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Sodium Percarbonate On Montmorillonite K10: An Ecofriendly And Efficient Supported Reagent For Oxidation Of Phenols To Quinones

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ABSTRACT

A solid state method for the oxidation of phenols to corresponding quinones is described using sodium percarbonate on wet montmorillonite K10 as oxidant. This method is very simple and carried out in ambient temperature, short time and solvent free condition.

KEYWORDS

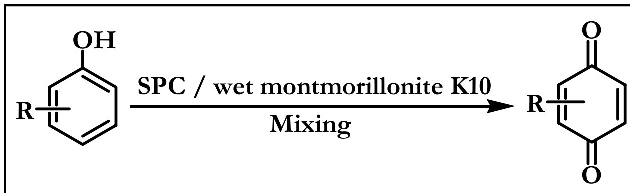
Oxidation;
Sodium percarbonate;
Phenols;
Quinones;
Montmorillonite K10.

INTRODUCTION

It is well known that many quinone derivatives possess bioactivity e.g. anthrocycline antibiotics[1] and the tetracyclic quinone streptonigrin[2]. Some quinones are also useful as intermediates in the preparation of medicines, e.g. anthracyclinones which was accomplished via a diels-alder cycloaddition using quinone rings[3]. Since substituted phenols are usually inexpensive, the oxidation of phenols constitutes a general method for the synthesis of substituted quinones. In this regard a variety of oxidizing reagents are available such as ceric ammonium nitrate[4], chromium(IV) salts[5], N-bromosuccinimide[6], cobalt and manganese salts in the presence of oxygen[7], hydrogen peroxide[8,9], potassium nitrosodisulfonate[10], and sodium nitrosodisulfonate[11]. Most of these reagents involve metal ions and solvents that are not ecofriendly. There is 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 waste generation. During the course of our studies on organic transformations[12], herein we report a facile oxidation of phenols to quinones in solid state using sodium percarbonate on wet montmorillonite K10 as oxidant.

Sodium percarbonate($Na_2CO_3 \cdot 1.5H_2O_2$=SPC) is a peroxygen compound and very inexpensive large scale industrial chemical which is extensively used in the detergent industry as a bleaching and antiseptic agent[13,14]. Thus, SPC, which can be considered as a 'dry carrier' of hydrogen peroxide, is an attractive oxidizing agent[15,16]. So it has been used for oxidation of sulfides[16], amines[16,17], organoboranes[18], as well as for the epoxidation of olefins[16] and hydrolysis of nitriles to amides[19]. A mixture of SPC and silica gel in aqueous DMF has been shown to be highly effective in the nef oxidation[20].

Different types of phenols were subjected to the oxidation by simple admixing with SPC and wet montmorillonite K10(85% w/w). The process involves grinding of phenols with SPC and wet montmorillonite K10 using a pestle and mortar. After thoroughly grinding, each phenol has especial color within 1-5 min which indicates the completion of the reaction as revealed by TLC examination.



SCHEME 1: Oxidation of phenols to quinones using sodium percarbonate on wet montmorillonite K10

RESULTS AND DISCUSSION

A solid state method for the oxidation of phenols to corresponding quinones is described using sodium percarbonate on wet montmorillonite K10 as oxidant. Sodium percarbonate is a cheap, large-scale industrial chemical that is nontoxic and relatively stable solid and is thus simple to handle on a large scale and permit accurate dosage. This method is very simple and carried out in ambient temperature, short time and solvent free condition.

Supported SPC on wet montmorillonite K10 is an excellent oxidant for phenols to quinones as shown in SCHEME 1. In most cases the optimum mole ratio between phenol and SPC is found to be 1:2.5 which delivers quinones in efficient yields.

SPC does not oxidized phenols in the absence of surface. As shown in TABLE 1 reaction efficiency and yields on montmorillonite K10 show a very good enhancement comparing with those performed on the silica gel and alumina. TABLE 2 lists a variety of phenol oxidized with supported SPC to the corresponding quinones. All yields refer to isolated products.

TABLE 1: Oxidation of phenols to quinones using SPC[a]

Entry	Substrate	Yield %		
		wet montmorillonite K10	wet silica gel	wet alumina
1	Hydroquinone	91	43	39
2	2,6-dimethylphenol	75	37	35

[a]All yields refer to isolated products

TABLE 2: Oxidation of phenols to quinones using sodium percarbonate on wet montmorillonite K10

Entry	Substrate	product	Time/min	Yield/ %[a]
1	Phenol	1,4-benzoquinone	5	55
2	Hydroquinone	1,4-benzoquinone	2	91
3	2-methylphenol	2-methyl-1,4-benzoquinone	3	68
4	3-methylphenol	2-methyl-1,4-benzoquinone	3	71
5	2,6-dimethylphenol	2,6-dimethyl-1,4-benzoquinone	3	75
6	1-naphthol	1,4-naphthoquinone	5	50
7	1,4-dihydroxy naphthalene	1,4-naphthoquinone	2	75
8	3-methoxyphenol	3-methoxy-1,4-benzoquinone	5	55

[a]All yields refer to isolated products

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EXPERIMENTAL

General procedure for the oxidation of phenols to quinines: SPC(2.5mmol) and wet montmorillonite (85% w/w 1g) were mixed thoroughly. Then phenol (1 mmol) was added and mixed using a pestle and mortar. After the completion of the reaction(TLC), the product was extracted with chloroform, washed with 5% NaOH aqueous solution and dried over Na_2SO_4. The solvent was evaporated and the product purified by short column chromatography over silica gel and identified by its m.p., IR and ^{1}HNMR spectroscopic properties.

CONCLUSION

In summary we have extended successfully the application of SPC/wet montmorillonite K10 to the oxidation of phenols to quinones. Meanwhile this method offers some advantages in term of simplicity of performance, solvent free condition, ambient temperature, superior yield and very low reaction time.

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