

Electroreduction of Organic Compounds, XVIII [1]

Electrochemical Dehalogenation of Chlorinated Dibenzofurans and Dibenzo-*p*-dioxins in Methanol

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Electroreduction, Chlorinated Dibenzofurans, Chlorinated Dibenzo-*p*-dioxins, Dehalogenation

Mono and polyhalogenated dibenzofurans and dibenzo-*p*-dioxins are electrochemically reduced in a divided cell in technical methanol at a lead cathode.

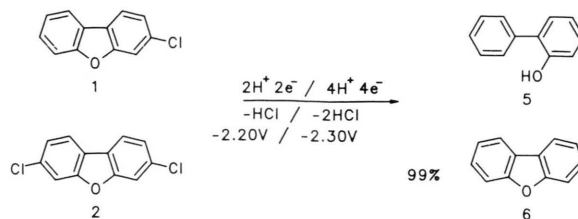
Disposal of halogenated aromatic compounds is predominantly achieved by high temperature incineration [2] or reduction with alkali metals [3, 4]. Microbial degradation of such xenobiotica is also under investigation [5].

In some cases electrochemical dehalogenation proved to be a particularly promising alternative [6–10]. Farwell, Beland and Geer [8] report on the electrochemical dehalogenation of all 12 chlorinated benzenes in dimethylsulfoxide at a mercury electrode whereas during our recent investigations [11] we obtained the same results in a protic medium by using methanol and a lead cathode [6].

After the successful dechlorination of substituted benzenes and biphenyls we now wish to report on the electrochemical reduction of chlorinated dibenzofurans and chlorinated dibenzo-*p*-dioxins. Our experiments were carried out in a divided cell with the aid of an anionic exchange membrane. At current densities of 30 mA/cm² yields could be optimized with increasing concentrations of the educts.

Among the dibenzofurans the 3-chloro-derivative (**1**) and the dichlorinated isomers, 3,7-dichlorodibenzofuran (**2**), 2,3-dichlorodibenzofuran (**3**) and 2,8-dichlorodibenzofuran (**4**) were investigated.

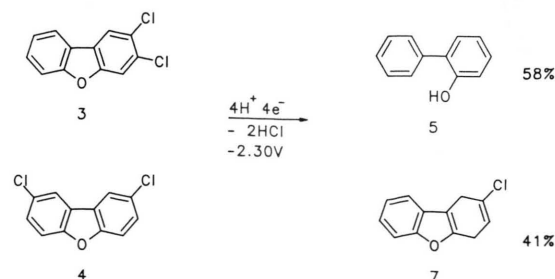
Compound **1** and **2** furnished a mixture of 2-hydroxybiphenyl (**5**) and dibenzofuran (**6**) in an



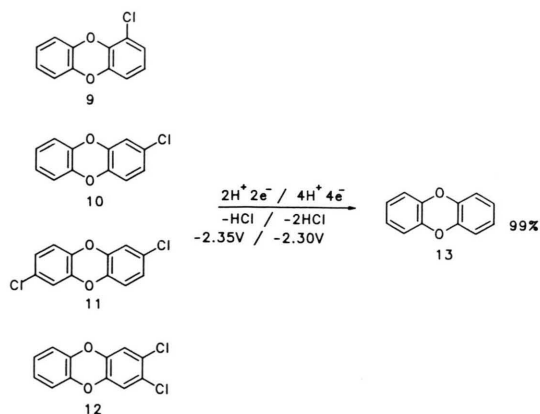
overall yield of 99% (see Fig. 1). The monochloro derivative **1** gave a mixture of 65% **5** and 34% **6** while proportions were 96:3 in the dichlorinated **2**. Besides the two main products GC/MS- as well as GC/IR-investigations revealed the presence of several byproducts in very small amounts which all showed at least one intact aromatic ring.

Under the same conditions, compounds **3** and **4** were transformed to a mixture of **5** and a chlorinated dihydroarene, to which we assign the structure of 1,4-dihydro-2-chlorodibenzofuran (**7**). The conversion was 99%, and the products were formed in a ratio of approximately 6:4 (see Fig. 2). As indicated by the characteristically large coupling constant $^5J_{1,4} = 7.6$ Hz, the ¹H NMR spectrum of **7** clearly shows the partial structure of a 1,4-dihydroarene. The presence of only five protons in said system point to a chloro substituent, however, due to the small amount of the isolated product, we could not determine the substitution pattern. We nevertheless suggest structure **7** since according to Fig. 3 a chloro substituent at pos. 3 would have been easily removed during the electroreduction.

