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Novel Template-Directed Anodic Phenol-Coupling Reaction

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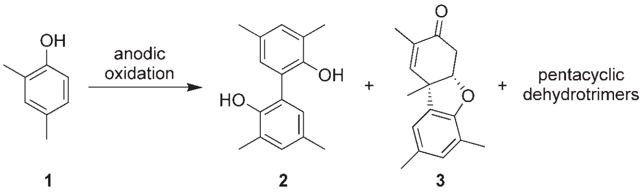
Abstract: Substituted phenols were anodically coupled to the corresponding 2,2′-biphenols via tetraphenoxy borate derivatives. This electrochemical method is particularly useful for methyl-substituted substrates, such as 2,4-dimethyl phenol. The selective *ortho*-coupling reaction can be easily performed on a multikilogram scale.

Keywords: borates • C–C coupling • electrochemistry • oxidation • phenols

Introduction

The oxidative-coupling reaction of phenolic substrates plays a significant role in the synthesis of natural products.[1] Several methodologies have been elaborated for the oxidative-coupling process of electron-rich arenes. In particular, the selective *ortho*-coupling of phenols has been addressed by numerous catalytic and stoichiometric approaches, in which sterically hindered *tert*-butylated phenols, as well as naphthols, represent preferred substrates.[2] Simple phenols, such as 2,4-dimethyl phenol (**1**), tend to result in polycyclic byproducts,[3] and, therefore, are not useful substrates (Scheme 1).



Scheme 1. Electrochemical oxidation of 2,4-dimethyl phenol (**1**).

If oxophilic polyvalent Lewis acids, such as $FeCl_3$, are employed, an intermediate template containing the metal centre is anticipated. This often results in the desired *ortho*–*ortho* coupling product.[4] To exploit other reagents for the oxidative transformation, covalently tethered phenolates were successfully applied. Various elements, such as Ti, Zr, Si and P, have been studied as oxophilic centres for enolates and phenolates in oxidative-coupling processes.[5] The best synthetic versatility was obtained for the silicon-based systems.[6]

Because the oxidation of a tethered system will significantly weaken the bond between the centre tether and the phenolate, only very oxophilic elements appear to be suitable. Furthermore, the possibility of higher coordination numbers limits the stability of such tethers, due to exchange processes on the metal centre. Consequently, phenoxy borates should be ideal substrates in terms of tethered phenolates. Surprisingly, the oxidation of boron phenolates has not yet been described in the coupling reaction to the corresponding biphenols. Because we have a particular interest in the selective dehydrodimerisation of simple substrates, such as 2,4-dimethyl phenol (**1**), we developed a novel concept for the anodic-coupling process of methyl-substituted phenols, which is also feasible on larger scale.[7]

Results and Discussion

In preliminary studies on the template-directed electrochemical synthesis of 2,2′-biphenol **2** from 2,4-dimethyl phenol (**1**), the crude product **4** from the condensation reaction of **1** with boric acid was subjected directly to anodic oxidation resulting in the desired dehydrodimer **2** (Scheme 2). Moreover, the intramolecular C–C coupling reaction took

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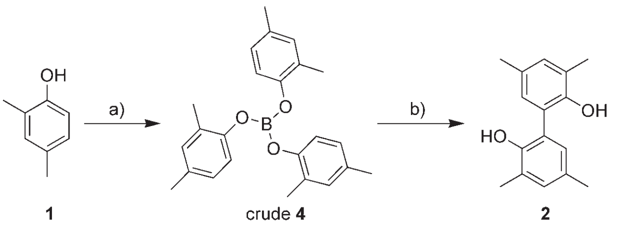
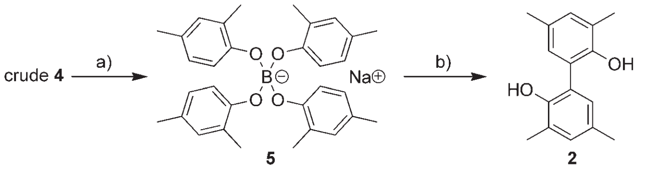


Scheme 2. Boron-templated synthesis of **2**. Reagents: a) $B(OH)_3$, toluene, 12 h reflux on a Dean–Stark trap, quantitative yield; b) electrochemical oxidation, Bu_4NBF_4, CH_2Cl_2, RT, then hot water (60 °C), citric acid, 37–46 %.[8]

place with high chemoselectivity in favour of **2**. The ratio of biphenol **2** to *Pummerer's* ketone **3** from the direct conversion of **1** in methanol, 1:10, was reversed to 12:1 with a yield of 46 % of **2** by using crude **4**.[3,7]

Upon studying the impact of the borate tether, it appeared that crude condensation products of **1** and boric acid, consisting of stoichiometries other than 3:1, also worked in the anodic process.[8] Mass-spectrometric investigation of all these crude borates **4** indicated the presence of several trigonal borate species, such as boroxines and other polynuclear phenoxy borate derivatives.[9] Surprisingly, analytically pure boric acid ester **4** obtained by distillation in high vacuum (10^{-4}–10^{-5} mbar) did not undergo the anodic conversion. However, the stoichiometry of **4** is not optimal for an efficient synthesis of **2**, because one phenyl moiety on the borate should remain unaffected. Because of the indistinct nature of the electrochemically active compound in crude **4**, and a suboptimal orientation of phenyl substituents on a trigonal borate, a novel template was developed by extending the triphenyl borate to the anionic tetraphenoxy borate **5** (Scheme 3).



