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Efficient oxidative dimerization of 1-naphthols to 2,2′-binaphthyls with dioxygen mediated by semiconductors

Tsuyoshi Otsuka, Iwao Okamoto, Eiichi Kotani and Tetsuya Takeya*

Showa Pharmaceutical University, 3-3165 Higashi-tamagawagakuen, Machida, Tokyo 194-8543, Japan

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Abstract—A novel and efficient oxidative dimerization of 1-naphthols **1** with dioxygen in the presence of several semiconductors including SnO_2, ZrO_2, and activated charcoal as catalytic mediators took place selectively to give the corresponding 2,2′-binaphthols **2** or 2,2′-binaphthyl-1,1′-quinones **3** in excellent yields without light irradiation. Among these semiconductors, the catalytic activity of SnO_2 could be fully restored by appropriate reactivation treatment after oxidation. The products **2** and **3** should be useful as synthetic intermediates for natural binaphthyls.

So-called oxidative dimerization and oxidative coupling of hydroxyarenes commonly involve oxidative dehydrogenation and subsequent C–C or C–O coupling of the resulting arenyl radical. The oxidative dimerization of hydroxyarenes such as naphthols and phenols is one of the most important tools of modern organic synthesis and is often used in biomimetic or chemical synthesis of natural products and binaphthols used as chirality inducers.[1] For instance, a number of methods have been developed for the preparation of binaphthols and their derivatives by the oxidative coupling of naphthols. This has been achieved by using a variety of oxidants, such as metal salts, Ag(I), Pb(IV), Fe(III), Mn(III), Cu(II), etc., in homogeneous solution.[2] In most cases, however, the coupling reactions are not catalytic but require more than stoichiometric amounts of oxidants. There are a few exceptions employing such catalyst systems as CuCl–(OH)·TMEDA complex or $VO(acac)_2$ under dioxygen (O_2) as coupling reagents.[2a,3] In the oxidation of naphthols, the use of homogeneous oxidants often leads to poor selectivity and low yield of the desired products, accompanied with side reactions, so that the reactions are difficult to control. Recently, solid Lewis acids,[4] have been used, such as $FeCl_3$ as heterogeneous catalysts, either alone or in binary combinations such as $CuSO_4/Al_2O_3$ and $FeCl_3$/montmorillonite, with aerial oxygen or dioxygen for oxidative coupling of 2-naphthols.

The replacement of current stoichiometric oxidations for the production of fine chemicals with environmentally benign catalytic oxidations is one of the major tasks in green chemistry.

Dioxygen seems to be an ideal oxidant for such purposes, as well as in biomimetic synthesis of natural products, because the supply is ample, and the molecule environmentally friendly and nontoxic. In addition, dioxygen participates in metabolic processes in mammalians and plants.[5] Further, various semiconductors (SC),[6a,b] particularly titanium dioxide (TiO_2),[6c] are extensively used as sensitizers in heterogeneous photocatalytic oxidations. They are particularly useful from an environmental viewpoint, because they are almost nontoxic, stable, and inexpensive. Several such reactions have been reported, including oxygenations and oxidative cleavage.[6]

From the practical and environmental viewpoints, SC should be advantageous as heterogeneous catalysts, and it is expected that dioxygen can be effectively used for the facile regeneration of such catalysts in a catalytic cycle. As far as we know, there have been no reports to date on oxidative dimerization of 1-naphthols (NPOH) with dioxygen using SC in the absence of light irradiation.

In this paper, we report a novel and efficient oxidative dimerization of NPOH **1** to 2,2′-binaphthyl derivatives **2**

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* Corresponding author. Tel./fax: +81-42-721-1579; e-mail: takeya@ac.shoyaku.ac.jp

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or **3** with dioxygen as the oxidant, mediated by several SC.

Preliminary experiments on the oxidative dimerization were done with NPOH **1a** as a substrate, without light irradiation. Several SC[6] and solvents saturated with dioxygen [namely, TiO_2, Nb_2O_5, SnO_2, ZrO_2, activated charcoal (Act-C),[7] etc., and CH_2Cl_2, MeCN, $MeNO_2$, etc.] were investigated, and the results are shown in Table 1. The best result was obtained with Act-C in MeCN (entry 1). That is, the reaction of **1a** using the Act-C/O_2 reagent system in the presence of O_2 in MeCN afforded selectively the so-called Russig's Blue,[8a] 2,2′-binaphthyl-1,1′-quinone (**3a**; BNPQ), in excellent yield. A similar result was obtained in the dark.

