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Unsymmetrical Anodic C–C Coupling of 2,6-Di-*tert*-butyl-4-methylphenol

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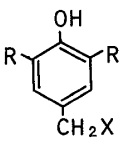
Cyclic voltammetry of 2,6-di-*tert*-butyl-4-methylphenol (**1**) in acetonitrile in the presence of an aliphatic amine such as ethyl-, diethyl-, or triethylamine shows an ill-defined anodic wave——a so-called kinetic wave——around 0.5 V *vs.* aqueous saturated calomel electrode, indicating an electron-transfer process preceded by a slow chemical reaction. Based on the estimated pK_a value of **1** ($pK_a = 12.55$ in water at 25 °C), the chemical reaction was ascribed to a slow hydrogen-bonding association of **1** and the added amine. Controlled potential electrolysis of **1** at the potential of the anodic wave gave an unsymmetrical dimer, 2,6-di-*tert*-butyl-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4-methyl-2,5-cyclohexadiene-1-one, as the main product. Side-chain aminated derivatives of **1**, Ar-CH_2NHEt, Ar-CH_2NEt_2, and Ar-$CH_2N^+NEt_3$ (Ar = 3,5-di-*tert*-butyl-4-hydroxyphenyl), are suggested to be the intermediates; that is, the process of dimer formation is explained in terms of cross-coupling of the phenoxyl radicals derived from **1** and the side-chain aminated phenols followed by expulsion of the aminomethyl group.

Keywords——electrochemical oxidation; cyclic voltammetry; controlled potential electrolysis; 2,6-di-*tert*-butyl-4-methylphenol; oxidative dimerization; phenol coupling

Electrochemical oxidation of 2,6-di-*tert*-butyl-4-methylphenol (**1**) gives various nuclear and side-chain substituted products depending upon the electrolysis conditions.[1] Examples of C–C dimerization of **1** are limited because the active ring positions are blocked by alkyl groups. Formation of the stilbenequinone **4** and its precursor **5** has been suggested in the oxidation of **1** in acetonitrile,[2] though a question was raised later as to whether the dimers were formed during the time-scale of the electrolysis.[3] The diphenoquinone **6** was isolated on electrolysis of **1** in methanol containing sodium methoxide, and a process *via* 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde was proposed.[4]

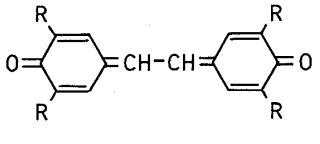


1 : X = H

2 : X = NEt_2

3 : X = N^+Et_3 ClO_4^-

R = *tert*-Bu



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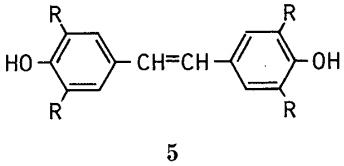

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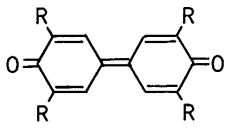

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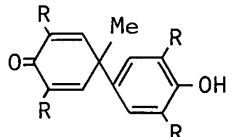

7

Chart 1

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In the course of studies on electrochemical side-chain substitution of **1**, we have found that the unsymmetrical dimer **7** is produced when **1** is electrolyzed in acetonitrile containing aliphatic amines. Although **7** has been obtained by the reactions of **1** with oxygen in the presence of copper-amine catalyst[5] and with iodine in the presence of ethylenediamine,[6] the reaction process was not elucidated in detail. Other investigators also reported the formation of **7** from **1**, but only as a minor product.[7] Ronlán has obtained **7** in the electrochemical oxidation of an equimolar mixture of **1** and 2,6-di-*tert*-butylphenol in acetonitrile, and has proposed a reaction process, in which the unoxidized form of the latter phenol attacks the phenoxonium ion derived from **1** by a two-electron transfer.[8] In the present case, since 2,6-di-*tert*-butylphenol is absent in the system, the process leading to the dimer **7** will be different and seems worthy of a detailed investigation. The results obtained are expected to provide information on the mechanism of the chemical transformation of **1** to the dimer **7**.