Scheme 3. Electrochemical synthesis of **2** via tetraphenoxy borate **5**. Reagents: a) Na, **1**, THF;[10] b) electrochemical oxidation, then hot water (60 °C), citric acid.

The synthesis of sodium tetraphenoxy borate **5** was performed by using a recently reported protocol and provides the desired templated phenolate in large quantities.[10] Despite time-consuming preparation of pure **4**, the corresponding tetragonal species **5** is readily accessible as a pure crystalline compound. The enhanced coordination number from three to four leads to a higher proximity of phenoxy moieties. This results in several beneficial aspects; for example, the maximum coordination number at the boron centre enhances the stability of the templated system. Furthermore, the appropriate stoichiometry in phenolate moieties is achieved. A good preorientation at the reactive subunits brings the individual *ortho* positions into proximity to support the selective oxidative-coupling transformation. The main advantage for anodic conversions of **5** is based on the anionic nature of the electrochemically active substrate. Consequently, the tetraphenoxy borate migrates in the electric field to the anode. Due to the ionic character of **5**, it combines the function of substrate and supporting electrolyte in a single compound! Thus, no additional electrolyte is required for the electrolysis.

Electroanalytic experiments with borate **5** were performed by using cyclic voltammetry (CV) and revealed, as expected, an irreversible oxidation process (Figure 1).

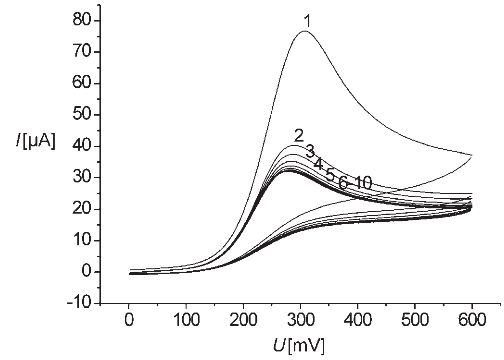


Figure 1. Cyclic voltammogram of **5** (5×10^{-3} M in 0.1 M Bu_4NClO_4/CH_3CN; vs.Ag/0.01 M $AgNO_3$ in 0.1 M Bu_4NClO_4/CH_3CN; 100 mV s^{-1}; 10 cycles).

The intensity of the oxidation peak decreases as the CV experiment progresses and levels off at about 32 μA after seven cycles, indicating an equilibrium of mass transport to and from the electrode. The maximum peak potential experiences a slight shift to lower potential from about 300 to 278 mV. This can be explained by an EC_{irr} mechanism, which characterises an electron-transfer process that is followed by an irreversible chemical reaction.[11] Nevertheless, for practical reasons, the electrochemical experiments towards the synthesis of bulk quantities of biphenol **2** were performed under galvanostatic conditions. The extent of the overoxidation processes leading to undefined decomposition products is determined clearly by the reaction conditions. Therefore, solvent and temperature of the electrolysis were systematically varied (Table 1).

The anodic conversion of **5** requires a solvent, which exhibits adequate polarity to support the dissociation of the sodium borate as electrolyte. ^{11}B NMR studies revealed sufficient stability of **5** in the applied solvents, and during electrolysis no interference with the templated substrate was anticipated.[10] Although not a common solvent for anodic oxidations, THF was employed because **5** exhibits an excellent solubility therein. However, no current flow could be induced, indicating that **5** is dissolved, but not dissociated into ion pairs (Table 1, entry 1). The same phenomenon was observed for propylencarbonate and *tert*-butanol based electrolytes. Switching to a methanolic solution resulted in a cur-

Table 1. Electrochemical oxidation of **5**.