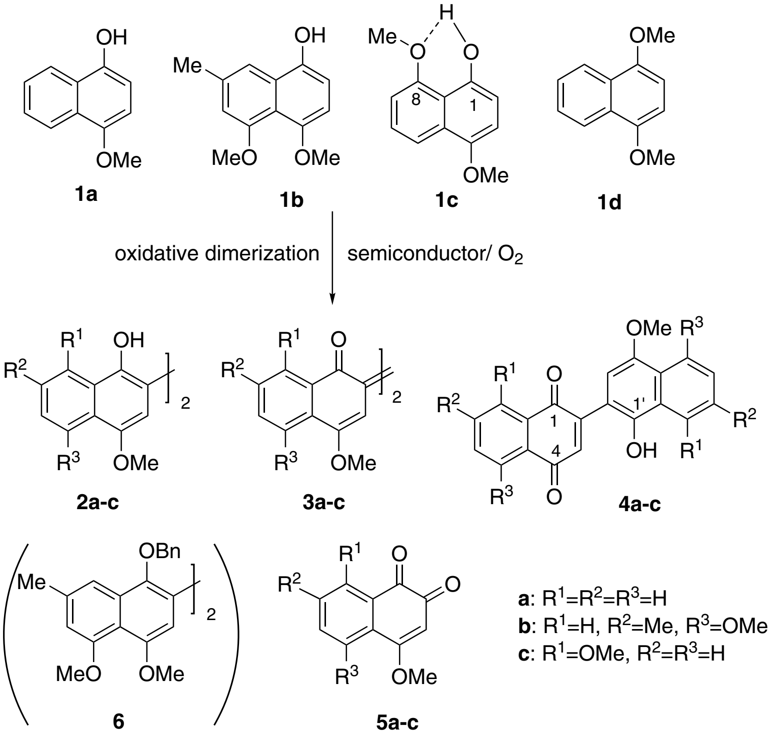
In the case of using the ZrO_2/O_2 system in CH_2Cl_2, BNPQ **3a** was obtained as a major product along with the *ortho*-naphthoquinone **5a** as a by-product (entry 2). However, good results were not obtained with the Nb_2O_5/O_2 or the TiO_2/O_2 system (entries 3 and 4).

Furthermore, with the SnO_2/O_2 system in CH_2Cl_2, 2,2′-binaphthol (**2a**; BNPOH) and 1′-hydroxy-2,2′-binaphthyl-1,4-quinone (**4a**; HBNPQ) were obtained in yields of 67% and 28%, respectively (entry 5). A solvent effect of MeCN was only observed in the reaction with the SnO_2/O_2 system. When MeCN was used in place of CH_2Cl_2 under similar conditions, **4a** was not obtained at all, and in this case **2a** and **3a** were obtained in yields of 64% and 28%, respectively (entry 6). The reason for this is discussed below. The catalyst (SnO_2) could be easily recovered by simple filtration and washing with CH_2Cl_2, followed by drying at 130 °C for 12 h under reduced pressure before use. The recovered SnO_2 showed almost unchanged catalytic reactivity, since reaction of **1a** using the recovered SnO_2 in MeCN under identical conditions gave **2a** (64%) and **3a** (26%). However, recovered ZrO_2 and Act-C did not acquire full catalytic activity after the above reactivation treatment.

Similar reactions were explored using **1b** or **1c**,[9] which can be precursors for the synthesis of binaphthyl natural products (Table 1).[8]

In the case of **1b**, the best result was obtained with the ZrO_2/O_2 system in MeCN for 0.75 h, affording **3b** selectively in excellent yield (entry 8). The reaction with the SnO_2/O_2 system under similar conditions gave a complex mixture containing a substantial amount of **2b**. In order to isolate **2b**, we performed column chromatography of the reaction mixtures under various conditions. However, all the attempts were unsuccessful, producing mainly solid mixtures of **2b** and **3b**. Therefore, the mixture of **2b** and **3b** was treated with benzyl bromide/K_2CO_3 to give **6** (81%) as a major product together with nonreacted **3b** (2%) (entry 9).