This paper reports the results of cyclic voltammetry and controlled potential electrolysis of **1** and its side-chain aminated derivatives **2** and **3** in acetonitrile containing aliphatic amines. The phenols **2** and **3** will be shown to be the intermediates to the dimer **7** in the electrolysis of **1** with added diethylamine and triethylamine, respectively.

Results and Discussion

Figure 1 compares the cyclic voltammograms of **1** in acetonitrile under various conditions. All potentials were measured against an aqueous saturated calomel electrode (S.C.E.). The voltammetric peak without added base (Fig. 1, A) is ascribed to the oxidation of undissociated form of **1** to the corresponding phenoxonium ion *via* two successive one-electron transfers coupled with deprotonation from the phenolic oxygen.[3,9,10] The voltammogram in the MeCN–Et_4NOH system (Fig. 1, B) agrees well with that reported by Evans *et al.*,[11] and its anodic peak represents the one-electron reversible oxidation of the phenolate ion of **1** to 2,6-di-*tert*-butyl-4-methylphenoxyl radical (**8**).[10,11]

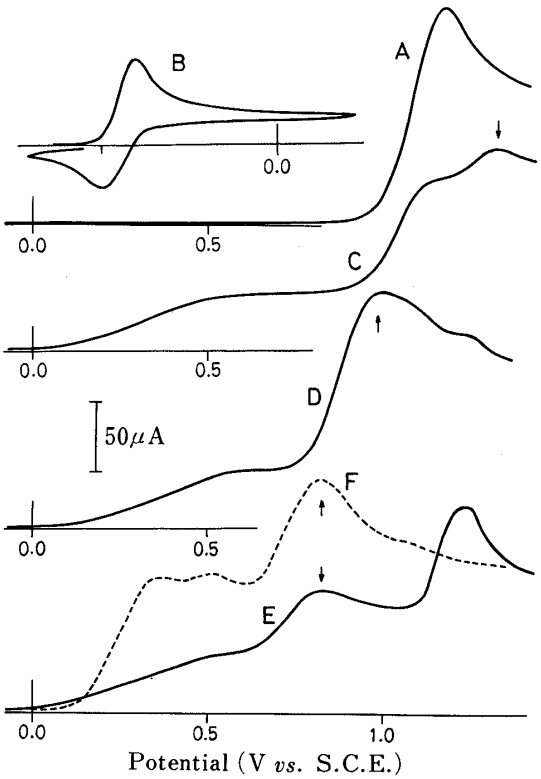

Fig. 1. Cyclic Voltammograms of the Phenol **1** (A—E) and 2,4,6-Trimethylphenol (F) in Acetonitrile

A, **1** without added base; B, **1** with Et_4NOH (1 eq); C, **1** with $EtNH_2$ (3 eq); D, **1** with Et_2NH (3 eq); E, **1** with Et_3N (3 eq); F, 2,4,6-trimethylphenol with Et_3N (3 eq). The concentration of the substrate was *ca.* 5 mM. Supporting electrolyte, 0.1 M $NaClO_4$ for A and C—F, and 0.1 M Et_4NClO_4 for B. Glassy carbon anode (area = 0.071 cm^{-1}); voltage sweep rate, 50 $mV\,s^{-1}$; at 25 °C. The voltammetric peaks indicated by arrows are due to the oxidation of added amines. The reverse sweep curves of A and C—E are omitted for simplicity: no cathodic peak indicating a reversible oxidation was observed.

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In the presence of an aliphatic amine, **1** showed a drawn-out anodic wave around 0.5 V (Fig. 1, C—E), the shape of which indicates an electron transfer process preceded by a slow chemical reaction.[12] The considerations described in the next paragraph strongly suggest that the chemical reaction involved is not slow dissociation of **1** to the phenolate ion but a slow hydrogen-bonding association of **1** with the added amine. Thus, the electrode process is attributable to one-electron transfer from the hydrogen-bonded complex to give the phenoxyl radical **8**. Under the voltammetric conditions, the radical **8** will be converted to the quinone methide **10** by disproportionation or *via* a coupling product **9** (see Chart 3), because further electron removal from **8** will not take place, at least below 0.8 V,[10] and no cathodic counterpart was observed for the anodic wave.

