

## An Organic Catalytic System for Dehydrogenative Oxidation

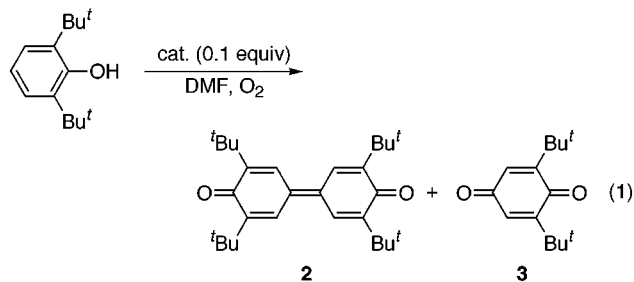
Toshikazu Hirao\* and Shinya Fukuhara

Department of Applied Chemistry, Faculty of Engineering,  
Osaka University, Yamada-oka, Suita,  
Osaka 565-0871, Japan

Received May 8, 1998

Organic compounds possessing relevant redox functions may potentially serve as catalysts in oxidation reactions, but stoichiometric amounts of the oxidant are usually required. In a previous paper,<sup>1</sup> derivatives of coenzyme PQQ were shown to participate in a reversible redox cycle with oxygen in dehydrogenative oxidation. Furthermore, a synthetic metal catalytic system has been devised that makes use of the redox properties of  $\pi$ -conjugated polymers such as polyanilines.<sup>2</sup> This finding suggests that an aniline oligomer may function as an oxidation catalyst. We herein report the catalytic action of *N,N*-bis(4'-aminophenyl)-1,4-benzoquinone diimine derivative **1** as an aniline trimer.<sup>3</sup>

Treatment of 2,6-di-*tert*-butylphenol with a catalytic amount of *N,N*-bis(4'-aminophenyl)-1,4-benzoquinone diimine (**1a**) under atmospheric oxygen resulted in oxidation to the diphenoquinone **2** as a major product and the benzoquinone **3** (eq 1). This result is in sharp contrast



to the fact that such efficient catalytic activity was not observed with *N,N*-diphenyl-1,4-benzoquinone diimine (**1b**) as shown in Table 1. This difference is probably attributable to the redox potentials of **1**.<sup>4</sup> A better result was obtained by use of the tetramethyl-substituted catalyst (**1c**).

The reaction under argon drastically decreased the yield without formation of the quinone **3**, indicating that the catalytic cycle is achieved under oxygen. The reduced form of the oxidant is considered to be the *N,N*-bis(4'-aminophenyl)-1,4-phenylenediamine **4a** or **4c**, which was

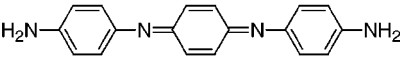
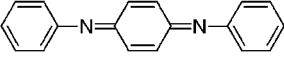
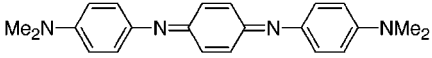


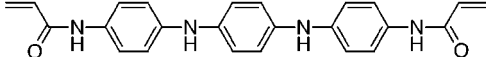
(1) Ohshiro, Y.; Itoh, S.; Kurokawa, K.; Kato, J.; Hirao, T.; Agawa, T. *Tetrahedron Lett.* **1983**, 24, 3465.

(2) Hirao, T.; Higuchi, M.; Ikeda, I.; Ohshiro, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 194. Higuchi, M.; Ikeda, I.; Hirao, T. *J. Org. Chem.* **1997**, 62, 1072.

(3) Wei, Y.; Yang, C.; Ding, T. *Tetrahedron Lett.* **1996**, 37, 731. The suggestion of Prof. Wei is acknowledged.

(4) The redox potential was measured with the reduced phenylenediamine derivative **4** because the quinone diimine moiety of **1** was inactive for CV measurement (see ref 5):  $E_{1/2} = 0.19, 0.39, 0.57$  V for **4a** and **4c**,  $0.98$  V for *N,N*-diphenyl-1,4-phenylenediamine (**4b**) versus  $\text{Ag}/\text{Ag}^+$ . These potentials are not corrected for the junction potential. For 1.0 mM dichloromethane solution of ferrocene, the  $E_{1/2}$  value is 0.51 V with 0.13 V for the peak separation.