In the case of **1c**, the best result was obtained with the SnO_2/O_2 system in MeCN. This oxidative coupling was very sluggish, but selectively afforded **2c** in good yield (entry 11). In all experiments with **1c** using various semiconductors, a longer period of reaction was required for completion of the reaction, in comparison with the cases of **1a**–**b**. This may be owing to the influence of the hydrogen-bond formation[10] between the



Scheme 1.

Table 1. Semiconductor-mediated oxidative dimerization of naphthol **1** in the presence of dioxygen (O_2)[a]

Entry	NPOH	Reagent	Solvent	Temperature (°C)	Time (h)	Product (isolated yield, %)			
1	**1a**	Act-C[b]	MeCN	70	16	**3a** (95)			
2	**1a**	ZrO_2	CH_2Cl_2	23	1.5	**3a** (75)	**5a** (17)		
3	**1a**	Nb_2O_5	CH_2Cl_2	23	3.5	**3a** (51)	**5a** (43)		
4	**1a**	TiO_2	CH_2Cl_2	23	0.5	**2a** (4)	**3a** (15)	**4a** (18)[g]	**5a** (20)
5	**1a**	SnO_2	CH_2Cl_2	23	72	**2a** (67)	**4a** (28)		
6	**1a**	SnO_2	MeCN	70	29	**2a** (64)	**3a** (28)		
7	**1a**	SnO_2	$MeNO_2$	23	72	**2a** (81)	**3a** (6)		
8	**1b**	ZrO_2	MeCN	70	0.75	**3b** (96)			
9[d]	**1b**	SnO_2	CH_2Cl_2	23	24	**6** (81)[c]	**3b** (2)	**4b** (3)[g]	
10[d]	**1c**	ZrO_2	MeCN	70	70	**2c** (68)	**3c** (14)	**4c** (trace)[g]	
11[d]	**1c**	SnO_2	MeCN	70	136	**2c** (86)			
12	**1d**	SnO_2	CH_2Cl_2	23	72	No reaction			
13[e]	**1b**	Ag_2O	$CHCl_3$	23	0.5	**6** (30)[c]	**3b** (34)	**5b** (8)	
14	**2a**	SnO_2	MeCN	70	0.75	**3a** (93)			
15[f]	**1a**	ZrO_2	CH_2Cl_2	23	1.5	No reaction			

[a] General procedure: a slurry of semiconductor powder [Act-C (1 g)[b], SnO_2 (5 g), ZrO_2 (5 g), Nb_2O_5 (5 g), or TiO_2 (1 g)] and **1a** (0.25 mmol) in a dioxygen-saturated solvent (MeCN, CH_2Cl_2, or $MeNO_2$; 10 mL) was vigorously stirred at an appropriate temperature (23 or 70 °C) under normal laboratory light. Similar results were obtained in the dark. These semiconductors are commercially available (Wako Pure Chemical Industries, Ltd, Japan).

[b] With activated charcoal.

[c] Yield from **1b**.

[d] Unreacted NPOHs **1** were also recovered: entry 9, **1b** (14%); entry 10, **1c** (8%); entry 11, **1c** (12%).

[e] With Ag_2O (1.5 equiv) under air.

[f] This reaction was carried out under air. CH_2Cl_2 as a solvent was used without any treatment.

[g] Structures **4** were elucidated by analyses of IR, ^1H NMR, ^{13}C NMR spectra, with the aid of 2D NMR spectral analyses, and transformation to the corresponding 2,2′-binaphthoquinones by the reaction with 69% HNO_3. The ^1H NMR spectra of compounds **4** showed the presence of a naphtholic OH at the C-1′ position (δ 8.51 in **4a**; δ 8.60 in **4b**; δ 9.41 in **4c**). The ^{13}C NMR spectra of compounds **4** displayed the presence of two carbonyl carbons at the C-1 and C-4 positions (δ 184.5, 188.5 in **4a**; δ 183.2, 185.3 in **4b**; δ 183.6, 188.3 in **4c**).

hydroxyl proton (at C1) and the methoxyl group (at C8) in **1c**, as shown in Scheme 1, though this remains to be confirmed.

