

## Electroreduction of Organic Compounds. 31 [1]

## Electroreduction of 2- and 3-Chlorodibenzofuran in Deuterated Methanol

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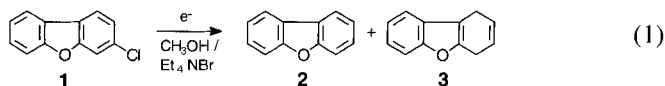
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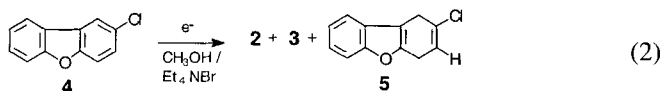
**Abstract.** The cathodic reduction of dibenzofuran (**2**), 2-chlorodibenzofuran (**4**), and 3-chlorodibenzofuran (**1**) in deuterated methanol is investigated. The Birch-type reduction product 1,4-dibenzofuran (**3**) is formed from **1** via **2**, whereas 2-chloro-1,4-dihydrodibenzofuran (**5**) is obtained as by-product besides

**3** from **4** as starting compound. Deuterium is only incorporated into the reduction products if  $\text{CH}_3\text{OD}$  or  $\text{CD}_3\text{OD}$  but not if  $\text{CD}_3\text{OH}$  are used. This observation is strongly indicative of a polar mechanism involving protonation rather than a radical mechanism with hydrogen atom abstraction to be operative.

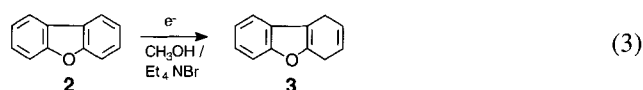
In the last few years we have successfully extended the electroreductive dehalogenation of aromatic chlorides [2] and aliphatic chlorides [3] to the use of methanol and methanol–water mixtures as solvents for preparative electrolyses. Lead proved to be a suitable cathode material. In the course of these investigations different chlorodibenzofurans including the four isomeric monochlorodibenzofurans were studied. Starting with 1-, 3- and 4-chlorodibenzofuran the identical reaction products dibenzofuran **2** and 1,4-dihydrodibenzofuran **3** are formed. The proportion of **2** and **3** obtained, for example from 3-chlorodibenzofuran **1** (Eq. 1), depends on the reduction potential ( $-2.0$  V or  $-2.5$  V vs. SCE) and the reaction time.



In contrast to this, 2-chloro-1,4-dihydrodibenzofuran **5** was formed during the electrolysis of the 2-chloro-derivative **4** as the main product besides smaller amounts of **2** and **3** (Eq. 2).



As one should expect, the dihydroproduct **3** is also formed by the electrolysis of dibenzofuran **2** itself (Eq. 3):



In order to get insight into the mechanism of the reactions we have performed electrolyses in specifically deuterated solvents ( $\text{CD}_3\text{OD}$ ,  $\text{CH}_3\text{OD}$ , and  $\text{CD}_3\text{OH}$ ) and looked for the incorporation of deuterium. The total deuterium content of the products **2** and **5** was determined by mass spectrometry, the distribution within all molecules by  $^1\text{H}$  NMR-spectroscopy.

The separation of the mixtures resulting from reaction (1) and (2) by preparative GC achieved pure dibenzofuran but not 1,4-dihydrodibenzofuran, which always contained dibenzofuran. It was, however, not possible to interpret the aromatic part of the  $^1\text{H}$  NMR spectrum quantitatively because the peaks in question overlap.

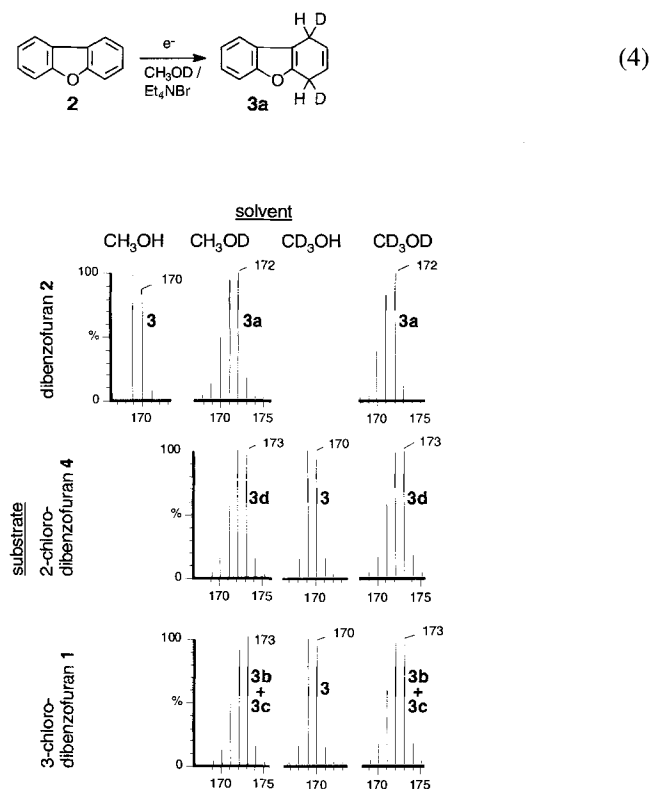
## Results and Discussion

## Electroreduction of Dibenzofuran 2

Figure 1 shows the molecular peaks in the mass spectra of the hydrogenated products **3**, which are formed by electroreduction of **2**, **4**, and **1** in methanol and its deuterated derivatives as solvents. Due to the intense ( $\text{M}^+-1$ )-peaks ( $m/z = 169$  for **3** from **2**) the degrees of deuteriation cannot be determined from the mass spec-

tra since the partially deuterated compounds would give rise to ( $M^+ - 2$ )-peaks of unknown intensity by splitting off  $^2\text{H}$ .

The peak areas in the  $^1\text{H}$  NMR spectra of **3** and **3a** (Fig. 2) clearly demonstrate that 98% deuterium is introduced into each the 1- and the 4-position upon hydrogenation of **2** in  $\text{CH}_3\text{OD}$  (Eq. 4). Obviously, the deuterium in the product can only stem from the hydroxyl ( $\text{OD}$ -) group of this solvent. This result is confirmed by the outcome of the electrolysis in  $\text{CD}_3\text{OD}$ . The methyl deuterons do not cause any difference in the mass spectra of the products beyond the estimated experimental error ( $\pm 5\%$ ). This implies the mechanism to be an ionic one.