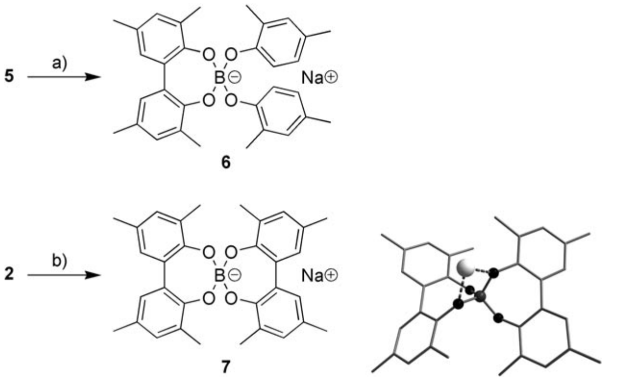
Entry	Electrolyte	Scale [g][a]	T [°C]	Recovery of **1** [%][b]	Yield of **2** [%]	Yield of **3** [%]
1	**5** (0.15 M) in THF	20[c]	20	99	–	–
2	**5** (0.15 M) in MeOH	20[c]	20	1	11	10
3	**5** (0.15 M) in DMF	20[c]	20	65	2	–
4	**5** (0.15 M) in CH_3CN	20[c]	20	2	24	4
5	**5** (0.15 M) in CH_3CN	20[c]	40	11	46	–
6	**5** (0.15 M) in CH_3CN	90[d]	40	–	85	–
7	**5** (0.12 M) in CH_3CN	3000[e]	40	28[f]	63[f]	n.d.

[a] Total mass of electrolyte. [b] After work-up. [c] With 8 cm^2 Pt electrode, 12.5 mA cm^{-2}. [d] With 21 cm^2 Pt electrode, 12.5 mA cm^{-2}. [e] In 734 cm^2 graphite capillary-gap cell, 15 mA cm^{-2}.[14] [f] Determined by GC using internal standard.

rent flow under moderate terminal voltage, but provided low yields of the desired product **2**. Unfortunately, the conversion of **5** in methanol was accompanied by formation of the undesired *Pummerer's* ketone **3** and severe decomposition, so only small quantities of phenol **1** could be recovered (entry 2). The electrochemical oxidation of **5** in DMF gave only sluggish formation of **2** and considerable decomposition (entry 3). If acetonitrile was applied, moderate yields of **2** were obtained and, again, extensive side reactions to polyphenolic products took place (entry 4). Because, in some cases, electrochemical oxidations benefited by elevated temperatures, the most promising run at ambient conditions was repeated at 40 °C (entry 5). In fact, the increased reaction temperature almost doubled the yield of **2**, and furthermore, the amount of recovered phenol **1** rose significantly relative to the conversion at room temperature. A higher electrolysis temperature of up to 60 °C did not improve the yield of **2**.

In many runs, the electrolyses of **5** stopped after 50 % conversion, indicated by a rapid rise in the terminal voltage. Therefore, ^{11}B NMR studies were performed to monitor the reaction progress. A vanishing signal at 3.2 ppm clearly demonstrated the consumption of borate **5**, whereas the signal for a product emerged at 6.3 ppm. To clearly identify the observed product or intermediate, biphenoxybis(phenoxy) borate **6** and bis(biphenoxy) borate **7**, which represent the anticipated intermediates after the first and the second intramolecular C–C bond formation, respectively, were examined more closely (Scheme 4).

The synthesis of borate **6** was accomplished by simple ligand exchange starting from the corresponding tetraphenoxy borate **5** and one equivalent of biphenol **2**. Because borate **6** exhibits lower solubility than **5**, direct crystallisation from the reaction mixture occurred. The liberated phenol **1** remains dissolved and was removed along with the filtrate. Borate **6** was obtained as an analytically pure powder. In contrast, borate **7** was synthesised directly from boric acid and **2**, followed by addition of sodium methanolate according to a modified protocol.[12] In addition, a single crystal of **7** was obtained that could be used for X-ray analysis. The structural features of bis(biphenoxy) borate **7** are quite similar to those observed for most tetraphenoxy borates.[10] The boron–oxygen distances of about 1.47 Å and an elongated tetrahedral geometry of **7** are also characteristic for **5** and its derivatives.[10]



Scheme 4. Synthesis of borates **6** and **7** (including the molecular structure of **7** obtained by X-ray analysis). Reagents: a) **2**, THF, RT, 69 %; b) $B(OH)_3$, methanol, 1 h reflux, then NaOMe, 77 %.

According to CV experiments, precursor **5** is more-readily oxidised than borates **6** and **7** (Figures 1–3 and Table 2).

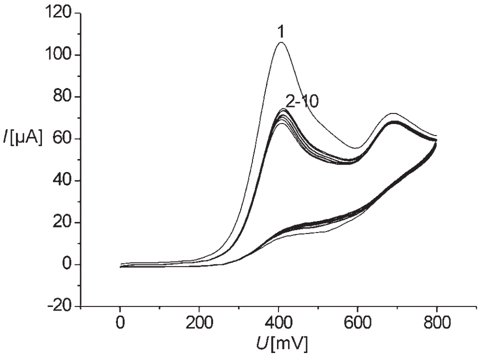


Figure 2. Cyclic voltammogram of **6** (5×10^{-3} M in 0.1 M Bu_4NClO_4/CH_3CN; vs.Ag/0.01 M $AgNO_3$ in 0.1 M Bu_4NClO_4/CH_3CN; 100 mV s^{-1}; 10 cycles).

