Cleavage of Oximes, Semicarbazones, and Phenylhydrazones with Supported Potassium Permanganate

Ahmad Shaabani,*a Soheila Naderi,a Abbas Rahmati,a Zahra Badri,a Maria Darvishi,a Donald G. Leeb

a Department of Chemistry, Shahid Beheshti University, P.O. Box 19839-4716, Tehran, Iran
b Department of Chemistry and Biochemistry, University of Regina, SK S4S 0A2, Canada
Fax +98(21)2403041; E-mail: a-shaabani@cc.sbu.ac.ir
Received 25 May 2005

Abstract: Potassium permanganate supported on manganese(II) sulfate or activated manganese dioxide can be used effectively for the oxidative cleavage of oximes and semicarbazones under solvent-free conditions and for the cleavage of phenylhydrazones in dichloromethane. The residue that remains after extraction of the organic products, primarily manganese oxides, can be recycled, making the process, in theory, infinitely sustainable.

Key words: oximes, semicarbazones, phenylhydrazones, potassium permanganate

Imine derivatives of carbonyl compounds, such as oximes, semicarbazones, and phenylhydrazones, which are used extensively for the purification and characterization of carbonyl compounds, may be prepared as illustrated in Scheme 1.

Scheme 1

Because of their hydrolytic stability, oximes are also used as carbonyl protectors from which the parent carbonyl compounds must be regenerated at the completion of a synthetic procedure. Regeneration of the carbonyl compound requires the use of mild reagents and reaction conditions that will cleave the C=N bond without modification to the rest of the molecule.

Furthermore, since oximes can also be prepared from non-carbonyl compounds, the generation of carbonyl compounds from them provides an alternative method for the preparation of aldehydes and ketones.

Over the last two decades, the use of solid supports in synthetic chemistry has become popular and in recent years the use of supported reagents under solvent-free conditions has opened up new and surprisingly useful approaches to chemistry. Among oxidants, supported potassium permanganate has proven to be a reagent whose reactions are easily adapted to solvent-free conditions.

Recently, several reports of the oxidative cleavage of oximes, semicarbazones, or phenylhydrazones with potassium permanganate supported on alumina, silica gel, zeolites, and montmorillonite K10 have appeared. However, in spite of the high potential utility of potassium permanganate adsorbed to these solid supports, the reactions are not completely optimized because the coproduct of the oxidation, manganese dioxide, cannot be easily separated from these solid supports when the reaction has been completed. The reaction residue must, therefore, be consigned to a landfill site. This prevents the recycling of the manganese dioxide, as shown in Scheme 2, and diminishes the possibility of developing a sustainable process. Therefore, the discovery of new conditions for the oxidative degradation of organic compounds with potassium permanganate that result in the deposition of manganese dioxide in a recyclable form is a prime objective of our laboratories.

Scheme 2

In previous papers we have shown that a recyclable byproduct can be obtained if activated manganese dioxide is used as a solid support for potassium permanganate. In this paper, we wish to report additional progress on this procedure. The results are of potential importance from an environmental perspective because the production of recyclable byproducts is an essential requirement for a sustainable process.

Herein, we describe procedures for the cleavage of oximes and semicarbazones with supported potassium permanganate under solvent-free conditions, and the cleavage of phenylhydrazones in dichloromethane solutions. When either manganese(II) sulfate or activated manganese dioxide is used as a support to the oxidant (Scheme 3), the organic products are obtained in good yields and the inorganic products are recyclable.

The results obtained from five variations of an optimized procedure have been summarized in Table 1.
The yields from the reaction using finely powdered, but unsupported, potassium permanganate are compared with those obtained when activated manganese dioxide or manganese(II) sulfate are added to the potassium permanganate (in each case, 1.00 g of either MgSO4·H2O or MnO2 was added to 1.00 g of KMnO4). Experimentation also revealed that addition of a small amount of water to the oxidant often improved yields and shortened reaction times, as indicated by the data in Table 1.

From consideration of these results (Table 1) and those previously reported,16 it is apparent that finely powdered potassium permanganate is not a satisfactory general purpose oxidant for use under solvent-free conditions or in dichloromethane. However, addition of either activated manganese dioxide or manganese(II) sulfate markedly increases the yields, especially if some moisture is present. Although the difference is marginal for some reactions, generally, the use of activated manganese dioxide gives better yields.

It was necessary to carry out the oxidative cleavage of phenylhydrazones in dichloromethane because the reactions under solvent-free conditions were so vigorous that they often burst into flame.

It has been known for many years that manganese(II) ions act as catalysts for the oxidation of certain organic compounds with potassium permanganate in aqueous solutions.16,17 Therefore, it is not surprising to observe that addition of manganese(II) ions aids the oxidation of the organic compounds described here. At this time, any suggestion of the role manganese(II) plays would be highly speculative; however, it is possible that the initial interaction between potassium permanganate and manganese(II) would be an electron transfer that results in the formation of manganese(III) ions, which could act as a catalyst for these reactions.18

It is also known that manganese dioxide supported on silica gel can be used to cleave oximes.19 Hence, it is not surprising that activated manganese dioxide is a good solid support for solvent-free potassium permanganate oxidation.

Potassium permanganate supported on manganese(II) sulfate or activated manganese dioxide can be used effectively for the oxidative cleavage of oximes and semicarbazones under solvent-free conditions and for the cleavage of phenylhydrazones in dichloromethane. Addition of a small amount of water usually results in higher yields and shorter reaction times.

