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Electrooxidative Coupling of Phenols. I. Product-Selective Electrosynthesis of 2,2',6,6'-Tetra-tert-butyl-1,1'-biphenol from 2,6-Di-tert-butylphenol

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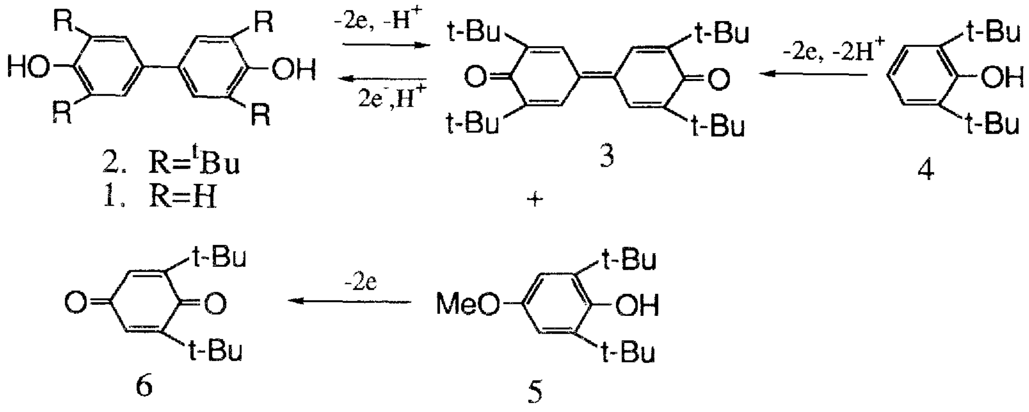
Summary: Biphenol electrosynthesis is achieved in a divided cell by a set of redox reactions from 2,6-di-tert-butylphenol (**4**) via the corresponding diphenoquinone **3**. Phenol **4** can also lead to either the corresponding biphenol **2** or diphenoquinone **3** in a product-selective manner by electrooxidation in an undivided cell. The choice of solvent is a crucial factor for the product-selectivity.

Biphenols attract much attention as core materials for new functional polymers and liquid crystals.$^{1)}$ The electrooxidative coupling of phenols has long been the tactics for biphenol synthesis.$^{2)}$ However, the electrooxidation of 2,6-di-tert-butylphenol (**4**) in an MeOH-$LiClO_4$-(Pt) system gives a mixture of 2,2'-6,6'-tetra-tert-butyl-1,1'-biphenol (biphenol **2**)(30%), 3,3',5,5'-tetra-tert-butyl-1,1'-biphenylidene-4,4'-quinone (diphenoquinone, **3**)(40%), and others (30%).$^{3)}$ Recently, the diphenoquinone **3** was isolated as a major product in an attempt to synthesis metal phenoxylate complexes.$^{4)}$ Indirect electrooxidation of **4** also provides **3** in high current efficiency.$^{5)}$ However, these conversion methods lack a straightforward access to the biphenol **2**. In this paper, we report two product-selective procedures for the preparation of biphenol **2**, a potential precursor of 4,4'-dihydroxy-1,1'-biphenyl **1**, through diphenoquinone **3**.



The anodic oxidation of 2,6-disubstituted phenols generally gives the corresponding dimeric products along with oxidized monomers as minor products. The high chemoselectivity may be attained by elucidation of crucial factors in relation to the destiny of reaction intermediates.[6)] Actually, we have studied the effects of anode material, anode potential, solvent, substrate concentration, electrolyte, additive, pH, temperature, stirring rate and atmosphere on the ratio of the products.[7)] However, the comprehension of decisive factors for the product-selectivity have not yet been clarified. We developed two procedures for the preparation of the biphenol **2** as follows: [Method A], a set of redox reaction which consists of the anodic oxidation of **4** in a MeOH/CH_2Cl_2(1:1)-$LiClO_4$ (0.3 M)-(Pt) system in a divided cell and the subsequent electroreduction is performed by changing the current direction. [Method B], a paired reaction which comprises both anodic oxidation of **4** leading to **3** in the anode cell, and the cathodic reduction of **3** in the cathode cell leading to **2**, is realized simultaneously. Taking the solubility of **3** into the consideration, a 1:1 mixed solution of MeOH/CH_2Cl_2 was employed and the results are compiled in Table 1.

Table 1. Electrosynthesis of diphenol 2 from 4 via 3 in a divided cell.[a)]

Entry	Substrate (mmol)	Reaction mode	Current density mA/cm^2	F/mol	Product, Yield (%)[b)] 2	3	4	6
1	4 (0.8)	anode	0.5-0.8	2.0	5.1	88.0	-	-
2[c)]	3 (1.0)	cathode	1.0	2.3	93.6	3.6	-	-
3	2 (0.2)	anode	"	2.6	-	94.9	-	-
4	4 (0.5)	change of current direction	"	(+)2.4 (-)1.45	92.8	4.1	-	-
5[d)]	4 (3.0)	"	"	"	72.0	-	-	6.3
6[c)]	(+)4 (1.0)	paired reaction	1.0	2.5	-	84.7	4.2	3.3
	(-)3 (1.0)		"	"	92.5	6.1	-	-

a) Carried out in a MeOH-CH_2Cl_2 (1:1)(20ml)-0.3M $LiClO_4$-(Pt)(2x3cm^2) system at 0-5 °C. b) Yields are isolated ones. c) 0.06ml of concentrated H_2SO_4 are added and 20 minutes of Argon bubbling are made in the cathodic compartment. d) same as c) but just before the reduction step.

