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# Highly Selective Electrosynthesis of Biphenols on Graphite Electrodes in Fluorinated Media

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**Abstract:** The direct and selective phenol coupling reaction that provides biphenols still represents a challenge in organic synthesis. The recently developed electrosynthesis on boron-doped diamond anodes with fluorinated additives was developed further to allow the application to less-expensive electrodes and fluorinated media. This advanced protocol allows the highly selective anodic phenol coupling reaction on graphite with a broad scope.

Introduction

In many fields of organic chemistry biphenols represent a common structural motif, in particular in natural product synthesis<sup>[1]</sup> and in technical applications.<sup>[2]</sup> In homogeneous catalysis biphenols have an outstanding role as ligands or starting materials thereof. Some methylated biphenols, for example, 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenyl (**2**), are important as backbone compounds for powerful ligand systems.<sup>[3,4,5]</sup> Furthermore, recent investigations have revealed that biphenoxyborates-based electrolytes exhibit an outstanding electrochemical stability. Thus, they were applied as novel electrolyte systems to super capacitor cells.<sup>[6]</sup>

Because of the high significance of methylated biphenols, selective and efficient synthetic methods are required for their preparation. Unfortunately, despite their simple archi-

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tecture a reliable and sustainable synthesis is challenging. Direct oxidation of methyl-substituted phenols by conventional oxidation methods or anodic treatment mostly results in a complex mixture of products—where the desired biphenol represents only a minor component.<sup>[7]</sup> Purification of such multicomponent mixtures is costly and time consuming. In addition to C–C bond formation, C–O coupling with subsequent rearrangements and integration of additional phenol units takes place leading to unique polycyclic scaffolds.<sup>[8]</sup> This allows molecular diversity within very few steps by overoxidation (Scheme 1).<sup>[9]</sup>



Scheme 1. Product distribution for the oxidation reaction of simple phenols.

Oxidative treatment of phenols by inorganic oxidants, for example, peroxodisulfate, or transition-metal cations in high oxidation states, for example, Fe<sup>3+</sup>, V<sup>5+</sup>, Cr<sup>6+</sup>, or Mn<sup>7+</sup> gives rise to excessive reagent waste. Electrosynthetic methods provide an outstanding atom economic and efficient approach because only electrons are shifted. In this case, no leaving functionalities are necessary and only hydrogen atoms are sacrificed. Consequently, excessive reagent waste could be avoided. Moreover, a large variety of useful electrochemical protocols for C-C bond formation has been developed in the past.<sup>[10,11]</sup> To overcome the challenges of undesired phenol-coupling pathways an electrochemical protocol based on a boron template strategy was successfully established.<sup>[12]</sup> Because a direct synthesis would allow a preparative short-cut, we focused on this practical one-step procedure. Unfortunately, only very few examples for the selective anodic biphenol synthesis using common electrode

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materials such as platinum or graphite exist. The electrooxidation of vanillin and eugenol on platinum in basic media into the corresponding natural occurring biphenols has been reported.<sup>[13,14]</sup> Owing to the high costs of platinum, carbon electrode materials are definitely more attractive for technical applications. Unfortunately, the conversion of simple methylated phenols like *para*-cresol or 2,4-dimethylphenol (1) lead to the formation of the corresponding Pummerer's ketone derivative 3 and not to the biphenol.<sup>[15]</sup> Significant progress was achieved by the use of boron-doped diamond (BDD) electrodes. Their unique electrochemical properties open up new synthetic pathways because oxyl radicals are easily formed in aqueous media. Through this approach a direct and selective electrosynthesis of 2 to 2,4-dimethylphenol (1) was developed.<sup>[16]</sup> However, the substrate scope was limited to only a few phenols. With the addition of fluorinated alcohols, for example, 1,1,1,3,3,3-hexafluoroisopropanol (10), the method became more general.<sup>[17]</sup> As fluorinated alcohols such as 10 tremendously enhance the lifetime of highly reactive spin centers,[18] this modified electrolysis allows the conversion of various electron-rich and halogenated phenols in a selective manner.<sup>[19]</sup> The stabilizing effect might be attributed to the trapping of intermediate oxyl species in a hydrogen-bonding network.<sup>[20]</sup> The non-nucleophilic and redox stable properties of 10 are often exploited in oxidative conversions.<sup>[21]</sup> Moreover, in this way the nonsymmetrical biphenol **30** was obtained exclusively.<sup>[22]</sup> This discovery opened up the pathway for the first anodic phenol-arene cross-coupling reaction, which enables the selective electrosynthesis of various nonsymmetrical biaryls. Therefore, the strategy belongs to the current cutting-edge approaches of modern arylation methods.<sup>[22]</sup> As the technical application of BDD electrodes is still challenging and the technical use of highly fluorinated alcohols like 10 is nonpracticable, this strategy has to be transferred to more simple and less costly electrode/electrolyte systems. Herein, we report the successful modification and application of the electrolysis protocol using readily available graphite electrodes. A technical electroorganic synthesis is mostly realized with graphite electrodes.<sup>[23]</sup> A variety of additives were tested in respect to selectivity, yield, and scope of substrates.