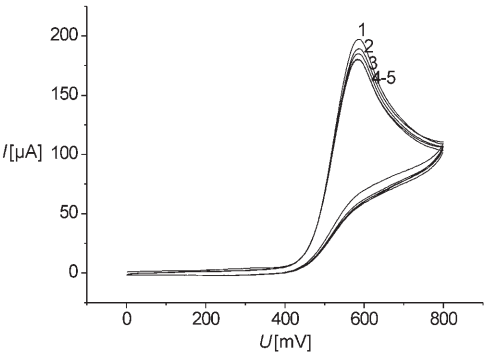


Figure 3. Cyclic voltammogram of **7** (1×10^{-2} M in 0.1 M Bu_4NClO_4/CH_3CN; vs.Ag/0.01 M $AgNO_3$ in 0.1 M Bu_4NClO_4/CH_3CN; 100 mV s^{-1}; 5 cycles).

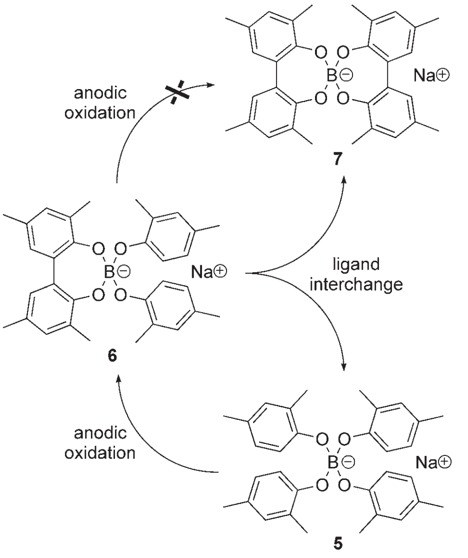
Table 2. ^{11}B NMR (64 MHz, CD_3CN, RT) and CV data for borates **5**, **6** and **7**.

Entry	Borate	δ [ppm]	E_{pa} [mV]
1	**5**	3.21	278
2	**6**	6.26	412, 692
3	**7**	7.99	586

Two oxidation processes can be detected for borate **6**, as it contains two redox-active ligands: the biphenol chelate and two equal phenol moieties (Figure 2; Table 2, entry 2). As anticipated, borate **7** requires the highest potential for the initial oxidation step (Figure 3; Table 2, entry 3).

Comparison of the ^{11}B NMR data of **5**–**7** with samples taken from the electrolysis reaction mixture indicated borate **6** with $\delta = 6.3$ ppm as a sole product from the oxidation of **5** (Table 2). As soon as tetraphenoxy borate **5** was completely consumed, the conversion stagnated and no formation of **7** by the second oxidation sequence was observed. Furthermore, a control experiment revealed that **6** could not be oxidised to **7** under the elaborated conditions, thus, the process had to be limited to 50 % maximum yield. As the first C–C bond formation is accomplished, the conformational freedom of the remaining phenolates in **6** is drastically restricted. The repulsive interaction between the *ortho*-methyl groups of the phenoxy and biphenoxy ligands inhibits the oxidative-coupling process, because the appropriate geometry for the intramolecular attack is sterically hindered. Nevertheless, the most dramatic effect was observed upon scaling up the electrolysis of **5** under optimised reaction conditions. The reaction volume was enlarged by a factor of 4.5, whereas the surface of the electrodes was increased by a factor of only 2.5. This resulted in a prolonged electrolysis time and provided a surprising yield of biphenol **2** of 85 % (Table 1, entry 6). An explanation for this unexpected reaction outcome was found by serendipity: the NMR tube containing the solution of borate **6** in deuterated solvent was stored for a few weeks and the ^{11}B NMR data for this sample were recorded again.[13] Surprisingly, apart from **6**, two further compounds were indicated by smaller signals at 3.2 and 8.0 ppm, matching borates **5** and **7**, respectively. Thus, two molecules of the mixed borate **6** undergo a slow ligand interchange to form the more symmetric borates **5** and **7** (Scheme 5).

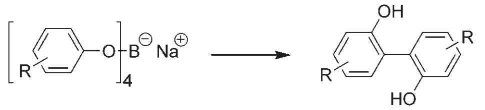
This ligand interchange overcomes the supposed conversion limit of 50 %. By disproportion of the electrochemically inactive intermediate **6** and regeneration of the reactive tetraphenoxy borate **5**, new substrate for the intramolecular-coupling reaction is provided in situ and the effective yield of **2** can be increased to 85 % (Scheme 5). The electrochemical conversion at elevated temperatures seems to be beneficial and the key to a reasonably fast ligand exchange. A large reservoir of reaction mixture provides a continuous supply of **5** for the anodic process. The driving force for the ligand exchange is the formation of the strongly entropically favoured bischelated borate **7**. Interestingly, the relatively low solubility of **6** allows a direct monitoring of the ligand interchange. Upon application of almost half of the calculated current, a significant amount of precipitate, consisting of **6**, is formed. Further electrolysis dissolves the solid intermediate completely.



