



MICROWAVE ASSISTED Fe(III) CATALYSED OXIDATION OF PHENOL BY HYDROGEN PEROXIDE SUPPORTED ON ALUMINA

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ABSTRACT

Hydrogen peroxide readily oxidized phenols to corresponding quinones in the presence of Fe(III) as a catalyst, both are supported on alumina. The reaction was carried out under microwave irradiation. The effects of Fe(III) catalyst and microwave irradiation reduces the time of reaction and the yield of product was also improved.

Keywords: Oxidation; Hydrogen peroxide; Alumina; Microwave; Phenol and quinones

INTRODUCTION

Natural product having a benzoquinone structure which a wide variety of biological activities such as cardiovascular, antitumor, antibacterial, antigerminative and antiprotozoal activity¹. Trimethyl-p-benzoquinone and 2,3-dimethoxy-5-methyl-p-benzoquinone are especially valuable as starting materials for the synthesis of vitamin E and coenzyme Q, therefore these are important for medicine². 2-methyl-1,4-naphthoquinone and vitamin K3 constitutes an important additive in animal feed, which is used commercially in large quantities, furthermore, benzoquinones are important fine chemicals in industry and are as useful dienophiles in chemical transformation and synthesis of many natural product³.

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 reaction in organic chemistry. Therefore it is essential to establish simple, convenient, economical and environmentally friendly methods for the oxidation of phenol to quinones. In this regard a variety of oxidizing systems such as hydrogen peroxide and methyloxorhenium(VII)⁴, benzeneselenic acid and benzeneselenic anhydride⁵, ceric ammonium nitrate⁶, N-bromosuccinimide (NBS)⁷, hydrogen peroxide⁸, NO₂/O₂⁹, PbO₂¹⁰, Ag₂O¹¹, NaIO₄¹², Ag₂CO₃/Celite¹³ and sensitized photo-oxidation method¹⁴ have been reported.

Recently a heterogeneous catalytic method for the oxidation of phenols to quinones using chromium silicate and hydrogen peroxide has been reported¹⁵, oxidation of phenol to quinines 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 method¹⁶. Fe(III) is a good catalyst in many oxidation reactions. Fe(III) catalysed oxidation of thiols to disulfide by urea- hydrogen peroxide adduct¹⁷, Fe(III) catalysed ozonation of phenol¹⁸, Fe(III) oxidation of β-O-4 lignin model¹⁹ and Fe (TSPc) catalysed oxidation of a non-pphenolic lignin model²⁰. So we here use Fe(III) as a catalyst.

EXPERIMENTAL

All melting points were determined by open capillary tube method and are uncorrected. IR spectra were recorded (KBr) on FT-IR unicorn maltson 1000 spectrophotometer. ¹H-NMR spectra were recorded on Bruker Ac-80 (80 MHz) spectrometer in CDCl₃ using TMS as internal standard and chemical shifts are

indicated in δ ppm. Chemicals were purchased from commercial suppliers and were used without any further purification. All products are known compounds and The progress of the reaction was monitored on precoated silica gel 60 F254 plates (Merck) using different solvent systems. Spectral data (IR and NMR spectra) confirmed the structures of the synthesized compounds.

Oxidation of phenol in to quinines

Typical procedure: Phenol (0.94 g, 10 mmol) ground with 6-7 g alumina. dil. H₂SO₄ 6-7 drop added to it mix with spatula. FeCl₃ 0.05 g mix with this mixture and add 5 ml 30% hydrogen peroxide to this mixture. After this irradiate this reaction mixture under microwave irradiation for specific time. Product will be separated by CH₂Cl₂. evaporated CH₂Cl₂ to get product.

Oxidation of other phenol was carried out by similar procedure. Reaction condition and yields of isolated product are given in table 1.

1,4-Naphthoquinone, yellow solid, mp 127 °C (lit.²² 128.5 °C), FT-IR (KBr):3030, 1650,1620, 1310, 1076, 905 cm⁻¹, ¹H-NMR (CDCl₃) δ 7.0 (s) δ 7.6-7.7 (m).

2,6-Dimethyl-1,4-benzoquinone, yellow solid, mp 72 °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 56 °C (lit.²² 57 °C), FT-IR (KBr):3030, 1660,1590, 1385, 1320, 1142, 1063, 840 cm⁻¹, ¹H-NMR (CDCl₃) δ 1.9 (s) 6.7 (s).

2-Methyl-1,4- benzoquinone, yellow purple solid, mp 69 °C (lit.²² 68-70 °C), FT-IR (KBr):3030, 1648,1348, 1100, 920 cm⁻¹, ¹H-NMR (CDCl₃) δ 2.0 (s) δ 6.5-6.6 (m)

1,4-Benzoquinone, yellow solid, mp 112-114 °C (lit.²² 114-117 °C), FT-IR (KBr):3030, 1650,1311, 1075, 1900 cm⁻¹, ¹H-NMR (CDCl₃) δ 6.7 (s).

RESULTS AND DISCUSSION

We here report the 30% aqueous hydrogen peroxide in the presence of Fe (III) supported on alumina under microwave irradiation serve as oxidants for a variety of phenol as shown in the generalized Scheme 1. Oxidation was carried out under microwave using phenol, catalyzed ratio of Fe (III), hydrogen peroxide and alumina. We compare the effect of Fe (III) and microwave on the oxidation of phenols. We saw that when reaction carried out under microwave using Fe (III) supported on alumina, reaction time get reduced and the yield of product increased. In conclusion hydrogen peroxide in the presence of Fe (III) supported on alumina under microwave irradiation, is a mild and effective alternative for the oxidation of phenol to corresponding quinines in a good yield.

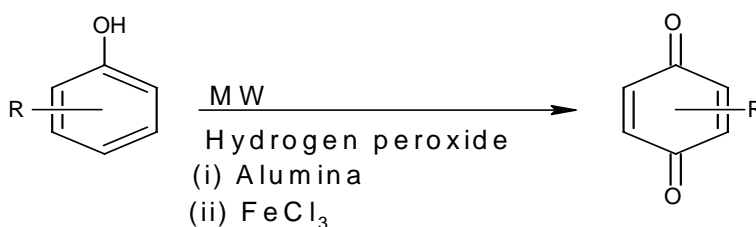
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Scheme 1.

Table-1: Oxidation of phenols to the quinones using hydrogen peroxide.

Substrate	Product	A. Time in min./ Yield%	B. Time in min./ Yield%	C. Time in min./ Yield%
Phenol	1,4-benzoquinone	60 /35	3.5 / 40	2.80 / 48
2-methylphenol	2-methyl-1,4- benzoquinone	40 /60	3.0/55	2.65 / 62
3-methylphenol	2-methyl-1,4- benzoquinone	65 /40	4.20 / 45	3.5 / 55
1-naphthol	1,4-naphthoquinone	130 /40	5.0 / 45	3.50 / 55
1,4dihydroxynaphthalen	1,4-naphthoquinone	80 /50	3.0 / 55	2.60 / 65
2,6-dimethylphenol	2,6-dimethyl-1,4-benzoquinone	35 /70	2.90/70	2.50 / 70
2,3-dimethylphenol	2,3-dimethyl-1,4-benzoquinone	50 /60	2.0 / 65	1.70 / 77
1,4-dihydroxybenzene	1,4-benzoquinone	55 /60	2.0 / 65	1.50 / 70

A. Conventionally without solid support

B. Supported on alumina under microwave irradiation.

C. Supported on alumina in the presence of Fe(III) under microwave irradiation.

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