Synthesis of Naphthalenediols by Aerobic Oxidation of Diisopropylnaphthalenes Catalyzed by *N*-Hydroxyphthalimide (NHPI)/α,α′-Azobisisobutyronitrile (AIBN)

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Received: October 11, 2003; Accepted: January 28, 2004

Abstract: Naphthalenediols were successfully synthesized in a one-pot reaction through the oxidation of diisopropylnaphthalenes with air catalyzed by *N*-hydroxyphthalimide (NHPI) combined with α,α′-azobisisobutyronitrile (AIBN) followed by decomposition with sulfuric acid. Thus, the oxidation of 2,6-diisopropylnaphthalene with air (20 atm) in the presence of AIBN (3 mol %) and NHPI (10 mol %) in CH_3CN at 75 °C for 21 h followed by treatment with 0.3 M H_2SO_4 gave 2,6-naphthalenediol in 92% yield.

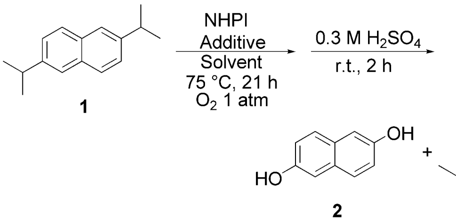
Keywords: homogeneous catalysis; hydroperoxides, *N*-hydroxyphthalimide; oxidation; radicals

Phenols and naphthols are an important class of compounds needed for the syntheses of dyes, pharmaceuticals and polymers. In particular, naphthalenediols are essential components of intelligent polymers such as engineering plastics and liquid crystalline polymers. 2,6-Naphthalenediol (**2**) has attracted much attention for its chemical and physical properties as a liquid crystalline monomer material. A classical process for the production of **2** is based on the sulfonation of naphthalene followed by alkali fusion of the resulting sulfonates.[1] However, **2** is difficult to synthesize in high yield by this method, which results in a complex mixture of several sulfonated products. It has been reported that the reaction of β-naphthol with hydrogen peroxide in the presence of a Lewis acid like SbF_5 produces **2**, but this method also brings about a mixture of several regioisomeric naphthalenediols.[2] There have been several patents on the synthesis of **2** by the oxidation of 2,6-diisopropylnaphthalene (**1**) followed by treatment of the resulting 2,6-bis(2-hydroxy-2-propyl)naphthalene with H_2O_2 and H_2SO_4.[3]

The phenol synthesis through cumene hydroperoxide obtained by the aerobic oxidation of isopropylbenzene is well known as the Hock process. Recently, this methodology was applied to the synthesis of 2,6-bis(1-hydroperoxy-1-methylethyl)naphthalene (**4**) and 2-isopropyl-6-(1-hydroperoxy-1-methylethyl)naphthalene (**5**).[4] In a previous paper, we have reported the aerobic oxidation of methylbenzenes like toluene and xylene to the corresponding carboxylic acids using *N*-hydroxyphthalimide (NHPI) as a key catalyst.[5] In addition, we reported the epoxidation of olefins with ethylbenzene hydroperoxide, generated *in situ* from the aerobic oxidation of ethylbenzene by NHPI, in the presence of $Mo(CO)_6$.[6] This fact shows that the NHPI-catalyzed oxidation of alkylbenzenes can be applied to the synthesis of alkyl hydroperoxides from alkylbenzenes.[7] ly, Sheldon et al. have reported phenol synthesis by means of the NHPI-catalyzed aerobic oxidation of cyclohexylbenzene.[8]

We now report an efficient synthesis of naphthalenediols *via* aerobic oxidation of diisopropylnaphthalenes catalyzed by NHPI and AIBN.

The aerobic oxidation of **1** was chosen as a model reaction and was carried out in the presence of catalytic amounts of AIBN and NHPI under various conditions (Table 1).



(1)

Compound **1** was allowed to react under O_2 (1 atm) in the presence of AIBN (3 mol %) and NHPI (10 mol %) in CH_3CN (5 mL) at 75 °C for 21 h followed by treatment of the reactants with 0.3 M sulfuric acid at room temperature for 2 h, leading to **2** in 81% yield along with 6-isopropyl-2-naphthol (**3**) (18%) (run 1). This shows that **1** is completely oxidized with O_2 by NHPI to give selectively **4** upon treatment with sulfuric acid leading to **2**. When the reaction was carried out using 5 mol % or 1 mol % of NHPI, a considerable amount of **3** was

DOI: 10.1002/adsc.200303168

Table 1. Oxidation of **1** with O_2 by NHPI under various conditions.[a]