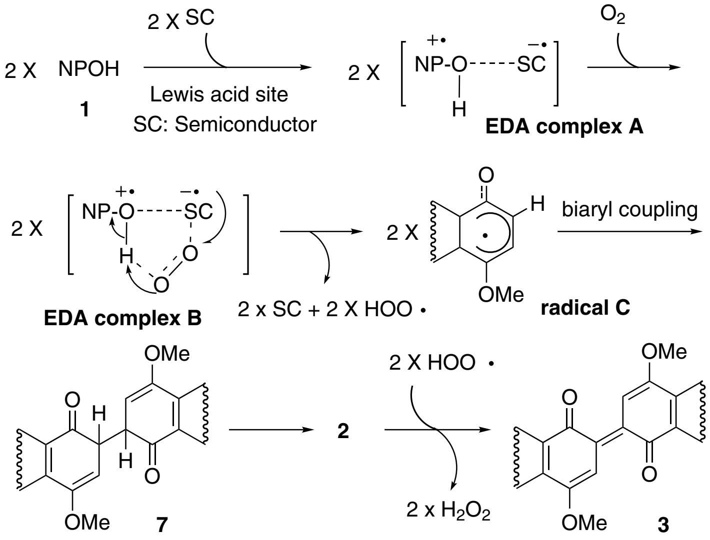
On the other hand, in the case of the naphthol-ether **1d** with the SnO_2/O_2 system, the reaction did not proceed under similar conditions (entry 12). Finally, the reaction of **1b** with the well-known oxidant Ag_2O in chloroform was examined, but gave only a mixture of the coupling product and its oxidized quinone (entry 13).

The noteworthy features of the above reactions were as follows. The hydroxyl group in **1a**–**c** was required for the formation of the binaphthyl derivatives, based on the result of entry 12. The SC-mediated oxidation of **1a**–**c** in the presence of O_2 made it possible to control the synthesis in the direction of either **3** or **2**. For example, the reaction of **1a** or **1b** with the Act-C/O_2 or the ZrO_2/O_2 system afforded the corresponding **3a** or **3b** in excellent yield, respectively, while the reaction of **1c** with the SnO_2/O_2 system gave **2c** in high yield. The SC were essential for the catalysis of the present oxidation, since it did not proceed in their absence. The resulting products **2**, **3**, and **4** would be useful synthetic intermediates for naturally occurring diosindigo B, biramentaceone and violet-quinone.[8b,c]

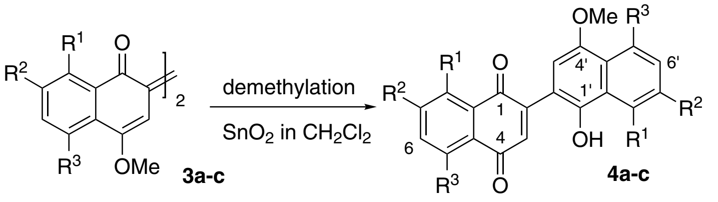
In order to confirm the formation mechanism of **3** in the present oxidation, for example, the reaction of **2a** with the SnO_2/O_2 system was carried out to give **3a** in high yield(entry 14 in Table 1). No reaction occurred in the absence of O_2 under similar conditions. The above results indicate that **3** is produced via **2** by the oxidation of **1**.

The proposed mechanism for the SC-mediated oxidative dimerization of NPOH **1** using O_2 is illustrated in Scheme 2. This is analogous to that proposed for the oxidative reaction of 1-naphthols with the $SnCl_4/O_2$ system reported previously by us.[11] This reaction is initiated by the formation of the electron donor–acceptor (EDA) complex **A** between **1** and a Lewis acid site on the SC surface. Subsequent processes proceed on the SC surface. The SC (semiconductor), such as SnO_2, ZrO_2 or Act-C, plays an important role in the present oxidation. That is, it acts not only as a characteristic Lewis acid catalyst, but also as a mediator for electron transfer. Alternatively, O_2 may act as a one-electron acceptor from the anion-radical species ($SC^{-}\cdot$) and a one-proton acceptor from the cation-radical species ($NPOH^{+}\cdot$) within complex **B**. Finally, the resulting hydroperoxy radicals act as a two-hydrogen acceptor from **2**.

