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Oxidative Transformation of Organic Compounds Using Bis(1,10-phenanthroline)silver(II) Peroxydisulfate as a Twin Catalyst/Oxidant

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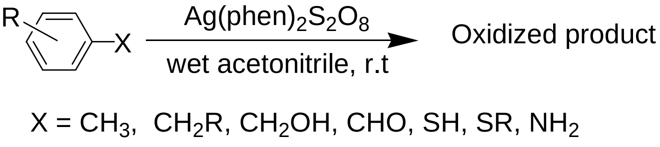
This work is dedicated to Professor Habib Firouzabadi on the occasion of his 65th birthday and also his retirement

The mild and efficient oxidation of a variety of organic functional groups with a twin catalyst/oxidant, *bis*(phenanthroline)silver(II) peroxydisulfate, [Ag(phen)$_2$]S$_2$O$_8$, is reported. This reagent shows high selectivity and the type of obtained products and the extent of oxidation are strongly dependent to the type of the functional groups and oxidant/substrate molar ratios.

Keywords: Silver(II), Peroxydisulfate, Oxidation, Electron transfer

INTRODUCTION

Peroxydisulfates have been successfully employed for selective oxidation of a wide variety of organic and inorganic oxidizable compounds [1]. It is one of the strongest oxidizing agents and is even stronger than H_2O_2 (standard redox potential in aqueous solution is estimated to be 2.01 V compared to 1.77 for H_2O_2 [2]. Oxidation reactions involving with this ion are relatively slow at ordinary temperatures, but are catalyzed by adding transition metal ions [3-14]. Silver ion is a well-known catalyst for peroxydisulfate oxidations [11-14]. Addition of Ag(II) salts has remarkable effect on the oxidation reactions using peroxydisulfate salts. Ag(II) is itself obtained from oxidation of $AgNO_3$ by strong oxidizing agents such as peroxydisulfate ion but it is unstable due to its powerful oxidizing nature in solution (standard redox potential 1.98 V) and must be stabilized by coordination with organic ligands, most notably the nitrogen-containing heterocycles [15]. To the best of our knowledge, tetrapyridinesilver(II) peroxydisulfate is the only peroxydisulfate oxidant which fulfills all requirements and has been used intelligently as an effective oxidizing agent for the oxidation of several classes of organic compounds [16-17]. It contains Ag(II) as catalyst partner, pyridine as a N-donor stabilizing ligand, and peroxydisulfate as oxidant partner. This complex slowly decomposes and liberates pyridine; and so, has a low lifetime. In addition, it needs the excess of pyridine to facilitate the oxidation transformation. In this study, we wish to report for the first time on the use of bis(1,10phenanthroline)silver(II) peroxydisulfate, [Ag(phen)$_2$]S$_2$O$_8$ as a selective and efficient oxidant for oxidation of the different functional groups in wet acetonitrile at room temperature (Scheme 1).



Scheme 1. Oxidation of different functional groups using [Ag(phen)$_2$]S$_2$O$_8$

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EXPERIMENTAL

Bis(1,10-phenanthroline)silver(II) peroxydisulfate was prepared according to the reported procedure [15]. Oxidation products were characterized by comparison with authentic samples (IR, ^{1}H NMR, TLC, and mp).

General Procedure for the oxidation of organic substrates with [Ag(phen)$_2$]S$_2$O$_8$

To a solution of a substrate (1 mmol) in 10 ml of wet acetonitrile (H_2O/acetonitrile; 1/20), [Ag(phen)$_2$]S$_2$O$_8$ (0.5-3 mmol) was added and stirred at room temperature for 0.15-5 h. The progress of the reaction was monitored by TLC (CCl_4:MeOH 5:1 or *n*-heptane:ethylacetate 4:1). The reaction was left for 30 min to precipitate all inorganic residues and then filtered. The solid was washed with acetonitrile (3×5 ml). The combined organic phases was evaporated and the crude product was purified by flash chromatography (silica gel). In the case of sulfonic acids, the oily crude products were isolated as their sodium salts on adding saturated sodium bicarbonate solution.

