

Electroreduction of Organic Compounds, 34 [1]. Cathodic Dehalogenation of Chloroarenes with Electron-Donating Substituents

Olaf Kranz and Jürgen Voss

Institut für Organische Chemie der Universität Hamburg,
Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Reprint requests to Prof. Dr. Jürgen Voss. Fax: +49 (0) 40 42838 5592.
E-mail: voss@chemie.uni-hamburg.de

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The electrochemical reduction of chlorinated arenes with electron-donating substituents, *i. e.* chlorotoluenes, -anisoles and -phenols, is studied. Preparative electrolyses are run in various solvent-supporting electrolytes under potentiostatic and galvanostatic conditions at lead or carbon cathodes. A partial and mostly regioselective hydrodechlorination of compounds with two or more chloro substituents is possible under suitable conditions. The replacement of one single chloro substituent, in particular in a *para*-position, is difficult. Highly toxic and persistent oligochloro derivatives are thus transformed into less problematic compounds with a low degree of chlorination. The chlorine content of real-life materials such as extracts of soil contaminated with chlorinated phenols and Nitrofen[®] can also be significantly decreased by electroreduction.

Key words: Electrolysis, Dehalogenation, Chloroarenes

Introduction

Now as before, chlorinated organic compounds play a role in technical syntheses as they represent useful materials with favourable properties which are suitable intermediates for synthesizing follow-up compounds with wide-spread applications. However, these products themselves and some of the by-products such as polychlorinated dibenzofurans and dibenzo-*p*-dioxins which are formed during the technical syntheses and during uncontrolled incineration processes are not only toxic but also in many cases very persistent. Some of them have become nearly ubiquitous and the development of methods for their degradation is therefore important and necessary [2–4].

Over the last decade we have investigated the cathodic reduction of chlorinated arenes such as oligochlorobenzenes [5, 6], polychlorinated biphenyls (PCB) [5, 6], naphthalenes (PCN) [6, 7], dibenzofurans (PCDF) [6, 8, 9], and dibenzo-*p*-dioxins (PCDD) [6, 8]. Besides the direct electroreduction we also studied a Ni(0)-mediated variant [6, 10] and the electrocarboxylation process [1, 6]. All these substrates are more or less electron-deficient compounds which exhibit relatively low reduction potentials. On the other hand, chlorinated arenes with electron-donating substituents

are also environmentally relevant compounds. They are expected to be more difficult to reduce because their electron density is decreased. We present here our results on the cathodic reduction of these classes of compounds.

Results and Discussion

Electroreduction of chlorinated toluenes

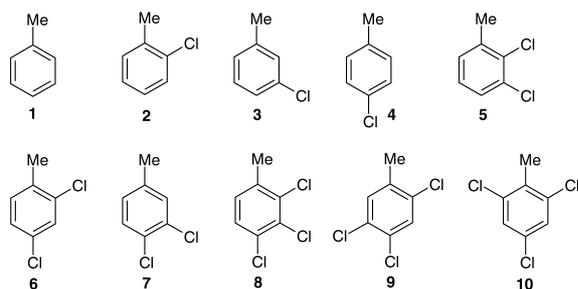
Chlorinated toluenes, *e. g.* 2-chloro- (**2**) and 4-chlorotoluene (**4**), are especially used for the industrial production of pesticides and dyes [11]. Polychlorinated toluenes have also been proposed as substitutes for PCB in hydraulic systems [12]. Suitable procedures for the degradation of these compounds are therefore required. For example, chlorotoluenes can be dechlorinated by catalytic hydrogenation [13–17].

Having performed some preliminary experiments 14 years ago [18], we have now studied the cathodic dechlorination of the monochloro- (**2–4**), dichloro- (**5–7**), and trichlorotoluenes (**8–10**) in a comprehensive way.

Table 1 shows the polarographic half-wave reduction potentials of chloroarenes **2–10**. Expectedly, the number of steps corresponds to the number of chloro substituents. According to the cyclic voltamograms all

Table 1. Polarographic half-wave potentials $E_{1/2}$ vs. Ag/AgBr of chlorotoluenes and chloroanisoles in DMF.

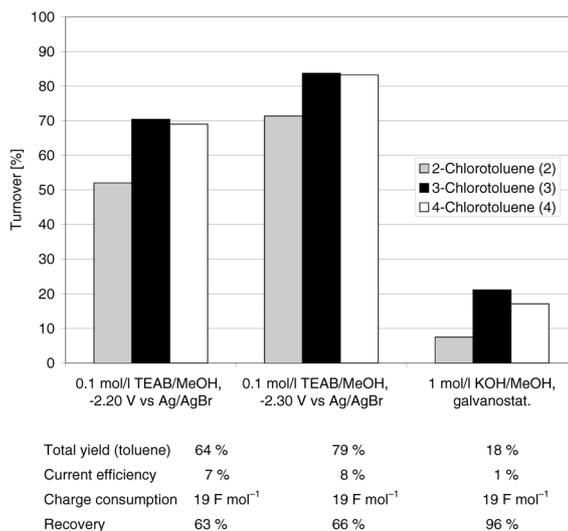
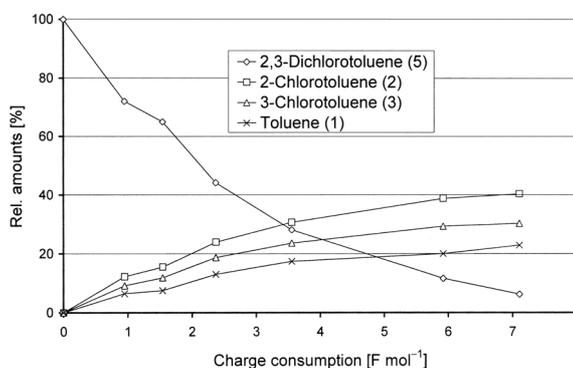
Compound	$E_{1/2}$ [V]			
2-Chlorotoluene (2)	-2.10			
3-Chlorotoluene (3)	-2.09			
4-Chlorotoluene (4)	-2.10			
2,3-Dichlorotoluene (5)	-2.10	-1.89		
2,4-Dichlorotoluene (6)	-2.09	-1.84		
3,4-Dichlorotoluene (7)	-2.10	-1.88		
2,3,4-Trichlorotoluene (8)	-2.08	-1.82	-1.53	
2,4,5-Trichlorotoluene (9)	-2.10	-1.85	-1.62	
2,4,6-Trichlorotoluene (10)	-2.10	-1.83	-1.60	
2-Chloroanisole (12)	-2.04			
3-Chloroanisole (13)	-2.03			
4-Chloroanisole (14)	-2.05			
2,3-Dichloroanisole (15)	-2.05	-1.81		
2,4-Dichloroanisole (16)	-2.03	-1.77		
3,4-Dichloroanisole (17)	-2.06	-1.78		
3,5-Dichloroanisole (18)	-2.04	-1.80		
2,3,4-Trichloroanisole (19)	-2.02	-1.73	-1.49	
2,4,6-Trichloroanisole (20)	-2.04	-1.74	-1.51	
2,3,4,5-Tetrachloroanisole	-2.06	-1.78	-1.58	-1.33
2,3,4,6-Tetrachloroanisole	-2.06	-1.78	-1.61	-1.35
2,3,5,6-Tetrachloroanisole	-2.08	-1.84	-1.61	-1.37
Pentachloroanisole (21)	-2.08	-1.82	-1.61	-1.35 -1.10



steps are irreversible, *i. e.*, the electron uptake is accompanied by the rapid elimination of a chloride anion. An inspection of the reduction potentials does not allow a prediction of any regioselectivity.

Equimolar mixtures of the three isomers **2–4** were electrolysed in methanol on a preparative scale under potentiostatic and galvanostatic conditions. Tetraethylammonium bromide (TEAB) or potassium hydroxide were used as electrolyte. The results are shown in Fig. 1.

