

**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-ethanediybis(*p*-toluenesulphonamide) 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.^{10,14} Since organic solvents are expensive and hazardous, dry media technique has attracted much attention recently because open vessels can be used.¹⁵

Potassium ferrate(VI) (K_2FeO_4), a hexavalent iron is a nontoxic compound¹⁶ has been introduced recently by Delaude et al. as a novel oxidizing reagent.¹⁷ However, there are a few examples for the use of potassium ferrate(VI) on mineral support for oxidation of organic substrates,^{17,18} for regeneration of carbonyl compounds from acetals, ketals and hydrazones,^{19,20} for oxidative deprotection of trimethylsilyl ethers and tetrahydropyranyl ethers.^{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.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.

Results and Discussion

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

Table 1. Regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones using K_2FeO_4/K_2SO_4 supported on montmorillonite K-10 under microwave irradiation.

Substrate	Product ^a	Reaction time (min)	Yield ^b (%)
1a	2a	2	98
1b	2b	2	98
1c	2c	1	98
1d	2d	3	95
1e	2e	3	95
1f	2f	2	93
1g	2g	3	91
1h	2h	2	97
1i	2i	3	96
1j	2j	3	97
1k	2k	3	96
1l	2l	3	97
1m	2m	3	98
1n	2n	3	92

^a All products were characterized by their bp or mp, in comparison with authentic samples, and IR spectra.

^b Yields are based on isolated products.

Experimental

2,4-Dinitrophenylhydrazones were synthesized from corresponding carbonyl compounds according to the literature.²⁵ All products were known and characterized by comparison of their mp or bp and IR spectra with those of authentic samples.^{25,26} Potassium ferrate(VI) was prepared according to the literature data¹⁷ 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

1. A. E. Gillam, T. F. West, *J. Chem. Soc.* **1945**, 95–98.
2. E. B. Hershberg, *J. Org. Chem.* **1948**, 13, 542–546.
3. G. S. Zhang, H. Gong, D. H. Yang, M. F. Chen, *Synth. Commun.* **1999**, 29, 1165–1170.
4. T. W. Green, P. G. M. Wutz, *Protective Groups in Organic Synthesis*; Wiley, New York, 1991.
5. P. J. Kocienski, *Protecting Groups*; Thieme, New York, 1994.
6. D. N. Kirk, C. J. Slade, *Tetrahedron Lett.* **1980**, 21, 651–655.
7. B. C. Ranu, D. C. Sarkar, *J. Org. Chem.* **1988**, 53, 878–879.
8. P. Laszlo, E. Polla, *Synthesis* **1985**, 439–440.
9. S. Narayanan, V. S. Srinivasan, *J. Chem. Soc. Perkin Trans. 2* **1986**, 1557–1559.
10. A. Khazaei, R. Ghorbani, *Molecules* **2002**, 7, 717–720.
11. a) G. S. Zhang, D. H. Yang, M. F. Chen, *Synth. Commun.* **1998**, 28, 2221–2226;
b) G. W. Kabalka, R. D. Pace, P.P. Wadgaonkar, *Synth. Commun.* **1990**, 20, 2453–2457.
12. C. B. Khouv, C. Partl, J. A. Lalenger, M. E. Davis, *J. Catal.* **1994**, 149, 195–210.
13. a) A. McKillop, D. W. Young, *Synthesis* **1979**, 401–420;
b) A. McKillop, D. W. Young, *Synthesis* **1979**, 481–500;
c) J. H. Clark *Catalysis of Organic Reactions by Supported Inorganic Reagents*; VCH, New York, 1994.
14. a) A. Abramowitch, *Org. Prep. Proced. Int.* **1991**, 23, 685–711;
b) S. Caddick, *Tetrahedron* **1995**, 51, 10403–10432.
15. a) R. S. Varma, J. B. Lamture, M. Varma, *Tetrahedron Lett.* **1993**, 34, 3029–3032;
b) R. S. Varma, R. Dahiya, *Tetrahedron Lett.* **1997**, 38, 2043–2044;
c) S. Bhar, S. K. Chaudhuri, *Tetrahedron* **2003**, 59, 3493–3498.
16. W. A. Kneppor, *Encyclopedia of Chemical Technology*; John Wiley, New York, 1981, 13, 735.
17. L. Delaude, P. Laszlo, *J. Org. Chem.* **1996**, 61, 6360–6370.
18. a) L. Delaude, P. Laszlo, P. Lehance, *Tetrahedron Lett.* **1995**, 36, 8505;
b) S. Caddick, L. Murtagh, R. Weaving, *Tetrahedron Lett.* **1999**, 40, 3655–3656.
19. M. M. Heravi, M. Tajbakhsh, S. Habibzadeh, M. Ghassemzadeh, *Monatsh. Chem.* **2001**, 132, 985–988.
20. M. M. Heravi, M. Tajbakhsh, S. Habibzadeh, M. Ghassemzadeh, *Phosphorus Sulfur* **2002**, 177, 2299–2302.
21. M. Tajbakhsh, M. M. Heravi, S. Habibzadeh, *Phosphorus Sulfur* **2003**, 178, 361–364.
22. M. Tajbakhsh, M. M. Heravi, S. Habibzadeh, *Phosphorus Sulfur* **2001**, 176, 191–194.
23. M. M. Hashemi, Y. A. Beni, *Synth. Commun.* **2001**, 31, 295–299.
24. G. W. Thompson, L. T. Ockerman, J. M. Schreyer, *J. Am. Chem. Soc.* **1951**, 73, 1379–1381.
25. R. L. Shriner, R. C. Fuson, D. Y. Curtin, T. C. Morrill, *The Systematic Identification of Organic Compounds*; John Wiley, New York, 1980.
26. C. J. Pouchert, *The Aldrich Library of IR Spectra*; Aldrich Chemical Co., Milwaukee, 1981.

Povzetek

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