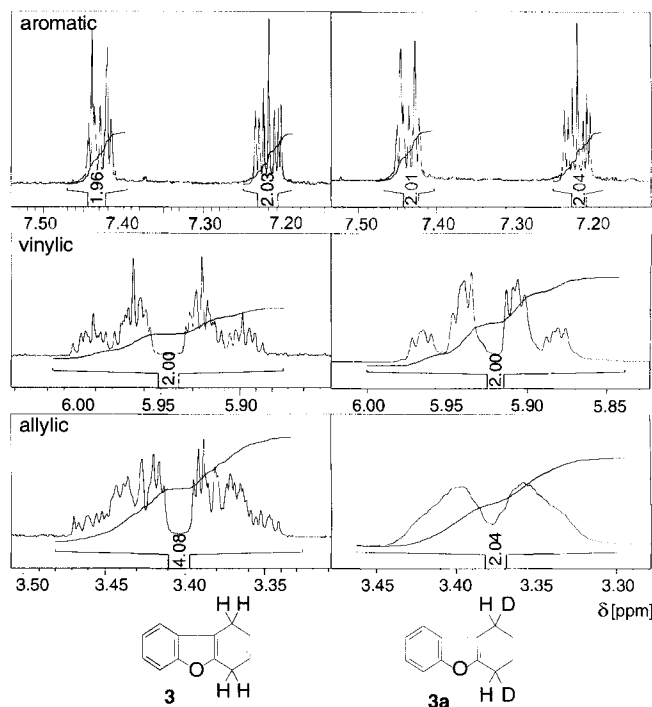


**Fig. 1** Molecular peaks in the mass spectra of the 1,4-dihydrodibenzofurans **3**, **3a**, **3b + 3c**, **3d**, formed during the electrolysis reactions (1) to (6)

### Electroreduction of 3-Chlorodibenzofuran **1**

Dibenzofuran **2a** which is formed during electrolysis of **1** in  $\text{CH}_3\text{OD}$  or  $\text{CD}_3\text{OD}$  contains 96.2% or 96% respectively monodeuterodibenzofuran. **2a** contains 96.0% if the electrolysis is carried out in  $\text{CD}_3\text{OD}$ , as determined by mass spectrometry.

As one would expect, the incorporation of deuterium into dibenzofuran **2a** occurs exclusively in the 3-position. This is evidenced by its  $^1\text{H}$  NMR spectrum (see Fig. 3) showing a signal intensity of only 50% for the corresponding protons (3-H and 7-H!). It is further sup-



**Fig. 2** Relevant sections of the  $^1\text{H}$  NMR spectra of the 1,4-dihydrodibenzofurans **3** and **3a**

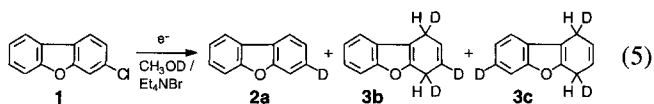
ported by changes in the signal splittings of 1-H, 2-H and 4-H (Fig. 3), which is due to the different couplings with 3- $^2\text{H}$ .

The situation is more complicated in the case of 1,4-dihydrodibenzofuran **3b + 3c** produced in the same experiment from **2a** because in principle both, the deuterated and the undeuterated benzene ring can be hydrogenated.

As a result, deuterium is found both, in the aromatic and the hydrogenated rings (**3c**) or only in the hydrogenated ring (**3b**). The  $^1\text{H}$  NMR-spectrum of this mixture cannot be fully evaluated because the signals of 6-H and 9-H as well as 7-H and 8-H overlap. However, deuterium contents of 97% in the 1- and the 4-position of the reaction product **3b + 3c** and correspondingly of 93% for the product of the electrolysis in  $\text{CH}_3\text{OD}$  are calculated if the signal intensity of the vinylic proton 2-H is equated with 100%. Thus, the deuterium in **3b** and **3c** resulting from substitution and 1,4-addition nearly completely originates from the OD-group of  $\text{CH}_3\text{OD}$ . In the same way as in the unsubstituted dibenzofuran case electrolyses in  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  confirmed that the hydroxyl groups were the only sources of hydrogen. Products with identical mass spectra were yielded by electrolyses in  $\text{CD}_3\text{OD}$  and in  $\text{CH}_3\text{OD}$  as well as by electrolyses in  $\text{CD}_3\text{OH}$  and in  $\text{CH}_3\text{OH}$ , respectively.

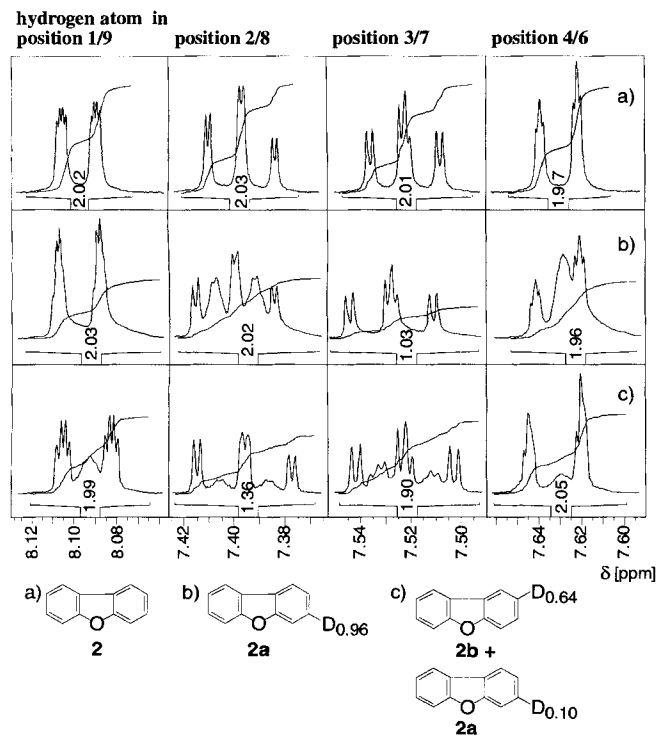
The analogous course of the two electrohydrogenations (Eq. 4) and (Eq. 5) is furthermore evidenced from the corresponding mass spectra. Whereas the isotopic

patterns in the molecular ions are quite similar a shift of exactly one mass unit is observed (cf. Fig. 1). A trans-



**Table 1** Deuterium contents (%) of the hydroxyl groups in the solvent before and after the electrolyses of **1** and **4**

Solvent	Substrate			
	before	<b>4</b> after	before	<b>1</b> after
CH <sub>3</sub> -OD	98.4	98.2	98.3	98.4
CD <sub>3</sub> -OH	0.4	0.3	—	0.6
CD <sub>3</sub> -OD	98.7	98.6	97.9	98.0



**Fig. 3** Relevant sections of the <sup>1</sup>H NMR spectra of the dibenzofurans **2** (authentic sample) of **2a** obtained from **1** and of (**2b**+**2a**) obtained from **4**

fer of hydrogen from methyl groups of the solvent and, consequently, a radical mechanism can therefore be excluded.

