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Electrocatalytic Oxidative Coupling Reaction of Naphthols and Naphthol Ethers on a TEMPO Modified Graphite Felt Electrode

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2- Naphthol and 2-methoxynaphthalene were quantitatively oxidized to the corresponding 1,1'-binaphthyls in more than 90% current efficiency on a graphite felt electrode coated with a thin poly(acrylic acid) layer immobilizing 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxyl (4-amino-TEMPO). 1-Naphthol and 1-methoxynaphthalene were also completely converted to the predicted 1,1'-, 1,2'-, and 2,2'- positioned coupling products. The reaction proceeds via electrocatalytic oxidation of the modified-TEMPO species. The electrode was not inactivated during electrolysis and could be used repeatedly.

Since the oxidative coupling of naphthols and their derivatives to dimeric products is a useful reaction in chemical and biochemical synthesis, many oxidation methods have been studied,[1] but few electrochemical methods have been reported.[2,3] The reason might be that electrolysis of naphthols easily deposits a polymer film on electrodes and can not continue due to diminishing of electric current. On the other hand, organic oxoammonium salts,[4] which can be easily prepared from nitroxide radicals such as 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) by a one-electron oxidation, have been explored as selective oxidizing agents for several organic functional groups in organic solvents.[5,6] However, it is reported that the oxoammonium salt oxidizes naphthols to quinones and does not produce binaphthyls.[5] Bobbitt first succeeded in the coupling reaction of a phenolic alkaloid, corypalline, with the oxonium tetrafluoroborate derived from TEMPO in acetonitrile (CH_3CN)-H_2O solution in the presence of $KHCO_3$ (yield 81%).[7,8] We have been developing a TEMPO-modified graphite felt (GF) electrode for various kinds of preparative, organic electrosynthesis.[9-11] Recently, we have found that the TEMPO-modified electrode oxidizes naphthols and methoxynaphthalenes electrocatalytically to yield dimeric products in excellent yield and current efficiency.

The modified electrode[12] used in this study was a graphite felt (WDF, National Electric Carbon Corp.) coated with a thin poly(acrylic acid)(MW: 1400000) layer. The carboxyl groups of the poly(acrylic acid) layer (ca. 40 nm) were attached to 4-amino-TEMPO (64%), crosslinked with hexamethylenediamine (16%) and butylated (20%). The density of TEMPO on the electrode was 24.4 μmol/cm^3.

The cyclic voltammograms of naphthols and methoxynaphthalenes measured in the same electrolyte conditions as below, showed two oxidation peaks after the second scan which were more positive than + 0.6 V vs. Ag/0.1 M $AgNO_3$ in CH_3CN. The electrochemical behavior of these substrates was complicated, as demonstrated by the previous investigators.[2,3] However, the TEMPO-modified GF electrode afforded a well defined electrocatalytic peak at ca. + 0.55 V in the presence of the substrates even when the scan was repeated. A

current-potential curve of 2-naphthol on the TEMPO-modified GF electrode (0.3 x 0.3 x 0.5 cm^3) is exemplified in Fig. 1.