Obviously the dechlorination of 3-chlorotoluene (**3**) and 4-chlorotoluene (**4**) occurs to a similar extent whereas the turnover of 2-chlorotoluene (**2**) is lower. The same order, *meta* = *para* > *ortho*, was observed for the hydrogenation under rhodium- [14] or palladium/C-catalysis [15]. This selectivity can be explained by an effect of steric hindrance through the *or-*

Fig. 1. Results of the electroreduction of the monochlorotoluenes **2–4**.Fig. 2. Course of the potentiostatic electroreduction of 2,3-dichlorotoluene (**5**) at -2.10 V in 0.1 M methanolic TEAB solution.

tho-methyl substituent. The total product yields were 64% of toluene (**1**) at -2.20 V vs. Ag/AgBr and 79% of **1** at -2.30 V vs. Ag/AgBr, and the current efficiencies were 7–8% for the electrolyses under potentiostatic conditions. Due to the volatility of toluene (**1**), the recovery was only 60–70% depending on the duration of the electrolyses. The yield of **1** was only 18% when the electroreduction was performed under the more practical galvanostatic conditions in methanolic potassium hydroxide solution. The selectivity in favour of the dehalogenation of **3** and **4** was more pronounced in this case. Due to the predominant hydrogen evolution, the current efficiency for the desired dechlorination process dropped to only 1%.

Substrate	Charge consumption [F mol ⁻¹]	Recovered substrate [%]	Product distribution [%]					Current efficiency [%]
			^a	2	3	4	1	
5	7.1 ^b	6	–	40	31	–	23	33
5	34 ^c	49	–	25	8	–	18	4
6	2.3 ^b	46	–	6	–	48	n.d. ^d	46
6	33 ^c	47	–	32	–	19	2	3
7	4.7 ^b	36	–	–	12	46	6	30
7	35 ^c	36	–	–	21	26	17	5
8	36 ^b	n.d. ^d	n.d. ^d	12	5	60	23	12
8	36 ^c	8	59 ^e	16	2	12	3	5
9	18 ^b	n.d. ^d	11 ^f	26	21	37	4	20
10	18 ^b	2	25 ^g	45	–	28	n.d. ^d	19

^a Dichlorotoluenes formed from the trichlorotoluenes; ^b potentiostatic conditions (–2.10 to –2.20 V vs. Ag/AgBr, *cf.* Experimental), 0.1 M TEAB in MeOH; ^c galvanostatic conditions (1.0 A, 509 A m⁻²), 1 M KOH in MeOH; ^d not detectable; ^e 3% **5** + 55% **6** + 1% **7**; ^f 4% **6** + 1% **7** + 6% 2,5-dichlorotoluene; ^g 6% **6** + 19% 2,6-dichlorotoluene.

In order to learn more about the regioselectivity we studied the dechlorination of the dichlorotoluenes **5–7**. The reduction potential was adjusted at –2.10 V. In addition, galvanostatic electrolyses were performed. The results are compiled in Table 2.

No significant product selectivity was observed in the case of 2,3-dichlorotoluene (**5**). Since, however, the ratio of the three products **1**, **2**, and **3** remained nearly constant during the electrolysis (*cf.* Fig. 2 which corresponds to entry 1 in Table 2), again a preferred reduction of the *meta*-substituent is probable.

A turnover of 51% of **5** and a current efficiency of 4% was achieved in methanolic potassium hydroxide solution under galvanostatic conditions. The electroreduction of 2,4-dichlorotoluene (**6**) led to **4** as the main product. Obviously, in this case the steric effect of the methyl group is over-compensated by the electronic substituent effect of the second chloro substituent. As one would expect, the electroreduction of 3,4-dichlorotoluene (**7**) also yielded 46% of **4** as the main product besides 12% of **3** and 6% of **1**. Galvanostatic electroreduction of **6** and **7** led to mixtures of products. Possibly due to the absence of the easily reducible intermediate **3**, only a very small amount of **1** was formed from **6**.

Finally, the trichlorotoluenes **8–10** were electrolysed. The potentiostatic reduction of 2,3,4-trichlorotoluene (**8**) at –2.20 V (entry 7 in Table 2) was remarkably regioselective. Mainly **4** was formed with 60% yield besides considerable 23% of toluene (**1**) but only 12% of **3** and 5% of **2**. The successive elimination of chloro substituents thus occurs *via* **6** and **4** whereas **5** and **7** are minor products even during the course of the electrolysis (*cf.* Fig. 3 which corresponds

Table 2. Electroreduction of the dichlorotoluenes **5–7** and the trichlorotoluenes **8–10** with Pb-cathodes.

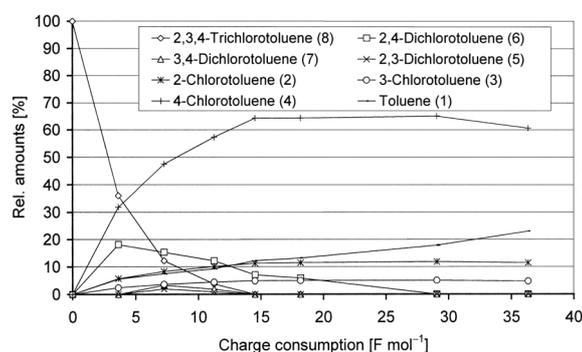


Fig. 3. Course of the potentiostatic electroreduction of 2,3,4-trichlorotoluene (**8**) at –2.20 V in 0.1 M methanolic TEAB solution.

to entry 7 in Table 2). The galvanostatic reduction of 2,3,4-trichlorotoluene (**8**) (entry 8 in Table 2) led to **6** as the main product (55%).

When 2,4,5-trichlorotoluene (**9**) was electrolysed at –1.65 V a partial dechlorination occurred which was, however, not regioselective. Continuation of the electrolysis at –2.10 V (entry 9 in Table 2) led to the expected products **4** (37%), **2** (26%), **3** (21%) and **1** (4%). The electroreduction of 2,4,6-trichlorotoluene (**10**) at –1.65 V resulted in the formation of 2,6-dichlorotoluene (33%) and **6** (8%); this mixture was further dechlorinated at –2.10 V (entry 10 in Table 2) to form, finally, **2** (45%) and **4** (28%).

Electroreduction of chlorinated anisoles

The single electron transfer, which is the initial step of the electroreduction of an arene, is impeded by the strong +M-effect of a methoxy substituent. The elimination of chloride anions from chloroanisoles

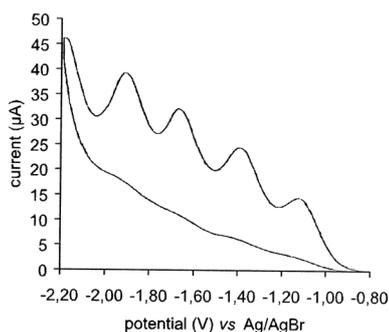
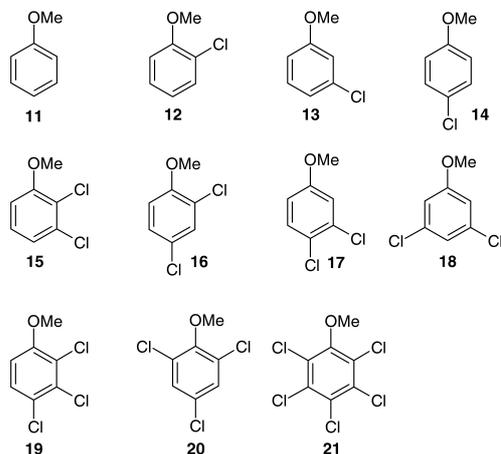


Fig. 4. Cyclic voltammogram of pentachloroanisole (**21**) in DMF at a scan rate of 400 mV s^{-1} .

should therefore occur at substantially more negative potentials as compared with arenes carrying electron-withdrawing substituents such as chlorobenzoic esters [19]. Unexpectedly however, this effect turned out to be not more pronounced than that of a methyl substituent in the chlorotoluenes as demonstrated by the polarographic reduction potentials shown in Table 1.

One reduction step is found for each chloro substituent in the molecule. This is exemplified in Fig. 4 showing the five irreversible reduction steps of pentachloroanisole (**21**). The first reduction potential is shifted to less negative values with an increasing number of chloro substituents (200–300 mV each), but no significant effect of the position of the substituents on the half-wave potentials is observed (*cf.* Table 1). Regioselective dechlorination was found when the selected congeners **12**–**21** were electrolysed on a preparative scale under protic conditions [20].



In general, the observed order of dechlorination was *meta* > *ortho* > *para* as one would expect on ac-

Table 3. Potentiostatic electroreduction ($-2.20 \text{ V vs. Ag/AgBr}$) of the monochloro- **12**–**14**, dichloro- **15**–**18** and trichloroanisoles **19** and **20** in methanolic TEAB solution at a Pb-cathode.