#### Electroreduction of 2-Chlorodibenzofuran **4**

Electroreduction of 2-chlorodibenzofuran **4** in CH<sub>3</sub>OD, CD<sub>3</sub>OH, or CD<sub>3</sub>OD yields monodeuterodibenzofuran with a deuterium content of 73.3/86.1%, 1.6%, or 87.1/

85.1%, respectively (determined by mass spectrometry). Two conclusions can be drawn from this result.

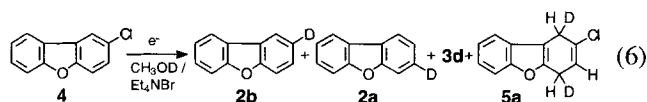
Firstly, the deuterium again stems from the hydroxyl rather than the methyl groups. Secondly, the observed deuterium content of only 73–87% significantly deviates from the expected value (>96%) and the reproducibility of this result is poor as demonstrated in two independent experiments.

This latter result requires an explanation. We therefore performed an electrolysis of **4** in methanol with perdeutero-tetrabutylammonium bromide, (C<sub>4</sub>D<sub>9</sub>)<sub>4</sub>NBr, as supporting electrolyte. In order to increase the yield of dibenzofuran the electrolysis was run for 24 h at a potential of –2.0 V instead of –2.5 V (*vs.* SCE). A deuterium content of 9%, well above the experimental error, was detected in the product. Thus the loss of deuterium in the reaction product **2a** + **2b** obtained by electroreduction of **4** can be explained by the assumption that Hofmann elimination of the tetraalkylammonium cations takes place by reaction with the methoxide anions generated at the cathode. The observation of 27% protonation *versus* only 9% deuteration should be due to the isotope effect.

The content of deuterium in the hydroxyl group was determined before and after the dehalogenation. However, no significant loss of deuterium was observed in any of the six reactions studied (cf. Tab. 1).

The substitution of chlorosubstituents takes a more complicated course in the case of 2-chlorodibenzofuran **4** as compared with 3-chlorodibenzofuran **1**. Deuterium is incorporated into the 2-position as well as into the 3-position. This is obvious from the signal intensities and the changes of the signal pattern of 2-H in the <sup>1</sup>H NMR spectrum (cf. Fig. 3, **2a** + **2b**). The presence of deuterium in the 1- and in the 4-position cannot be excluded with certainty (*i.e.* beyond the experimental error of 5%).

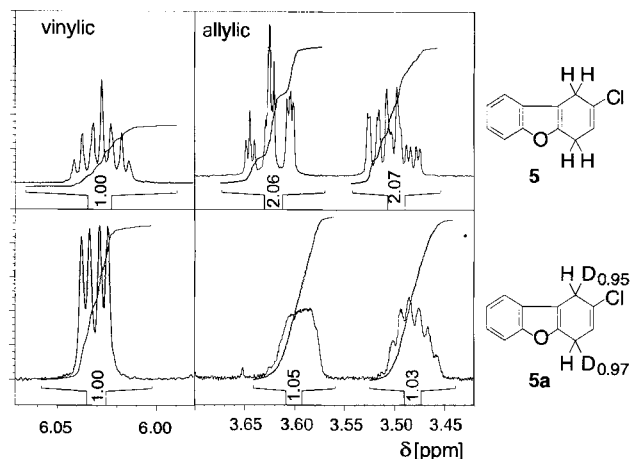
Contamination of 2-chlorodibenzofuran (**4**) with 3-chlorodibenzofuran (**1**) was excluded by GC.



The reaction product **3d** is a mixture of trideutero-1,4-dihydrodibenzofurans according to the mass spectra (cf. fig. 1). From the presence of two reaction products **3b** + **3c** formed in reaction (5) and the fact that 2- and 3-deuterodibenzofuran **2b** and **2a** are formed in reaction (6) we infer that the components of **3d** are [1,2,4-D<sub>3</sub>], [1,3,4-D<sub>3</sub>], [1,4,7-D<sub>3</sub>] and [1,4,8-D<sub>3</sub>] 1,4-dihydrodibenzofuran.

A deuterium content of 96% is observed for the formation of **5a** (electrolysis in CH<sub>3</sub>OD, cf. Fig. 4) where-

as only 2% deuteration is found in **5a** after electrolysis in CD<sub>3</sub>OH. This is, once more, indicative of the hydroxyl groups to be the main if not the only source of hydrogen in the products. It is particularly obvious from the <sup>1</sup>H NMR signal of 3-H which appears as a doublet of doublets in **5a** instead of a triplet of triplets with identical coupling constants in **5** ( $J_{1,3} = 1.6$  Hz,  $J_{3,4} = 3.7$  Hz).



**Fig. 4** Relevant sections of the <sup>1</sup>H NMR spectra of the 2-chloro-1,4-dihydrodibenzofurans **5** and **5a**

## Conclusion

Birch reduction, *i.e.* 1,4-dihydrogenation, occurs if dibenzofuran (**2**) is electrolysed in methanol. The chloro-substituent in 3-chlorodibenzofuran (**1**) is replaced by hydrogen during the electrolysis, which results in the formation of **2** and, subsequently 1,4-dihydrodibenzofuran **3**. On the other hand 2-chlorodibenzofuran (**4**) is not exclusively transformed into **3** but significant amounts of 2-chloro-1,4-dihydrodibenzofuran (**5**) are formed, obviously by direct dihydrogenation of **4**.