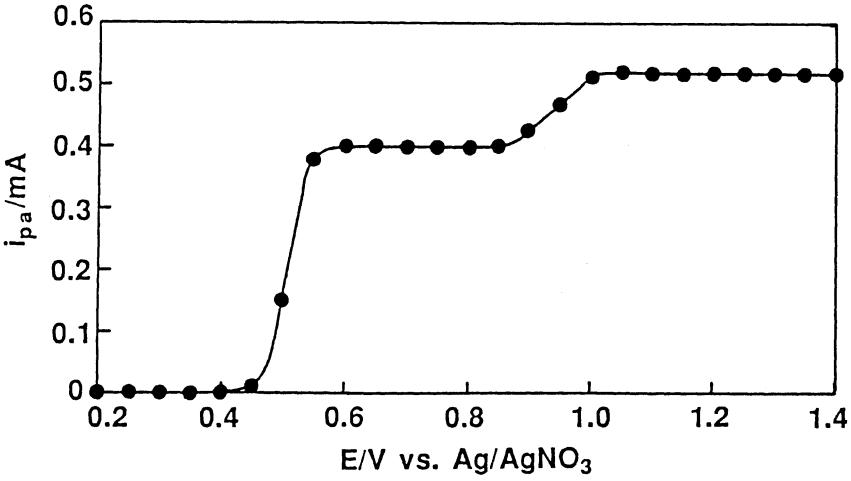


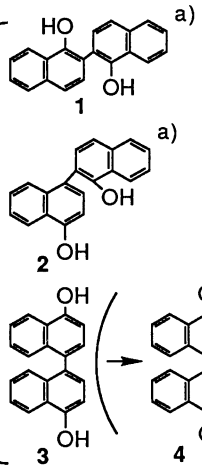
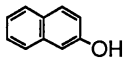
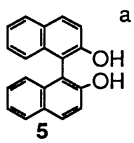
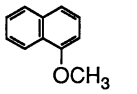
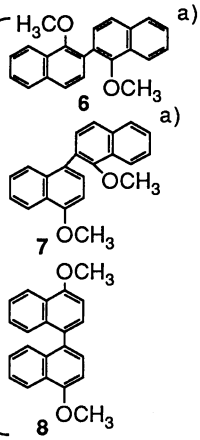
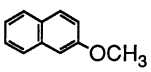
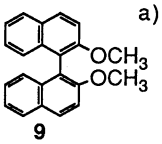
Fig. 1. Current-potential curve of 2-naphthol on TEMPO-modified GF chip (0.3 x 0.3 x 0.5 cm^3) electrode in 0.2 M $NaClO_4/CH_3CN$.

Guided by the current-potential curve in Fig. 1, preparateve, potential-controlled electrolysis at + 0.6 V on the TEMPO-modified GF electrode (5 x 2 x 0.5 cm^3) was performed in CH_3CN solution using an H-type divided cell separated by cationic exchange membrane (Nafion 117). The anolyte contained 50 mmol of substrate, 20 mmol of tetralin as a gas chromatographic (GC) standard, 50 mmol of 2,6-lutidine and 8 mmol of sodium perchlorate ($NaClO_4$) in a total volume of 40 ml. The catholyte was 40 ml CH_3CN solution containing 8 mmol of $NaClO_4$. After the electrolysis was over (examined by GC : Unicarbon A-100, column temp 220 °C, inj. temp 260 °C), the anolyte was concentrated. Dichloromethane (100 ml) was added, and the mixture was washed with 0.1 M HCl and H_2O and dried with sodium sulfate. In a specific example the pale brown reaction mixture of 1-naphthol was fed into a silica gel column (Wako Gel C-200, 3 cm ϕ x 1.5 m), and fractionated (ethyl acetate:ethanol = 4:1, 2:1, 1:1 and 1:2 v/v, each volume of 1.5 l). The recrystallized (**1**, **2**, and **3** from toluene and **4** from benzene) fractions weighed: **1**, 0.81 g (11.3%); **2**, 2.58 g (36.1%); **3**, 3.12 g (43.6%); and **4**, 0.22 g (3.1%) (See the structures in Table 1). The total yield was 94.1%. Other reaction mixtures were similarly treated, and the products were indentified by conventional methods.

Table 1 shows the results of the macroeletrolysis. The conversion of each run was 100% and the current efficiency was more than 90%. The electrode was not deactivated. 2-Naphthol and 2-methoxynaphthalene were quantitatively oxidized to single products of 2,2'-dihydroxy-1,1'-binaphthyl (**5**) and 2,2'-dimethoxy-1,1'-binaphthyl (**9**), respectively. 1-Naphthol and 1-methoxynaphthalene afforded three kinds of 1,1'-, 1,2'-, and 2,2'-binaphthyl compounds as predicted. The coupling products were racemic (no optical rotation). Blank electrolysis at + 0.6 V on the bare GF in the same conditions did not yield any coupling product. The reaction mechanism for the naphthols is estimated to proceed via coupling of naphthyl radicals which were formed by deprotonation following one electron transfer from naphthols to a oxoammonium ion of TEMPO. The redox reaction of TEMPO will be a one electron process between TEMPO and its oxoammonium ion, because there is no inactivation of the electrode.[11]

The above results show that the TEMPO-modified GF yields excellent electrocatalytic coupling reactions of naphthols and methoxynaphthalenes without deactivation of the electrode and the method can be used for macrosynthesis of binaphthyl compounds. Further study on this type of modified electrode is now underway.