Substrate	Charge consumption [F mol ⁻¹]	Product distribution [%]				Current efficiency [%]
		12	13	14	11	
12	31	62	–	–	38	2.5
13	31	–	21	–	79	5.5
14 ^a	31	–	–	89	11	< 1
14 ^b	48	–	–	75	20 ^c	8
15	38	20–26	48–60	–	20–27	6.5
16	38	< 1	–	> 99	n.d. ^d	5
17	38	–	3	92	5	6
18 ^e	38	–	52	–	48	8
18 ^e	58	–	45	–	55	5
18 ^f	58	–	64	–	36	5
19 ^g	45	1	2	90	5	9
19 ^h	16	4	1	79	13	26
20	45	< 1	–	> 99	n.d. ^d	9

^a 200 mg **14**; ^b 1000 mg **14**; ^c + 4% 1-chloro-4-methoxy-1,4-cyclohexadiene; ^d not detectable; ^e membrane: Permion 4035; ^f membrane: Reichelt MA 3475; ^g 200 mg **19**; ^h 600 mg **19**.

count of the +M-effect of the methoxy group [21]. The yields of anisole (**11**) were 79%, 38%, and 11%, respectively, when 3-chloro- (**13**), 2-chloro- (**12**), and 4-chloroanisole (**14**) were electroreduced with the same consumption of electricity (31 F mol⁻¹). The current efficiencies of only 1–6% could be improved to 8–15% by increasing the normally applied substrate concentrations of 14 mM to 70 mM. In case of **14** also the chemical yield increased from 11% to 20% of **11**.

As it was expected from the results above, **14** was also formed as the main final product by the electrolysis of 2,4-dichloro- (**16**), 3,4-dichloro- (**17**), 2,3,4-trichloro- (**19**) and 2,4,6-trichloroanisole (**20**), whereas 2,3-dichloroanisole (**15**) gave a mixture of **11**, **12**, and **13**. About equal amounts of **11** and **13** were formed from 3,5-dichloroanisole (**18**). For comparison, we varied the charge consumption and used two different anion exchange membranes in this case. However, the result was not improved substantially. All yields are compiled in Table 3.

According to its electroanalytical data (*cf.* Table 1 and Fig. 4), pentachloroanisole (**21**) should rather easily release three or four chloro substituents on electroreduction. In fact, the potentiostatic electrolysis at -2.20 V predominantly led to 4-chloroanisole (**14**) (51%), and anisole (**11**) (26%), with smaller amounts of 2-chloro- (**12**, 5%) and 3-chloroanisole (**13**, 14%). As we have found in other cases [6], a trace (< 2%) of

Cathode material	Substrate amount [mmol]	Charge consumption [F mol ⁻¹]	Total turnover ^a [%]	Relative turnover [%]			Current efficiency [%]
				12	13	14	
Lead ^b	2.1	35	32	31	37	29	2
Lead ^c	10.9	8.5	9	8	12	7	2
Lead ^d	2.1	40	4	n.d. ^e	n.d. ^e	n.d. ^e	0.2
Carbon ^b	2.2	30	18	19	23	11	1
Carbon ^b	10.0	9.3	48	52	56	38	10
Carbon ^c	10.8	8.6	14	15	20	9	3

^a Total yield of **11**; ^b 0.1 M TEAB in MeOH; ^c 0.1 M TEAB in MeOH/H₂O 80:20 (v/v); ^d 0.1 M TEAB in MeOH/H₂O 50:50 (v/v); ^e not detectable.

Table 4. Potentiostatic electroreduction (−2.20 V vs. Ag/AgBr) of an equimolar mixture of the three chloroanisoles **12**–**14** at a lead or carbon cathode in varying SSE.^{b–d}

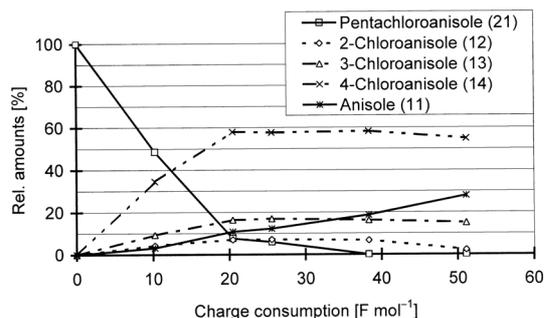


Fig. 5. Course of the potentiostatic electroreduction of pentachloroanisole (**21**) at −2.20 V in 0.1 M methanolic TEAB solution.

a hydrogenated species, possibly the Birch-type product 1-chloro-4-methoxy-1,4-cyclohexadiene, was detected. The current efficiency was 10%, *i. e.* higher than in the case of anisoles with fewer chloro substituents. Fig. 5 shows a typical course of an electrolysis of **21**.

The formation of **14** as the main final product is obvious, whereas its two isomers **12** and **13** appear as intermediates, which are further reduced to anisole. Only small amounts of dichloro-, trichloro- and tetrachloroanisoles (< 5% in total) can be detected during the starting phase of the electrolysis. Even at a reduction potential of only −1.10 V it was not possible to eliminate one chloro substituent selectively. Instead, a very complex product mixture was obtained. Once again, it contained 31% of **14** and 21% of **16** + **20**, *i. e.*, products that result from the predominant elimination of *meta*-chloro substituents. Only 3% of different tetrachloroanisole isomers were detected (*cf.* Experimental Section).

In the case of chlorinated anisoles, we have performed electrolyses under varying experimental conditions (*cf.* Table 4 and 5) in order to find a method which would be more suitable for practical applications. The commonly used lead cathodes tend to be corroded during the electrolysis. Furthermore lead, being a toxic

heavy metal, is not a good choice in view of a possible contamination of the environment. We explored therefore the suitability of carbon felt as cathode material, which has also been used for the electrodechlorination of dichloro- and trichlorophenoxyacetic acids [22]. In addition, we wanted to substitute our standard solvent-supporting electrolyte (SSE), TEAB in dry methanol, and tried to use the cheaper sodium bromide or even potassium hydroxide in aqueous methanol instead. Table 4 shows the results of our experiments with an equimolar mixture of **12**, **13**, and **14** as the test substrate.

The product distribution was determined by GLC. The turnover degree was calculated for each component separately. The amount of **11** as well as the current efficiencies correspond to the total turnover of the particular electrolysis. The data of Table 4 demonstrate that the total turnover and the current efficiencies, as referred to the rate of dehalogenation, significantly decrease with increasing content of water in the electrolyte, irrespective of the cathode material and the concentration of starting material used. Due to the enhanced decomposition of water, the turnover dropped to 4% in 50% aqueous methanol and no dechlorination at all took place in pure water. The use of a carbon felt cathode instead of a lead foil also led to a decrease of the turnover from 32% to 18%. It could, however, be improved to 48% at 10% current efficiency by applying a higher substrate concentration (entry 5 in Table 4). We have observed this effect in other cases too (see above). It may be due to a decrease of the protic nature of the double layer. The observed order of the dechlorination rates was *meta* > *ortho* > *para* in all cases.

Further experiments aimed at an optimisation of the electrolyses were performed with 2,3,4-trichloroanisole (**19**). The results are shown in Table 5.

As expected, a higher degree of dehalogenation (*i. e.* the sum of the weighted percentages of dichloro-,

Table 5. Electroreduction of 2,3,4-trichloroanisole **19** under varying conditions.