### **Results and Discussion**

When performing a constant-current electrolysis various parameters can be adjusted to control the electrolysis. The most important are: electrode material, current density, amount of applied electricity, and the composition of the respective electrolyte system. Our experience from previous investigations has shown that it is useful to establish suitable electrolysis conditions first. The oxidative coupling reaction of 2,4-dimethylphenol (2) on graphite anodes served as a model system, because this electrooxidation was intensively investigated in the recent past (Scheme 2).<sup>[24]</sup> In the course of the study several electrolyte compositions were tested. The electrolyses were carried out in an undivided cell with a



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Scheme 2. Selective electrosynthesis of biphenol 2 on graphite.

volume of 30 mL, where the phenolic substrate (52 wt %) served as the major component. For stabilizing reactive intermediates and minimizing overoxidation of the biphenols, fluorinated solvents were added only in small quantities (4–9 mL).

The ionic liquids **5–7**, which are based upon quaternary ammonia salts, were employed as supporting electrolytes because they were the most appealing in tests based on past studies (Scheme 3).<sup>[25]</sup> To prevent degradation, electrolysis



Scheme 3. Ionic liquids as supporting electrolytes in anodic phenol coupling reactions. Pyr=pyrrolidine.

was stopped before complete conversion of the phenolic starting material. Advantageously, the desired biphenols were obtained by simple and practical purification steps. After electrolysis, abundant starting material was recovered by short-path distillation. Subsequent column chromatography of the crude product on silica gel or crystallization from isopropanol/water mixtures yielded the biphenols (see the Supporting Information). The results of the optimization studies are summarized in Table 1. Initial reactions were carried out with 1,1,1,3,3,3-hexafluoroisopropanol (10, HFIP) as an additive and 5 as the supporting electrolyte. When high current densities were chosen, biphenol 2 was isolated in yields of 50-60% (entries 1 and 2), but also a significant amount of polymeric by-product was observed. In addition, the inner cell resistance has increased significantly during electrolysis.

A partial conversion of 1 with the application of 0.77 F per mol and a constant current of 10 mA cm<sup>-2</sup> revealed the best result with respect to yield and minimizing side reactions (entry 3). Lowering the current density (entry 4) or the quantity of 10 resulted in no improvement (entry 5). When a 3–5 fold quantity of supporting electrolyte was employed the applied cell voltage decreased to 50%, but the yield of biphenol 2 did not improve (entries 6 and 7). Switching to ionic liquid 6 as the supporting electrolyte, led to similar results (entry 8). As 10 is still relatively costly an alternative additive was required. In anodic oxidation of arenes, trifluoroacetic acid (19; TFA) is a common electrolyte component. In previous studies of analogous phenol coupling on boron-doped diamond, 19 proved to be dramatically inferior as an additive.<sup>[16]</sup> However, different results were observed

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Table 1.	Screening for ge	eneral condi-	tions in the se	lective synthesis	of biphenol or	n graphite e	electrodes by	constant c	urrent electroly	sis of <b>1</b> in a	n undivid-
ed cell.											

	Fluorinated additive (wt%)	Supporting electrolyte (wt%)	Electricity <sup>[a]</sup> [F per mol of phenol]	$U_{\max}\left[\mathbf{V} ight]$	$j [{ m mAcm^{-2}}]^{[b]}$	<i>T</i> [°C]	Yield of <b>2</b> [%] <sup>[c,d]</sup> (isolated)	CE [%] <sup>[e]</sup>	Recovered 1 [%] <sup>[f]</sup>
1	10 (45)	<b>5</b> (3)	1.00	27	20	30	66 (60)	53	19
2	10 (45)	<b>5</b> (3)	0.77	22	20	30	51	49	25
3	10 (45)	5 (3)	0.77	17	10	30	66 (55)	50	42
4	10 (45)	5 (3)	0.77	13	5	30	49 (49)	35	44
5	10 (28)	5 (4)	0.77	21	10	30	49 (49)	36	44
6	10 (43)	5 (9)	0.77	8	10	30	47	35	43
7	<b>10</b> (41)	5 (14)	0.77	10	10	30	53	38	40
8	10 (45)	<b>6</b> (3)	0.77	17	10	30	54 (51)	43	39
9	<b>19</b> (45)	<b>5</b> (3)	1.00	14	10	50	51 (45)	41	19
10	<b>19</b> (45)	<b>5</b> (3)	0.77	18	10	30	67 (64)	55	37
11	<b>19</b> (45)	7 (3)	0.77	20	10	30	- (51)	43	35

