MICROWAVE ASSISTED REGENERATION OF CARBONYL COMPOUNDS FROM 2,4-DINITROPHENYLHYDRAZONES WITH POTASSIUM FERRATE(VI) SUPPORTED ON MONTMORILLONITE K-10

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Abstract

2,4-Dinitrophenylhydrazones were efficiently and rapidly converted to their corresponding carbonyl compounds with supported potassium ferrate(VI) under microwave irradiation.

Keywords: regeneration, potassium ferrate, 2,4-dinitrophenylhydrazones

Introduction

2,4-Dinitrophenylhydrazones and other derivatives of carbonyl compounds are important intermediates in organic synthesis because of their use in the characterization and purification1-4 of carbonyl compounds and play an important role in the protection of these compounds.5-9 Thus, the regeneration of carbonyl compounds from the corresponding 2,4-dinitrophenylhydrazones under mild conditions is an attractive process in organic synthesis. Several such procedures for regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones have been reported, for example: with Dowex-50 cation exchange resin,7 clayfen,8 potassium boromate,9 N,N–dibromo-1,2-ethanediylbis(p-toluene sulphonamide) under microwave irradiation,10 etc. Although some of these reactions are carried out under mild conditions, some of them have a drawback of using expensive oxidant, strong oxidative conditions, need of freshly prepared reagents, tedious work-up, or they are often hazardous.3,4,11 Thus, there is a continuous need either to improve the existing protocols or to introduce new reagents to permit faster reaction, milder conditions, easier work-up and eco-friendly procedures.

Prompted by stringent environment protection laws in recent years, there is an increasing interest in the use and design of eco-friendly reagents, solid and solvent free reactions.12,13 Application of microwave irradiation technique is currently under
intensive examination.\textsuperscript{10,14} Since organic solvents are expensive and hazardous, dry media technique has attracted much attention recently because open vessels can be used.\textsuperscript{15}

Potassium ferrate(VI) (K$_2$FeO$_4$), a hexavalent iron is a nontoxic compound\textsuperscript{16} has been introduced recently by Delaude et al. as a novel oxidizing reagent.\textsuperscript{17} However, there are a few examples for the use of potassium ferrate(VI) on mineral support for oxidation of organic substrates,\textsuperscript{17,18} for regeneration of carbonyl compounds from acetals, ketals and hydrazones,\textsuperscript{19,20} for oxidative deprotection of trimethylsilyl ethers and tetrahydropyranyl ethers.\textsuperscript{21,22}

We have previously reported a convenient method for the regeneration of carbonyl compounds by oxidative cleavage of carbon-nitrogen double bond with molecular oxygen in presence of copper(I) chloride/kieselgur.\textsuperscript{23} Herein, we wish to report that a mixture of potassium ferrate(VI) and potassium sulfate supported on montmorillonite K-10 can regenerate carbonyl compounds from 2,4-dinitrophenylhydrazones under microwave irradiation in high to excellent yields.

\textbf{Results and Discussion}

Potassium ferrate(VI) can be prepared easily by oxidizing ferric nitrate with sodium hypochlorite and subsequent treatment with potassium hydroxide.\textsuperscript{24} The synthesis of this reagent has been improved, and it has been claimed to be a low polluting oxidizer.\textsuperscript{17}

Our approach to a clean and efficient regeneration of carbonyl compounds from 2,4-nitrophenylhydrazones is to make use of the mixture of potassium ferrate(VI) and potassium sulfate supported on montmorillonite K-10. When the supported reagent was mixed with benzaldehyde 2,4-dinitrophenylhydrazone, and the mixture placed into a microwave oven, the reaction was completed in 2 min in 98\% yield. The work-up procedure involves addition of diethyl ether, mere filtration, evaporation of the solvent, and passing the residue through a small column of silica gel using suitable solvent. The advantage of using microwave irradiation is supported by the fact that this reaction, with exactly the same ratio of reagent and catalysts, could be completed in an oil bath at a comparable temperature of 55 °C in 38 h in 90\% yield. On the other hand, it remained incomplete after 2 min in a similar oil bath.
It is noteworthy to mention that the above reaction remained incomplete under microwave irradiation, when supported potassium ferrate(VI) was used without potassium sulfate, even with a higher ratio of reagent 1:K$_2$FeSO$_4$ (1:3) or longer microwave irradiation time (7 min). Our experiments indicated that potassium sulfate mixed with potassium ferrate(VI) stabilizes the ferrate against decomposition and inhibits clumping of the solid material, and therefore can improve the ability of the reagent.