Cathode material	Charge consumption [F mol ⁻¹]	Degree of dechlorination [%]	Product distribution [%]				Current efficiency [%]
			16	17	14	11	
Lead ^a	16	68	< 1	< 1	79 ^b	13	26
Carbon ^a	16	54	25	14	54	4	20
Lead ^c	16	66	1	< 1	91	2	25
Carbon ^c	29	35	61	31	7	n.d. ^d	7
Carbon ^c	16	53	4	3	54	14	20
Lead ^e	24	42	19	15	38	2	11
Carbon ^e	52	21	32	24	3	n.d. ^d	2
Lead ^f	106	42	34	34	25	1	2
Carbon ^f	189	35	29	32	20	< 1	1
Lead ^g	711	58	11	13	62 ^h	2	0.5

^a Potentiostatic conditions (-2.20 V vs. Ag/AgBr), 0.1 M TEAB in MeOH; ^b + 4% **12** and 1% **13**; ^c potentiostatic conditions (-2.20 V vs. Ag/AgBr), 0.1 M TEAB in MeOH/H₂O 80:20 (v/v); ^d not detectable; ^e potentiostatic conditions (-2.20 V vs. Ag/AgBr), 1 M NaOH + 0.1 M NaBr in MeOH/H₂O 80:20 (v/v); ^f galvanostatic conditions (2.0 A or 3.0 A), 1 M KOH in MeOH; ^g galvanostatic conditions (3.0 A), 1 M KOH in MeOH/H₂O 75:25 (v/v); ^h + 1% **12** + 9% **13**.

monochloro- and unsubstituted anisoles) was achieved with a lead cathode as compared with the carbon felt. The amount of remaining dichloroanisoles was significantly higher when carbon felt was used. Similar results were observed after the addition of 20% of water to the solvent. The electrolyses at carbon cathodes were also less reproducible due to the ill-defined surface of fibre tissue and hence the varying current densities. In addition, the lower overall conductivity of carbon compared to a metal led to a considerable warming in case of high currents applied.

As a further experimental parameter, the supporting electrolyte was changed since the bromide anions of TEAB are oxidised to bromine at the anode, which should be avoided in view of a technical application. We tested sodium and potassium hydroxide. The degree of dechlorination was, however, much lower even at a lead cathode (see Table 5). This could be due to the smaller size of the cations, which influences the polarity of the double layer. Furthermore, the lack of a well-defined anodic reaction may influence the electroreduction. Last but not least, corrosion of the lead cathode is considerably higher in the strongly alkaline media. Interestingly, also the regioselectivity is lost, *i. e.*, 2,4-dichloro- (**16**) and 3,4-dichloroanisole (**17**) are formed in equal amounts.

Electroreduction of chlorinated phenols

Large quantities of chlorinated phenols have been produced industrially for decades. They were used as intermediates for the synthesis of pesticides, *e. g.* dichlorophenoxyacetic acid (2,4-D) and Nitrofen[®]

[(**36**), *cf. Electroreduction of real-life material*], as protecting material for wood, and for other purposes [23]. Although the production of chlorinated phenols is declining and has been totally discontinued in several countries, they still remain severe environmental pollutants because of their pronounced persistency and toxicity [24], their ubiquitous occurrence and because they represent the precursors of the polychlorinated dibenzofurans and dibenzo-*p*-dioxins. The biological [25,26] and the chemical degradation of chlorinated phenols by reductive [27–30] or oxidative [31,32] processes have therefore been the target of several different investigations. Electrochemical procedures have also been studied [33]. Besides the anodic oxidation [34–38], which seemed promising for the degradation of mono- and dichlorophenols, the mechanism of the cathodic reduction of chlorophenols [39] and the preparative electroreduction of pentachlorophenol **32** [40] have been explored. Most of these methods exhibit significant drawbacks with a view to practical applications. The direct electrooxidation of **25**, for instance, yields 2,7-dichlorodibenzo-*p*-dioxin as the product [34]. We were therefore interested in the behaviour of chlorinated phenols during the cathodic reduction and have studied the mono-, di-, tri-, tetra- and pentachloro derivatives **23**–**34**, of which **27** is the starting material for the production of 2,4-D and Nitrofen[®] (**36**).

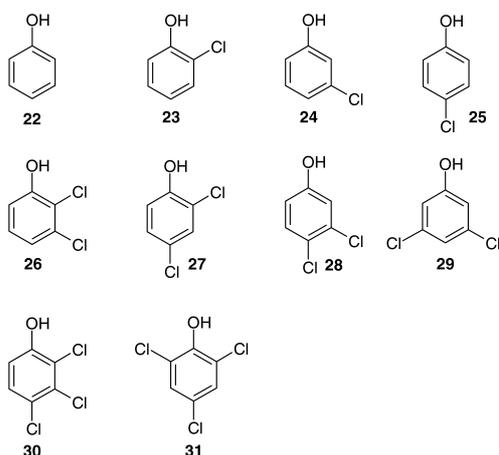
The strong +M-effect of the hydroxy substituent causes a very pronounced negative shift of the reduction potential of chlorophenols. In addition, the phenols are deprotonated under the basic conditions in the electrolyte and the resulting phenolate anions

Substrate	Cathode material	Charge consumption [F mol ⁻¹]	Recovered substrate [%]	Product distribution [%]					Current efficiency [%]
				27	23	24	25	22	
26	Carbon ^{a,b}	683	66	–	17	10	–	7	0.1
27	Carbon ^{a,b}	730	11	–	4	–	76	9	0.3
28	Lead ^b	730	n.d. ^c	–	–	16	39	45	0.4
28	Carbon ^{b,d}	730	8	–	–	9	73	8	0.3
28	Carbon ^{a,b}	547	43	–	–	9	41	7	0.2
29	Lead ^b	608	57	–	–	41	–	2	0.1
29	Carbon ^{b,d}	1094	30	–	–	62	–	8	0.1
30	Lead ^e	291	1	9	6	2	68	14	1.3
30	Carbon ^{b,d}	620	6	53 ^f	3	1	20	4	0.5
31	Lead ^e	146	3	33	10	–	51	3	2
31	Carbon ^{a,b}	660	43	39	n.d. ^c	–	13	5	0.4
32	Lead ^e	103	3	29 ^g	15	n.d. ^c	28	4	6

Table 6. Galvanostatic electroreduction of the dichlorophenols **26–29**, the trichlorophenols **30** and **31** and pentachlorophenol (**32**) in varying SSE.

^a Carbon felt; ^b aqu. 0.1 M NaOH + 0.1 M Na₂SO₄; ^c not detectable; ^d carbon fibres; ^e 1 M KOH in MeOH; ^f + 2% **26** + 11% **28**; ^g + 14% 2,5-dichlorophenol.

are even less easily to reduce although their solubility is increased in hydroxylic solvents. The reduction potentials of **23–31** could therefore not be determined in our standard SSE, which is decomposed at -2.2 V. In an inert SSE the half-wave potentials of the monochlorophenols are found at ca. -2.8 V (vs. Ag/AgCl) [41].



The preparative electroreduction of the three monochlorophenols **23–25** was performed in methanolic potassium hydroxide solution at a lead cathode under galvanostatic conditions. The anodic and cathodic compartments of the cell were divided by a cation exchange membrane. The three isomers were electrolysed as an equimolar mixture. Phenol (**22**) was found as the only product. Hydrogenated compounds could not be detected. The low total yield of 12% of **22** and the extremely low current efficiency of only 0.3% could not be increased by a change of the conditions, *e. g.* the use of a carbon felt instead of a lead cathode or aqueous sodium hydroxide as electrolyte. The

electroreduction was, however, regioselective. The conversion of **23**, **24** and **25** was 21%, 15% and 2%, respectively, *i. e.*, the ease of dechlorination follows the order *ortho* > *meta* \gg *para*. Due to the decomposition of the SSE at the necessary, extremely negative potentials, a satisfactory controlled potential electrolysis in TEAB/methanol was not possible.

2,3-Dichloro- (**26**), 2,4-dichloro- (**27**), 3,4-dichloro- (**28**) and 3,5-dichlorophenol (**29**) were electrolysed as single compounds. Galvanostatic conditions with lead or carbon cathodes were applied and aqueous sodium hydroxide containing sodium sulfate to increase the conductivity was used as SSE. The results are shown in Table 6.

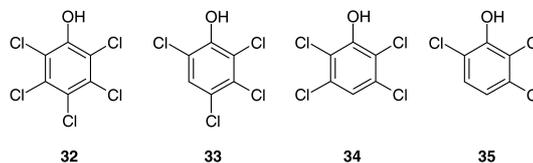
Again, the current efficiency was poor (0.1–0.4%) due to pronounced hydrogen evolution. The rate of dehalogenation was, however, higher. At least, one chloro substituent was removed easily from most substrates. As expected from the electrolysis results of **23–25**, an *ortho*-chloro substituent was first split off selectively followed by a *meta*-chloro substituent if present. But at a lead cathode even the *para*-chloro substituent of **28** could be replaced by hydrogen to a considerable extent, with 45% of phenol being formed (entry 3 in Table 6).