If CH<sub>3</sub>OD or CD<sub>3</sub>OD are used as solvent instead of CH<sub>3</sub>OH incorporation of deuterium into the products occurs. However, no deuteration is observed in CD<sub>3</sub>OH. This is strongly indicative of an ionic mechanism involving proton transfer rather than a radical mechanism for the electroreduction.

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## Experimental

Melting points (corrected): Electrothermal. – NMR spectra: Bruker WH 400. – IR spectra: ATI Mattson "Genesis"-FT-IR. – GC-MS: GC 8000 (equipped with a 30m SE 54 column)

and MD 800 quadrupole-MS (EI, 70 eV), Fisons Instruments. The deuterium content of the hydroxyl group as listed in table 1 was determined before and after the electrolysis (each sample was taken from the completely built up cell). The solvent was distilled off and was treated with CaH<sub>2</sub> to afford a hydrogen mixture of H<sub>2</sub> and HD. The ratio of these two was determined by mass spectroscopy.

**Nitration of Dibenzofuran** [4]: A suspension of dibenzofuran (100 g, 0.59 mol) in 400 ml glacial acetic acid was carefully treated with fuming HNO<sub>3</sub>,  $\rho = 1.52$  (100 g, 1.59 mmol). After the addition of 50 g the dark red solution was warmed to 60 °C to start the exothermic reaction. A crystalline precipitate was formed. The remaining HNO<sub>3</sub> was added. After stirring at 95 °C for 1 h the mixture was left at room temperature overnight. The reaction product was filtered off and extracted with boiling ethanol (2×500 ml). The crude product was vacuum dried and recrystallized from glacial acetic acid to afford 81 g of 3-nitrodibenzofuran (64%), *m.p.* = 182 °C (ref. [4c]: 182 °C). – IR (KBr):  $\nu/\text{cm}^{-1} = 3102$  (w), 1629 (m), 1605 (w), 1526 (s), 1458 (m), 1342 (s), 1198 (m), 873 (m), 846 (m), 821 (s), 760 (s), 735 (s), 563 (w), 419 (w).

The ethanol extract was concentrated *in vacuo*, affording 20 g of a mixture of 2- and 3-nitrodibenzofuran. The 2-nitro-derivative was extracted with ether and chromatographed on silica gel with petroleum ether/ethylacetate (3:1) providing 5.0 g pure 2-nitrodibenzofuran (5%), *m.p.* = 135–137 °C (ref. [5]: 143 °C). – IR (KBr):  $\nu/\text{cm}^{-1} = 3099$  (w), 2925 (m), 2853 (w), 1602 (m), 1586 (m), 1526 (s), 1468 (m), 1445 (m), 1343 (s), 1250 (m), 1200 (s), 1020 (m), 894 (m), 842 (m), 822 (m), 748 (s), 718 (m), 689 (m), 604 (w), 421 (w).

**3-Aminodibenzofuran**: 3-Nitrodibenzofuran (40 g, 188 mmol) and 2 g Raney nickel were suspended in 2 l ethanol, and the mixture was heated to reflux. Hydrazinium hydroxide (80%, 35.2 g, 563 mmol) was added dropwise. After 2 h some more Raney nickel was added carefully and the mixture was refluxed for 2 h. The catalyst was filtered off. The solution was reduced to 1 l, boiled up with charcoal, filtered again, and reduced in volume to 300 ml. By that a part of the product crystallized out. The supernatant solution was decanted into 2 l water and the white precipitate was filtered with suction. The product was dissolved in ether, dried over MgSO<sub>4</sub> and recrystallized from an ethanol–water mixture (1:1). The yield was 30.7 g (89%). *m.p.* = 96–97 °C (ref. [4a,c]: 94 °C). – IR (KBr):  $\nu/\text{cm}^{-1} = 3441$  (w), 3362 (w), 3289 (m), 3059 (w), 1638 (s), 1605 (s), 1507 (m), 1458 (s), 1423 (m), 1306 (w), 1188 (w), 1152 (m), 1129 (s), 1016 (w), 846 (m), 814 (m), 751 (s), 722 (m).

**2-Aminodibenzofuran**: 2-Nitrodibenzofuran (6.5 g, 30.5 mmol) and Raney Nickel (400 mg) in 300 ml ethanol and hydrazinium hydroxide (80%, 5.7 g, 91.1 mmol) are treated as described above. The product was chromatographed on silica gel with petroleum ether/ethylacetate (3:1), yielding 4.0 g (72%) 2-aminodibenzofuran. *m.p.* = 115–117 °C (ref. [5]: 117 °C). – IR (KBr):  $\nu/\text{cm}^{-1} = 3428$  (s), 3345 (s), 3046 (w), 2954, 2923 (w), 1629 (s), 1614 (s), 1601 (s), 1487 (s), 1450 (s), 1351, 1323 (m), 1282, 1232 (m), 1192 (s), 1180 (s), 1153, 1126, 1106, 941, 865, 838, 806, 767, 754, 732, 623, 578, 563, 515, 424.

**3-Chlorodibenzofuran (1)**: A solution of 3-aminodibenzofuran (23.5 g, 128.3 mmol) in 65 ml 6M HCl was diazotized with a

