

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

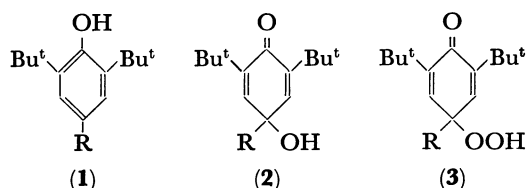
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Synopsis. The oxygenation of 4-alkyl-2,6-di-*t*-butylphenols in diethylamine containing sodium amide under mild conditions afforded the corresponding *p*-quinols in excellent yields.

The synthesis of *p*-quinols has been developed by the oxidation of the corresponding phenols involving Co(II)–Schiff's base complex catalyzed oxygenation¹⁾ and thallium triperchlorate oxidation,²⁾ and also by the reduction of the appropriate *p*-benzoquinones with alkyl-lithium compounds.³⁾ The reduction of hydroperoxides formed from appropriate phenols by oxidation with O₃⁴⁾ or hydrogen peroxide-molybdenum complex⁵⁾ 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)}

a; R = Bu^t, b; R = Prⁱ, c; R = Et, d; R = MeTABLE 1. THE FORMATION OF *p*-QUINOLS BY OXYGENATION 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	<i>t</i> -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 ₂ S	NaNH ₂	5	6	20	90
	Me ₂ S	<i>t</i> -BuOK	5	6	20	90

a) Yields by isolation.

We now find that the oxygenation of 2,6-di-*t*-butylphenols in HNEt₂ containing NaNH₂ 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 HNEt₂ containing excess NaNH₂ 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 HNEt₂ to **2**, the formation of **2** by oxygenation should proceed *via* the hydroperoxide intermediate. Replacement of the solvent with NEt₃ 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 samples¹⁾ (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.