

NOVEL OXIDATION OF PHENOLS TO QUINONES BY HYDROGEN PEROXIDE IN THE PRESENCE OF COBALT(II) AND MANGANESE(II) ACETATE

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Abstract

Hydrogen peroxide readily oxidizes phenols to the corresponding quinones in the presence of cobalt(II) acetate or manganese(II) acetate as catalyst.

Introduction

Quinones are a family of compounds which many of them possess bioactivity *e.g.* anthrocycline antibiotics¹ and the tetracyclic quinone streptonigrine.² 2-Methyl-1,4-naphthoquinone, vitamin K₃, constitutes an important additive in animal feed, which is used commercially in large quantities. Furthermore, alkyl substituted *p*-benzoquinones serve as useful dienophiles in Diels-Alder reactions and are versatile starting materials in synthesis of many natural products. Thus, trimethyl-*p*-benzoquinone and 2,3-dimethoxy-5-methyl-*p*-benzoquinone are especially valuable starting materials for the synthesis of vitamin E and coenzyme Q and therefore, are important for medicine.³

Since substituted phenols are usually quite inexpensive and readily available, they serve as desirable starting materials for the synthesis of benzoquinones, which constitute important oxidation reactions in organic chemistry. Therefore it is essential to establish simple, convenient, economical and environmentally friendly methods for the oxidation of phenols to quinones. In this regard a variety of oxidizing systems such as hydrogen peroxide and methyloxorhenium (VII),⁴ molecular oxygen and oxygen carrying Co(II) chelate complex,⁵ benzeneselenic acid and benzeneselenic anhydride,⁶ potassium nitrosodisulfonate⁷ and sodium nitrosodisulfonate,⁸ Br₂,⁹ HgO and Hg(OCOCF₃)₂,¹⁰ ceric ammonium nitrate (CAN),¹¹ PbO₂,¹² NO₂/O₂,¹³ BaMnO₄,¹⁴ FeCl₃,¹⁵ Ag₂O,¹⁶ NaIO₄,¹⁷ Ag₂CO₃/Celite¹⁸ and sensitized photo oxidation method¹⁹ have been reported.

Recently a heterogeneous catalytic method for the oxidation of phenols to quinones using chromium silicate and hydrogen peroxide has been reported.²⁰ Oxidation of phenols to quinones by molecular oxygen catalyzed by a mixture of the cobalt and

manganese salts of *p*-amino benzoic acid supported on silica gel is another heterogeneous catalytic method.²¹

Results and discussion

We now report that 30% aqueous hydrogen peroxide, in the presence of cobalt(II) acetate and manganese(II) acetate serves as an oxidant for a variety of phenols as shown in the generalized Scheme 1.

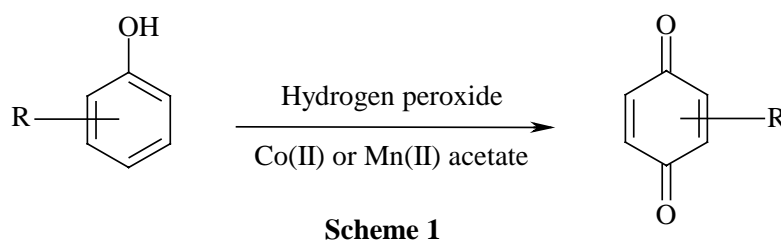


Table 1. Oxidation of phenols to the quinones using hydrogen peroxide in the presence of cobalt(II) acetate and manganese(II) acetate.^a

Substrate	Product ^b	Time (min)	Yield ^c (%)	Yield ^d (%)	Yield ^e (%)
phenol	1,4-benzoquinone	60	35	30	40
2-methylphenol	2-methy-1,4-benzoquinone	30	70	70	70
3-methylphenol	2-methy-1,4-benzoquinone	50	65	60	65
1-naphthol	1,4-naphthoquinone	120	45	40	45
1,4-dihydroxynaphthalen	1,4-naphthoquinone	60	60	50	50
2,6-dimethylphenol	2,6-dimethyl-1,4-benzoquinone	30	75	60	65
2,3-dimethylphenol	2,3-dimethyl-1,4-benzoquinone	60	55	45	50
1,4-dihydroxybenzene	1,4-benzoquinone	60	60	50	60

^a All reactions were carried out in acetic acid using 20:1 phenol-catalyst molar ratio.