The diphenoquinone **3** was formed in high yields together with small amounts of **2** (entry 1). Independently, the cathodic reduction of **3** in low concentrations (0.2 mmol) into **2** proceeded in high conversion yield under the same conditions and is facilitated by adding a few drops of concentrated sulfuric acid in higher concentration conditions (entry 2). In addition, the oxidation of **2** under the conditions of entry 1 afforded the diphenoquinone **3**, preferentially (entry 3). Next, we turned to realize a "one-pot" synthesis of biphenol **2** from the phenol **4** by switching the current direction when 2.4 Faradays/mol of electricity were passed [method A]. Thus, the first produced diphenoquinone 3 was reduced into the biphenol **2** in 92.8% overall yield (entry 4). Taking into consideration the results obtained in entry 2, the eletrolysis of **4** in higher concentration (3 mmol) was tried with adding sulfuric acid and making a bubbling of argon just before the reduction step and reasonable result was obtained compared with that of entry 4 (entry 5).

Another possibility for the conversion is laid on the performance of a paired reaction [method B]. It is interesting to examine whether the oxidation of **4** and the reduction of diphenoquinone 3 are not disturbed each other on running the electrolyses together in a divided cell. The result (entry 6) clearly shows that there is no mutual perturbation.

Parallel investigations in an undivided cell were conveyed by changing MeOH/CH_2Cl_2 ratios as shown in Table 2. Apparently, the diphenoquinone **3** was obtained preferentially in a less methanolic methylene dichloride solution (entry 2). In contrast, around 75% of methanolic solution tends to give the biphenol **2** as a major product (entry 1). Addition of a drop of sulfuric acid brought about high selectivity upon the formation of **2** but less efficiency on conversion (entry 3).

Table 2. Electrooxidation of phenol 4 in an undivided cell.a)

Entry	Solvent system MeOH/CH_2Cl_2	Current mA/cm^2	Density F/mol	Conversion (%)	Product, Yield (%)b) **2**	**3**	**6**
1	(3:1)	2.0	3.5	87.6	62.7	-	6.7
2	(1:9)	"	4.5	97.0	1.5	81.1	4.6
3c)	(3:1)	"	3.6	73.9	67.8	1.6	3.4

a) A 0.1M solution of **4** in a MeOH-CH_2Cl_2 (20ml)-0.3M $LiClO_4$-(Pt)(2x3cm^2) system was electrolysed under 2mA/cm^2 at 0-5 °C. b) yields are isolated ones. c) With 3 drops of concentrated H_2SO_4.

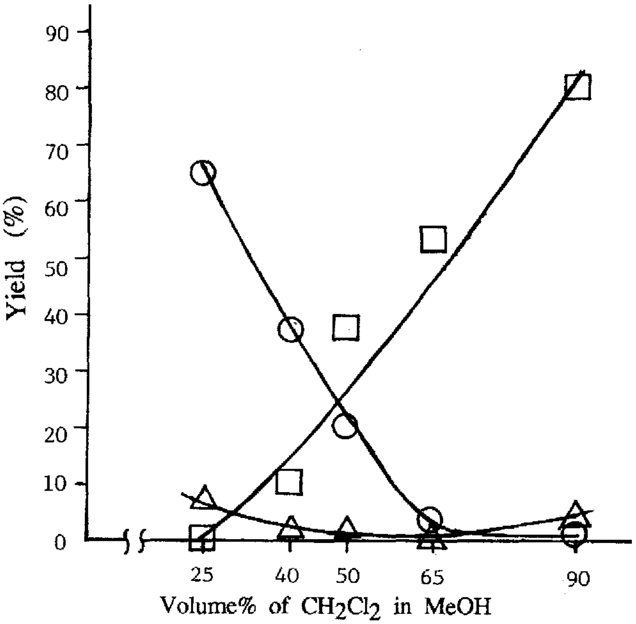


Figure 1. Relationships between yields of biphenol 2, diphenoquinone 3, and benzoquinone 6, under varying ratio of CH_2Cl_2 / MeOH. 2; ○, 3; □, 6; △.

The reaction features in the mixed solvent systems are plotted in Fig. 1. Obviously, the present mixed solvent systems are suitable for the nucleus-nucleus coupling rather than methoxylation at the aromatic nucleus. The yield of 2 increases in proportion to the percentage of methanol up to 75%. However, the solubility of 3 decreases sharply over the 75% methanol solution. At present, we have no evidence for the rationalization of the reason from where such selectivities arise in the mixed solvent system.

The method described here is of obvious preparative value in terms of energy-saving features due to a unique paired precess. Further study for optimization aimed at practical operation is currently under active progress in our laboratory.

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7) Details will be reported by a full paper in due course.

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