<sup>[</sup>a] In the range of 0.77–1.00 F per mol of phenol applied electricity; the product precipitated affecting an increased cell resistance. Consequently, the cell voltage abruptly rose. [b] j=current density [c] Yield based on recovered starting material. [d] Yields of **2** were estimated by gas chromatography using pentadecane as an internal standard. Yield of isolated product is given in parenthesis. [e] Current efficiency (CE) is defined as the quotient of electricity consumed for the synthesis of **2** by total applied electricity. [f] Unchanged starting phenol **1** was recovered by short-path distillation. CE=current efficiency,.

in this study: Elevated temperature lowered the cell resistance, but it seemed to be unfavorable with respect to yield (entry 9). When the electrolysis was performed at 30 °C, the yield of isolated **2** was slightly improved with an acceptable current density (entry 10). Use of the more common imidazolium-based ionic liquid **7** did not ameliorate the result (entry 11). A major challenge in the direct oxidation of 2,4dimethylphenol (**1**) is the control of product selectivity. Consequently, the effect of additives on the product distribution was studied in more detail. As mentioned above, biphenol **2**, Pummerer's ketone derivative **3**, and some pentacyclic scaffolds were the major products.

Upon oxidation of 1 on a platinum anode in basic media the C–O coupling product 3 dominates.<sup>[7]</sup> By switching to BDD anodes and neutral water-containing electrolytes the selectivity inverted towards the biphenol 2.<sup>[15]</sup> Applying a variety of additives (8-20) to electrolysis of 1 on graphite anodes for the selective formation of biphenol 2 turned out to be suitable for the synthesis of 3. However, a new byproduct was observed that could not yet be clearly assigned. Mass spectrometry measurements indicated the formation of a dehydrotrimer 4 (Scheme 4). The X-ray crystal structure analysis of a single crystal could not unequivocally assign the molecular structure. Analysis of the NMR spectra indicated the presence of two isomers. Atropic isomers could be excluded because temperature dependent spectroscopy did not change the number of signals. By GC no method could be established to separate these isomers. Derivatization with propionic acid anhydride confirmed the presence of two regioisomers 4a and 4b, as NMR analysis of the product clearly showed two different, but very similar compounds. Products 4a and 4b are formed by overoxidation of the targeted biphenol 2. The biphenol 2 served as the substrate for a terphenol coupling reaction. The terphenols only differ in the connectivity on the central benzene moiety.

The results of the screening for additives are summarized in Table 2. By performing the electrolysis with the simplest



Scheme 4. Major products obtained by anodic treatment of 1 on graphite.

fluorinated alcohol 1,1,1-trifluoroethanol (8, TFE) the biphenol product 2 was obtained in good yield and selectivity (entry 1). A longer fluorinated carbon chain, for example, in 1H,1H,5H-octafluoropentanol 9, led to decreased yield and selectivity (entry 2). Use of hexafluoroisopropanol (10) improved the formation of biphenol 2 significantly. Thus, the selectivity of 2 versus 4 was determined as 17:1. Ketone 3 was only detected in trace amounts (<1%; entry 3). Although replacing a CF<sub>3</sub> moiety by a phenyl group was expected to show similar results,<sup>[17]</sup> only moderate yield and selectivity were found when 11 (entry 4) was employed. Installation of an additional fluorine group on the phenyl moiety (entry 5) or a CF<sub>3</sub> substituent gave comparable results (entry 6). Although the use of enol 14 led to the exclusive formation of the desired biphenol 2, it was formed in 20% yield with only moderate efficiency (entry 7). In the case of methane sulfonic acid (16) similar data were obtained (entry 9). Slight improvement was observed by the addition of acetic acid (17; entry 10) or its trichloro analogue 18 (entry 11). However, the acidic nature of the additive did not seem to be crucial. The application of fluorinat-