Scheme 5. Conversion of **6** to borates **5** and **7** by ligand interchange.

In an attempt at a large-scale synthesis of biphenol **2**, the electrochemical conversion of **5** was performed in a capillary-gap cell[14] on a 3 kg scale. Again, the yield could be improved relative to the primal 20 g batch. Notably, the reaction outcome indicated only slight decomposition processes and provided 63 % yield of **2** (Table 1, entry 7). A single crystallisation from toluene/heptane provided a high-quality product **2** with marginal loss of material.[7] Furthermore, the electrolysis can be performed on inexpensive graphite electrodes.

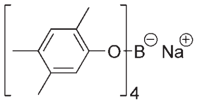
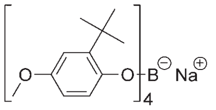
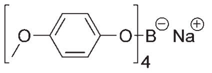
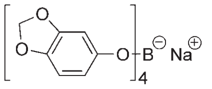
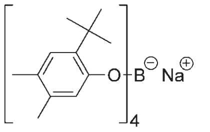
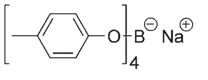
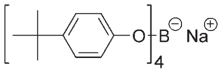
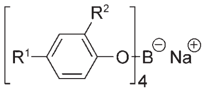
The strategy for the template-directed electrochemical synthesis of 2,2′-biphenols was extended to further substrates of potential interest (Scheme 6 and Table 3).



Scheme 6. Template-directed electrochemical synthesis of 2,2′-biphenols. Reagents: Pt electrodes, CH_3CN, 40 °C, then hot water (60 °C), citric acid.

The method was optimised for **5** and was tested on several other borates without specific optimisation modifications. Nevertheless, biphenols **8**–**14** were obtained in moderate to good yields by using the borate-tethered oxidative-coupling reaction. The beneficial scale-up phenomenon observed in the conversion of borate **5** in terms of ligand interchange was not found to occur in the oxidation of other substrates. However, particularly electron-rich phenoxy borates gave reasonable yields of the corresponding biphenols, such as

Table 3. Template-directed electrochemical synthesis of 2,2′-biphenols.

Entry		Borate	Yield [%] (biphenol)	Current efficacy [%]
1	**5**		85 (**2**)	66
2	**8a**		66 (**8**)	52
3	**9a**		58 (**9**)	36
4	**10a**		48 (**10**)	61
5	**11a**		34 (**11**)	26
6	**12a**		30 (**12**)	18
7	**13a**		30 (**13**)	51
8	**14a**		20 (**14**)	41
9	**15a**: $R^1=H, R^2=CH_3$ **16a**: $R^1=Cl, R^2=H$ **17a**: $R^1=R^2=H$		– – –	n.d. n.d. n.d.

hexamethyl-substituted **8** (Table 3, entry 2) and alkoxy-substituted **9** and **10** (Table 3, entries 3 and 4). Due to potential overoxidation, the use of highly electron-rich borate **11a** or sterically demanding substrate **12a** resulted in low current efficacies (Table 3, entries 5 and 6). Solely *para*-alkyl-substituted phenoxy borates underwent the electrochemical oxidation in low-to-moderate yields with decreased selectivity (Table 3, entries 7 and 8). The anodic conversion of **13a** and **14a** provided the desired 2,2′-biphenols, as well as small amounts of the corresponding 2-hydroxy-4′,5-dialkyl diphenyl ethers by means of an O–C coupling reaction.[15] If borates of *ortho*-cresol (**15a**), 4-chlorophenol (**16a**) or phenol (**17a**) were subjected to this transformation, no conversion was obtained (Table 3, entry 9).

Although the methodology presented herein is limited to substrates with electron-donating substituents in the *para* position of the phenoxy moieties, it represents a feasible tool for the large-scale electrochemical synthesis of 2,2′-biphenols.

Conclusion

If electron-rich phenols containing a substituent in the *para* position are templated as tetraphenoxy borates, an anodic conversion yields the *ortho*-coupled products selectively. Remarkably, tetraphenoxy borates serve as substrates and supporting electrolyte in the electrolysis. The novel methodology was optimised for 2,4-dimethyl phenol and provides 85 % of pure biphenol after hydrolytic work-up. Ligand interchange of the boron template is crucial for high conversions and can be monitored by ^{11}B NMR spectroscopy. The templated electrochemical biphenol synthesis can be applied on a multikilogram scale and provides a highly pure product. The scope of the anodic conversion was successfully extended to a variety of electron-rich substrates.