Next, to throw light on whether HBNPQ **4** is formed by acid-induced demethylation or oxidative demethylation of the enol-ethers **3** in the reaction of **1** in CH_2Cl_2 (entries, 4, 5, and 9 in Table 1), the reactions of **3a**–**c** with various reagents in the absence of O_2 in CH_2Cl_2 or MeCN were examined (Scheme 3). The results are summarized in Table 2. With SnO_2 in CH_2Cl_2, selective demethylation of **3a**–**c** proceeded efficiently to give **4a**–**c** under mild conditions in high yield (entries 1, 3, and 4). Similar results were obtained in the dark. These results indicate that the formation of **4** from **3** does not require dioxygen and light, but requires SnO_2. Alternatively, the formation of the hydroxyl group (at C-1′) in **4** from **3** requires a proton (H^+) or a hydrogen source. This suggests the participation of a Brønsted acid (Sn–OH) site



Scheme 2.



Scheme 3.

Table 2. Demethylation of the enol-ethers **3** to **4** with various reagents in the absence of O_2[a]

Entry	Substrate	Reagent	Solvent	Time (h)	Product (%)[b]
1	**3a**	SnO_2	CH_2Cl_2	19	**4a** (94)
2	**3a**	SnO_2	MeCN	72	No reaction
3	**3b**	SnO_2	CH_2Cl_2	2	**4b** (95)
4	**3c**	SnO_2	CH_2Cl_2	2	**4c** (93)
5[c]	**3a**	ZrO_2	CH_2Cl_2	72	**4a** (12)
6	**3a**	Act-C	CH_2Cl_2	72	No reaction
7[d]	**3a**	HCl	CH_2Cl_2	8	**4a** (91)

[a] General procedure: a slurry of semiconductor powder [SnO_2 (5 g), ZrO_2 (5 g) or Act-C (1 g)] and **3** (0.25 mmol) in an argon-saturated solvent (CH_2Cl_2 or MeCN) was vigorously stirred at 23 °C under normal laboratory light. Similar results were obtained in the dark.

[b] Isolated yield.

[c] Together with recovered **3a** (40%).

[d] Using 10% HCl aqua.

on the SnO_2 surface, because proton sources, such as water (H_2O) and acids were not used in the work-up after the reaction according to general procedure described in Table 2. Early infrared studies (IR spectroscopy) of the adsorption of carbon monoxide (CO) on the SnO_2 surface explicitly showed the existence of Sn–OH sites on the SnO_2 surface.[12b] Indeed, the reaction of **3a** with HCl as a Brønsted acid in place of SnO_2 gave **4a** in good yield (entry 7). Accordingly, **4** is concluded to be formed by demethylation of **3** at Sn–OH sites on the SnO_2 surface.

In order to examine the reason why MeCN has the solvent effect described above, the reaction of **3a** using MeCN in place of CH_2Cl_2 as a solvent was carried out under similar conditions. Surprisingly, this reaction did not proceed at all (entry 2). In the above case, as well as in the case of entry 6 in Table 1, **4a** was presumably not obtained because the interaction between the Sn–OH sites and the carbonyl group in **3a** is blocked by the MeCN molecules, which bind to the Sn–OH sites, based on a report described below. Yates and co-workers[12c] observed that the adsorption of MeCN on Brønsted acid sites of a metal oxide surface, such as TiO_2, by means of IR spectroscopy. The reaction with ZrO_2 under similar conditions gave **4a** in low yield, while no reaction occurred with Act-C. These results indicate that the formation of **4** by the reaction of **1** or **3** can be well controlled when ZrO_2 or Act-C as a catalyst and MeCN are employed.

In this study, we found that heterogeneous SC, such as SnO_2, ZrO_2 and Act-C, are efficient solid oxidation catalysts for the oxidative dimerization of NPOH **1** to 2,2′-binaphthyl derivatives **2** or **3** using dioxygen as an oxidant.

In particular, SnO_2 is a useful and convenient catalyst for the selective synthesis of 2,2′-binaphthols **2** and for selective O-demethylation of the enol-ether **3** to **4**. The SnO_2-mediated oxidations appear to be free from possible environmental pollution, since the reagent is nontoxic and can be recycled.

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