		Additive	Yield of <b>2</b> [%] <sup>[b]</sup>	CE [%]	Product ratio <b>2/3/4</b> <sup>[c]</sup>
1	8	F <sub>3</sub> COH	48	32	$13:<1^{[d]}:1$
2	9		38	27	$8:<1^{[d]}:1$
3	10	F <sub>3</sub> C ≻−ОН F <sub>3</sub> C	55	49	17:<1 <sup>[d]</sup> :1
4	11	CF3	21	14	4::1
5	12	CF3	15	14	8::1
6	13	F <sub>3</sub> C OH	6	5	6:3:1
7	14	O OH CF3	20	8	_
8	15	0 НО- <sup>5</sup> -ОН О	trace <sup>[e]</sup>	_	_
9	16	O -S-OH O	6	4	15:2:1
10	17	ОН	20	14	6:-:1
11	18	сі₃с он	18	10	7:-:1
12	19	F <sub>3</sub> COH	64	53	16:-:1
13	20	Б <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> C ОН	49 <sup>[f]</sup>	43	7:-:1

Table 2. Influence of additives on the product distribution in the electrolysis of  $\mathbf{1}^{[a]}$ 

[a] General electrolysis conditions: graphite electrodes, constant current  $j=10 \text{ mA cm}^{-2}$ , Q=0.77 F per mol of phenol **1**, 30 °C, 3 wt% of [Et<sub>3</sub>NMe] [O<sub>3</sub>SOMe] (**5**), 45 wt% of additive, and 52 wt% of phenol **1**. [b] Yield based on recovered starting material. [c] Product ration was estimated from gas chromatographic analysis of the crude product. [d] **3** was observed in quantities far below 1%. [e] A black, highly viscous oil was formed containing only small quantities of **2**. [f] Owing to low conductivity the electrolysis was carried out at 50 °C.

ed carboxylic acids, for example, TFA (19) turned out to be beneficial for the electrolysis. In this way the formation of ketone **3** was suppressed and biphenol **2** was selectively obtained in 64% yield of isolated product (entry 12). In the case of heptafluorobutyric acid (20) the conditions were not improved any further. However, additive **20** is favorable for conversions at higher temperature (entry 13). Fortunately, the novel electrolysis protocol is not limited to substrate **1**. Thus, a variety of substituted phenols were subjected to the optimized electrolysis conditions. A selection of biphenol products is shown in Scheme 5. In all cases the *ortho-ortho* biphenols **21–25** were obtained in a highly selective manner or even exclusively. In this way the hexamethylated biphenol **21** was accessible and isolated in 30% yield. As a result of its electron-rich nature, the overoxidation of **21** is ob-



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Scheme 5. Scope of the electrochemical synthesis of biphenols.

served. Remarkably, several halogenated biphenols were formed upon direct oxidation of the corresponding phenols.

The electrolysis on graphite is particularly superior to the transformation of halogenated phenols at boron-doped anodes, for example, the conversion of 2-bromo-4-methylphenol led to dibromobiphenol **22** in 76% yield. The electrolysis of an electron-poor phenol, such as 2-fluoromethylphenol still provided the corresponding biphenol **23**. In the conversion of chlorinated cresols both regioisomers *para*chloro- and *ortho*-chlorocresol was coupled and formed biphenols **24** and **25**, respectively.

Notably, electrolysis of 4chloro-2-methylphenol yielded the dibenzofuran derivative **26** as a by-product in 6% yield. The molecular structure was verified by X-ray crystal structure analysis of a suitable single crystal (see the Supporting In-



formation). No analogous by-products were detected upon electrolysis of other phenols. These findings represent a significant improvement of selectivity because in the past electrolysis of halogenated phenols led to multicomponent product mixtures only.<sup>[26]</sup> In the course of our studies, benzyland *tert*-butyl-substituted substrates were tested. Upon electrolysis according to the protocol, complex product mixtures were obtained. The desired biphenolic species were observed, but represented a minor component because random transfer of *tert*-butyl or benzyl moieties was detected. Thus, purification of these mixtures was pointless. These facts indicate a reaction pathway that proceeds via a cationic species, which can liberate cationic fragments thus leading to the observed multicomponent mixture.

