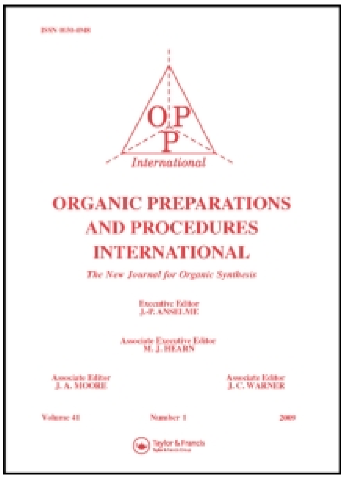


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

FERROUS SULFATE PROMOTED CONVERSION OF *N,N*-DIMETHYLHYDRAZONES AND PHENYLHYDRAZONES TO CARBONYL COMPOUNDS

Aayesha Nasreen[a]; Srinivas R. Adapa[a]
[a] Inorganic Division, Indian Institute of Chemical Technology, Hyderabad, INDIA

To cite this Article Nasreen, Aayesha and Adapa, Srinivas R.(1999) 'FERROUS SULFATE PROMOTED CONVERSION OF *N,N*-DIMETHYLHYDRAZONES AND PHENYLHYDRAZONES TO CARBONYL COMPOUNDS', Organic Preparations and Procedures International, 31: 5, 573 — 575

To link to this Article: DOI: 10.1080/00304949909355344

URL: http://dx.doi.org/10.1080/00304949909355344

FERROUS SULFATE PROMOTED CONVERSION OF *N,N*-DIMETHYLHYDRAZONES AND PHENYLHYDRAZONES TO CARBONYL COMPOUNDS[†]

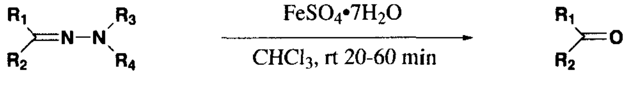
Submitted by
(06/24/99)

Aayesha Nasreen and Srinivas R. Adapa*

Inorganic Division, Indian Institute of Chemical Technology
Hyderabad - 500 007 INDIA

Derivatives of carbonyl compounds such as *N,N*-dimethylhydrazones and phenylhydrazones serve as important synthetic intermediates, used for the purification and characterization of carbonyl-containing molecules and as protective groups.[1-3] Extensive studies on the deprotection of these derivatives have been carried out using various catalysts[4-7] which are not satisfactory when sensitive groups are present elsewhere in the molecule. Consequently, there is a need for the development of protocol using readily available and safer reagents.

There has been increased activity in metal ion-promoted/catalyzed hydrolysis of functional groups, particularly acid derivatives due to their relevance to biochemical processes.[8a] It has been proposed that metal ions make the functional groups more susceptible to nucleophilic attack through complexation. In addition, other factors such as activation of nucleophiles, stabilization of the leaving groups and entropic assistance may facilitate the reaction. The few data available indicate that metal ions may retard or promote the hydrolysis of imines depending on whether they form two or less chelate rings with the imine. [8b,9a-b]



1 2

$R_3, R_4 = CH_3$
$R_3 = H, R_4 = Ph$

Recently anhydrous ferrous sulfate has been used for the deprotection of 1,1-diacetals.[9c] This communication reports the use of ferrous sulfate catalyst in chloroform at room temperature for the cleavage of *N,N*-dimethylhydrazones and phenylhydrazones to carbonyl compounds.

The results shown in the Table indicate that the deprotection of *N,N*-dimethylhydrazones and phenylhydrazones by ferrous sulfate appears to have wide applicability for the regeneration of carbonyl compounds under mild conditions.

TABLE 1. Yields of Carbonyl compounds from hydrazones with ferrous sulfate.

Carbonyl Compound	N,N-Dimethyl-hydrazone (%)	Time (min.)	Phenyl-hydrazone (%)	Time (min.)	bp./ (mp.) (°C)	lit. bp. (mp.)[a] (°C)
$C_6H_5COCH_3$	90	45	90	60	200	202
4-$MeOC_6H_4CHO$	91	45	90	60	247	248

TABLE 1. Continued...