Experimental Section

General remarks: All reagents used were of analytical grade. Solvents were desiccated if necessary by standard methods. Column chromatography was performed on silica gel (particle size 63–200 μm, Merck, Darmstadt, Germany) by using mixtures of cyclohexane with ethyl acetate as eluents. Melting points were determined by using a melting point apparatus SMP3 (Stuart Scientific, Watford Herts, UK) and were uncorrected. Microanalyses were performed by using a Vario EL III (Elementar-Analysensysteme, Hanau, Germany). Cyclic voltammetry experiments were performed by using a BAS 100B electrochemical analyzer (BASi, West Lafayette, USA) using an Ag/Ag^+ reference electrode, a glassy-carbon working electrode and a Pt auxiliary electrode. ^{1}H NMR spectra were recorded at 25 °C by using a Bruker ARX 300, AMX 300 or AMX 400 instrument (Analytische Messtechnik, Karlsruhe, Germany). Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS as internal standard or traces of $CHCl_3$, [D_5]DMSO, [D_7]THF or CD_2HCN in the corresponding deuterated solvents. ^{11}B NMR spectra were recorded at 25 °C by using a Bruker AC 200 spectrometer with external calibration relative to $BF_3{\cdot}Et_2O$. Mass spectra were obtained by using a MAT8200, MAT95XL (Finnigan, Bremen, Germany) or MS50 (Kratos, Manchester, England) apparatus employing EI and by using a Quattro LC (Waters-Micromass), or Micro TOF (Bruker) apparatus employing ESI and HRMS (negative mode).

3,3′,5,5′-Tetramethyl-2,2′-biphenol (2): Sodium[tetrakis(2,4-dimethylphenoxy)borate] (**5**) (9.93 g, 19.2 mmol) was dissolved in acetonitrile (100 mL) and transferred into a nondivided, standard electrolysis cell[16] equipped with two platinum sheets as anode and cathode, respectively. At 40 °C, a galvanostatic electrolysis with a current density of 12.5 mA cm^{-2} was performed. During electrolysis, the polarity was reversed every 60 s to avoid electrode coating. After complete reaction (ca. 4.9 F) the electrolysis was stopped and citric acid was added (ca. 1.60 g, 8.3 mmol). The reaction mixture was diluted with hot water (60 °C, 300 mL), stirred for 5 min and extracted with *tert*-butyl methyl ether (TBME, 3 × 70 mL). The combined organic layers were washed with brine (80 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (cyclohexane/ethyl acetate 98:2, then 95:5) yielded **2** as colourless solid (7.82 g, 32.3 mmol, 85 %). M.p. 135 °C (cyclohexane, value in ref. [17]: m.p. 134–135 °C); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.27$ (s, 12H; CH$_3$), 5.04 (s, 2H; OH), 6.85 (s, 2H; 4-H), 6.98 ppm (s, 2H; 6-H); elemental analysis calcd (%) for $C_{16}H_{18}O_2$ (242.13): C 79.31, H 7.49; found: C 79.21, H 7.35.

Sodium[(3,3′,5,5′-tetramethyl-2,2′-biphenoxy)bis(2″,4″-dimethylphenoxy)-borate] (6): The solution of sodium[tetrakis(2,4-dimethylphenoxy)borate] (**5**) (0.49 g, 0.9 mmol) and 3,3′,5,5′-tetramethyl-2,2′-biphenol (**2**) (0.23 g, 0.9 mmol) in THF (5 mL) was stirred for 2 h at RT. The reaction mixture was concentrated to half the volume and stored for 12 h at 4 °C. The crystalline precipitate was isolated by filtration and subsequent washing with diethyl ether (2 mL). Drying in high vacuum yielded **6** as colourless solid (0.32 g, 0.6 mmol, 69 %). ^{1}H NMR (300 MHz, [D$_8$]THF): $\delta = 2.01$ (s, 6H; CH$_3$), 2.07 (s, 6H; CH$_3$), 2.10 (s, 6H; CH$_3$), 2.26 (s, 6H; CH$_3$), 6.56 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.8 Hz, 2H; 5″-H), 6.67 (d, ^4J(H,H) = 1.8 Hz, 2H; 3″-H), 6.77 (s, 2H; 4-H), 6.95 (d, ^4J(H,H) = 1.8 Hz, 2H; 6-H), 7.21 ppm (d, ^3J(H,H) = 8.3 Hz, 2H; 6″-H); ^{13}C NMR (75 MHz, [D$_8$]THF): $\delta = 17.59$ (CH$_3$), 17.83 (CH$_3$), 20.77 (CH$_3$), 20.96 (CH$_3$), 119.44, 126.39, 126.93, 127.58, 127.78, 129.07, 130.30, 130.68, 130.73, 132.24, 153.72, 155.46 ppm; ^{11}B NMR (64 MHz, [D$_8$]THF): $\delta = 5.44$ ppm; HRMS: calcd for $C_{32}H_{34}BO_4$ $[M-\mathrm{Na}]^-$: 493.2556; found: 493.2547.