Run	NHPI (mol %)	Additive (mol %)	Solvent	Conv. [%]	Yield [%][b]	
					2	**3**
1	10	AIBN (3)	CH_3CN	> 99	81	18
2	5	AIBN (3)	CH_3CN	> 99	67	23
3	1	AIBN (3)	CH_3CN	78	19	50
4	0	AIBN (3)	CH_3CN	19	n.d.	19
5	10		CH_3CN	No Reaction		
6[c]	10	$Co(OAc)_2$ (0.5)	CH_3CN	81	n.d.	6
7	10	NO_2 (0.5)	CH_3CN	28	n.d.	3
8	10	AIBN (3)	AcOH	5	n.d.	1
9	10	AIBN (3)	AcOEt	> 99	58	19
10	10	AIBN (3)	PhCN	> 99	57	16
11[d]	10	AIBN (3)	CH_3CN	> 99	92	1
12[e]	10	AIBN (3)	CH_3CN	93	55	37

[a] **1** (3 mmol) was allowed to react with O_2 (1 atm) in the presence of NHPI and additive in CH_3CN (5 mL) at 75 °C for 21 h, followed by the addition of 0.3 M H_2SO_4 (1 mL) at 25 °C for 2 h.

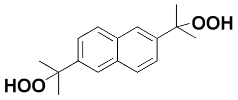
[b] Based on **1** used.

[c] **6** (20%) and **7** (10%) were obtained.

[d] Under air (20 atm).

[e] For 3 h.

formed (runs 2 and 3). Removing of NHPI from the oxidation system resulted in lower conversion (run 4). The oxidation did not take place in the absence of AIBN under these conditions (run 5). Although the oxidation of **1** proceeded by adding a very small amount of $Co(OAc)_2$ in place of AIBN, the selectivity to **2** and **3** was drastically decreased (run 6). This is because the Co ions promote the redox decomposition of the resulting hydroperoxides like **5** to 2-(2-hydroxy-2-propyl)-6-isopropylnaphthalene (**6**) (20%) and its dehydrated product (**7**), etc.



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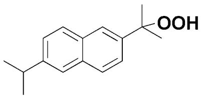

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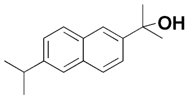

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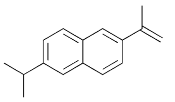

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In a previous paper, we showed that NO_2 can abstract the hydrogen atom from the hydroxyimide moiety of the NHPI to generate phthalimide *N*-oxyl (PINO) which abstracts the hydrogen atom from the isopropyl moiety of **1**.[8] Thus, the oxidation of **1** was examined by a combination of NHPI with NO_2 instead of AIBN (run 7). However, the reaction proceeded in low conversion to result in undesired products. This may be attributed to *in situ* formation of HNO_2 and/or HNO_3 from NO_2 in the course of the reaction since these acids induce the decomposition of **5** to **3**, which inhibits the radical chain reaction.

We next examined the effect of several solvents in the present oxidation of **1** (runs 8–10). In contrast to the NHPI-catalyzed aerobic oxidation of methylbenzenes to benzoic acids by NHPI where acetic acid was the best solvent, the employment of acetic acid in the present oxidation under these conditions led to a considerable decrease of the conversion of **1**, and the yields of **2** and **3** were very low. This is believed to be due to the fact that the resulting hydroperoxides **4** and **5** react with acetic acid to form **2** and **3** that serve as radical inhibitors in the aerobic oxidation of **1**. The same oxidation in AcOEt and PhCN afforded **2** and **3** in somewhat lower yields than in CH_3CN. From an industrial viewpoint, it is important to run the oxidation with air instead of pure oxygen. Thus, the oxidation of **1** under air (20 atm) was examined and found to afford **2** in high yield (92%) together with a very small amount of **3** (1.4%) (run 11). When the reaction was stopped after 3 h under these conditions, **2** and **3** were obtained in 55% and 37% yields, respectively, at 93% conversion of **1** (run 12).

In order to obtain information on the reaction course of the present reaction, the oxidation of **1** with O_2 (1 atm) under the influence of AIBN and NHPI at 75 °C was followed as a function of time (Fig. 1).

From Figure 1 it can be seen that about 93% of **1** was converted at 3 h to **4** and **5** which led to **2** and **3** upon treatment with sulfuric acid, respectively. Subsequently, **5** was slowly oxidized to **4** and the yield of **2** reached a maximum at 21 h.