Table 1. The Results of Electrocatalytic Coupling Reaction of Naphthols and Naphthol Ethers on TEMPO-Modified Electrode

Substrate	Product	Charge passed[b) C	Current efficiency/%	Isolated yield[c) %	Selectivity %	Turnover number
	 1 a)	5233	92.2	11.3	12	49
	2 a)			36.1	38	156
	3 + 4			43.6 (3.1)	46 (4)	189 (16)
	 5 a)	5042	95.7	98.6	100	410
	 6 a)	5188	93.0	6.8	8	33
	7 a)			37.5	40	164
	8			49.6	52	213
	 9 a)	5155	93.6	96.6	100	410

a) Racemic mixture.
b) Substrates were completely consumed (100% conversion).
c) Calculated from the isolated product weight divided by the theoretical product weight by percent.

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12) Detailed preparation method will published later. A similar method was reported in T. Osa, Y. Kashiwagi, J. M. Bobbitt, and Z. Ma, "Electroorganic Synthesis," ed by R. D. Little and N. L. Weinberg, Marcel Dekker, Inc., New York, (1991), p.343.
13) Spectral data are as follows. **1**: ^{1}H NMR (acetone-d$_6$) δ 7.2 (m, 8H, ArH), 7.9 (m, 4H, ArH), 8.67 (bs, 2H, ArOH). Mp 221-223 °C (lit.[14] mp 220 °C). **2**: ^{1}H NMR (acetone-d$_6$) δ 7.1 (m, 8H, ArH), 7.8 (m, 4H, ArH), 8.62 (bs, 2H, ArOH). Mp 248-249 °C (lit.[15] mp 250 °C). **3**: ^{1}H NMR (acetone-d$_6$) δ 7.3 (m, 8H, ArH), 8.0 (m, 4H, ArH), 8.95 (bs, 2H, ArOH). Mp 296-298 °C (lit.[16] mp 297-299 °C, lit.[17] mp 298-300 °C, lit.[15] mp 342 °C). **4**: ^{1}H NMR (CDCl$_3$) δ 7.1-7.9 (m, 12H, ArH). ν_{max} : 1290, 1325, 1585, 1650 cm^{-1}. Mp 121-123 °C (lit.[17] no melting point). MS(EI) m/e 284 (M^+). **5**: ^{1}H NMR (acetone-d$_6$) δ 7.2 (m, 8H, ArH), 8.0 (m, 4H, ArH), 8.7 (bs, 2H, ArOH). Mp 217-219 °C (lit.[14] mp 219 °C). MS(EI) m/e 286 (M^+). **6**: ^{1}H NMR (CDCl$_3$) δ 3.72 (s, 6H, OCH$_3$), 7.3 (m, 8H, ArH), 7.9 (m, 4H, ArH). Mp 119-121 °C (lit.[18] mp 122 °C, lit[17] mp 120-122 °C). **7**: ^{1}H NMR (CDCl$_3$) δ 3.40 (s, 3H, OCH$_3$), 4.05 (s, 3H, OCH$_3$), 6.96 (d, J =8 Hz, 1H, ArH), 7.30-8.00 (m, 9H, ArH), 8.30-8.45 (m, 2H, ArH); lit.[17] ^{1}H NMR (CDCl$_3$) δ 3.41 (s, 3H, OCH$_3$), 4.07 (s, 3H, OCH$_3$), 6.92 (d, J =8 Hz, 1H, ArH), 7.20-7.95 (m, 9H, ArH), 8.20-8.24 (m, 2H, ArH). Mp 126-128 °C (lit.[17] mp 125.5-126.5 °C, lit[19] mp 122-124 °C). **8**: ^{1}H NMR (CDCl$_3$) δ 3.70 (s, 6H, OCH$_3$), 7.3 (m, 8H, ArH), 7.9 (m, 4H, ArH). Mp 262-264 °C (lit.[17] mp 259-260 °C, lit[19] mp 258-260 °C). **9**: ^{1}H NMR (CDCl$_3$) δ 3.67 (s, 6H, OCH$_3$), 7.2 (m, 8H, ArH), 7.8 (m, 4H, ArH); lit.[20] ^{1}H NMR for (R)- or (S)-isomer δ 3.69 (s, 6H, OCH$_3$), 7.27 (m, 8H, ArH), 7.89 (m, 4H, ArH). Mp 202-204 °C (lit.[21] mp 195 °C). MS(EI) m/e 314 (M^+).
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