Sodium[bis(3,3′,5,5′-tetramethyl-2,2′-biphenoxy)borate] (7): The warm suspension (50 °C) of boric acid (0.77 g, 12.4 mmol) in methanol (25 mL) was combined with the warm solution (50 °C) of 3,3′,5,5′-tetramethyl-2,2′-biphenol (**2**) (6.00 g, 24.8 mmol) in methanol (25 mL) and the reaction mixture was heated for 10 min under reflux conditions. The resulting solution was chilled to 0 °C and sodium methanolate (2.3 mL of a 5.4 M solution in methanol, 12.4 mmol) was added dropwise, followed by immediate formation of a precipitate. The desired product was filtered off and subsequently washed with cold methanol (10 mL). The filtrate was concentrated under reduced pressure and a second crop was isolated as described above. Drying in high vacuum provided **7** as colourless solid (4.92 g, 9.6 mmol, 77 %). Single crystals of **7** for X-ray analysis were obtained along with the second crop from methanol. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 2.00$ (s, 12H; CH$_3$), 2.29 (s, 12H; CH$_3$), 6.91 (s, 4H; 4-H), 6.97 ppm (s, 4H; 6-H); ^{13}C NMR (75 MHz, CD$_3$CN): $\delta = 17.53$ (CH$_3$), 20.96 (CH$_3$), 128.51, 129.64, 130.13, 130.74, 131.72, 153.16 ppm; ^{11}B NMR (64 MHz, CD$_3$CN): $\delta = 7.99$ ppm; HRMS: calcd for $C_{32}H_{32}BO_4$ 491.2399 $[M-\mathrm{Na}]^-$; found: 491.2288.

General procedure for the anodic oxidation of sodium[tetrakis-(phenoxy)borates]: The corresponding sodium[tetrakis(phenoxy)borate] was dissolved in acetonitrile and transferred into a nondivided, standard electrolysis cell[16] equipped with two platinum sheets as anode and cathode, respectively. At 40 °C a galvanostatic electrolysis with a current density of 12.5 mA cm^{-2} was performed. During electrolysis, the polarity was reversed every 60 s to avoid electrode coating. Completion of the reaction was indicated by a sudden increase in the terminal voltage, at which point the electrolysis was stopped. Citric acid (ca. 0.30 g, 1.6 mmol) was added and the reaction mixture was diluted with hot water (100 mL) followed by stirring for 5 min and extraction with *tert*-butyl methyl ether (TBME, 3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried (MgSO$_4$) and concentrated in vacuo. Purification by column chromatography yielded the corresponding biphenol as colourless solid.

3,3′,5,5′,6,6′-Hexamethyl-2,2′-biphenol (8): Sodium[tetrakis(2,4,5-trimethylphenoxy)borate] (**8a**) (2.96 g, 5.2 mmol), acetonitrile (25 mL), 5.0 F, subjected to column chromatography (cyclohexane/ethyl acetate 98:2, then 95:5) yielded **8** (1.83 g, 6.8 mmol, 66 %); m.p. 169 °C (cyclohexane, value in ref. [18]: m.p. 136–138 °C); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.86$ (s, 6H; CH$_3$), 2.25 (s, 12H; CH$_3$), 4.56 (s, 2H, OH), 7.02 ppm (s, 2H; 4-H); elemental analysis calcd (%) for $C_{18}H_{22}O_2$ (270.37): C 79.96, H 8.20; found: C 79.94, H 8.16.

3,3′-Di-*tert*-butyl-5,5′-dimethoxy-2,2′-biphenol (9): Sodium[tetrakis(2-*tert*-butyl-4-methoxyphenoxy)-borate] (**9a**) (0.97 g, 1.3 mmol), acetonitrile (14 mL), 6.4 F, subjected to column chromatography (cyclohexane/ethyl acetate 98:2, then 95:5) yielded **9** (0.54 g, 1.5 mmol, 58 %); m.p. 226 °C (cyclohexane, value in ref. [19]: m.p. 228–229 °C); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.42$ (s, 18H; CH$_3$), 3.76 (s, 6H; OCH$_3$); 5.00 (s, 2H; OH), 6.61 (d, ^4J(H,H) = 3.1 Hz, 2H; 6-H), 6.95 ppm (d, ^4J(H,H) = 3.1 Hz, 2H, 4-H); elemental analysis calcd (%) for $C_{22}H_{30}O_4$ (358.47): C 73.71, H 8.44; found: C 73.64, H 8.44.

5,5′-Dimethoxy-2,2′-biphenol (10): Sodium[tetrakis(4-methoxyphenoxy)-borate] (**10a**) (2.11 g, 4.0 mmol), acetonitrile (25 mL), 3.1 F, subjected to column chromatography (cyclohexane/ethyl acetate 75:25, then 70:30) yielded **10** (0.93 g, 3.8 mmol, 48 %); m.p. 125 °C (cyclohexane, value in ref. [20]: m.p. 125–126 °C); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 3.75$ (s, 6H; OCH$_3$), 6.52 (brs, 2H; OH), 6.78–6.82 (m, 4H; 4-H, 6-H); 6.87 ppm (d, ^3J(H,H) = 8.8 Hz, 2H; 3-H); elemental analysis calcd (%) for $C_{14}H_{14}O_4$ (246.26): C 68.28, H 5.73; found: C 67.99, H 5.69.