Removal of the organic products by extraction leaves a residue that consists primarily of manganese oxides containing small amounts of potassium permanganate. Since industrial processes for recycling and reoxidizing manganese dioxide to permanganate are well established, the reactions are, in theory, infinitely sustainable.13 The reactions, therefore, represent progress in the search for methods that can be applied to make chemistry more environmentally friendly.

Oxidation of Oximes and Semicarbazones; General Procedure

The five oxidants were prepared and used under identical conditions. The first oxidant was prepared by grinding KMnO4 (1.00 g), using a pestle and mortar, until a fine powder was obtained. A second oxidant was prepared in exactly the same way with the exception that MnSO4·H2O (1.00 g) was added to the KMnO4 (1.00 g). For the third oxidant, activated MnO2 (1.00 g) was added to finely ground KMnO4 (1.00 g). The fourth and fifth oxidants were prepared in the same way as the second and third oxidants, but with the addition of a small amount of H2O (0.3 mg).

These oxidants were placed in five separate round-bottom flasks and to each flask was added the oxime or semicarbazone (1.0 mmol). The reactants were stirred continuously at r.t. using a magnetically controlled stirring bar; TLC was used to monitor the progress of the reactions until the oxime or semicarbazone had completely reacted or until a reasonable amount of time had elapsed. Then, CH2Cl2 (15 mL) was added to each flask and the mixtures were filtered through a sintered glass funnel. The residues were washed with additional CH2Cl2 (2 × 10 mL) and the solvent collected from each reaction was combined and evaporated on a flash evaporator. The yields were determined by GC analysis or by weight after preparation of 2,4-dinitrophenylhydrazone derivatives. All products are known compounds and were characterized from their well-defined 1H NMR spectra.

Oxidation of Phenylhydrazones; General Procedure

The oxidations were completed similarly to those described above using the first three oxidants, except that CH2Cl2 (15 mL) was added to the oxidant before using it in the reaction with the phenylhydrazone.

Acknowledgment

Financial assistance from the Research Council of Shahid Beheshti University of Iran is gratefully acknowledged.

References

## Table 1  Oxidative Cleavage of Oximes, Semicarbazones and Phenylhydrazones to the Corresponding Aldehydes and Ketones

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yield (%) (Time)</th>
<th>KMnO₄ (unsupported)</th>
<th>KMnO₄/MnSO₄·H₂O (moisture added)</th>
<th>KMnO₄/Mn₂O₃ (moisture added)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde oxime</td>
<td>45 (90 min)</td>
<td>72 (75 min)</td>
<td>79 (45 min)</td>
<td>84 (40 min)</td>
</tr>
<tr>
<td>p-Methylbenzaldehyde oxime</td>
<td>41 (90 min)</td>
<td>71 (70 min)</td>
<td>80 (44 min)</td>
<td>84 (30 min)</td>
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<tr>
<td>p-Methoxybenzaldehyde oxime</td>
<td>46 (90 min)</td>
<td>65 (65 min)</td>
<td>70 (40 min)</td>
<td>85 (30 min)</td>
</tr>
<tr>
<td>p-Nitrobenzaldehyde oxime</td>
<td>41 (110 min)</td>
<td>49 (100 min)</td>
<td>55 (75 min)</td>
<td>82 (45 min)</td>
</tr>
<tr>
<td>Acetophenone oxime</td>
<td>49 (120 min)</td>
<td>75 (90 min)</td>
<td>78 (50 min)</td>
<td>81 (30 min)</td>
</tr>
<tr>
<td>Ethyl phenyl ketone oxime</td>
<td>48 (90 min)</td>
<td>71 (85 min)</td>
<td>78 (50 min)</td>
<td>82 (30 min)</td>
</tr>
<tr>
<td>p-Methylacetophenone oxime</td>
<td>45 (150 min)</td>
<td>73 (100 min)</td>
<td>80 (75 min)</td>
<td>94 (45 min)</td>
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<td>p-Chloroacetophenone oxime</td>
<td>43 (180 min)</td>
<td>70 (120 min)</td>
<td>82 (90 min)</td>
<td>80 (60 min)</td>
</tr>
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<td>83 (110 min)</td>
<td>90 (90 min)</td>
<td>90 (75 min)</td>
</tr>
<tr>
<td>p-Nitroacetophenone oxime</td>
<td>12 (360 min)</td>
<td>81 (150 min)</td>
<td>85 (90 min)</td>
<td>93 (60 min)</td>
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<td>&lt;5 (50 min)</td>
<td>77 (50 min)</td>
<td>73 (50 min)</td>
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<tr>
<td>p-Methylacetophenone semicarbazone</td>
<td>10 (270 min)</td>
<td>68 (35 min)</td>
<td>77 (60 min)</td>
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<tr>
<td>p-Chloroacetophenone semicarbazone</td>
<td>25 (210 min)</td>
<td>76 (120 min)</td>
<td>88 (210 min)</td>
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<tr>
<td>Acetophenone phenylhydrazone</td>
<td>50 (9 h)</td>
<td>65 (9 h)</td>
<td>70 (9 h)</td>
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<tr>
<td>p-Methylacetophenone phenylhydrazone</td>
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<td>62 (8 h)</td>
<td>68 (8 h)</td>
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<tr>
<td>p-Chloroacetophenone phenylhydrazone</td>
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<td>58 (10 h)</td>
<td>68 (10 h)</td>
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<tr>
<td>Benzophenone phenylhydrazone</td>
<td>40 (10 h)</td>
<td>68 (10 h)</td>
<td>58 (10 h)</td>
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