Subjecting 2-naphthol (27) to the elaborated protocol to form BINOL (28) failed. As 27 is insoluble in TFA (19) and the melting point of the substrate is 123 °C, the reaction was carried out at 100 °C. Therefore, heptafluoroacetic acid (20) was used instead of TFA. This modification of the protocol enabled a successful conversion (Scheme 6). However,

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Scheme 6. Electrosynthesis of BINOL (28).

avoiding the overoxidation of BINOL is, in this, case challenging. The BINOL product can be synthesized electrochemically by a TEMPO-mediated process.<sup>[27]</sup>

As recently reported,<sup>[21]</sup> an unexpected coupling product was discovered for the anodic transformation of 4-methylguaiacol (**29**) on boron-doped diamond in hexafluoroisopropanol **10**. These conditions provide the *ortho-meta* homocoupling product **30** exclusively. Consequently, the electrolysis of guaiacol **29** was carried out according to the elaborated protocol at graphite anodes using TFA as the additive (Scheme 7).



Scheme 7. Electrooxidation of guaiacol **29** to give the nonsymmetrical biphenol **30**.

With the less expensive electrode/electrolyte system the nonsymmetrical biphenol **30** was the only coupling product and was isolated in approximately 55% yield. Different electrolyses were performed by applying various amounts of electric current (Table 3). The best combination with respect

Table 3. Electrolysis of 29 by applying various amounts of electricity.<sup>[a]</sup>

	Electricity [F per mol of <b>29</b> ]	Yield of <b>30</b> [%] <sup>[b]</sup>	CE [%]	Recovered <b>29</b> [%] <sup>[c]</sup>
1	0.77	55	45	31
2	0.9	57	31	49
3	1.0	54	36	33
4	2.0	35	13	21

[a] General electrolysis conditions: graphite electrodes, constant current  $j=10 \text{ mA cm}^{-2}$ , 30°C, 3 wt% of [Et<sub>3</sub>NMe] [O<sub>3</sub>SOMe] (**5**), 45 wt% of additive, and 52 wt% of phenol **29**. [b] Yield based on recovered starting material. [c] Unchanged starting phenol **29** was recovered by short-path distillation.

to product yield and current efficiency was achieved after application of 0.77 F of electricity per mol of **29** (entry 1). Treatment with more electricity (0.9 or 1.0 F) gave similar yields, but owing to overoxidation processes the current efficiencies were lower (entries 2 and 3). When passing 2 F of electricity per mol of **29**, both the yield and the current efficiency dropped dramatically. The electrolysis resulted in a deep brown viscous reaction mixture (entry 4).

## Conclusion

The combination of readily available TFA and common graphite electrodes is a powerful electrode/electrolyte system. For the TFA/graphite anode system a similar reactivity profile as for boron-doped diamond was found. The scope of the phenol coupling is strikingly similar. The protocol is suitable for a range of electron-rich and halogenated phenols. Moreover, even homocoupling reaction of 4-methylguaiacol resulting in a nonsymmetrical biphenol was possible. This inexpensive approach can be used instead of the boron-doped diamond electrodes in the synthesis of biphenol using electroorganic methods. Because graphite is the preferred technical electrode material, a scale-up for this electroorganic method is viable. The protocol seems to be an outstanding tool for electroorganic conversions and will be applied to other transformations, which are typically performed on boron-doped diamond, and reported in due course.

#### **Experimental Section**

General procedure for electrolysis of phenols on graphite electrodes: A solution of phenol derivative (52 wt%), [Et<sub>3</sub>NMe] [O<sub>3</sub>SOMe] (5, 3 wt%), and additive (45 wt%) was transferred into a undivided standard electrolysis cell equipped with two graphite electrodes. At 30°C a galvanostatic electrolysis with a current density of 10 mA cm<sup>-2</sup> was performed. After complete reaction (0.77–1.00 F permol of phenol) the electrolysis was stopped, the electrolyte transferred into a flask by methanol (in the case of acidic additives) or toluene (in the case of alcoholic additives) and the solution was concentrated in vacuo. Solvents were recovered by distillation or column chromatography. Unchanged starting material was recovered by short-path distillation (140°C (oil bath temperature),  $10^{-2}$  mbar).

Modified procedure for electrolysis of 2-naphthol (27) on graphite electrodes: A solution of 2-naphthol (27, 22 wt%, 10 g, 0.07 mol), [Et<sub>3</sub>NMe] [O<sub>3</sub>SOMe] (5, 7 wt%, 3 g, 0.012 mol), and heptafluorobutyric acid (20, 71 wt%, 20 mL) was transferred into a undivided standard electrolysis cell equipped with two graphite electrodes. At 100 °C, a galvanostatic electrolysis with a current density of 10 mA cm<sup>-2</sup> was performed. After complete reaction (0.77 F per mol of phenol) the electrolysis was stopped, the electrolyte transferred into a flask by methanol and the solution was concentrated in vacuo.

For workup and further synthetic procedures as well as analytical details see the Supporting Information.

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