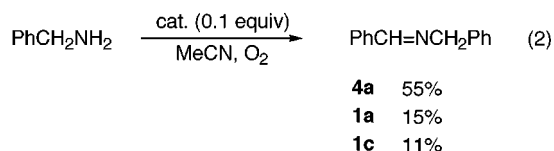
Table 1. Oxidation of 2,6-Di-*tert*-butylphenol

cat.	yield, % ( <b>2</b> : <b>3</b> )
	77 (81 : 19)
<b>1a</b>	
—————	10 (99 : $\leq 1$ )
<b>1a<sup>a</sup></b>	16 (100 : 0)
	10 (99 : $\leq 1$ )
<b>1b</b>	
	99 (86 : 14)
<b>1c</b>	
	84 (83 : 17)
<b>4a</b>	
	99 (87 : 13)
<b>4c</b>	
	83 (89 : 11)
<b>4d</b>	
<b>polymer - 4d</b>	89 (99 : $\leq 1$ )

<sup>a</sup> Under argon. The other reactions were carried out under atmospheric oxygen.

found to serve as a catalytic oxidant. *N,N*-Bis(acryloyl) derivative **4d** worked similarly. The catalytic activity was also observed with the corresponding polymer of **4d**, although **4d** is not soluble in DMF. It should be noted that the selectivity for **2** was higher with the heterogeneous catalyst **4d**.

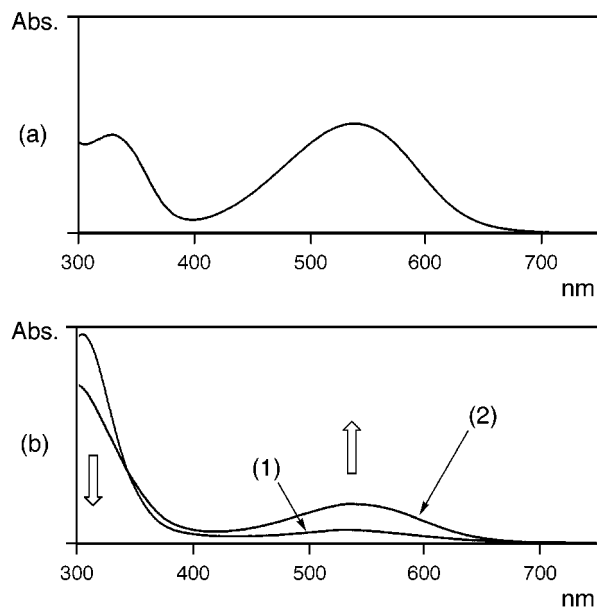
This method is applied to the dehydrogenative oxidation of benzylamine to *N*-benzylidenebenzylamine (eq 2).



The latter formation is explained by dehydrogenation to benzylideneamine and subsequent transamination with benzylamine. A distinct difference in catalytic activity was observed between **1a** and **4a** as shown in eq 2. This difference is probably due to the presence of the amine protons of **4a**, which is consistent with the result that a proton is required for the formation of a reversible redox cycle of polyanilines.<sup>5</sup> In the case of oxidation of the phenol, a proton source is available from the substrate.

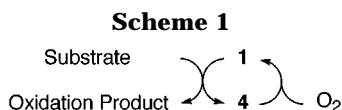
As mentioned above, the catalysis appears to depend on a reversible redox cycle of **1** under oxygen. The broad

(5) Higuchi, M.; Imoda, D.; Hirao, T. *Macromolecules* **1996**, 29, 8277.

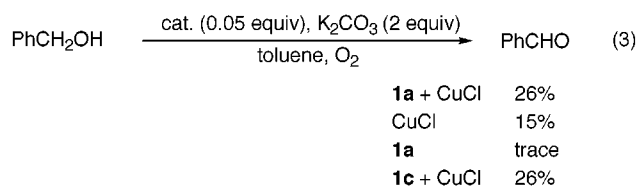


**Figure 1.** UV-vis spectra. (a)  $[1\mathbf{a}] = 5.0 \times 10^{-5}$  M; solvent MeCN. (b) (1) treatment with benzylamine at 70 °C for 5 h under argon; (2) treatment at room temperature for 9 h under atmospheric oxygen.

absorption around 540 nm in the UV-vis spectrum of **1a** (Figure 1a), which is possibly assigned to the CT band between the benzenoid and quinoid moieties, disappeared on treatment with benzylamine at 70 °C under argon. This spectral change implies the reduction of **1a** to **4a**. The absorption reappeared to some extent upon contact with atmospheric oxygen (Figure 1b). The phenylenediamine **4a** was also detected by  $^1\text{H}$  NMR in the reaction mixture obtained similarly in acetonitrile- $d_3$ . These results support the catalytic cycle of **1** or **4** shown in Scheme 1.



The combination of polyanilines and a copper or iron salt is revealed to form an efficient complex catalytic system,<sup>2</sup> and the imine moiety of **1c** is capable of coordinating to transition metals.<sup>6</sup> Benzyl alcohol was allowed to undergo the dehydrogenation to benzaldehyde on treatment with a catalytic amount of copper(I) chloride and **1a** or **1c** in the presence of potassium carbonate (eq 3). Both catalytic components are essential for the



effective conversion. Since the azodicarboxylate has been reported to serve as a hydrogen acceptor,<sup>7</sup> **1** might also play a similar role in the present oxidative transformation.