2,3,4-Trichlorophenol (**30**) and 2,4,6-trichlorophenol (**31**) were electrolysed galvanostatically, each of the two both in methanolic potassium hydroxide at a lead cathode and in aqueous sodium hydroxide/sulfate at a carbon felt cathode (Table 6). Expectedly, **30** led to **25** (68%) and **27** (9%) as the main products. Smaller amounts of **23** and **24** as well as 14% of **21** were found as by-products (lead cathode), with only 1% of starting compound **30** being recovered (entry 8 in Table 6). In the case of **31**, the product mixture (lead cathode) also consisted of **25** (51%) and **27** (33%) as the main

products besides **23** (10%) and phenol (**21**, 3%) as by-products (entry 10 in Table 6). Only 3% of the starting compound **31** was recovered. The results were less satisfactory when carbon fibres and water were used (entries 9 and 11 in Table 6). In summary, one can state that a partial dechlorination of the dichloro- and trichlorophenols to form mainly 4-chlorophenol (**25**) is well possible by cathodic reduction in methanolic potassium hydroxide whereas the use of an aqueous electrolyte and carbon cathodes is less favourable.

The electroreduction of pentachlorophenol (**32**) should lead to a complex multi-component mixture of products, and this is indeed found. Considerable analytical problems arise from this fact and we have reported on these in detail [42]. The results can be summarized as follows. Potentiostatic electrolyses in methanolic solution at a low reduction potential of -1.50 V and at low current densities led to a total turnover of only 48%. Mainly one *meta*- or the *para*-chloro substituent was removed and, in accordance with the statistical expectation, 2,3,4,6-tetrachlorophenol (**33**) and 2,3,5,6-tetrachlorophenol (**34**) were formed with 26% and 13% yield besides 5% of **31** and 1% of its isomer 2,3,6-trichlorophenol (**35**). If the controlled potential electroreduction of **32** was run for a prolonged time (charge consumption of 65 F mol^{-1}) at -2.20 V, 96% of the starting compound was consumed. However, a disappointing complex mixture of 12% tetrachlorophenols (**33**, **34**), 34% trichlorophenols (20% **31**, 11% **35**), 42% dichlorophenols and 8% 2-chlorophenol (**23**) but without phenol (**22**) was formed [42]. Substitution of chlorine in the *meta*-position also occurred during the independent potentiostatic electroreduction of the two tetrachlorophenols **33** and **34** at -1.70 V, which we have studied for comparison. After a charge consumption of 11 F mol^{-1} **34** was transformed into **35** (13%) and **26** (3%) under *meta*-substitution whereas **33** gave **31** (41%) and **27** (6%) under *meta*-substitution besides only 6% of **35** (*para*-substitution) and 5% of 2,4,5-trichlorophenol (*ortho*-substitution). Complex product mixtures resulted from electrolyses of the tetrachlorophenols at -2.20 V with charge consumptions of 35 F mol^{-1} (*cf.* Experimental Section). In the case of **33** the yields of dichloro- and trichlorophenols were 45% and 47%, respectively, besides 3% of 2-chlorophenol (**23**) and 4% of recovered **33**. Similarly, **34** yielded 8% monochloro- (mainly **23**), 41% dichloro- and 35% trichlorophenols with 16% recovered starting material **34**. The galvanostatic electrore-

duction of pentachlorophenol (**32**) led to a good total turnover of 97%. Expectedly, 4-chloro- (**25**, 28%) and 2,4-dichlorophenol (**27**, 29%) were the main products (entry 12 in Table 6). Only traces of trichloro- and tetrachlorophenols were found in the product mixture.



Putting together these results, a reasonable pathway of the consecutive steps can be deduced [42]. From a practical point of view on the other hand, the electroreduction under galvanostatic conditions is more important. Fortunately, the galvanostatic electroreduction of **32** in methanolic potassium hydroxide at a high current density of 255 A m^{-2} (see above) provided a more satisfying result. In summary, one can state that the electroreductive transformation of pentachlorophenol **32** into mono- and dichlorophenols, which are much less dangerous pollutants, can be achieved under suitable and practical conditions. Removal of the last chloro substituent to form phenol (**22**) is however not possible.

Electroreduction of real-life material

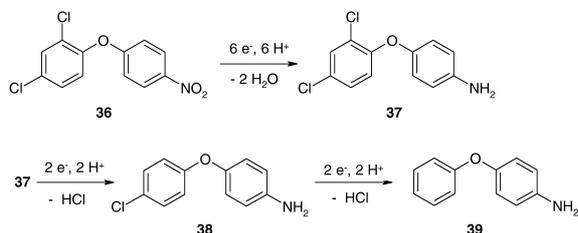
Within the context of a governmental project on soil remediation in which we were involved, we have studied the electrochemical reduction of the extract of a highly contaminated soil. The soil specimen from a former industrial site at Bitterfeld, Germany, was extracted with toluene in a Soxhlet apparatus. A careful analysis of this extract revealed a high content of chlorinated nitrodiphenyl ethers including the notorious [43] *Nitrofen*[®] [2,4-dichloro-4'-nitrodiphenyl ether (**36**)], chloronitrobenzenes and chlorophenols (Table 7). It has been shown that *Nitrofen*[®] is one of the most abundant contaminants in soils at the agrochemical production centres of the former GDR [44]. As recently as in 2002 public concern arose in Germany when considerable amounts of this pesticide were found in a granary near Berlin which was still in use.

Polarographic half-wave potentials of **36** and related compounds are also given in Table 7. These data and the respective cyclic voltamograms of chlorinated nitroarenes show that as expected, nitro groups are reduced first (in two steps) before dechlorination occurs.

Table 7. Concentrations of the main contaminants in the soil specimen studied and polarographic half-wave potentials $E_{1/2}$ vs. Ag/AgBr in DMF.

Compound	Concentration [mg/kg dry soil]	$E_{1/2}$ [V]			
Nitrofen® (36)	8600	-2.01	-1.72	-1.27	-0.59
4-Chloronitrobenzene	750			-1.29	-0.51
2,4,6-Trichlorophenol (31)	2000	-	-	-	-
2,4-Dichlorophenol (27)	1800	-	-	-	-

After removal of the solvent the soil extract was electrolysed under galvanostatic conditions in methanolic potassium hydroxide at a lead cathode. After a suitable work-up procedure the product distribution was determined by GLC and GLC-MS coupling. Three products had been formed from Nitrofen® (36): 4-amino-2',4'-dichlorodiphenyl ether (37, 6%), 4-amino-4'-chlorodiphenyl ether (38, 76%) and 4-aminodiphenyl ether (39, 18%). Thus, the nitro group was completely reduced and mostly one *ortho*- or both the chloro substituents were removed. No starting material could be detected. The 4-chloronitrobenzene was totally transformed into 4-chloroaniline without any dechlorination. As expected from the above mentioned results, the chlorinated phenols 27 and 31 were partially dechlorinated, with 24% of 23 being formed mainly at the expense of 31, the amount of which decreased from 37% to 6% by the electrolysis.



Conclusions

The cathodic reduction of chloroarenes is, as expected, impeded if substituents with inductive (methyl) or mesomeric (methoxy, hydroxy) electron-donating effects are present. This is evident from their half-wave reduction potentials. Nevertheless, a preparative scale electroreduction is possible under potentiostatic as well as under galvanostatic conditions. In particular, compounds with two or more chloro substituents are dechlorinated to a large extent. In nearly all cases the monochloro derivatives can be obtained, whereas the

complete removal of the chloro substituents is more difficult. The best results are obtained by use of lead cathodes with a methanolic tetraethylammonium bromide solution as solvent-supporting electrolyte. Carbon felt cathodes and potassium or sodium hydroxide solutions with substantial water contents can also be applied, although the efficiency is considerably lower. Real-life material, such as extracts of soils that are contaminated with chloroarenes can also be treated, with a significant decrease of the degree of chlorination being achieved.

Experimental Section

Melting points (corrected): Electrothermal. – NMR spectra: AMX 400 (Bruker). GC: GC 4200 (Carlo-Erba) and GC 8000 (Fisons) equipped with a DB 1701 column (J & W Scientific). – GC-MS: GC 8000 (Fisons) equipped with a 30 m DB 5 MS or a 50 m FFAP MS column in combination with an MD 800 quadrupole-MS (EI, 70 eV, Fisons).