In the hydrogen-bonding equilibria between phenols and amines in aprotic media (Chart 2), both the proton-transfer equilibrium constant K_{PT} and the association constant K_{AS} have been shown to decrease with decrease in the ΔpK_a value defined as $\Delta pK_a = pK_a(\geqslant NH^+) - pK_a(ArOH)$.[13,14] The K_{PT} value in CCl_4 is essentially zero when the ΔpK_a value

$$ArOH + N\leqslant \underset{}{\overset{K_{AS}}{\rightleftharpoons}} \underset{[A]}{ArOH\cdots\cdots N\leqslant} \overset{K_{PT}}{\rightleftharpoons} \underset{[B]}{ArO^-\cdots\cdots HN^+\leqslant}$$

Chart 2

is reduced to 1.28 [4-chlorophenol ($pK_a = 10.65$) and octylamine ($pK_a = 9.37$)], though the K_{AS} value is still significant ($K_{AS} = 41$).[13] Similar results have been obtained in CD_3CN [$K_{PT} = 0$ for $\Delta pK_a = 0.82$: phenol ($pK_a = 9.89$) and propylamine ($pK_a = 10.71$)];[14] the K_{AS} value was not reported. The ΔpK_a values for **1** and the amines used in the present study are estimated to be less than -1.5,[15] and hence the contribution of the polar structure [B] (Chart 2) will be negligible under the voltammetric conditions. The association of **1** or 2,4,6-trimethylphenol with triethylamine was examined in CCl_4 according to the reported procedure,[13] though similar attempts in acetonitrile were unsuccessful. As shown in Fig. 2, the absorption of the non-hydrogen-bonded hydroxyl group of the trimethylphenol at around 3650 cm^{-1} decreased to *ca.* 1/2 in the presence of triethylamine, while that of **1** was essentially unchanged. Since it can be shown from the reported results[13,14] that linear correlations exist between log K_{PT} and log K_{AS} in CCl_4 and between log K_{PT}'s in CCl_4 and in CD_3CN, the results in Fig. 2 suggest that

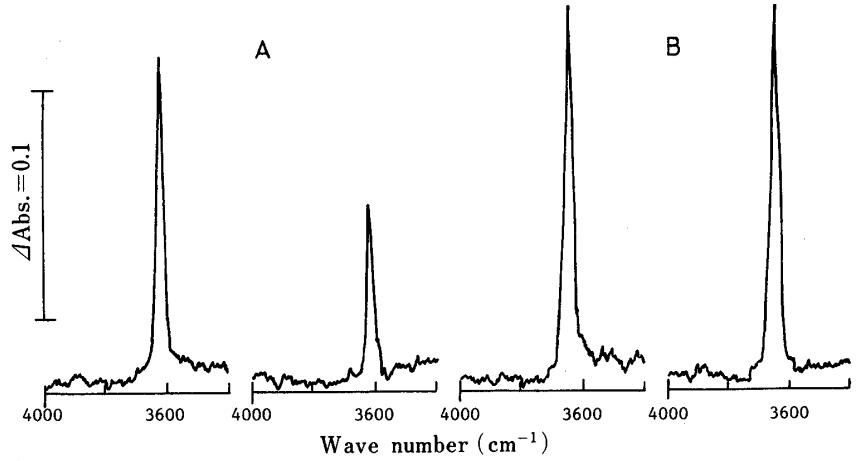

Fig. 2. Infrared Absorption Band of the Hydroxyl Group of the Phenol **1** and 2,4,6-Trimethylphenol in CCl_4

A, 2,4,6-trimethylphenol (0.052 M) without added base (left) and with Et_3N (0.15 M) (right); B, **1** (0.052 M) without added base (left) and with Et_3N (0.15 M) (right).

