*Synthetic Communications*®, 40: 725–731, 2010
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903013705

# REGENERATION OF AROMATIC CARBONYL COMPOUNDS FROM THE CORRESPONDING OXIMES USING TETRAPYRIDINE SILVER(II) PEROXYDISULFATE IN ACETONITRILE AND AQUEOUS MEDIA

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***The results of the recovery of both aldehyde and ketone carbonyl functionalities from the oxime derivatives in aromatic carbonyl compounds using tetrapyridine silver(II) peroxydisulfate [$Ag(py)_4S_2O_8$] as a stable, mild, and efficient oxidizing agent is reported. Yields in excess of 85% were achieved at room temperature in both acetonitrile and aqueous media, making the method versatile and suitable for a wide range of aromatic carbonyl oximes.***

***Keywords***: Acetonitrile; carbonyl; oxime; peroxydisulfate ion; water

## INTRODUCTION

The protection of functional groups, including aldehydes and ketones, is often necessary during total organic synthesis.[1] For aldehydes and ketones, oximes have been useful derivatives as protecting groups because they are stable under a wide range of reaction conditions. Additionally, oximes are important mediators for the purification and characterization of aldehydes and ketones.[2] Oximes may also be used fruitfully as intermediates for the synthesis of amines[3] and nitriles.[4]

Recently, a number of methods for the blocking and recovery of the carbonyl functionalities using the oxime derivative have been reviewed,[5] and they include (a) hydrolysis under the acidic[6] or neutral[7] reaction conditions, (b) oxidation using chromium(VI),[8] manganese(VII), (IV), (III),[9] thallium(III),[10] cerium(IV),[11] and lead(IV),[12] (c) halogenation[13] and halogenated compounds,[14] (d) reduction using $LiAlH_4$,[15] $Na_2S_2O_4$,[16] $Fe(CO)_5$,[17] $TiCl_4/NaI$[18] and $VCl_2$,[19] (e) enzymatic methods,[20] and (f) microwave irradiation.[21] A number of these methods require drastic reaction conditions or the use of toxic and expensive compounds, making them undesirable.

Received December 9, 2008.

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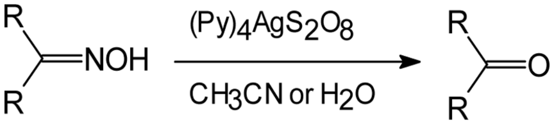
An alternate method for the regeneration of the protected carbonyl functionality from the oxime derivative is oxidation with the peroxydisulfate ion, $S_2O_8^{-2}$. The peroxodisulfate ion is a strong oxidizing agent with a standard redox potential of 2.01 V in aqueous solution.[22] The reactions of organic compounds using peroxydisulfate derivatives have been reported using tetrabutyl ammonium peroxydisulfate,[23] bis(1-benzyl)-4-aza-1-azoniabicyclo [2.2.2] octane peroxodisulfate,[24] benzyl triphenyl phosphonium peroxodisulfate,[25] polymer-supported-peroxydisalfate,[26] Amberlyst-supported peroxodisulfate,[27] and *n*-butyl phenyl phosphonium peroxodisulfate.[28] However, little attention has been paid to the oxidative cleavage of oximes by peroxodisulfates and, in particular, to the conversion of oxime derivatives to their corresponding carbonyl compounds.[23–28] This article reports on the oxidation of a variety of aromatic oximes using tetrapyridine silver(II) peroxydisulfate,[29] producing the corresponding carbonyl compounds in good yield and using mild reaction conditions, because the reactions were carried out at room temperature in both acetonitrile and aqueous media (Scheme 1). The oxidizing agent, tetrapyridine silver(II) peroxydisulfate, was selected because it is easily prepared in good yield (95%) from an aqueous solution of silver nitrate, pyridine, and potassium peroxodisulfate.