2.5M solution of  $\text{NaNO}_2$  (8.85 g/52 ml, 128.3 mmol) in water. It was added to a solution of  $\text{CuCl}$  (16.9 g, 171 mmol) in 70 ml conc.  $\text{HCl}$  and kept at 70 °C for 1 h. The product was steam-distilled, extracted with ether and dried over  $\text{MgSO}_4$ . Chromatography on silica gel with petroleum ether/ethylacetate (3:1) provided 6.2 g 3-chlorodibenzofuran (24%) as a white solid. *m.p.* = 92–94 °C (ref. [4c]: 101 °C). – IR (KBr):  $\nu/\text{cm}^{-1}$  = 3097 (w), 3087 (w), 3072 (w), 1601 (m), 1589 (s), 1448 (s), 1419 (s), 1342 (m), 1190 (m), 1064 (m), 897 (m), 817 (s), 748 (s), 719 (m). –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.32 (dd, 1H, H-2,  $J_{1,2}$  = 8.2 Hz,  $J_{2,4}$  = 1.9 Hz), 7.35 (ddd, 1H, H-8,  $J_{7,8}$  = 8.3 Hz,  $J_{8,9}$  = 7.7 Hz,  $J_{6,8}$  = 1.1 Hz), 7.46 (ddd, 1H, H-7,  $J_{7,8}$  = 8.3 Hz,  $J_{6,7}$  = 7.3 Hz,  $J_{7,9}$  = 1.4 Hz), 7.56 (ddd, 1H, H-6,  $J_{6,7}$  = 8.3 Hz,  $J_{6,8}$  = 1.1 Hz,  $J_{6,9}$  = 0.7 Hz), 7.57 (dd, 1H, H-4,  $J_{2,4}$  = 1.9 Hz,  $J_{1,4}$  = 0.3 Hz), 7.84 (dd, 1H, H-1,  $J_{1,2}$  = 8.2 Hz,  $J_{1,4}$  = 0.3 Hz), 7.91 (ddd, 1H, H-9,  $J_{8,9}$  = 7.7 Hz,  $J_{7,9}$  = 1.4 Hz,  $J_{6,9}$  = 0.7 Hz). –  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 156.5 (quart.), 156.3 (quart.), 132.7 (quart.), 127.4 (tert.), 123.5 (quart.), 123.3 (tert.), 123.1 (tert.), 123.0 (quart.), 121.2 (tert.), 120.6 (tert.), 112.3 (tert.), 111.8 (tert.). – MS:  $m/z$  (%) = 205(4), 204(30,  $\text{M}^+$ ), 203(12), 202(88,  $\text{M}^+$ ), 173(7), 167(4,  $\text{M}^+ - \text{Cl}$ ), 166(1), 148(1), 147(2), 140(13), 139(100), 138(17), 137(13), 113(22), 112(5), 111(21), 110(10), 109(5), 102(6), 101(18), 100(4), 99(12), 98(14), 97(6), 89(16), 88(10), 87(35), 86(26), 85(11), 75(20), 74(32), 73(12), 69(35), 65(4), 64(4), 63(40), 62(25), 61(11), 56(7), 55(5), 53(4), 51(15), 50(21).

**2-Chlorodibenzofuran (4):** 2-Aminodibenzofuran (1.25 g, 6.8 mmol), dissolved in 3.5 ml 6M  $\text{HCl}$  was diazotized with  $\text{NaNO}_2$  (474 mg/2.8 ml, 6.8 mmol) and reacted with  $\text{CuCl}$  (903 mg, 9.1 mmol, 1.3 eq.) as described above. The crude product was purified by chromatography on silica gel with hexane/ethylacetate (20:1). The yield was 330 mg (24%). *m.p.* = 102 °C (ref. [6]: 102–103 °C). – IR (KBr):  $\nu/\text{cm}^{-1}$  = 3068 (w), 2924 (w), 1622 (w), 1462 (s), 1441 (s), 1267 (w), 1244 (w), 1201 (s), 1105 (m), 1064 (m), 814 (s), 752 (s), 694 (m). –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.35 (ddd, 1H, H-8,  $J_{8,9}$  = 7.7 Hz,  $J_{7,8}$  = 7.3 Hz,  $J_{6,8}$  = 1.1 Hz), 7.40 (dd, 1H, H-3,  $J_{3,4}$  = 8.7 Hz,  $J_{1,3}$  = 2.2 Hz), 7.47 (dd, 1H, H-4,  $J_{3,4}$  = 8.7 Hz,  $J_{1,4}$  = 0.6 Hz), 7.48 (ddd, 1H, H-7,  $J_{6,7}$  = 8.3 Hz,  $J_{7,8}$  = 7.3 Hz,  $J_{7,9}$  = 1.4 Hz), 7.56 (ddd, 1H, H-6,  $J_{6,7}$  = 8.3 Hz,  $J_{6,8}$  = 1.1 Hz,  $J_{6,9}$  = 0.7 Hz), 7.90 (dd, 1H, H-1,  $J_{1,3}$  = 2.2 Hz,  $J_{1,4}$  = 0.6 Hz), 7.91 (ddd, 1H, H-9,  $J_{8,9}$  = 7.7 Hz,  $J_{7,9}$  = 1.4 Hz,  $J_{6,9}$  = 0.7 Hz). –  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 156.8 (quart.), 154.5 (quart.), 128.2 (quart), 127.9 (tert.), 127.2 (tert.), 125.7 (quart.), 123.4 (quart), 123.0 (tert.), 120.8 (tert.), 120.5 (tert.). – MS:  $m/z$  (%) = 205(2), 204(23,  $\text{M}^+$ ), 203(10), 202(70,  $\text{M}^+$ ), 173(5), 167(3,  $\text{M}^+ - \text{Cl}$ ), 147(2), 140(11), 139(100), 138(17), 137(14), 113(24), 112(6), 111(29), 110(15), 109(5), 102(5), 101(15), 100(5), 99(16), 98(19), 97(8), 89(19), 88(12), 87(45), 86(36), 85(14), 76(4), 75(25), 74(45), 73(16), 69(33), 64(5), 63(50), 62(33), 61(14), 56(7), 55(6), 53(5), 51(22), 50(30), 49(4), 40(17), 39(31), 38(23).

### Electrolyses (General procedure)

All electrolyses were carried out in a divided glass-cell (2×15 ml, anion-exchange membrane Permion 4035) with a lead disc electrode, a platinum net as counterelectrode and a silver wire as reference electrode. The potential was controlled with

a Wenking potentiostat HP 77. All glassware and the electrodes were dried overnight at 110 °C. It was not necessary to work under nitrogen because of the hydrogen evolution.

In order to clean the surface of the lead electrode it was dipped into aqua regia and conc.  $\text{HCl}$  and was washed with hot distilled water and methanol. The cell was built up and filled with methanol (2×15 ml) and tetraethylammonium bromide (2×0.32 g = 0.1M solution). The magnetic stirrer was switched on, the potential was adjusted (–2.2 V vs.  $\text{Ag}/\text{AgBr}$ ) and the substrate was added.

The catholyte was poured into 100 ml water, acidified with 4M  $\text{HCl}$  and extracted with 3×30 ml chloroform. A small sample was kept for GC/MS-measurements. The remaining solution was concentrated *in vacuo* and weighed.