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TABLE I. Results of Controlled Potential Electrolysis[a]

No.	Phenol (Amount, mmol)	Amine (Amount, mmol)	S.E.[b]	F/mol[c]	*n*-Value[d]	Products (Yield, %)[e]
1	**1** (1)	$EtNH_2$ (1)	A	1	2.1	**1** (52), **7** (42)
2		(3)	A	1	1.8	**1** (56), **7** (40)
3		(5)	A	1	1.8	**1** (50), **7** (39)
4		(5)	A	2	2.4	**1** (18), **7** (80)
5		Et_2NH (1)	B	1	2.2	**1** (53), **7** (42)
6		(3)	B	1	1.8	**1** (55), **7** (37)
7		(5)	B	1	2.0	**1** (52), **7** (38)
8		(5)	B	2	2.4	**1** (16), **7** (83)
9		Et_3N (1)	C	1	1.9	**1** (48), **7** (19), **3** (23)
10		(3)	C	1	1.9	**1** (48), **7** (21), **3** (25)
11		(5)	C	1	2.0	**1** (51), **7** (32), **3** (9)
12		(5)	C	2	2.4	**1** (16), **7** (78), **3** (9)
13	**1** (0.7), **2** (0.3)	Et_2NH (3)	B	1	—	**1** (30), **7** (72), **6** (3)
14	**1** (0.5), **2** (0.5)	(3)	B	1	—	**1** (22), **7** (56), **6** (15)
15	**2** (1)	(3)	B	1	—	**2** [f], **7** (0), **6** (46)
16	**2** (1)	(3)	B	2	—	**2** [f], **7** (0), **6** (71)
17	**1** (0.5), **3** (0.5)	Et_3N (3)	C	1	—	**1** (21), **7** (55), **6** (12), **3** (Trace)
18	**1** (0.5), **2** (0.5)	Et_2NH (3)	B	0.2	—	**1** (42), **7** (15), **6** (3), HCHO (*ca.* 100)[g]
19	**1** (0.5), **3** (0.5)	Et_3N (3)	C	0.2	—	**1** (39), **7** (15), **6** (5), HCHO (*ca.* 100)[g]

a) Electrolysis was carried out in MeCN (50 ml) at ambient temperature by using a one-compartment cell with a glassy carbon plate as the anode and a platinum foil as the cathode; the anode potential was 0.5 V *vs.* S.C.E. *b*) Supporting electrolyte (0.1 M): A, $EtNH_3ClO_4$; B, $Et_2NH_2ClO_4$; C, Et_3NHClO_4. *c*) The electrolysis was discontinued when the indicated amount of electricity (based on the total amount of the substrates) had been consumed. *d*) Based on the amount of **1** consumed. *e*) Based on the total amount of the substrates (1 mmol): determined by HPLC. *f*) The yield could not be determined by HPLC. *g*) Based on the amount of **6** and **7** produced.

the extent of the hydrogen-bonding association of **1** and triethylamine is also very small in acetonitrile. Further support for the slow hydrogen-bonding association of **1** and the added amine in the electrode process is the observation that the trimethylphenol gave well-defined voltammetric peaks in the presence of triethylamine (Fig. 1, F).[16] In the case of the trimethylphenol, the equilibrium concentration of the structure [A] (Chart 2) must be considerable, but the contribution of the polar structure [B] should again be negligible: $\Delta pK_a = -0.06$.[15]

Table I summarizes the results of controlled potential electrolysis in acetonitrile under various conditions: the anode potential was 0.5 V throughout.

Electrolysis of **1** in the presence of ethyl- or diethylamine gave the unsymmetrical dimer **7** as the main product *via* an overall two-electron process (runs 1—8). The amount of added amine excess with respect to **1** had little effect on the results (runs 1—3 and 5—7), except that the time required to consume the indicated amount of electricity (1 F/mol) decreased with increase in the concentration of the amine.[17] In the presence of triethylamine, the side-chain aminated phenol **3** was formed together with the dimer **7**, and the yield of **3** decreased at higher amine concentration while that of **7** increased (runs 9—11).

The results in runs 13—17 strongly suggest, when compared with those in runs 6 and 10, that the side-chain aminated phenols **2** and **3** are the intermediates in the formation of **7** during the electrolysis of **1** in the presence of diethyl- and triethylamine, respectively, that is, **7** is formed from **1** and its side-chain aminated derivatives. In run 14, for example, the amount of **1** consumed in the electrolysis is 0.28 mmol while that of **7** formed is 0.28 mmol. If **7** is formed only from **1**, the amount of **7** would be at most 0.14 mmol. Oxidation of the phenol **2** alone did not give **7** but gave the symmetrical dimer **6** (runs 15 and 16).

