

Oxidative transformation of organic compounds using bis(bipyridine)silver(II) peroxydisulfate

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Abstract

Bis(bipyridine)silver(II) peroxydisulfate selectively oxidizes a variety of organic functional groups in good to excellent yields and in moderately conditions. The type of products and the extent of oxidation are strongly dependent to the oxidant/substrate molar ratio.

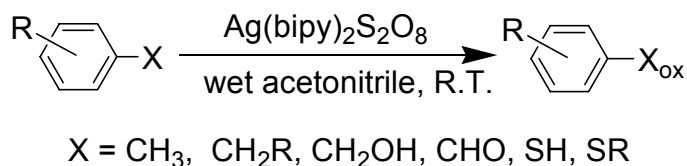
Keywords: Silver(II), peroxydisulfate, oxidation, electron transfer

Introduction

The availability of selective oxidants for selective functional group transformation of organic compounds is of obvious importance to research in organic chemistry. Peroxydisulfate in several cases fulfills most requirements.¹ The peroxydisulfate ion, $S_2O_8^{2-}$, is one of the strongest oxidizing agents and is even stronger than H_2O_2 . The standard redox potential is estimated to be 2.01 V (1.77 for H_2O_2) in aqueous solution.² $S_2O_8^{2-}$ oxidation frequently proceeds by an initial *O,O*- bond breakage to give, the radical anion SO_4^- , which appears to be a very effective electron transfer oxidizing agent.¹

Many peroxydisulfate oxidations have been studied kinetically. Reactions involving this ion are relatively slow at ordinary temperatures, but are catalyzed by adding transition metal ions.³⁻¹⁴ Silver ions are well-known catalysts 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 by strong oxidizing agents such as peroxydisulfate ion but is rather 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 compounds containing both Ag(II) and peroxydisulfate which has been recognized as an effective oxidizing agent for the oxidation of several classes of organic compounds.^{16,17} This complex is slowly decomposed

and liberates pyridine; so, has a low lifetime. In addition, it needs to excess pyridine to facilitate the oxidation transformation. In this study, we wish to report the first and wide application of the more stable bis(bipyridine)silver(II) peroxydisulfate, $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$ in oxidation of different functional groups (Scheme 1).



Scheme 1

Results and Discussion

Oxidation of a series of organic compounds were performed using $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$ in wet acetonitrile at room temperature (Scheme 1, Tables 1-2). In all cases, the known product was characterized using NMR and IR spectroscopies and TLC/GC chromatography and comparison of its melting point with authentic sample. Oxidation of benzylic methyl and methylene groups proceeded well 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 benzyl alcohols were converted to the corresponding aldehydes and to acids using oxidant/substrate 1 to 3 molar ratios, respectively (Table 1, entries 1-6). One of the most advantages of bis(bipyridine)silver(II) peroxydisulfate lies in its application in the oxidation of relatively less-active benzylic protons to the corresponding aldehydes and ketones (Table 1, entries 7-10). This one pot oxidation negates the use of commonly corrosive oxidants used for this purpose.

Oxidation of aldehydes to the corresponding acids also 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).

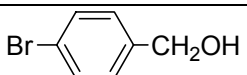
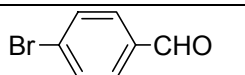
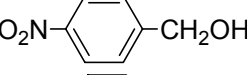
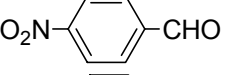
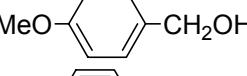
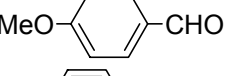
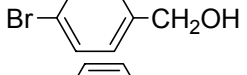
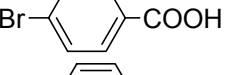
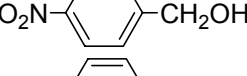
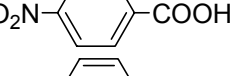
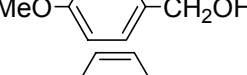
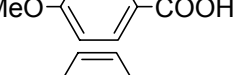
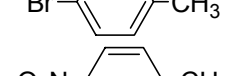
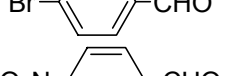
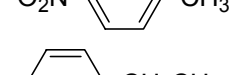
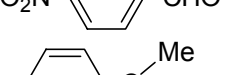
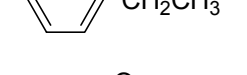
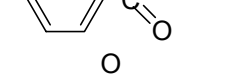
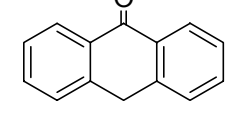
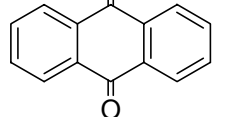
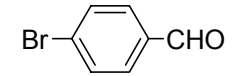
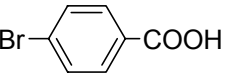
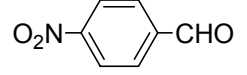
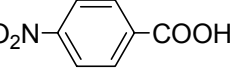
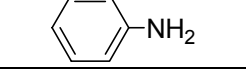
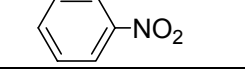
In the case of aniline (Table 1, entry 13), oxidation was proceeded well to nitrobenzene with the formation of an unidentified by-product.

Similar selectivities were observed in sulfur compounds. Thiols were converted to the corresponding disulfides immediately with 0.5 mmol of the oxidant (Table 2, entries 1-2) while were oxidized to the corresponding sulfonic acids with higher oxidant molar ratios and reaction time (Table 2, entries 3-4). Again, oxidation of disulfide to the corresponding sulfonic acid was proceeded well with almost same condition as the one pot conversion of thiols to sulfonic acids (Table 2, entry 5).