### Electrolysis of 3-Chlorodibenzofuran (1) in $\text{CH}_3\text{OD}$

Substrate: 147 mg (0.725 mmol), charge: 4 F, chem. yield 69%, current efficiency: 42%; products (GC): 3-chlorodibenzofuran: 1%, dibenzofuran (**2a**): 32%, 1,4-dihydrodibenzofuran (**3b+3c**): 64%, other: 3%.

#### [3-D]Dibenzofuran (2a)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): as shown in Fig. 3. – MS:  $m/z$  (%) = 171(1), 170(14), 169(100,  $\text{M}^+$ ), 168(4), 141(9), 140(49), 139(8), 115(5), 114(8), 113(4), 90(5), 89(5), 88(6), 87(8), 86(6), 85(14), 75(7), 74(7), 70(10), 69(7), 64(7), 63(11).

#### [1,3,4- $D_3$ ]1,4-Dihydrodibenzofuran (3b) and [1,4,7- $D_3$ ]1,4-Di-hydrodibenzofuran (3c)

MS:  $m/z$  (%) = 175(1), 174(13), 173(100,  $\text{M}^+$ ), 172(89), 171(47), 170(10), 146(4), 145(18), 144(52), 143(29), 142(13), 141(15), 140(6), 119(3), 118(26), 117(43), 116(20), 115(6), 114(4), 104(4), 91(8), 90(9), 89(6), 88(7), 87(10), 86(8), 85(4), 79(4), 78(6), 77(7), 76(9), 75(10), 74(7), 73(5), 72(10), 71(10), 70(5), 66(4).

### Electrolysis of 3-Chlorodibenzofuran (1) in $\text{CD}_3\text{OH}$

Substrate: 157 mg (0.77 mmol); charge: 4 F; chem. yield 65%; current efficiency: 44%; products (GC): 3-chlorodibenzofuran: 12%, dibenzofuran (**2**): 14%, 1,4-dihydrodibenzofuran (**3**): 70%, other: 4%.

#### Dibenzofuran (2)

MS:  $m/z$  (%) = 170(1), 169(13), 168(100,  $\text{M}^+$ ), 140(5), 139(33), 138(2), 114(3), 113(5), 89(3), 88(2), 87(3), 86(2), 84(5), 75(2), 74(2), 69(4), 63(4), 62(2).

#### 1,4-Dihydrodibenzofuran (3)

MS:  $m/z$  (%) = 172(1), 171(13), 170(98,  $\text{M}^+$ ), 169(100), 168(14), 155(3), 153(1), 152(1), 151(1), 144(2), 143(1), 142(12), 141(43), 140(4), 139(18), 127(2), 116(4), 115(35), 114(3), 113(4), 102(2), 89(5), 88(2), 87(3), 86(2), 85(3), 84(2), 77(2), 76(2), 75(3), 74(3), 71(3), 69(2), 65(2), 63(7), 62(3), 57(3), 51(6).

### Electrolysis of 3-Chlorodibenzofuran (1) in $\text{CD}_3\text{OD}$

Substrate: 150 mg (0.74 mmol), charge: 5 F, chem. yield: 68%, current efficiency: 37%; products (GC): 3-chlorodibenzofuran: 9%, dibenzofuran (**2a**): 11%, 1,4-dihydrodibenzofuran (**3b+3c**): 66%, other: 14%.

**[3-D]Dibenzofuran (2a)**

MS:  $m/z$  (%) = 171(2), 170(11), 169(100,  $M^+$ ), 168(8), 142(3), 141(15), 140(83), 139(19), 115(13), 114(25), 113(13), 112(6), 111(8), 110(7), 99(7), 98(8), 90(17), 89(15), 88(23), 87(29), 86(22), 85(9), 84(20), 78(6), 77(5), 76(13), 75(27), 74(31), 70(11), 69(19), 65(5), 64(28), 63(45), 62(27), 61(11), 52(16), 51(28), 50(24).

**[1,3,4- $D_3$ ]1,4-Dihydrodibenzofuran (3b) and [1,4,7- $D_3$ ]1,4-Dihydrodibenzofuran (3c)**

MS:  $m/z$  (%) = 175(2), 174(16), 173(97,  $M^+$ ), 172(100), 171(58), 170(15), 169(3), 146(6), 145(31), 144(84), 143(58), 142(26), 141(27), 140(12), 119(10), 118(61), 117(108), 116(58), 115(19), 114(10), 113(5), 105(5), 104(10), 103(10), 102(6), 101(4), 100(4), 99(6), 98(5), 93(5), 92(10), 91(23), 90(26), 89(20), 88(23), 87(26), 86(19), 85(10), 80(5), 79(13), 78(19), 77(23), 76(29), 75(36), 74(22), 73(5), 72(13), 71(17), 70(9), 69(3), 67(10), 66(13), 65(24), 64(53), 63(48), 62(24), 61(8), 59(15), 58(6).

**Electrolysis of 2-Chlorodibenzofuran (4) in  $CH_3OD$  at  $-2.10$  V (vs. Ag/AgBr)**

Substrate: 100 mg (0.493 mmol), charge: 4 F, potential:  $-2.10$  V (vs Ag/AgBr), time of electrolysis: 2 h, chem. yield 81%, current efficiency: 47%; products (GC): 2-chlorodibenzofuran: 10%, dibenzofuran (2a+2b): 2%, 2-chloro-1,4-dihydrodibenzofuran (5a): 16%, 1,4-dihydrodibenzofuran (3d): 54%, other: 18%.

**[2-D]Dibenzofuran (2b) and [3-D]Dibenzofuran (2a)**

MS:  $m/z$  (%) = 170(10), 169(100,  $M^+$ ), 168(19), 141(12), 140(74), 139(33), 115(5), 114(26), 113(13), 111(4), 90(8), 89(18), 88(29), 87(36), 86(26), 85(16), 75(31), 74(38), 70(16), 64(24), 63(54), 62(35), 61(5), 52(13), 51(30), 50(30).