Differential pulse polarography: VA 663/Polarecord 626 (Metrohm). Cyclic voltammetry: VA-Scanner E 612 (Metrohm) with plotter Servotec 720 (Metrawatt). Potentials were measured in DMF vs. an internal Ag wire as reference electrode, which corresponds to the Ag/AgBr couple in the TEAB solution. They were not converted into potentials vs. the usually applied SCE because we have used different and varying solvents for the preparative scale electrolyses. This would require solvent corrections in each case to get comparable potentials.

Materials: 2,3,4-Trichlorotoluene (8) [45,46], 2,4,5-trichlorotoluene (9) [47,48] and 2,4,6-trichlorotoluene (10) [47,49] were prepared according to literature procedures. 2,4-Dichloroanisole (16) [50,51], 3,4-dichloroanisole (17), 3,5-dichloroanisole (18) [52,53], 2,4,6-trichloroanisole (20) [54] and pentachloroanisole (21) [55,56] were prepared by methylation of the corresponding phenols with dimethyl sulfate in aqu. NaOH [45]. 2,3,4,5-Tetrachlorophenol [57] was obtained by demethylation of 2,3,4,5-tetrachloroanisole with aqu. 48% HBr [45]. The other substrate compounds were commercially available.

Electrolyses (general procedure): The electrolyses on a preparative scale were performed either potentiostatically (Wenking HP 88, Bank Electronic) or galvanostatically (DC Power Supply 6247B, Hewlett Packard) in the divided cell (volume of the cathodic and anodic compartment: 100 mL each) shown in Fig. 6 [9]. The potentials and currents were measured by use of a digital voltmeter (Conrad-Electronic). The consumption of electric charge was monitored with a DC current counter (Conrad-Electronic). The cathodic and the anodic compartments were separated by anion- or cation-exchange membranes. Lead cathodes (Pb foil Merck, analytical grade, 99.97%) were purified before use by subsequent

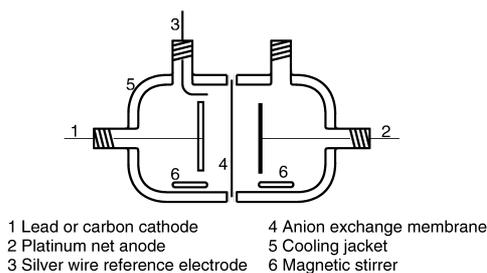


Fig. 6. Schematic setup of the divided batch cell.

rinsing with *aqua regia*, conc. HCl and hot water. Carbon felt cathodes (R&G GmbH Faserverbundwerkstoffe), in certain cases disentangled to fibre bunches, were extracted with acetone prior to use in order to remove textures and coating materials. They were fitted into the batch cell with a glass support.

Analytical protocol: During the electrolyses, samples of ca. 0.2–1.0 ml were taken from the catholyte for monitoring. They were diluted with the threefold amount of de-ionised water, acidified with half-conc. HCl and extracted with hexane (toluenes and anisoles) or diethyl ether (phenols and electrolysis products of the soil extract). The samples were dried over MgSO_4 and analysed by GLC.

After the end of the electrolysis the whole catholyte was treated in the same way. The product mixtures were isolated and analysed qualitatively and quantitatively by capillary GLC. The yields are corrected with respect to the recovery rates. The assignment of the peaks was performed by co-injection of reference compounds and comparison of the retention times. Standard solutions of the respective reference compounds with 1,2,4,5-tetramethylbenzene as internal standard were measured repeatedly for the quantitative determinations. The evaluation was performed automatically by use of the ChromCard software (Fisons). Relative response factors of the components were calculated and the peak areas corrected accordingly for the determination of the product distribution.

In addition, selected samples and the respective reference compound were studied by the GLC-MS coupling method.

In several cases, the phenols were transformed into the corresponding anisoles for the GLC analysis [58]. The electrolyte was extracted with diethyl ether and the extract was concentrated. The residue was dissolved in 20 ml acetone, an excess of iodomethane and K_2CO_3 were added and the mixture was refluxed for 12 h. After filtration the solution was diluted with diethyl ether and analysed by GLC as described above. The recovery was tested on examples and was found to be 75–88%. No selectivity for different chlorinated phenols was observed.

The capillary zone electrophoretic (CZP) analysis of chlorinated phenols has been described elsewhere [42].

Electroreduction of the chlorinated toluenes

All electrolyses were performed at Pb-cathodes with Reichelt Chemietechnik MA 3475 anion exchange membranes. A 0.1 M TEAB solution in MeOH was used as SSE in the case of controlled potential electrolyses (CPE). A 1 M KOH solution in MeOH was used in the case of controlled current electrolyses (CCE). The charge consumptions, current efficiencies for **5–10** and amounts of recovered substrate are given in Table 2.

The monochlorotoluenes were electrolysed as mixtures of each 203 mg (1.60 mmol) of **2**, **3** and **4**. CPE (–2.30 V, 20 F mol^{-1}); recovery: 66%; current efficiency: 8%; yield: 79% **1**; turnover: 71% **2**, 84% **3**, 83% **4**. CCE (1.0 A, 29 F mol^{-1}); recovery: 96%; current efficiency: 1.3%; yield: 18% **1**; turnover: 9% **2**, 25% **3**, 21% **4**.

2,3-Dichlorotoluene (**5**). CPE (–2.10 V); 507 mg (3.15 mmol) **5**; recovery: 84%; yields: 40% **2**, 31% **3**, 23% **1**. CCE (1.0 A); 531 mg (3.30 mmol) **5**; recovery: 76%; yields: 25% **2**, 8% **3**, 18% **1**.

2,4-Dichlorotoluene (**6**). CPE (–2.10 V); 517 mg (3.21 mmol) **6**; recovery: 83%; yields: 6% **2**, 48% **4**. CCE (0.5 A); 550 mg (3.42 mmol) **6**; recovery: 72%; yields: 32% **2**, 19% **4**, 2% **1**.

3,4-Dichlorotoluene (**7**). CPE (–2.10 V); 511 mg (3.17 mmol) **7**; recovery: 77%; yields: 12% **3**, 46% **4**, 4% **1**. CCE (1.0 A); 509 mg (3.16 mmol) **7**; recovery: 77%; yields: 21% **3**, 26% **4**, 17% **1**.

2,3,4-Trichlorotoluene (**8**). CPE (–2.20 V); 201 mg (1.03 mmol) **8**; recovery: 81%; yields: 12% **2**, 5% **3**, 60% **4**, 23% **1**. CCE (1.0 A); 201 mg (1.03 mmol) **8**; recovery: 77%; yields: 3% **5**, 55% **6**, 1% **7**, 16% **2**, 2% **3**, 12% **4**, 3% **1**.

2,4,5-Trichlorotoluene (**9**). CPE (–2.20 V); 202 mg (1.04 mmol) **9**; recovery: 71%; yields: 4% **6**, 1% **7**, 6% 2,5-dichlorotoluene, 26% **2**, 21% **3**, 37% **4**, 4% **1**.

2,4,6-Trichlorotoluene (**10**). CPE (–2.20 V); 204 mg (1.04 mmol) **10**; recovery: 69%; yields: 19% 2,6-dichlorotoluene, 6% **6**, 45% **2**, 28% **4**.

Electroreduction of the chlorinated anisoles

Controlled potential electrolyses of the monochloro-, dichloro- (Table 3) and trichloroanisoles (Table 3) and of pentachloroanisole (**21**) were performed at Pb-cathodes (working potential –2.20 V) with Permion 4035 anion exchange membranes if not stated otherwise. A 0.1 M TEAB solution in methanol was used as SSE. Charge consumptions and current efficiencies are given in Table 3.

2-Chloroanisole (**12**). 200 mg (1.40 mmol) **12**. Recovery: 57%; yield: 38% **11**.

3-Chloroanisole (**13**). 200 mg (1.40 mmol) **13**. Recovery: 57%; yield: 79% **11**.

4-Chloroanisole (**14**). – a) 200 mg (1.40 mmol) **14**. Recovery: 38%; yield: 11% **11**. – b) 1000 mg (7.00 mmol) **14**.