^b All quinones were fully characterized by their melting points and spectral data.

^c The reactions were carried out in the presence of manganese(II) acetate at room temperature.

^d The reactions were carried out in the presence of cobalt(II) acetate at room temperature.

^e The reactions were carried out in the presence of cobalt(II) acetate at 50 °C.

Oxidations were carried out at room temperature in acetic acid using 20:1 phenol-catalyst ratio and excess hydrogen peroxide. Increasing of temperature had almost no effect to the yields of these reactions. Thus, performing of these oxidation reactions in the presence of cobalt(II) acetate at 50 °C showed only a moderate increase of the reaction yields.

Two experiments have been performed to check the efficiency of our method: a) cobalt(II) acetate alone did not oxidize phenols and b) oxidation of phenols with hydrogen peroxide without metal catalyst was very slow and the quinones were obtained in lower yields. Table 1 shows a variety of phenols, which were oxidized with hydrogen peroxide in the presence of cobalt(II) acetate or manganese(II) acetate as catalyst to the corresponding quinones.

The data provided are optimum conditions such as quantity of catalyst, time and solvent for all the reactions.

Conclusions

In conclusion hydrogen peroxide in the presence of cobalt(II) or manganese(II) acetate is a mild and effective alternative for the oxidation of phenols to the corresponding quinones in good yields.

Experimental

All melting points are uncorrected. IR spectra were recorded (KBr) on FT-IR Unicam Mattson 1000 Spectrophotometer. ^1H NMR spectra were recorded on Bruker AC-80 (80 MHz) spectrometer in CDCl_3 using TMS as internal standard and chemical shifts are indicated in δ ppm. Chemicals were purchased from commercial suppliers and were used without further purification. All products are known compounds and they were identified by their melting points, IR and ^1H NMR spectroscopic properties. All yields refer to isolated products.

Oxidation of phenols into quinones. Typical procedure. Phenol (0.94 g, 10 mmol) was dissolved in 20 mL glacial acetic acid and cobalt(II) acetate tetrahydrate (0.09 g, 0.5 mmol) was added to this solution and then aqueous hydrogen peroxide (30%, 5 mL, 49.0 mmol) was added in portions over 60 minutes at room temperature along with stirring of reaction mixture. Then 15 mL water was added and the reaction mixture was neutralized with 10% aqueous sodium. The product was extracted with CH_2Cl_2 (3×10 mL), dried over Na_2SO_4 and evaporated to dryness. After sublimation 0.32 g (30% yield) of 1,4-benzoquinone was obtained.

Oxidation of the other phenols was carried out by similar procedure. Reaction conditions and yields of isolated products are given in Table 1.

1,4-Benzoquinone, yellow solid, mp 112–114 °C (lit.²² 114–117 °C), FT-IR (KBr): 3030, 1648, 1307, 1077, 1900 cm⁻¹, ¹H NMR (CDCl₃) δ 6.7 (s).

2-Methyl-1,4-benzoquinone, yellow purple solid, mp 69–71 °C (lit.²² 68–70 °C), FT-IR (KBr): 3030, 1653, 1345, 1100, 930 cm⁻¹, ¹H NMR (CDCl₃) δ 2.0 (s), δ 6.6–6.7 (m).

2,6-Dimethyl-1,4-benzoquinone, yellow solid, mp 71–73 °C (lit.²² 72 °C), FT-IR (KBr): 3030, 1648, 1300, 1100, 930 cm⁻¹, ¹H NMR (CDCl₃) δ 1.9 (s), 6.7 (s).

2,3-Dimethyl-1,4-benzoquinone, yellow red solid, mp 55–58 °C (lit.²² 57 °C), FT-IR (KBr): 3030, 1661, 1590, 1384, 1315, 1138, 1059, 846 cm⁻¹, ¹H NMR (CDCl₃) δ 1.9 (s), 6.7 (s).

1,4-Naphthoquinone, yellow solid, mp 127–128 °C (lit.²² 128.5 °C), FT-IR (KBr): 3030, 1648, 1610, 1307, 1076, 900 cm⁻¹, ¹H NMR (CDCl₃) δ 7.0 (s), δ 7.7–8.1 (m).

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Povzetek

V prisotnosti kobaltovega(II) acetata ali magnezijevega(II) acetata kot katalizatorja, vodikov peroksid z lahkoto oksidira fenole v ustrezne kinone.