**Mixture of [ $D_3$ ]1,4-Dihydrodibenzofuran isomers (3d)**

MS:  $m/z$  (%) = 175(1), 174(12), 173(95,  $M^+$ ), 172(98), 171(58), 170(14), 169(3), 146(6), 145(28), 144(80), 143(55), 142(23), 141(25), 140(12), 129(4), 128(4), 119(7), 118(56), 117(100), 116(52), 115(17), 114(10), 105(5), 104(9), 103(9), 102(5), 99(6), 98(4), 93(5), 92(9), 91(21), 90(24), 89(17), 88(22), 87(24), 86(17), 85(8), 79(12), 78(18), 77(21), 76(27), 75(32), 74(21), 73(12), 71(16), 70(11), 67(9), 66(12), 65(22), 64(47), 63(42), 62(20).

**[1,4- $D_2$ ]2-Chloro-1,4-dihydrodibenzofuran (5a)**

$^1H$  NMR (400 MHz,  $CDCl_3$ ): as shown in Fig. 4. – MS:  $m/z$  (%) = 208(9,  $M^+$ ), 207(5), 206(30,  $M^+$ ), 205(3), 204(1), 172(13), 171(100,  $M^+ - Cl$ ), 170(28), 169(12), 144(12), 143(85), 142(13), 141(48), 140(33), 139(8), 118(9), 117(67), 116(51), 115(19), 114(17), 113(8), 112(7), 111(8), 110(4), 104(7), 103(12), 102(8), 101(7), 100(7), 99(11), 98(7), 91(12), 90(21), 89(18), 88(29), 87(28), 86(20), 85(25), 79(7), 78(11), 77(21), 76(33), 75(41), 74(33), 73(8), 72(14), 71(30), 70(17).

**Electrolysis of 2-Chlorodibenzofuran (4) in  $CH_3OD$  at  $-1.80$  V (vs. Ag/AgBr)**

Substrate: 60 mg (0.296 mmol), charge: 4 F, potential:  $-1.80$  V (vs Ag/AgBr), time of electrolysis: 23 h, chem. yield: 69%, current efficiency: 26%; products (GC): 2-chlorodibenzofuran:

17%, dibenzofuran (2a+2b): 68%, 2-chloro-1,4-dihydrodibenzofuran (5a): 6%, 1,4-dihydrodibenzofuran (3d): 9%.

**[2-D]Dibenzofuran (2b) and [3-D]Dibenzofuran (2a)**

MS:  $m/z$  (%) = 171(1), 170(14), 169(100,  $M^+$ ), 168(7), 141(7), 140(37), 139(8), 115(4), 114(6), 113(3), 90(4), 89(5), 88(6), 87(7), 86(5), 85(3), 84(24), 76(4), 75(7), 74(7), 70(20), 69(19), 64(8), 63(13), 62(8).

**Mixture of [ $D_3$ ]1,4-Dihydrodibenzofuran isomers (3d)**

MS:  $m/z$  (%) = 175(2), 174(15), 173(100,  $M^+$ ), 172(94), 171(57), 170(19), 169(14), 168(1), 146(3), 145(15), 144(42), 143(26), 142(13), 141(15), 140(10), 119(3), 118(20), 117(34), 116(17), 115(7), 114(4), 105(2), 104(3), 103(3), 92(3), 91(8), 90(9), 89(7), 88(7), 87(15), 86(13), 85(9), 79(5), 78(8), 77(9), 76(11), 75(13), 74(9), 72(14), 71(23), 70(10), 70(24), 67(5), 66(6), 65(11), 64(24), 63(20), 62(10).

**[1,4- $D_2$ ]2-Chloro-1,4-dihydrodibenzofuran (5a)**

MS:  $m/z$  (%) = 209(2), 208(11,  $M^+$ ), 207(9), 206(34,  $M^+$ ), 205(8), 204(6), 203(4), 202(3), 172(19), 171(100,  $M^+ - Cl$ ), 170(33), 169(12), 144(7), 143(37), 142(9), 141(20), 140(16), 139(5), 138(2), 118(3), 117(18), 116(15), 115(6), 114(5), 103(5), 102(3), 91(3), 90(6), 89(6), 88(7), 87(7), 86(7), 85(24), 77(6), 76(10), 75(12), 74(9), 71(23), 70(37), 69(17), 65(5), 64(13), 63(15), 62(8).

**Electrolysis of 2-Chlorodibenzofuran (4) in  $CD_3OH$** 

Substrate: 104 mg (0.513 mmol), charge: 2.5 F, chem. yield 68%, current efficiency: 38%; products (GC): 2-chlorodibenzofuran: 19%, dibenzofuran (2): 4%, 2-chloro-1,4-dihydrodibenzofuran (5): 33%, 1,4-dihydrodibenzofuran (3): 33%, other: 11%.

**Dibenzofuran (2)**

MS:  $m/z$  (%) = 170(1), 169(15), 168(100,  $M^+$ ), 141(2), 140(15), 139(77), 138(2), 137(2), 114(11), 113(19), 111(5), 110(3), 98(6), 89(15), 88(11), 87(25), 86(17), 85(9), 84(17), 77(3), 76(3), 75(18), 74(23), 70(4), 69(20), 65(3), 64(5), 63(35), 62(21).

**1,4-Dihydrodibenzofuran (3)**

MS:  $m/z$  = 172(1), 171(13), 170(89,  $M^+$ ), 169(92), 168(12), 155(3), 144(3), 143(3), 142(25), 141(78), 140(7), 139(33), 116(14), 115(100), 114(9), 113(11), 102(9), 101(3), 98(5), 91(4), 90(4), 89(24), 88(8), 87(17), 86(11), 85(9), 84(5), 77(13), 76(12), 75(19), 74(20), 71(5), 70(13), 69(12), 65(10), 64(8), 63(40), 62(17), 61(4).

**2-Chloro-1,4-dihydrodibenzofuran (5)**

MS:  $m/z$  (%) = 207(1), 206(9,  $M^+$ ), 205(4), 204(29,  $M^+$ ), 203(3), 202(3), 171(1), 170(13), 169(100,  $M^+ - Cl$ ), 168(31), 167(1), 142(8), 141(61), 140(10), 139(54), 116(6), 115(60), 114(9), 113(14), 111(6), 110(4), 102(8), 101(5), 99(6), 98(6), 89(18), 88(8), 87(20), 86(13), 85(8), 84(15), 77(8), 76(10), 75(22), 74(21), 73(6), 70(18), 69(27), 65(6), 64(5), 63(35), 62(17), 61(6).