Recovery: 46%; yield: 30% **11** + 4% 1-chloro-4-methoxy-1,4-cyclohexadiene {MS (EI, 70 eV) m/z (%) = 146 (**11**) [M^+], 145 (**5**), 144 (**35**) [M^+], 143 (**6**), 142 (**2**), 129 (**3**) [$M^+ - CH_3$], 128 (**3**), 114 (**11**), [$M^+ - CH_2O$], 109 (**84**) [$M^+ - Cl$], 108 (**19**), 101 (**13**), 99 (**8**), 94 (**35**), 79 (**26**), 78 (**21**), 77 (**70**), 65 (**100**)}.

2,3-Dichloroanisole (**15**). 200 mg (1.13 mmol) **15**. Recovery: 58%; yields: 20–27% **11**, 20–26% **12**, 48–60% **13**.

2,4-Dichloroanisole (**16**). 200 mg (1.13 mmol) **16**. Recovery: 49%; yields: < 1% **11**, > 99% **14**.

3,4-Dichloroanisole (**17**). 200 mg (1.13 mmol) **17**. Recovery: 75%; yields: 5% **11**, 3% **13**, 92% **14**.

3,5-Dichloroanisole (**18**). – a) 200 mg (1.13 mmol) **18**. Entry 8 in Table 3; recovery: not determined; yields: 48% **11**, 52% **13**. – b) Entry 9 in Table 3; recovery: 47%; yields: 55% **11**, 45% **13**. – c) Reichelt Chemietechnik MA 3475 membrane; recovery: 62%; yields: 36% **11**, 64% **13**.

2,3,4-Trichloroanisole (**19**). – a) 200 mg (0.95 mmol) **19**. Entry 11 in Table 3; recovery: 58%; yields: 5% **11**, 1% **12**, 2% **13**, 90% **14**, 2% (**16** + **17**). – b) 600 mg (2.85 mmol) **19**. Entry 12 in Table 3; recovery: 49%; yields: 13% **11**, 4% **12**, 1% **13**, 79% **14**, < 1% (**16** + **17**).

2,4,6-Trichloroanisole (**20**). 200 mg (0.95 mmol) **20**. Recovery: not determined; yields: < 1% **11**, > 99% **14**.

Pentachloroanisole (**21**). – a) 123 mg (0.44 mmol) **21**. Reichelt Chemietechnik MA 3475 membrane; charge consumption: 85 F mol⁻¹; recovery: 62%; current efficiency: 10%; yields: 26% **11**, 5% **12**, 14% **13**, 51% **14**, 2% 1-chloro-4-methoxy-1,4-cyclohexadiene. – b) 51 mg (0.18 mmol) **21**. Reichelt Chemietechnik MA 3475 membrane; working potential: –1.10 V; charge consumption: 57 F mol⁻¹; recovery: not determined; current efficiency: 10%; yields: 2% **12**, 5% **13**, 31% **14**, 21% **16** + **20**, 13% 2,5-dichloroanisole, 12% **17**, 4% 2,4,5-trichloroanisole, 5% **21**.

Controlled potential electrolyses (working potential: –2.20 V, Reichelt Chemietechnik MA 3475 membranes) of equimolar mixtures of the monochloroanisoles **12**, **13** and **14** under varying conditions. Charge consumptions and current efficiencies are given in Table 4. – a) CPE 1 (entry 1 in Table 4); each 102 mg (0.71 mmol) **12**, **13** and **14**; 0.1 M TEAB/MeOH; Pb-cathode; recovery: 57%; yield: 32% **11**; turnover: 31% **12**, 37% **13**, 29% **14**. – b) CPE 2 (entry 2 in Table 4); each 531 mg (3.71 mmol) **12**, **13** and **14**; 0.1 M TEAB in MeOH/H₂O 80:20; Pb-cathode; recovery: 57%; yield: 9% **11**; turnover 8% **12**, 12% **13**, 7% **14**. – c) CPE 3 (entry 4 in Table 4); each 106 mg (0.74 mmol) **12**, **13** and **14**; 0.1 M TEAB/MeOH; carbon felt cathode; recovery: 57%; yield: 18% **11**; turnover: 19% **12**, 23% **13**, 11% **14**. – d) CPE 4 (entry 5 in Table 4); each 476 mg (3.33 mmol) **12**, **13** and **14**; 0.1 M TEAB/MeOH; carbon felt cathode; recovery: 50%; yield: 48% **11**; turnover: 52% **12**, 56% **13**, 38% **14**. – e) CPE 5 (entry 6 in Table 4); each 515 mg (3.60 mmol) **12**, **13** and **14**; 0.1 M TEAB in MeOH/H₂O 80:20; carbon felt cathode;

recovery: 52%; yield 14% **11**; turnover: 15% **12**, 20% **13**, 9% **14**.

Controlled potential (working potential: –2.20 V, Reichelt Chemietechnik MA 3475 membrane) and current controlled electrolyses of 2,3,4-trichloroanisole (**19**) under varying conditions. Charge consumptions and current efficiencies are given in Table 5. – a) CPE 1 (entry 2 in Table 5); 600 mg (2.84 mmol) **19**; 0.1 M TEAB/MeOH; carbon felt cathode; recovery: 40%; 20%; yields: 4% **11**, 2% **13**, 54% **14**, 25% **16**, 14% **17**. – b) CPE 2 (entry 3 in Table 5); 613 mg (2.90 mmol) **19**; 0.1 M TEAB in MeOH/H₂O 80:20; Pb-cathode; recovery: 77%; yields: 2% **11**, 2% **12**, 3% **13**, 91% **14**, 1% **16**. – c) CPE 3 (entry 4 in Table 5); 604 mg (2.86 mmol) **19**; 0.1 M TEAB in MeOH/H₂O 80:20; carbon felt cathode; recovery: 46%; yields: 7% **14**, 61% **16**, 31% **17**. – d) CPE 4 (entry 5 in Table 5); 620 mg (2.93 mmol) **19**; 0.1 M TEAB in MeOH/H₂O 80:20; carbon felt cathode; recovery: 65%; yields: 14% **11**, 1% **13**, 54% **14**, 4% **16**, 3% **17**, 23% **19**. – e) CPE 5 (entry 6 in Table 5); 593 mg (2.81 mmol) **19**; 1 M NaOH + 0.1 M NaBr in MeOH/H₂O 80:20; Pb-cathode; recovery: 75%; yields: 2% **11**, 3% **12**, 4% **13**, 38% **14**, 19% **16**, 15% **17**, 18% **19**. – f) CPE 6 (entry 7 in Table 5); 625 mg (2.96 mmol) **19**; 1 M NaOH + 0.1 M NaBr in MeOH/H₂O 80:20; carbon felt cathode; recovery: 48%; yields: 3% **14**, 32% **16**, 24% **17**, 41% **19**. – g) CCE 1 (2.0 A, entry 8 in Table 5); 598 mg (2.83 mmol) **19**; 1 M KOH/MeOH; Pb-cathode; recovery: 73%; yields: 1% **11**, 2% **13**, 25% **14**, 34% **16**, 34% **17**, 3% **19**. – h) CCE 2 (3.0 A); 250 mg (1.18 mmol) **19**; carbon felt cathode; recovery: 86%; yields: 2% **13**, 20% **14**, 29% **16**, 32% **17**, 16% **19**. – i) CCE 3 (3.0 A); 100 mg (0.47 mmol) **19**; 1 M KOH in MeOH/H₂O 75:25; Pb-cathode; recovery: 75%; yields: 2% **11**, 1% **12**, 9% **13**, 62% **14**, 11% **16**, 13% **17**, 2% **19**.

Electroreduction of the chlorinated phenols

The monochlorophenols **23**, **24** and **25** were electrolysed galvanostatically (2.0 A/1020 A m⁻², Pb-cathode, Reichelt Chemietechnik MC 3470 cation exchange membrane) as a mixture of each 105 mg (0.82 mmol) in 1 M KOH/MeOH. Charge consumption: 93 F mol⁻¹; recovery: 72%; current efficiency: 0.3%; turnover: 21% **23**, 15% **24**, 2.5% **25**; yield: 12% **22**.

The dichlorophenols **26–29** and the trichlorophenols **30** and **31** were electrolysed galvanostatically (3.0 A, Reichelt Chemietechnik MC 3470 cation exchange membrane) in 0.1 M NaOH/0.1 M Na₂SO₄/H₂O if not stated otherwise. The charge consumptions and current efficiencies are given in Table 6.