To assess the generality of the method, a variety of 2,4-dinitrophenylhydrazones were treated in a similar way to afford the parent carbonyl compounds in high to excellent yields (Scheme 1, Table 1). Cinnamaldehyde 2,4-dinitrophenylhydrazone was transferred to cinnamaldehyde by this method (93% yield), thus showing that the carbon-carbon double bond is not prone to the cleavage by this reagent under microwave irradiation. Overoxidation was also not observed.

**Conclusions**

In conclusion, the present procedure for regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones has all advantages of using iron salt as eco-friendly and nontoxic material, mild reaction conditions, easy work-up procedure, short reaction time, high to excellent yields, because of adding potassium sulfate to supported potassium ferrate(VI) and microwave irradiation without the use of expensive and hazardous organic solvents.
Table 1. Regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones using K₂FeO₄/K₂SO₄ supported on montmorillonite K-10 under microwave irradiation.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product ¹</th>
<th>Reaction time (min)</th>
<th>Yield ² (%)</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>2a</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>1b</td>
<td>2b</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>1c</td>
<td>2c</td>
<td>1</td>
<td>98</td>
</tr>
<tr>
<td>1d</td>
<td>2d</td>
<td>3</td>
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</tr>
<tr>
<td>1e</td>
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</tr>
<tr>
<td>1n</td>
<td>2n</td>
<td>3</td>
<td>92</td>
</tr>
</tbody>
</table>

¹ All products were characterized by their bp or mp, in comparison with authentic samples, and IR spectra.
² Yields are based on isolated products.

Experimental

2,4-Dinitrophenylhydrazones were synthesized from corresponding carbonyl compounds according to the literature. All products were known and characterized by comparison of their mp or bp and IR spectra with those of authentic samples. Potassium ferrate(VI) was prepared according to the literature data then it was mixed with potassium sulfate (4:2) and the mixture impregnated on montmorillonite K-10 (Aldrich Chemical LTD). Thin layer chromatography was done on precoated silica gel. IR spectra were recorded on FT-IR Unicam Mattson 1000 spectrophotometer. A Sears Kenmore microwave oven equipped with a turntable at full power (900 Watts) was used.

Regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones; general procedure

To a solution of 2,4-dinitrophenylhydrazone (2 mmol) in a minimum amount of diethyl ether (5 mL) a mixture of potassium ferrate(VI) (0.8 g, 2 mmol), potassium sulfate (0.35 g, 2 mmol) and montmorillonite K-10 (1.5 g) was added at room temperature, and the reaction mixture was thoroughly mixed using a vortex mixer. The air-dried adsorbed material (in a small beaker) was placed into an alumina bath inside
the microwave oven and irradiated for the time indicated in Table 1. The temperature of
the alumina bath (heat sink) inside the microwave oven was ca. 55 °C after 2 min of
irradiation. The progress of reaction was monitored by TLC (petroleum ether/ethyl
acetate, 4:1). After completion of reaction, the partial molten mixture was cooled to
room temperature and the product was extracted with diethyl ether and filtered.
Evaporation of solvent gave a crude product which was passed through a short column
of silica gel using a suitable solvent to regenerate the carbonyl compounds.

References
13. a) A. McKillop, D. W. Young, Synthesis 1979, 401–420;
b) A. McKillop, D. W. Young, Synthesis 1979, 481–500;
**Povzetek**

2,4-dinitrofenilhidrazone smo s pomočjo mikrovalov in kalijevega ferata(VI) na nosilcu hitro in uspešno pretvorili v ustrezne karbonilne spojine.