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Regioselective Oxidation of Phenols to *o*-Quinones with Dess-Martin Periodinane(DMP)

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Abstract: Regioselective oxidation of phenols to *o*-quinones with Dess-Martin periodinane is reported.

Keywords: Phenol, *o*-quinone, Dess-Martin periodinane.

O-quinones undergo a variety of reactions, for example, these species can be reduced to the corresponding catechol, in addition, as a highly reactive 8π-electron system, *o*-quinone display two 4π components as potential sites for Diels-Alder reaction[1]. Such versatility clearly suggests the unsymmetric *o*-quinone should be of considerable synthetic use. However, to the best of our knowledge, there are few but one[2] previous examples of regioselective procedure for the direct conversion of phenol into *o*-quinone. Oxidants such as Fremy'salt[3] and benzeneseleninic anhydride[4] are indiscriminate or favor oxidation of the para position unless blocked with a substituent.

Herein, we wish to describe regioselective oxidation of phenols to *o*-quinones mediated by Dess-Martin periodinane (DMP)[5,6]. The phenol (1eq) was dissolved in dichloromethane to give about 0.4mol/L solution, solid DMP (1eq) was added to this solution to give white suspension. Foil wrapped around the outside of the reaction vessel to prevent decomposition. After stirring for 20 min,the reaction mixture turns yellow or brown in every example. The reaction mixture was allowed to stir at room temperature until no start material existed (about 12 h) by TLC, then on usually workup to gave the *o*-quinone in 50 to 87% yield. The result are summarized in **Table 1**.

It is noted that 1-naphthol and 2-naphthol were oxidized to the same product 1,2-naphthaquione, while, 1-naphanol was reported to be oxidized by Fremy'salt to give 1,4-naphthaquinone dominantly.

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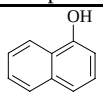
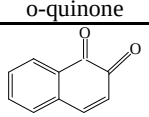
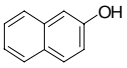
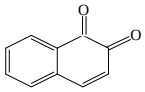
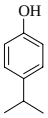
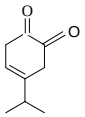
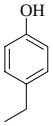
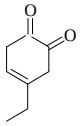
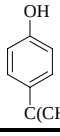
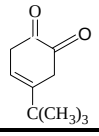
Table 1 Oxidation of phenol with DMP

Entry	phenol	o-quinone	Yield(%)
1			74
2			87
3			52
4			58
5			50

References and Notes

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7. Typical procedure: synthesis of 1, 2-naphthoquinone: To the solution of 1-naphthanol (1.45 g, 10 mmol) in dichloromethane (25 mL) was added solid DMP (3.75 g, 10 mmol). The reaction mixture was stirred at room temperature until no start material(about 12 h) by TLC. The mixture was washed successively with water (3×50 mL),brine(2×50 mL), dried(Na_2SO_4),filtered and the solvent evaporated to afford 1,2-naphthoquinone as a yellow solid. ^{1}H-NMR($CDCl_3$,400MHz) δppm: 8.14-8.11(m,1H); 7.53(td, 1H, J_1=7.52Hz,J_2=1.4Hz) 7.50-7.42(m,2H);7.39-7.37(m,1H);6.45(d,1H,J=10.4Hz).

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