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

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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 xenobiotics 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 aprotic 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 $^3J_{\text{H,H}} = 7.6$ Hz, the $^1$H 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. 3a 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-dichlorodibenzop-dioxin (11) and 2,3-dichlorodibenzop-dioxin (12). The electrolyses were carried out at a reduction potential of $-2.30$ V and $-2.35$ V against (Ag/AgCl/AgBr/Br₂). In all cases dechlorination...
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. The \(^1\)H NMR spectrum of 2 (CD\(_6\)D\(_6\)) showed the following data: \(\delta = 7.03\) (dd, H-2, H-8, \(J_{1,2} = 8.4\) Hz, \(J_{5,6} = 1.8\) Hz), 7.13 (d, H-1, H-9), 7.25 (d, H-4, H-6) ppm.

The \(^1\)H 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 (Ag/Ag\(^+\)/AgBr/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.


