

Solid state oxidation of phenols to quinones with ammonium persulfate/wet SiO₂

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A solid state method for the oxidation of phenols to quinones is described using ammonium persulfate/wet silica gel as oxidant

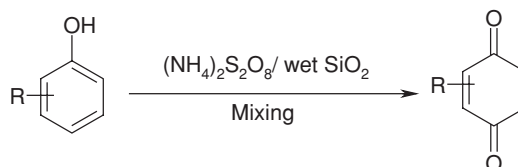
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Natural products having a benzoquinone structure show biologically important properties *e.g.* anthrocycline antibiotics¹ and the tetracyclic quinone streptiginine.² Furthermore benzoquinones are important fine chemicals in industry and are useful dienophiles in organic synthesis. Since substituted phenols are usually quite inexpensive and readily available, they serve as desirable starting materials for the synthesis of benzoquinones, formed by an important oxidation reaction; therefore it is essential to establish simple convenient methods for the oxidation of phenols to quinones. In this regard a variety of oxidising systems such as ceric ammonium nitrate (CAN),³ chromium(IV) salts,⁴ hypervalent iodine(III),⁵ *N*-bromosuccinimide (NBS),⁶ cobalt and manganese salts in the presence of oxygen⁷ and hydrogen peroxide^{8,9} have been reported. Most of the reagents involve metal ions and solvents that are not ecofriendly. There is an increasing emphasis on technological developments that deploy environmentally friendly reagents or proceed in the absence of solvent and preferably without a metal ion thereby reducing the generation of waste.

As part of our studies on the oxidation of organic compounds,¹⁰ herein we report a facile oxidation of phenols to quinones in the solid state using ammonium persulfate/wet SiO₂ as a benign oxidant.

Ammonium persulfate is relatively inexpensive, stable and easily handled oxidising agent in comparison to most oxidants usually employed for this transformation. The most common application of this reagent in the chemical industry is for bleaching.¹¹ It has also been used for the oxidation of alkenes,¹² thiols¹³ and for cleavage of semicarbazones and phenylhydrazones.¹⁴

Different types of phenols were subjected to the oxidation by simple admixing with ammonium persulfate and wet SiO₂ (60% w/w). The process in its entirety involves grinding of phenols with ammonium persulfate and silica gel using a pestle and mortar. After thoroughly grinding, each phenol has an especial colour within 1–5 min which indicates the completion of the reaction as revealed by TLC examination. In most cases, the optimum mole ration between phenol and ammonium persulfate is found to be 1:1 which delivers



quinones in efficient yields. The results of oxidation of phenols to quinones are summarised in Table 1.

In conclusion, the use of ammonium persulfate under solvent free conditions provides a remarkably simple and general oxidative protocol for the oxidation of phenols to quinones in good yields.

Experimental

General procedure for the oxidation of phenols to quinones: Ammonium persulfate (1 mmol) and wet SiO₂ (60% w/w 1 g) were mixed thoroughly. Then phenol (1 mmol) was added and the mixture ground using a pestle and mortar. After the completion of the reaction (TLC), the product was extracted with chloroform, washed with %5 NaOH solution and dried over Na₂SO₄. The solvent was evaporated and the product purified by column chromatography over silica gel (petroleum ether:ethyl acetate 4:1) and identified by its m.p., IR and ¹H NMR spectroscopic properties.

(i) *1,4-benzoquinone*: yellow solid, m.p. 114–116 °C (lit.¹⁵ 115–117 °C), IR(KBr) 3060, 1680, 1658, 1600, 1570, 1510 cm⁻¹, δ_H (CDCl₃) 6.8(s).

(ii) *2-methyl-1,4-benzoquinone*: yellow-purple solid, m.p. 69–71 °C (lit.¹⁵ 68–70 °C), IR(KBr) 3030, 1653, 1345, 1100, 930 cm⁻¹, δ_H (CDCl₃) 2.0(s), 6.6–6.7(m).

(iii) *2,6-dimethyl-1,4-benzoquinone*: yellow solid, m.p. 71–73 °C (lit.¹⁵ 72 °C), IR(KBr) 3030, 1648, 1300, 1100, 930 cm⁻¹, δ_H (CDCl₃) 1.9(s), 6.7(s).

(iv) *1,4-naphthoquinone*: yellow solid, m.p. 127 °C (lit.¹⁵ 128.5 °C), IR(KBr) 3030, 1675, 1610, 1590, 1485, 1330, 1320 cm⁻¹, δ_H (CDCl₃) 7.0(s), 7.7–8.2(m).

(v) *1,2-benzoquinone*: red-purple solid, decomposed at 60 °C (lit.¹⁵ 60–70 °C), IR(KBr) 3050, 2910, 1748, 1688, 1670, 1410, 1292 cm⁻¹.

(vi) *2-methoxy-1,4-benzoquinone*: yellow solid, m.p. 144–146 °C (lit.¹⁵ 145 °C), δ_H (CDCl₃) 6.23(s), 4.12(s), 3.36(m).

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Table 1 Oxidation of phenols to quinones using ammonium persulfate/wet SiO₂

Entry	Substrate	Product	Time /min	Yield /%
1	Phenol	1,4-Benzoquinone	3	55
2	Hydroquinone	1,4-Benzoquinone	1	92
3	2-Methylphenol	2-Methyl-1,4-benzoquinone	5	64
4	3-Methylphenol	2-Methyl-1,4-benzoquinone	5	60
5	2,6-Dimethylphenol	2,6-Dimethyl-1,4-benzoquinone	2	66
6	1-Naphthol	1,4-Naphthoquinone	4	52
7	1,4-Dihydroxynaphthalen	1,4-Naphthoquinone	3	65
8	2-Hydroxyphenol	1,2-Benzoquinone	5	76
9	3-Methoxyphenol	2-Methoxy-1,4-benzoquinone	4	61

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