The following chlorinated dibenzo-*p*-dioxins were selected: 1-chloro-dibenzo-*p*-dioxin (**9**) 2-chlorodibenzo-*p*-dioxin (**10**), 2,7-dichlorodibenzo-*p*-dioxin (**11**) and 2,3-dichlorodibenzo-*p*-dioxin (**12**). The electrolyses were carried out at a reduction potential of –2.30 V and –2.35 V against (Ag/Ag⁺/AgBr/Br[–]). In all cases dechlorination



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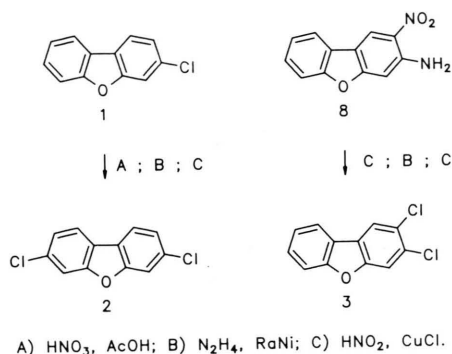
took place forming the parent compound, dibenzo-*p*-dioxin (**13**) in more than 99% yield (see Fig. 3).

Investigations on "Real-life"-samples containing minute amounts of chlorinated dibenzofurans and dibenzo-*p*-dioxins dissolved in a complex oil matrix were highly promising.

Experimental

Compounds **4–12** are commercially available (amchro, Sulzbach, Germany). Preparation of 3-chlorodibenzofuran (**1**) was described by Cullinane [12] and Oita, Johnson and Gilman [13]. The compound served as starting material for the synthesis of the 3,7-dichloroderivative (**2**) – m.p. 185°C – which was carried out in a nitration-reduction-Sandmeyer sequence according to Fig. 4. ^1H NMR spectra were run on a Bruker AC 250P at 250.133 MHz, TMS served as the internal standard. The ^1H NMR spectrum of **2** (C_6D_6) showed the following data: $\delta = 7.03$ (dd, H-2, H-8, $J_{1,2}, J_{8,9} = 8.4$ Hz, $J_{2,4}, J_{6,8} = 1.8$ Hz), 7.13 (d, H-1, H-9), 7.25 (d, H-4, H-6) ppm.

2,3-Dichlorodibenzofuran **3** – m.p. 133°C – was obtained from 3-amino-2-nitrodibenzofuran [14, 15] (see Fig. 4). The ^1H NMR spectrum of **3** (C_6D_6) showed the following data: $\delta = 7.00$ (m, 1H), 7.07 (m, 1H), 7.21 (m, 1H), 7.25 (s, 1H), 7.35 (m, 1H), 7.50 (s, 1H) ppm.



The ^1H NMR spectrum of the reduction product **7** (CDCl_3) showed the following data: $\delta = 6.8–7.62$ (m, H-6, H-7, H-8, H-9), 5.52 (m, H-3), 3.23 (dt, H-1a, H-1b), 2.88 (H-4a, H-4b) ppm; coupling constants are $J_{1,3} = 1.6$ Hz, $J_{1,4} = 7.6$ Hz, $J_{3,4} = 3.6$ Hz.

The synthesis of dibenzo-*p*-dioxin (**13**) followed the recently described procedure [16].

Electrolyses were potentiostatically (potentiostat ST 72; Bank Electronic, Göttingen, W-Germany) carried out at 20°C in a divided stationary cell. An anion exchange membrane Permion 4035 (Serva, Heidelberg, Germany) served as a diaphragm. The working electrode (cathode) consisted of a lead foil (99.97% purity, Merck, Darmstadt, Germany) while the anode was made of platinum. A silver wire ($\text{Ag}/\text{Ag}^+/\text{AgBr}/\text{Br}^-$) served as the reference electrode. A 0.25 M solution of methanolic tetraethylammonium bromide was used as the catholyte medium. About 0.5 mmol of the chlorinated substrate were dissolved; after consumption of the 1.5–20 fold of the theoretical charge the solution was diluted with water, acidified with hydrochloric acid to pH 5 and extracted with pentane.

Identification of the reaction products was carried out by GC/MS analysis (HP-GC 5970 series linked to a mass selective detector – MSD) of the dried extracts on a 50 m fused silica column coated with SE 54 and by GC/IR-analysis (HP-GC 5890 series II linked to a HP-IR-detector 5965 A) under the same gas chromatographic conditions.

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