RESULTS AND DISCUSSION

A series of organic compounds has been oxidized using [Ag(phen)$_2$]S$_2$O$_8$ in wet acetonitrile at room temperature with high to excellent yields and in moderately short reaction times (Tables 1-2). In all cases, the known products were characterized using NMR and IR techniques, TLC/GC chromatography and comparison of their melting point with authentic samples. Benzylic, methyl and methylene groups were converted into the corresponding carbonyl compounds with this reagent (Table 1, entries 1-10). Interestingly, the conversions were very selective and depended on the oxidant/substrate molar ratios. For example, 4-substituted benzylic alcohols were converted into the corresponding aldehydes using equimolar amount of oxidant and substrate while the required oxidant/substrate for their conversions into the corresponding carboxylic acid were three times more (Table 1, entries 1-6). One of the most advantages of bis(phenanthroline)silver(II) peroxydisulfate lies in its application in the oxidation of relatively less-active benzilic groups into the corresponding aldehydes and ketones (Table 1, entries 7-10).

This reagent has also been applied for oxidation of aldehydes into their corresponding carboxylic acids. The oxidation was proceeded well in almost the same time as one pot conversion of alcohols to acids but using lower oxidant molar ratio (Table 1, entries 11-12).

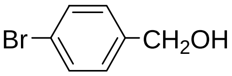
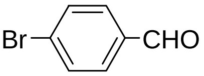
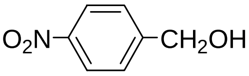
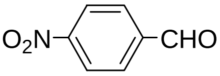
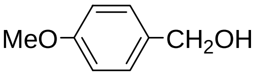
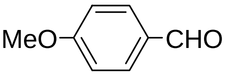
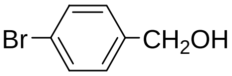
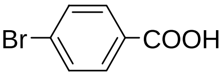
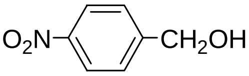
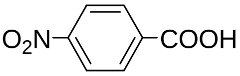
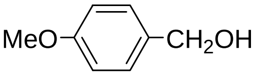
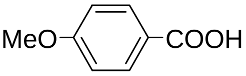
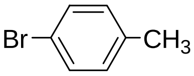
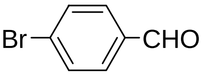
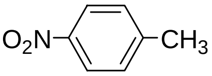
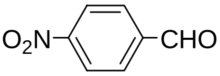
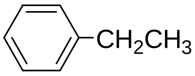
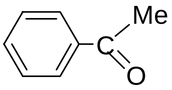
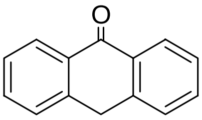
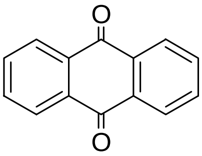
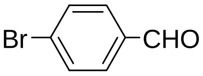
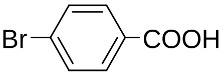
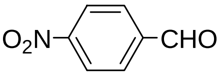
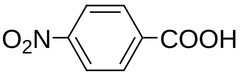
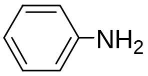
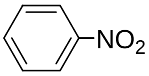
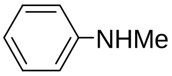
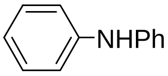
In the case of aniline (Table 1, entry 13), oxidation was proceeded well to nitrobenzene with the formation of an unidentified by-product. N,N-disubstituted anilines (Table 1, entries 14-15) were intact in the appropriate times but were converted into many unidentified products in long reaction times.

The reagent was also applied for a wide variety of sulfur compounds and similar selectivity was observed in these cases. Thiols were converted into the corresponding disulfides immediately with a lower oxidant/substrste ratio (0.5:1) (Table 2, entries 1-2) while they were oxidized into the corresponding sulfonic acids with a higher oxidant/substrate molar ratios 2:1 and reaction times, 30-45 min (Table 2, entries 3-4). Again, oxidation of a disulfide into the corresponding sulfonic acid was also performed well with almost the same reaction conditions used for direct conversion of thiols to sulfonic acids (Table 2, entry 5). The sulfides were selectively oxidized to the corresponding sulfoxide in good to excellent yields and at relatively shorter reaction times using equimolar amount of the oxidant (Table 2, entries 6-10). In comparison, the expected sulfoxide could not be obtained in significant amount using tetrabutylammonium peroxydisulfate as an oxidant [18]. In the case of methyl phenyl sulfide and benzylphenylsulfide (Table 2, entries 7, 9), the formation of sulfone as the minor product was also observed in 10% yield. Increasing the oxidant/substrate molar ratios to 2.5:1 affected this selectivity and the corresponding sulfone was produced as the major product together with a small amount of sulfoxide as minor product (Table 2, entries 11-12).