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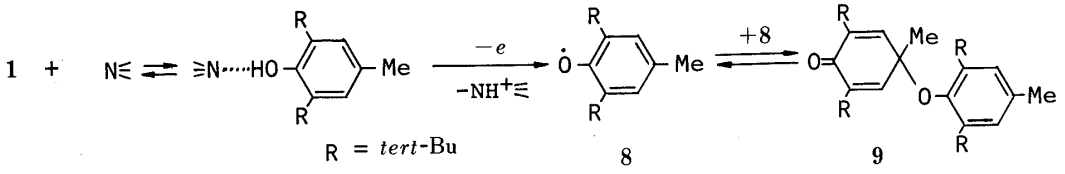
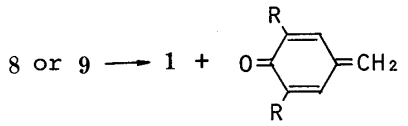
The pathway shown in Chart 3 is proposed for the formation of **7** from **1**. The process from the phenoxyl radical **8** to the quinone methide **10** (Eqs. 1 and 2) has been well documented in the chemical[18] and electrochemical[10] one-electron oxidation of **1**. The side-chain aminated phenols **2**, **3**, and **11** will be formed by the reaction of **10** with the corresponding amines (Eq. 3), as in the reaction of **10** with methanol[4] and pyridine[19] to afford 2,4-di-*tert*-butyl-4-methoxymethylphenol and 2,4-di-*tert*-butyl-4-(1-pyridinium)-methylphenol, respectively.



(1)



(2)

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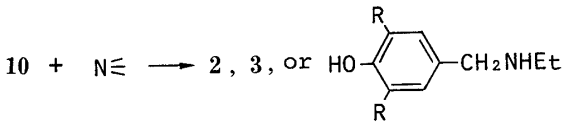

(3)

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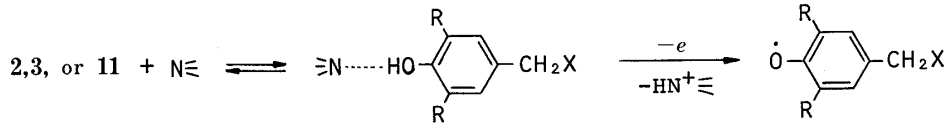
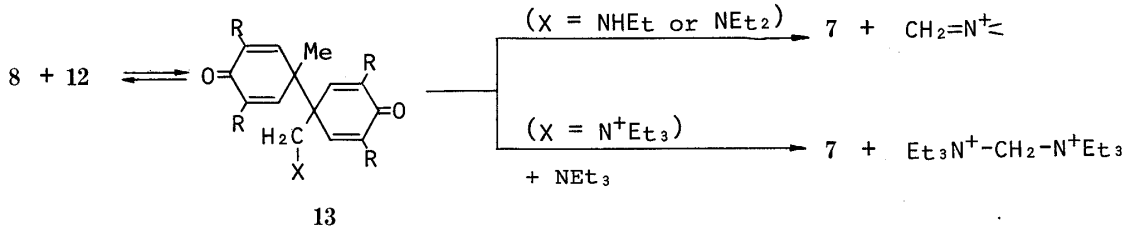


(4)

12

X = NHEt, NEt_2, or N^+Et_3

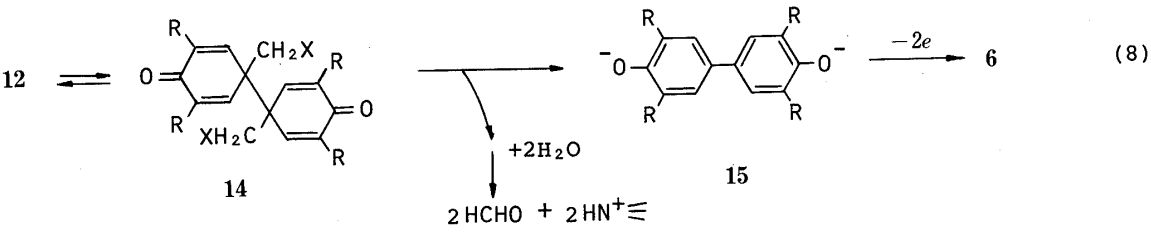


(5)