Sulfides were converted selectively to sulfoxide in good to excellent yields and at relatively shorter reaction times (Table 2, entries 6-8). In comparison, the expected sulfoxide could not be obtained in significant amount using tetrabutylammonium peroxydisulfate as an oxidant.¹⁸ In the


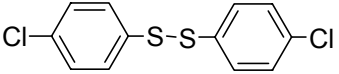
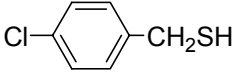
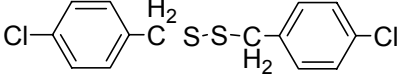
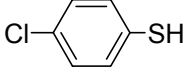
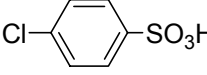
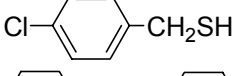
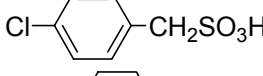
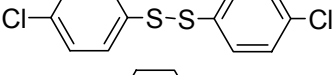
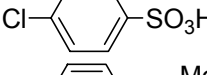
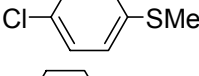
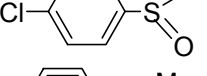
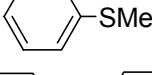
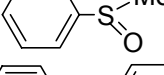
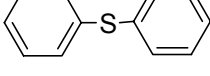
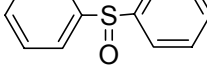
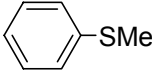
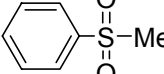
case of methyl phenyl sulfides, formation of sulfone as the minor product was also observed in 10% yield. Increasing the oxidant/substrate molar ratios affected this selectivity and sulfone was produced as the major product in addition of a small amount of sulfoxide as minor product (Table 2, entry 9). These results are very important because a crucial point to the successful oxidation is to avoid over-oxidation to sulfone.

Table 1. Some representative oxidation of oxygen and nitrogen containing organic compounds using $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$

Entry	Substrate	Oxidant Substrate	Product	Time (h)	Yield ^a (%)
1		1.0		0.5	90
2		1.0		1.5	75
3		1.0		0.5	95
4		3.0		4.0	95
5		3.0		5.0	85
6		3.0		4.0	100
7		2.0		2.0	95
8		2.0		2.0	85
9		2.0		1.5	95
10		2.0		2.0	80
11		2.0		4.0	95
12		2.0		4.0	75
13		2.0		0.5	85

^aIsolated yield. All products were purified and characterized by comparison with authentic samples (IR, ¹H NMR, TLC, and mp).

Table 2. Some representative oxidation of sulfur containing organic compounds using $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$

Entry	Substrate	Oxidant Substrate	Product	Time (h)	Yield ^a (%)
1		0.5		0.15	90
2		0.5		0.15	90
3		2.0		1.5	95
4		2.0		1.5	90
5		2.0		1.0	90
6		1.0		0.5	90
7 ^b		1.0		0.5	80(15)
8		1.0		0.5	82
9 ^c		2.5		0.5	85(10)

^aIsolated yield. All products were purified and characterized by comparison with authentic samples (IR, ¹H NMR, TLC, and mp). ^bThe yield in parenthesis is for sulfone as byproduct. ^cThe yield in parenthesis is for sulfoxide as byproduct.

Conclusions

A series of organic functional groups can be selectively oxidized using bis(bipyridine)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 $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$ as oxidant and catalyst.

Experimental Section

General Procedure. All yields refer to the pure isolated products which were characterized by comparison with authentic samples (IR, ^1H NMR, TLC, and mp).

Preparation of $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$

Bis(bipyridine)silver(II) peroxydisulfate was prepared according to the reported procedure.¹⁵ To a methanol solution of silver nitrate (0.51 g, 3 mmol), 2,2'-bipyridine (1.1 g, 7 mmol) was added and the bright yellow solution was allowed to stir at room temperature for 0.5 h. The solvent was removed and the yellow crystalline product ($[\text{Ag}(\text{bipy})_2]\text{NO}_3$) was poured into an cooled aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ (0.95 g, 3.5 mmol). After the solution has been left standing for 0.5 h, a brown crystalline compound was formed. The solution was filtered and the brown crystals was washed with cooled water and dried *in vacuo*. Yield 4.64 (76%). The product was characterized as $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$ based CHN elemental analysis, magnetic susceptibility, and UV-Vis spectroscopy. Anal. Calc. for $\text{AgC}_{20}\text{H}_{16}\text{N}_4\text{O}_8\text{S}_2$: C, 39.23, H, 2.63, N, 9.15, Found: C, 39.44, H, 2.48, N, 9.07. μ_{eff} (BM, 298 K), 1.84. λ_{max} (nm)(ϵ , $\text{l mol}^{-1}\text{cm}^{-1}$), 445 (1950).

General Procedure for the oxidation of organic substrates with $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$

To a solution of a substrate (1 mmol) in 10 ml wet acetonitrile, $[\text{Ag}(\text{bipy})_2]\text{S}_2\text{O}_8$ (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 or n-heptane:ethylacetate). The reaction was left for 30 min to settle all inorganic residues and filtered. The solid was washed with acetonitrile (3 \times 5 ml). The combined organic phases were 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.

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