2,3-Dichlorophenol (**26**). 107 mg (0.66 mmol) **26**. 1 M NaOH/1 M Na₂SO₄/H₂O; carbon felt cathode; recovery: 82%; yields: 7% **22**, 17% **23**, 10% **24**, 66% **26** (entry 1 in Table 6).

2,4-Dichlorophenol (**27**). 100 mg (0.61 mmol) **27**. 1 M NaOH/1 M Na₂SO₄/H₂O; carbon felt cathode; recovery: 81%; yields: 9% **22**, 4% **23**, 76% **25**, 11% **27** (entry 2 in Table 6).

3,4-Dichlorophenol (**28**). 100 mg (0.61 mmol) **28**. – a) CCE 1 (entry 3 in Table 6); Pb-cathode; recovery: 91%; yields: 45% **22**, 16% **24**, 39% **25**. – b) CCE 2 (entry 4 in Table 6); carbon fibre bunch cathode; recovery: 76%; yields: 8% **22**, 9% **24**, 73% **25**, 8% **28**. – c) CCE 3 (entry 5 in Table 6); carbon felt cathode; recovery: 69%; yields: 7% **22**, 9% **24**, 41% **25**, 43% **28**.

3,5-Dichlorophenol (**29**). – a) CCE 1 (entry 6 in Table 6); 200 mg (1.23 mmol) **29**; Pb-cathode, 5.0 A; recovery: 57%; yields: 2% **22**, 41% **24**, 57% **29**. – b) CCE 2 (entry 7 in Table 6); 100 mg (0.61 mmol) **29**; carbon fibre bunch cathode; recovery: not determined; yields: 8% **22**, 62% **24**, 30% **29**.

2,3,4-Trichlorophenol (**30**). – a) CCE 1 (entry 8 in Table 6); 101 mg (0.51 mmol) **30**, 1 M KOH/MeOH; Pb-cathode, 2.0 A; recovery: 66%; yields: 14% **22**, 6% **23**, 2% **24**, 68% **25**, 9% **27**. – b) CCE 2 (entry 9 in Table 6); 107 mg (0.54 mmol) **30**; carbon fibre bunch cathode; recovery 54%; yields: 4% **22**, 3% **23**, 1% **24**, 20% **25**, 2% **26**, 57% **27**, 11% **28**, 6% **30**.

2,4,6-Trichlorophenol (**31**). – a) CCE 1 (entry 10 in Table 6); 201 mg (1.02 mmol) **31**; 1 M KOH/MeOH; Pb-cathode, 2.0 A; recovery: 62%; yields: 3% **22**, 10% **23**, 51% **25**, 33% **27**, 3% **31**. – b) CCE 2 (entry 11 in Table 6); 134 mg (0.68 mmol); carbon felt cathode; recovery 78%; yields: 5% **22**, 13% **25**, 39% **27**, 43% **31**.

The tetrachlorophenols **33** and **34** were electrolysed potentiostatically at a Pb-cathode in 0.1 M TEAB/MeOH. The current efficiencies are given in Table 6.

2,3,4,6-Tetrachlorophenol (**33**). 153 mg (0.66 mmol) **33**. – a) CPE 1 (–1.70 V); recovery not determined; yields: 6% **27**, 6% **35**, 5% 2,4,5-trichlorophenol, 41% **31**, 40% **33**. – b) CPE 2 (–2.20 V); recovery not determined; yields: 3% **23**, 7% **26** + 2,5-dichlorophenol, 27% **27**, 11% 2,6-dichlorophenol, 5% **35**, 3% 2,4,5-trichlorophenol, 39% **31**, 4% **33**.

2,3,5,6-Tetrachlorophenol (**34**). 156 mg (0.67 mmol) **34**. – a) CPE 1 (–1.70 V); recovery: not determined; yields: 3% **26**, 13% **35**, 82% **34**. – b) CPE 2 (–2.20 V); recovery: not determined; yields: 7% **23**, 1% **24**, 29% **26**, 12% 2,6-dichlorophenol, 2% 2,3,5-trichlorophenol, 33% **35**, 16% **34**.

Pentachlorophenol (**32**) was electrolysed at a Pb-cathode. – a) CPE 1 (–1.50 V); 156 mg (0.58 mmol) **32**; 0.1 M TEAB/MeOH; recovery: not determined; current efficiency: 5%; yields: 5% **31**, 1% **35**, 26% **33**, 13% **34**, 52% **32**. – b) CPE 2 (–2.20 V); 156 mg (0.58 mmol) **32**; 0.1 M TEAB/MeOH; recovery: 77%; current efficiency: 8%; yields: 8% **23**, 8% **26** + 2,5-dichlorophenol, 17% **27**, 12% 2,6-dichlorophenol, 11% **35**, 1% 2,3,5-trichlorophenol, 20% **31**, 5% **33**, 7% **34**, 4% **32**. – c) CCE (entry 12 in Table 6); 144 mg (0.51 mmol) **32**; 1 M KOH/MeOH, 0.5 A; recovery:

78%; current efficiency: 6%; yields: 4% **22**, 15% **23**, 28% **25**, 29% **27**, 14% 2,5-dichlorophenol, 2% 2,4,5-trichlorophenol, 1% **31**, 3% **32**.

Electroreduction of a soil extract

Dried soil (16.5 g) from the Bitterfeld site was extracted for 48 h with toluene in a Soxhlet extractor. The solvent was evaporated to yield a residue (411 mg) which contained 143 mg of Nitrofen® (**36**), 12 mg of 4-chloronitrobenzene, 30 mg of 2,4-dichlorophenol (**27**), and 33 mg of 2,4,6-trichlorophenol (**31**) according to a GLC analysis. This extract was electrolysed galvanostatically (1.0 A, 509 A m⁻²) in 1 M KOH/MeOH by use of a Pb-cathode and a cation exchange membrane (Reichert Chemietechnik MC 3470). After a total charge consumption of 18000 A s the electrolyte was diluted with H₂O and first extracted with diethyl ether, then acidified with HCl and again extracted. Both extracts (295 mg in total) were analysed qualitatively (GC-MS coupling) and quantitatively (GLC). The first extract contained 7 mg (6%) of 4-amino-2',4'-dichlorodiphenylether (**37**), 75 mg (76%) of 4-amino-4'-chlorodiphenylether (**38**), 15 mg (18%) of 4-aminodiphenylether (**39**) and 9 mg of 4-chloroaniline. The acidic extract contained 0.3 mg of phenol (**22**), 5 mg of 2-chlorophenol (**23**), 11 mg of 4-chlorophenol (**25**), 34 mg of 2,4-dichlorophenol and 4 mg of 2,4,6-trichlorophenol (**31**).

37: MS (EI, 70 eV): m/z (%) = 257 (3) [M⁺], 255 (14) [M⁺], 253 (17) [M⁺], 219 (1), 183 (3), 154 (3), 147 (8), 145 (11), 135 (4), 133 (8), 127 (4), 111 (11), 109 (31), 108 (100) [C₆H₆NO⁺], 91 (6), 85 (6), 84 (6), 80 (75), 72 (25), 74 (28), 73 (15), 65 (39), 63 (28), 53 (28), 52 (22).

38: MS (EI, 70 eV): m/z (%) = 221 (11) [M⁺], 219 (44) [M⁺], 184 (1), 183 (1), 156 (6), 128 (4), 127 (3), 111 (13), 108 (100) [C₆H₆NO⁺], 80 (47), 75 (19), 65 (17), 63 (10), 53 (11), 52 (7).

39: MS (EI, 70 eV): m/z (%) = 186 (7) [M⁺], 185 (42) [M⁺], 169 (1), 168 (1), 157 (6), 156 (8), 130 (3), 129 (4), 128 (4), 109 (14), 108 (100) [C₆H₆NO⁺], 92 (3), 91 (3), 80 (94), 77 (64), 65 (28), 63 (17), 53 (26), 52 (17), 51 (42), 50 (17).

4-Chloroaniline: MS (EI, 70 eV): m/z (%) = 130 (3), 129 (22) [M⁺], 128 (8), 127 (100) [M⁺], 102 (6), 100 (19) [M⁺–NH₂], 99 (8), 92 (28) [M⁺–Cl], 91 (8), 78 (3), 75 (8), 74 (6), 73 (11), 65 (56), 63 (36).

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