13

$CH_2=N^+\equiv + H_2O \longrightarrow HCHO + H_2N^+\equiv$ (6)

$Et_3N^+-CH_2-N^+Et_3 + H_2O \longrightarrow HCHO + 2HN^+Et_3$ (7)



(8)

Chart 3

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Since under the conditions of Fig. 1, D and E the phenols **2** and **3** also showed ill-defined voltammetric waves similar to that of **1** in essentially the same potential region (not shown), oxidation of **2**, **3**, and **11** to the radical **12** seems reasonable in the controlled potential electrolysis (Eq. 4). Thus, the dimer **7** is considered to be formed by the cross-coupling of the radicals **8** and **12** *via* the intermediate dimer **13** (Eq. 5). Formation of formaldehyde (runs 18 and 19) supports the release of the aminomethyl group from **13**. In Eqs. 6 and 7, the water unavoidably contaminating the medium probably takes part in the hydrolysis. The dimer **6** has been shown to be formed by the coupling of 2,6-di-*tert*-butyl-4-formylphenoxyl radical followed by deformylation.[4] Similar dimerization of **12** seems reasonable (Eq. 8).

The exclusive formation of the unsymmetrical dimer **7** in the electrolysis of **1** (runs 1—8) and the predominance of **7** over the symmetrical dimer **6** in the electrolysis of a mixture of **1** and **2** (runs 13 and 14) or of **1** and **3** (run 17) can be qualitatively explained as follows. Molecular models suggest that the rotational freedoms of the aminomethyl group in **12**, not only as a whole but also with respect to each bond in the group, are lost to a considerable extent in the intermediates **13** and **14**, and hence in the transition state to them. Consequently, the coupling of **8** and **12** (Eq. 5) may be faster than the dimerization of **12** (Eq. 8). Moreover, during the course of electrolysis started with **1** alone, the concentration of **1** will be always in excess over the expected intermediate **2**, **3**, or **11**, that is, the radical **12** will find the radical **8** more often than another molecule of **12**. Tail-to-tail dimerization of the radical **8** should also take place, in addition to the head-to-tail dimerization to give **9** (Eq. 1), with a rate greater than that of the coupling of **8** and **12**. However, the release of the methyl group from the tail-to-tail coupled dimer will be difficult, as evidenced by the isolation of the unsymmetrical dimer **7**, and hence the tail-to-tail dimer, if formed, will dissociate back to the radical **8** as in the case[5,6] of **9**.

The effects of triethylamine concentration on the product distribution in the electrolysis of **1** (runs 9—11) cannot be explained simply. The slow rate of coupling of **8** and **12** with larger X group (N^+Et_3) and the requirement of another molecule of triethylamine for the release of the $-CH_2-N^+Et_3$ group in **13** (Eq. 5) may be responsible for the lower yield of **7** in the electrolysis at lower amine concentration. Formation of a head-to-tail coupled dimer similar to **9** from **8** and **12** might compete with the formation of **13**, when the rate of the latter process decreases. In such a dimer the radical **8** will constitute the dienone part, and the subsequent reaction of the dimer will afford the phenol **3** and the quinone methide **10**; the latter will be converted to **3** according to Eq. 3. Since the formation of **3** from **1** is a two-electron process, the yield of **7** will decrease while that of **3** will increase with decrease in the triethylamine concentration, when the electrolysis is discontinued in an early stage, *e.g.*, after passage of 1 F per mol of **1** in the present study.

Experimental

Materials——The phenol **1** was recrystallized from methanol–water. The phenol **2** was obtained by Mannich reaction of 2,6-di-*tert*-butylphenol according to the procedure reported for the preparation of 2,4,6-tris(diethylamino)-phenol,[20] and was purified and stored as the hydrochloride (mp 118 °C from ethanol–hexane). In the electrochemical experiments, the salt was neutralized with aqueous sodium bicarbonate and the resulting free base was extracted with ether. After being dried with Na_2SO_4, the ether was removed under reduced pressure and the residue was used as the substrate for voltammetry and controlled potential electrolysis. The phenol **3** was prepared by ethylation of **2** with ethyl iodide (in hexane; refluxed for 24 h; yield, 8%) followed by anion exchange with $AgClO_4$: mp 155 °C. *Anal.* Calcd for $C_{21}H_{38}ClNO_5$: C, 60.06; H, 9.12; N, 3.34. Found: C, 59.52; H, 9.18; N, 3.28. IR ν_{max}^{Nujol} cm^{-1}: 3580 (OH), 1100 (ClO_4). NMR ($CDCl_3$) δ: 1.44 (18H, s), 1.45 (9H, t, J=7 Hz), 3.24 (6H, q, J=7 Hz), 4.39 (2H, s), 5.50 (1H, s, –OH), 7.13 (2H, s, Ar).

