

Electrocarboxylations in the Naphthalene Series

1-Chloronaphthalene (**26**) forms a mixture of naphthalene (**27**), dihydro- and tetrahydronaphthalenes on direct electroreduction in methanol[18]. Electrocarboxylation gives a 37% yield of the expected 1-naphthoic acid (**28**) and a mixture of dihydronaphthalenedicarboxylic acids, according to MS analysis (Scheme 11). An identification of these components could not be achieved.

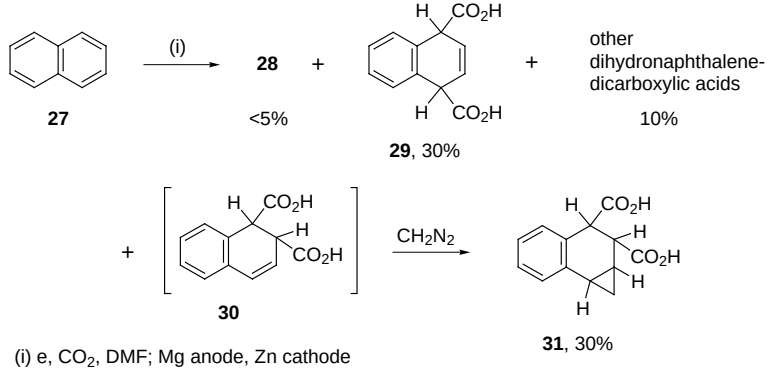


26 (27% recovered) **27**, 17% **28**, 37% 10%

(i) e, CO_2, DMF; Mg anode, Zn cathode

SCHEME 11

Di- or tetrahydronaphthalenes are not formed. Formation of 1,4-dihydronaphthalene-1,4-dicarboxylic acid (**29**) in the electroreduction of **27** in DMF at a mercury cathode in the presence of carbon dioxide has been observed[19] as early as 1959. We have applied our conditions to the electrocarboxylation of **27** and also obtained **29** together with its isomer **30** and a mixture of other dihydronaphthalenedicarboxylic acids (Scheme 12).



27 <5% **29**, 30% 10%

30 **31**, 30%

(i) e, CO_2, DMF; Mg anode, Zn cathode

SCHEME 12

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20. *Note added in proof*. Recently we have electrocarboxylated (at a zinc cathode) 1-chlorodibenzofuran, which is not easily accessible, and obtained a 76% yield of dibenzofuran-1-carboxylic acid.