**Electrolysis of 2-Chlorodibenzofuran (4) in  $CD_3OD$** 

Substrate: 107mg (0.528mmol), charge: 5F, chem. yield 76%, current efficiency: 32%; products (GC): 2-chlorodibenzofuran:

11%, dibenzofuran (**2a+2b**): 5%, 2-chloro-1,4-dihydrodibenzofuran (**5a**): 16%, 1,4-dihydrodibenzofuran (**3d**): 60%, other: 8%.

**[2-D]Dibenzofuran (2b) and [3-D]Dibenzofuran (2a)**

MS:  $m/z$  (%) = 171(3), 170(16), 169(100,  $M^+$ ), 168(15), 141(13), 140(64), 139(18), 115(8), 114(15), 113(9), 98(4), 90(9), 90(48), 89(11), 89(37), 88(15), 88(43), 87(19), 87(48), 86(13), 86(34), 85(24), 85(18), 80(10), 79(23), 78(35), 77(43), 76(9), 76(54), 75(17), 75(65), 74(18), 74(41), 73(10), 72(24), 71(31), 70(24), 70(17), 69(6), 68(7), 67(18), 66(1), 66(24), 65(5), 65(44), 64(16), 64(96), 63(29), 63(87), 62(17), 62(43), 61(6), 61(14), 59(28), 59(8), 58(10).

**Mixture of [D<sub>3</sub>]1,4-Dihydrodibenzofuran isomers (3d)**

MS:  $m/z$  (%) = 175(2), 174(16), 173(100,  $M^+$ ), 172(99), 171(57), 170(14), 169(3), 146(5), 145(23), 144(63), 143(41), 142(18), 141(19), 140(9), 119(6), 118(37), 117(63), 116(32), 115(10), 114(6), 104(6), 103(5), 93(3), 92(5), 91(13), 90(14), 89(10), 88(11), 87(15), 86(11), 85(6), 79(7), 78(10), 77(13), 76(15), 75(18), 74(11), 73(5), 72(11), 71(12), 70(8).

**[1,4-D<sub>2</sub>]2-Chloro-1,4-dihydrodibenzofuran (5a)**

MS:  $m/z$  (%) = 209(2), 208(10,  $M^+$ ), 207(7), 206(30,  $M^+$ ), 205(6), 204(3), 172(18), 171(100,  $M^+ - Cl$ ), 170(34), 169(14), 144(12), 143(70), 142(16), 141(38), 140(30), 139(7), 118(7), 117(50), 116(40), 115(16), 114(12), 113(6), 112(5), 111(5), 104(5), 103(9), 102(6), 101(5), 100(5), 99(7), 98(5), 91(8), 90(15), 89(14), 88(19), 87(20), 86(14), 85(20), 84(5), 79(4), 78(8), 77(15), 76(23), 75(28), 74(23), 73(5), 71(25), 70(28), 69(6).

**Electrolysis of 2-Chlorodibenzofuran (4) in CH<sub>3</sub>OH/δ<sub>36</sub>-TBAB**

Substrate: 100 mg (0.493 mmol), charge: 8.8 F, potential: – 2.2 V (vs Ag/AgBr), chem. yield 72%, current efficiency: 15%; products (GC): 2-chlorodibenzofuran: 8%, dibenzofuran (**2**): 4%, 2-chloro-1,4-dihydrodibenzofuran (**5**): 58%, 1,4-dihydrodibenzofuran (**3**): 28%, other: 2%.

**Dibenzofuran (2)**

MS:  $m/z$  (%) = 170(2), 169(24), 168(100,  $M^+$ ), 141(2), 140(20), 139(77), 138(2), 114(12), 113(20), 111(6), 110(4), 101(3), 99(3), 98(7), 89(17), 88(12), 87(26), 86(18), 85(10), 84(18), 77(4), 76(4), 75(19), 74(24), 70(6), 69(21), 65(3), 64(7), 63(37), 62(22), 61(7), 53(3), 51(16), 50(16).

**1,4-Dihydrodibenzofuran (3)**

MS:  $m/z$  (%) = 174(1), 173(8), 172(9), 171(17), 170(89,  $M^+$ ), 169(92), 168(12), 156(1), 155(3), 153(2), 152(1), 151(1), 144(8), 143(7), 142(27), 141(79), 140(8), 139(33), 127(3), 126(2), 118(4), 117(6), 116(16), 115(100,  $C_9H_7^+$ ), 114(10), 113(11), 102(9), 98(5), 91(5), 90(5), 89(24), 88(9), 87(18), 86(12), 85(10), 84(5), 78(4), 77(14), 76(13), 75(20), 74(21), 71(6), 70(13), 69(12), 65(11), 64(10), 63(42), 62(18).

**2-Chloro-1,4-dihydrodibenzofuran (5)**

MS:  $m/z$  (%) = 207(1), 206(11,  $M^+$ ), 205(6), 204(36,  $M^+$ ), 203(4), 202(6), 170(13), 169(100), 168(30), 149(2), 142(4), 141(33), 140(5), 139(27), 138(2), 116(3), 115(24), 114(4), 113(5), 102(5), 101(3), 89(9), 88(4), 87(8), 86(6), 85(6), 84(19), 77(3), 76(4), 75(10), 74(9), 70(20), 69(35), 63(12), 62(6), 57(8).

**Electrolysis of Dibenzofuran (2) in CH<sub>3</sub>OD**

Substrate: 150 mg (0.89 mmol), charge: 6.1 F, chem. yield 71%, current efficiency: 11%; products (GC): dibenzofuran: 37%, 1,4-dihydrodibenzofuran (**3a**): 61%, tetrahydroderivative: 2%.

**[1,4-D<sub>2</sub>]1,4-Dihydrodibenzofuran (3a)**

MS:  $m/z$  (%) = 174(1), 173(15), 172(100,  $M^+$ ), 171(95), 170(48), 169(11), 168(2), 156(3), 145(3), 144(16), 143(51), 142(18), 141(13), 140(12), 139(3), 118(4), 117(28), 116(28), 115(8), 114(4), 103(3), 91(4), 90(8), 89(6), 88(5), 87(6), 86(11), 85(6), 84(4), 78(5), 77(7), 76(8), 75(10), 74(7), 72(7), 71(16), 70(16), 69(6), 66(4), 65(5), 64(15), 63(17), 62(8).

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