Apparatus——Cyclic voltammetry was carried out as described previously.[21] Controlled potential electrolysis was performed in an undivided cyclindrical cell (35 × 75 mm or 50 × 100 mm) using a Hokuto Denko HA-104 potentiostat-galvanostat with a Hokuto Denko HF-201 coulometer and a Toadempa EPR-108 electronic recorder. A glassy carbon plate, a platinum foil, and an S.C.E. separated by an agar bridge were used as the anode, cathode, and

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reference electrode, respectively. High-performance liquid chromatography (HPLC) was carried out using a Waters 6000-A solvent delivery system with a U6K universal injector and a Shimadzu SPD-2A spectrophotometric detector: Bondapack C_{18}-Corasil and acetonitrile were used. Infrared (IR) and nuclear magnetic resonance (NMR) spectra were obtained on a JASCO A-202 spectrometer connected with a JASCO DP-A300 data processor and a Hitachi R-22 spectrometer, respectively.

Isolation of the Phenol 3 and the Dimers 6 and 7 in the Controlled Potential Electrolysis——Typical examples are described. The phenol **1** (800 mg, *ca.* 3.6 mmol) was subjected to electrolysis in acetonitrile (100 ml) containing triethylamine (18 mmol) and 0.1 M $NaClO_4$ at 0.5 V until 632 C, which corresponded to 1.8 F per mol of **1**, had been consumed. The acetonitrile was removed from the electrolyzed solution under reduced pressure, and the residue was extracted with ether (50 ml × 3). The ether was removed under reduced pressure, and the residue was subjected to preparative thin layer chromatography (PTLC) on silica gel with AcOEt–hexane (1 : 18) as the developing solvent to give the phenol **1** (156 mg, 20%) and the dimer **7** (360 mg, 47%). The structure of **7** [mp 158 °C (lit.[6] 154—156.5 °C) was verified by elemental analysis and by the IR and NMR[22] spectra. The residue from the ether extraction was washed with chilled water (10 ml × 3), and recrystallized from AcOEt–hexane to give the phenol **3** (221 mg, 21%). The phenol **2** (534 mg, *ca.* 1.8 mmol) was subjected to electrolysis in acetonitrile (90 ml) containing diethylamine (5.5 mmol) and 0.1 M $Et_2NH_2ClO_4$ at 0.5 V until 1.8 F per mol of **2** had been consumed. The electrolyzed solution was worked-up essentially as described above. The dimer **6** (184 mg, 49%) was separated from the ether extract by PTLC, and identified by comparing its IR and NMR spectra with those of an authentic sample.[4] The residue from the water washing (310 mg, 43%) was identified as the perchlorate salt of the phenol **2**.

General Procedure for the Electrolysis in Table I——An acetonitrile solution (50 ml) of the materials listed in Table I was subjected to electrolysis at 0.5 V until the indicated amount of electricity had been consumed. The electrolyzed solution was adjusted to 100.0 ml with acetonitrile in a volumetric flask, and the mixture was analyzed by HPLC. In runs 18 and 19, a part of the mixture was diluted with water[23] and formaldehyde was determined according to the method of Tannenbaum and Bricker.[24]

References and Notes

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23) Essentially the same results were obtained when the mixture was diluted with acetonitrile, provided that the determination was performed immediately. However, formaldehyde was found to be more volatile in acetonitrile than in water. This is the reason why the electrolysis in runs 18 and 19 was discontinued at an earlier stage (0.2 F/mol). When the electrolysis was continued until 1.0 F/mol had been consumed (*cf.* other runs in Table I), the amount of formaldehyde was always considerably less than the theoretical value even though the electrolyzed solution was worked-up with water.

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