In conclusion, the above-mentioned results indicate that the  $\pi$ -conjugate molecules possessing a reversible redox function contribute to the construction of an efficient organic and complex catalytic system under oxygen.

## Experimental Section

**Synthesis of 1 and 4.** The preparation of **1a**, **1c**, **4a**, and **4c** was carried out according to the reported method.<sup>3</sup> **4d** was prepared as follows. To a solution of **4a** (290 mg, 1.00 mmol) in DMF (25 mL) was added dropwise a solution of acryloyl chloride (181 mg, 2.00 mmol) and pyridine (313 mg, 4.00 mmol) in DMF (5 mL) at 0 °C under argon. Stirring was continued for an additional 5 h. The reaction mixture was concentrated under reduced pressure. Methanol (20 mL) was added to the obtained residue, which was filtered to remove the insoluble black solid. Reprecipitation of the concentrated filtrate from a saturated aqueous solution of  $\text{NaHCO}_3$  was carried out three times. Further reprecipitation from hexane (200 mL) gave 235 mg (59% yield) of **4d**. mp 213–214 °C (uncorrected, dec); IR (KBr) 3300, 1659, 1613, 1510, 1384, 1307, 822  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  9.91 (s, 2H), 7.80 (s, 2H), 7.48 (dd, 4H,  $J = 7.2, 1.8$  Hz), 6.98 (s, 4H), 6.92 (dd, 4H,  $J = 7.2, 1.8$  Hz), 6.40 (dd, 2H,  $J = 17.1, 10.5$  Hz), 6.20 (dd, 2H,  $J = 17.1, 2.1$  Hz), 5.69 (dd, 2H,  $J = 10.5, 2.1$  Hz); MS (FAB)  $m/z$ , 398 ( $M^+$ ). Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_2 \cdot 1.25\text{H}_2\text{O}$ : C, 68.47; H, 5.87; N, 13.31. Found: C, 68.20; H, 5.41; N, 13.66.

Polymerization was carried out by treatment of **4d** (40 mg, 0.10 mmol) in dichloromethane with benzoyl peroxide (2.4 mg, 0.01 mmol) at 80 °C for 24 h under argon in a sealed glass tube. The blue solid polymer (28 mg) was washed with dichloromethane and methanol and dried; mp >300 °C; IR (KBr) 3313, 1658, 1603, 1536, 1503, 1319, 1250, 823  $\text{cm}^{-1}$ . Anal. Found:  $\text{C}_{24}\text{H}_{22.46}\text{N}_{4.15}$ .

**A Representative Procedure for the Catalytic Oxidation of 2,6-Di-*tert*-butylphenol.** A mixture of 2,6-di-*tert*-butylphenol (206 mg, 1.00 mmol) and **1a** (29 mg, 0.10 mmol) in DMF (1 mL) was stirred at 70 °C for 40 h under atmospheric oxygen. Ether (50 mL) was added to the reaction mixture, which was filtered and concentrated. The yields of **2** and **3** were determined by GLC as shown in Table 1.<sup>2</sup>

**A Representative Procedure for the Catalytic Oxidation of Benzylamine.** A mixture of benzylamine (107 mg, 1.00 mmol) and **1a** (29 mg, 0.10 mmol) in acetonitrile (1 mL) was stirred at reflux for 24 h under atmospheric oxygen. Ether (50 mL) was added to the reaction mixture, which was filtered and concentrated. The yield of *N*-benzylidenebenzylamine was determined by GLC as shown in eq 2.<sup>2</sup>

**A Representative Procedure for the Catalytic Oxidation of Benzyl Alcohol.** To a mixture of **1a** (29 mg, 0.10 mmol), copper(I) chloride (9.9 mg, 0.10 mmol), and potassium carbonate (553 mg, 4.00 mmol) in toluene (2 mL) was added benzyl alcohol (216 mg, 2.00 mmol). The mixture was stirred at 90 °C for 24 h under atmospheric oxygen. Ether (50 mL) was added to the reaction mixture, which was filtered and concentrated. The yield of benzaldehyde was determined by GLC as shown in eq 3. Benzoic acid was not detected by GLC.

**Measurement of UV-Vis and  $^1\text{H}$  NMR Spectra in the Redox Process of 1a.** The oxidation reaction of benzylamine was carried out similarly as mentioned above at 70 °C for 5 h under argon. The obtained solution was diluted to ca.  $5 \times 10^{-5}$  M with acetonitrile for the measurement of the UV-vis spectrum. The solution was contacted with atmospheric oxygen at room temperature for 9 h to give the spectrum shown in Figure 1. For the measurement of the  $^1\text{H}$  NMR spectrum, acetonitrile- $d_3$  was used as a solvent.

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