5,5′-Dihydroxy-[6,6′]bi(benzo[1,3]dioxolyl) (11): Sodium[tetrakis(benzo-[1.3]dioxol-5-yloxy)borate] (**11a**) (1.63 g, 2.8 mmol), acetonitrile (25 mL), 5.2 F, subjected to column chromatography (cyclohexane/ethyl acetate 80:20, then 75:25) yielded **11** (0.51 g, 1.9 mmol, 34 %); m.p. 201 °C (cyclohexane, value in ref. [6]: m.p. 201–202 °C); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 5.91$ (s, 4H; 2-H), 6.50 (s, 2H; 4-H), 6.67 (s, 2H; 7-H), 8.87 ppm (brs, 2H; OH); elemental analysis calcd (%) for $C_{14}H_{10}O_6$ (274.23): C 61.32, H 3.68; found: C 61.35, H 3.47.

3,3′-Di-*tert*-butyl-5,5′6,6′-tetramethyl-2,2′-biphenol (12): Sodium-[tetrakis(2-*tert*-butyl-4,5-dimethylphenoxy)borate] (**12a**) (1.01 g, 1.4 mmol), acetonitrile (25 mL), 6.2 F, subjected to column chromatography (cyclohexane/ethyl acetate 98:2) yielded **12** (0.29 g, 0.8 mmol, 30 %); m.p. 163 °C (cyclohexane, value in ref. [21]: m.p. 161–162 °C); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.40$ (s, 18H; C(CH$_3$)$_3$), 1.82 (s, 6H; CH$_3$), 2.26 (s, 6H; CH$_3$), 4.80 (s, 2H; OH), 7.13 ppm (s, 2H; 4-H); elemental analysis calcd (%) for $C_{24}H_{34}O_2$ (354.53): C 81.31, H 9.67; found: C 81.36, H 9.56.

5,5′-Dimethyl-2,2′-biphenol (13): Sodium[tetrakis(4-methylphenoxy)borate] (**13a**) (2.23 g, 4.8 mmol), acetonitrile (25 mL), 2.3 F, subjected to column chromatography (cyclohexane/ethyl acetate 90:10, then 85:15) yielded **13** (0.60 g, 2.8 mmol, 30 %); m.p. 155 °C (cyclohexane, value in ref. [22]: m.p. 154–155 °C); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.31$ (s, 6H; CH$_3$), 6.01 (brs, 2H; OH), 6.87–6.90 (m, 2H; 3-H), 7.06–7.08 ppm (m, 4H; 4-H, 6-H); elemental analysis calcd (%) for $C_{14}H_{14}O_2$ (214.26): C 78.48, H 6.59; found: C 78.21, H 6.40.

5,5′-Di-*tert*-butyl-2,2′-biphenol (14): Sodium[tetrakis(4-*tert*-butylphenoxy)borate] (**14a**) (2.02 g, 3.2 mmol), acetonitrile (25 mL), 2.0 F, subjected to column chromatography (cyclohexane/ethyl acetate 90:10) yielded **14** (0.40 g, 1.3 mmol, 20 %); m.p. 196 °C (cyclohexane, value in ref. [23]: m.p. 207–208 °C); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.32$ (s, 18H; CH$_3$), 6.96 (d, ^3J(H,H) = 8.5 Hz, 2H; 3-H), 7.27 (d, ^4J(H,H) = 2.5 Hz, 2H; 6-H), 5.56 (brs, 2H; OH), 7.34 ppm (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.5 Hz, 2H; 4-H).

X-ray crystal-structure analysis for **7**: formula $C_{36}H_{48}BNaO_8$, $M = 642.54$, light-yellow crystal $0.60 \times 0.30 \times 0.10$ mm^3, $a = 20.647(1)$ $b = 8.087(1)$ $c = 21.940(1)$ Å, $\beta = 103.44(1)°$, $V = 3563.0(5)$ Å^3, $\rho_{\mathrm{calc}} = 1.198$ g cm^{-3}, $\mu = 0.093$ mm^{-1}, empirical absorption correction ($0.946 \leq T \leq 0.991$), $Z = 4$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 14017 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{-1}, 4222 independent ($R_{\mathrm{int}} = 0.048$) and 2456 observed reflections [$I \geq 2\sigma(I)$], 221 refined parameters, $R = 0.060$, $wR_2 = 0.172$, max. residual electron density 0.46 (−0.34) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Data sets were collected by using a Nonius KappaCCD diffractometer equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN[24], absorption correction Denzo[25], structure solution SHELXS-97[26], structure refinement SHELXL-97[27], graphics DIAMOND 3.0d (Crystal Impact, Bonn, Germany).

CCDC 298666 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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