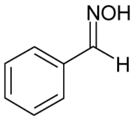
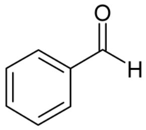
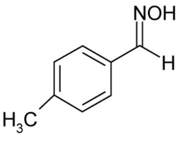
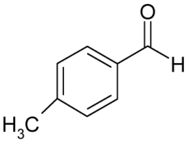
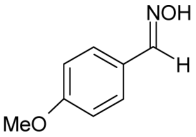
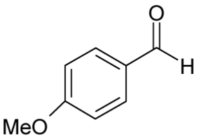
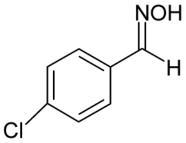
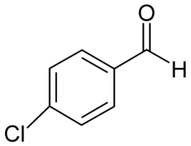
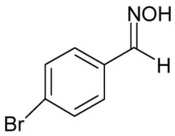
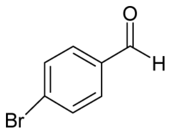
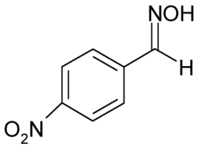
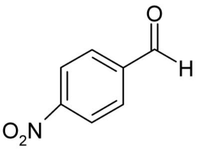
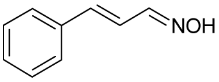
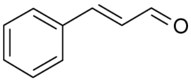
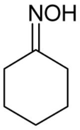
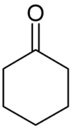
The yields and the times required for the reaction are listed in Table 1 for the oxidation of a range of aromatic oximes containing both electron-releasing and electron-withdrawing groups. In each case, the reaction regenerated the carbonyl derivative in good yield (85–90%), although the yield of product was found to depend on the nature of the substrate and reaction medium. For the aldehyde oximes examined, the reagent was found to be more reactive toward those containing the electron-releasing groups (entries 2 and 3). To achieve similar yields (85–90%) for oximes containing strong electron-withdrawing groups (entry 6), a longer reaction time was required (90–180 min). To assess the efficiency of the reagent for the regeneration of aromatic ketone-oximes, a series of reactions (entries 9 and 10) was carried out at room temperature, producing similarly good yields (85–95%) and further demonstrating the efficiency of this reagent. The reaction was carried out in both acetonitrile and aqueous media for each of the carbonyl–oximes systems. Good yields were achieved (>85%) in both media, although acetonitrile required longer reaction times to achieve these yields.

In summary, tetrapyridine silver(II) peroxydisulfate has been demonstrated to be an efficient reagent for the regeneration of carbonyl functionalities in aromatic compounds in yields of 80–95% from their corresponding oximes in both acetonitrile and aqueous media. Additionally, the reagent is cost-effective, readily available, and simple to prepare. The good yields of products from the range of oximes investigated in both aqueous and polar organic media with the further advantage of mild reaction conditions suggest that this novel method for the recovery of carbonyl functionalities from oximes has general applicability.



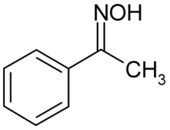
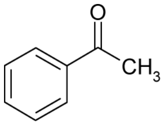
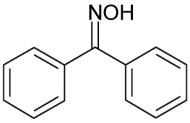
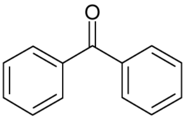
**Scheme 1.** Conversion of oximes to carbonyls.

**Table 1.** Deoximation by tetrapyridine silver(II) peroxodisulfate

| | | | $H_2O$ | | $CH_3CN$ | |
|---|---|---|---|---|---|---|
| Entry | Substrate | Product | Time (min) | Yield[a] (%) | Time (min) | Yield[a] (%) |
| 1 |  |  | 30 | 90 | 60 | 95 |
| 2 |  |  | 30 | 85 | 60 | 93 |
| 3 |  |  | 30 | 88 | 50 | 90 |
| 4 |  |  | 40 | 85 | 100 | 88 |
| 5 |  |  | 40 | 90 | 120 | 85 |
| 6 |  |  | 90 | 80 | 180 | 85 |
| 7 |  |  | 30 | 90 | 60 | 90 |
| 8 |  |  | 40 | 85 | 20 | 85 |

(*Continued*)

**Table 1.** Continued

| | | | $H_2O$ | | $CH_3CN$ | |
|---|---|---|---|---|---|---|
| Entry | Substrate | Product | Time (min) | Yield[a] (%) | Time (min) | Yield[a] (%) |
| 9 |  |  | 30 | 90 | 15 | 95 |
| 10 |  |  | 30 | 90 | 15 | 95 |

[a] Yields refer to the isolated products and 2,4-dinitrophenyl-hydrazine derivatives. Structures were confirmed by IR, $^{1}H$ NMR, $^{13}C$ NMR, and mp/bp.

## EXPERIMENTAL

Tetrapyridine silver(II) peroxodisulfate was prepared according to a reported method.[29] All the other reagents were purchased from Aldrich and used as supplied. The products were characterized by IR and $^{1}H$ NMR. The yields refer to the isolated regenerated carbonyl products or to the corresponding 2,4-dinitrophenyl-hydrazine derivatives.

### General Procedure

Tetrapyridine silver(II) peroxodisulfate (3 mmol) was added to a solution of oxime (1 mmol) in acetonitrile (8 ml) or water (8 ml). The mixture was stirred at room temperature. The progress of the reaction was followed by thin-layer chromatography. When the reaction was complete, silica gel (6 g) was added, and the solvent was evaporated under the reduced pressure. The resulting powder was added to the top of a short silica-gel column and purified using *n*-hexane–EtOAc in a 5:1 ratio as the eluent. Recovery of the pure carbonyl compounds was then achieved by evaporation of the solvent under the reduced pressure.

## ACKNOWLEDGMENT

The investigation has enjoyed the support of the Payam Noor University of Fariman and Mashhad.

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