BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (5), 1683 (1975)

Base-catalyzed Oxygenation of 2,6-Di-*t*-butylphenols. A Convenient Method for Preparation of *p*-Quinols

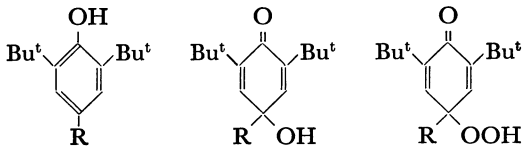
Akira NISHINAGA, Toshio ITAHARA, and Teruo MATSUURA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

(Received January 13, 1974)

Synopsis. The oxygenation of 4-alkyl-2,6-di-*t*-butylphenols in diethylamine containing sodium amide under mild conditions afforded the corresponding *p*-quinols in excellent yields.

The synthesis of *p*-quinols has been developed by the oxidation of the corresponding phenols involving Co(II)–Schiff's base complex catalyzed oxygenation[1] and thallium triperchlorate oxidation,[2] and also by the reduction of the appropriate *p*-benzoquinones with alkyllithium compounds.[3] The reduction of hydroperoxides formed from appropriate phenols by oxidation with O_2[4] or hydrogen peroxide-molybdenum complex[5] also affords *p*-quinols. No attempt has been made for a one-step synthesis of such *p*-quinols by simple oxygenation. We previously reported that the oxygenation of *t*-butylated phenols in *t*-BuOH or aprotic solvents such as DMF, DMSO, and HMPA containing *t*-BuOK leads to the exclusive formation of epoxyquinols, intramolecular decomposition products of the corresponding hydroperoxides.[6,7]



(**1**) (**2**) (**3**)

a; R=Bu^t, **b**; R=Pr^i, **c**; R=Et, **d**; R=Me

TABLE 1. THE FORMATION OF *p*-QUINOLS BY OXYGENETION OF **1**.

1	Solvent	Base	Base/1 mol/mol	Reaction time (hr)	Conversion (%)	**1** Yield (%)[a]
1a	$HNEt_2$	$NaNH_2$	5	4	100	**2a**, 86
	NEt_3	$NaNH_2$	5	6	30	90
	$HNEt_2$	*t*-BuOK	5	6	35	80
1b	$HNEt_2$	$NaNH_2$	5	6	100	**2b**, 92
1c	$HNEt_2$	$NaNH_2$	5	6	100	**2c**, 94
1d	$HNEt_2$	$NaNH_2$	5	6	100	**2d**, 95
	NEt_3	$NaNH_2$	5	6	40	90
	Me_2S	$NaNH_2$	5	6	20	90
	Me_2S	*t*-BuOK	5	6	20	90

a) Yields by isolation.

We now find that the oxygenation of 2,6-di-*t*-butylphenols in $HNEt_2$ containing $NaNH_2$ affords the corresponding *p*-quinols in excellent yields. This provides a convenient method for one-step synthesis of such *p*-quinols (**2**). The phenols (**1**) were dissolved in $HNEt_2$ containing excess $NaNH_2$ and bubbled with oxygen at room temperature. The products (**2**) could be isolated in crystalline form upon diluting the reaction mixture with ice-cooled water and were identified with authentic samples (IR and NMR). The results are summarized in the Table. Since the hydroperoxides (**3**) separately synthesized are easily reduced in $HNEt_2$ to **2**, the formation of **2** by oxygenation should proceed *via* the hydroperoxide intermediate. Replacement of the solvent with NEt_3 or of the base with *t*-BuOK reduces the reactivity (Table 1). Dimethyl sulfide is a good reducing reagent for **3** to **2** but the oxygenation of **1** in this solvent is largely inhibited (Table 1) probably due to competition of oxidation of the solvent itself.

Experimental

*Oxygenation of **1** in Diethylamine Containing Sodium Amide.* The phenols (1 mmol) were dissolved in diethyl amine (20 ml) containing sodium amide (5 mmol). Oxygen was bubbled through the solutions at room temperature for appropriate periods (see Table 1). The reaction mixtures were then poured into a large amount of ice-cooled water to give the *p*-quinols (**2**) as crystals, which were identified with authentic samples[1] (IR and NMR).

References.

1) A. Nishinaga, K. Watanabe, and T. Matsuura, *Tetrahedron Lett.*, **1974**, 1291.
2) Y. Yamada, K. Hosaka, H. Sanjoh, and M. Suzuki, *Chem. Commun.*, **1974**, 661.
3) A. Rieker, *Angew. Chem.*, **76**, 601 (1964).
4) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957); H. R. Gersmann and A. F. Bickel, *J. Chem. Soc.*, **1959**, 2711.
5) Y. Hayashi, S. Shioi, M. Togami, and T. Sakan, *Chem. Lett.*, **1973**, 651.
6) A. Nishinaga, T. Itahara, and T. Matsuura, *ibid.*, **1974**, 667.
7) A. Nishinaga, T. Itahara, and T. Matsuura, *Tetrahedron Lett.*, **1974**, 4481.