An extension of this oxidation to 2,7-diisopropylnaphthalene (**8**) with O_2 (1 atm) in the presence of

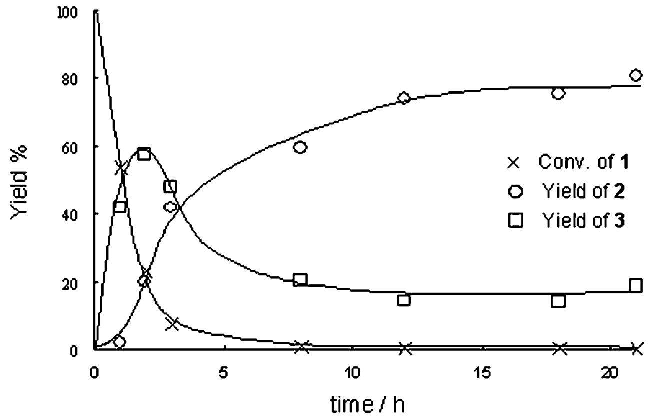
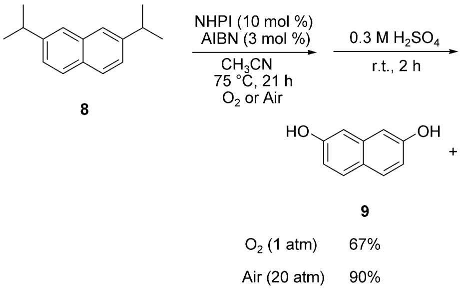


Figure 1. Time-dependence curves for the aerobic oxidation of **1**. Conditions: **1** (3 mmol) was allowed to react under O_2 (1 atm) in the presence of AIBN (3 mol %), NHPI (10 mol %) in CH_3CN (5 mL) at 75 °C, followed by the treatment with 0.3 M H_2SO_4.

NHPI (10 mol %) and AIBN (3 mol %) in CH_3CN (5 mL) at 75 °C for 21 h, followed by treatment with 0.3 M H_2SO_4 afforded 2,7-naphthalenediol (**9**) in 67% yield and 7-isopropyl-2-naphthol (**10**) (21%) [Eq. (2)].The same oxidation under pressure of air (20 atm) led to **9** in high yield (90%) along with a trace amount of **10**.



(2)

In conclusion, diisopropylnaphthalenes were found to be efficiently converted into the corresponding dihydroxynaphthalenes by the aerobic oxidation by NHPI in the presence of AIBN followed by treatment with sulfuric acid. The reduction of the amount of the catalyst employed is required for industrial application of the present method. Further investigations are underway in our laboratory.

Experimental Section

General

^{1}H and ^{13}C NMR spectra were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with TMS as the internal standard. Infrared (IR) spectra were measured as thin films on NaCl plate or KBr press disk. A GLC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-17). Mass spectra were determined at an ionizing voltage of 70 eV. All starting materials, catalysts, and initiators were purchased from commercial sources and used without further treatment. The yields of products were estimated from the peak areas based on the internal standard technique.

General Procedure for the Oxidation of Diisopropylnaphthalenes to the Naphthalenediols

An acetonitrile (5 mL) solution of the diisopropylnaphthalene (3 mmol), AIBN (3 mol %), and NHPI (10 mol %) was placed in a two-necked flask equipped with a balloon filled with O_2. The mixture was stirred at 75 °C for 21 h. The reaction mixture was treated with 0.3 M H_2SO_4 in CH_3CN (1 mL) at 25 °C for 2 h. Removal of the solvent under reduced pressure afforded a cloudy solution, which was purified by column chromatography on silica gel (*n*-hexane) to give the corresponding product. The products were characterized by ^{1}H and ^{13}C NMR, IR, and GC-MS, respectively.

Procedure for the Oxidation of Diisopropylnaphthalenes under Air (20 atm)

An acetonitrile (5 mL) solution of the diisopropylnaphthalene (3 mmol), AIBN (3 mol %), NHPI (10 mol %) was placed in a 50-mL teflon-coated autoclave, and 20 atm of air were charged. The solution was stirred at 75 °C for 21 h. The reaction mixture was treated with 0.3 M H_2SO_4 in CH_3CN (1 mL) at 25 °C for 2 h. The work-up was performed by the same method as described above. The products were identified by ^{1}H NMR, ^{13}C NMR, IR and GC-MS, respectively.

10: ^{1}H NMR : $\delta = 7.70-7.00$ (m, 6H), 4.94 (br, 1H), 3.07–2.97 (m, 1H), 1.32 (d, $J = 7.2$ Hz, 6H); ^{13}C NMR : $\delta = 153.2$, 147.0, 134.7, 129.4, 127.6, 127.5, 123.4, 122.6, 116.7, 109.2, 34.3, 24.0: HRMS (EI): calcd. for $C_{10}H_8O_2$ $[M-H]^+$: 160.0531; found: 160.0524.

Acknowledgements

This work was partially supported by a Grant-Aid for Scientific Research (KAKENHI) (S) (No. 13853008) from Japan Society for the Promotion of Science (JSPS), and DAICEL Chemical Industries, Ltd.

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