CONCLUSION

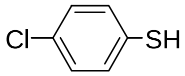
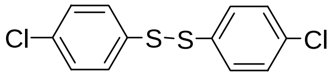
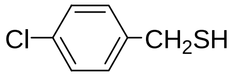
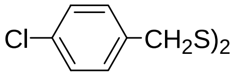
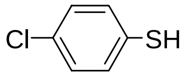
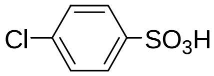
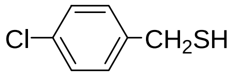
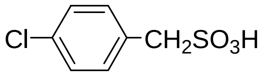
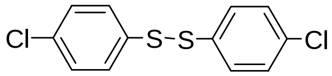
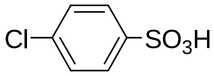
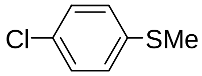
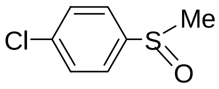
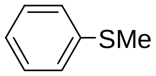
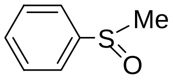
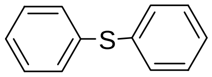
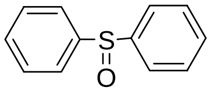
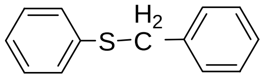
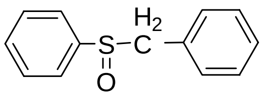
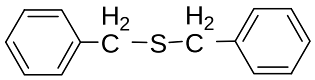
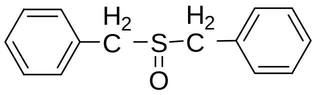
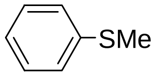
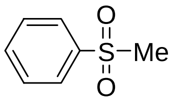
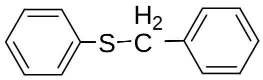
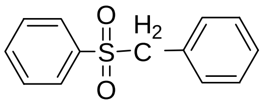
In conclusion, we have introduced a simple and efficient twin oxidnt/catalyst system for the selective oxidation of a wide variety of organic compounds using bis(1,10-phenanthroline) silver(II) peroxydisulfate .The ease of preparation and stability of the reagent, neutrality of reaction media, selectivity, and the mildness of the reaction condition are some of advantages, which should be mentioned. Excellent conversions and low reaction time may be due to mutual action of [Ag(phen)$_2$]S$_2$O$_8$ as oxidant and catalyst. The idea of application of bi-functional oxidant/catalyst compounds could

Table 1. Some representative oxidation of oxygen and nitrogen containing organic compounds using $[Ag(phen)_2]S_2O_8$

Entry	Substrate	*oxidant* / *Substrate*	Product	Time (min)	Yield [a] (%)
1		1.0		20	90
2		1.0		60	80
3		1.0		20	100
4		3.0		180	95
5		3.0		200	90
6		3.0		180	100
7		2.0		80	95
8		2.0		80	90
9		2.0		60	95
10		2.0		80	90
11		2.0		180	95
12		2.0		180	85
13		2.0		20	90
14		2.0	-	200	-
15		2.0	-	200	-

[a] Isolated yield, All products were purified and characterized by comparison with authentic samples (IR, ^{1}H NMR, TLC, and mp).

Table 2. Some representative oxidation of sulfur containing organic compounds using $[Ag(phen)_2]S_2O_8$

Entry	**Substrate**	*oxidant* / *Substrate*	**Product**	**Time (min)**	**Yield** [a] **(%)**
1		0.5		b	95
2		0.5		b	95
3		2.0		45	95
4		2.0		45	90
5		2.0		30	90
6		1.0		15	90
7 [c]		1.0		15	85(10)
8		1.0		15	90
9 [c]		1.0		20	80(10)
10		1.0		30	85
11 [d]		2.5		15	75(20)
12 [d]		2.5		20	60(20)

[a] Isolated yield, All products were purified and characterized by comparison with authentic samples

[b] Immediately

[c] The yield in parenthesis is for sulfone as the by-product

[d] The yield in parenthesis is for sulfoxide as the by-product.

be investigated in other reactions and developed for other well-known catalyst and/or oxidants.

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