Carbonyl Compound	N,N-Dimethyl-hydrazone (%)	Time (min.)	Phenyl-hydrazone (%)	Time (min.)	bp./ (mp.) (°C)	lit. bp. (mp.)[a] (°C)
C_6H_5CHO	85	20	92	30	178	179
$C_2H_5COCH_3$	88	30	88	45	78	80
$2\text{-}NO_2C_6H_4CHO$	90	25	90	45	44	45
$2,6(Cl)_2C_6H_3CHO$	88	45	86	40	71	70
$CH_3(CH_2)_3CHO$	94	30	92	40	102	104
$C_6H_{10}O$	86	45	90	45	156	155
$(CH_3)_3CCOCH_3$	92	45	91	60	117	116
C_3H_7CHO	95	45	92	45	75	74
$2Br\text{-}4,5(OCH_2O)C_6H_2CHO$	90	30	88	40	128	129[b]

a) A. I.Vogel, *"A Text Book of Practical Organic Chemistry "* 3rd ed., Longman group. London. (1973). b) Dictionary of Organic Compounds. VIth ed, Vol. 2, Chapman and Hall. London.

EXPERIMENTAL SECTION

The preparation of *N,N*-dimethylhydrazones and phenylhydrazones was quantitative.[10] All chemicals and solvents were obtained from commercial sources and used without further purification.^{1}H NMR were recorded at 90 MHz in $CDCl_3$ solvent, IR spectra were obtained on G.C. FTIR using Vartan Nicolet USA apparatus, EI mass spectra were determine by using V.G. Micromass 7070H and Finnigan Mat 1020B apparatus. Melting points were determine on Veego digital automatic melting point apparatus and are uncorrected. The reaction proceeds well in other solvents such as ethyl acetate, toluene, acetonitrile, heptane and 1,2 dichloroethane with excellent yields for benzaldehyde, acetophenone , ethyl methyl ketone etc. showing the generality and applicability of this procedure in large scale preparations.

General Procedure.- To a solution of the hydrazone (5 mmol) in chloroform (10 mL) was added ferrous sulfate (0.139 mg, 5 mmol), and the reaction mixture was stirred for 20-60 min upon completion of the reaction as indicated by TLC. The solid was separated by filtration and the filtrate was washed with water. The dried organic layer was evaporated under reduced pressure to afford the product which was purified by column-chromatography on silica gel with ethyl acetate-hexane, 7:3 as eluent.

Similarly the conversion of *N,N*-dimethylhydrazones and phenylhydrazones to the corresponding carbonyl compounds in solvents such as ethyl acetate, toluene, acetonitrile, heptane and 1,2 dichloroethane could be performed using the same procedure as described above.

Acknowledgement.- The authors heartily acknowledge Dr. K. V. Raghavan Director of IICT and Dr. B. M. Chowdhary, HOD of Catalysis Division, for their encouragement and support.

REFERENCES

†. IICT Communication No 4262.

1. a) T. W. Greene and P. G. W. Wuts, *"Protective Groups in Organic Synthesis"*, 2nd ed. John Wiley & Sons, New York, 213 **(1991)**; b) R. H. Sharpo and M. J. Heart, *J. Am. Chem. Soc.*, **89**, 5734 (1967); c) J. Friedman and H. Shechter, *ibid.*, **83**, 3159 (1961); d) G. W. Kabalka and S. T. Summer, *J. Org. Chem.*, **46**, 1217 (1981); e) G. Rosini and R. Ballini, *Synthesis.*, 228 (**1983**).

2. a) H. J. E. Loewenthal, *in "Protective Groups in Organic Chemistry"*, J. F. W. McOmie., ed., Plenum Press, New York, 340 **(1973)**; b) D. N. Kirk and C. J. Slade, *Tetrahedron Lett.*, **21**, 65 (1980); c) W. F. McGuckin and E. C. Kendall, *J. Am. Chem. Soc.*, **74**, 5811(1952).

3. a) A. M. Gillam, T. F. West, *ibid.*, **67**, 95 (1945); b) E. B. Hershberg, *J. Org. Chem.*, **13**, 542 (1948); c) E. J. Eisenbraun, R. P. Wesley, R. M. Budhram and B. Dewprasad, *Chem. Ind., (London).*, 549 (**1989**); d) B. C. Ranu and D. C. Sarkar, *J. Org. Chem.*, **53**, 878 (1988) and references cited therein; e) M. Curini and U. Costatino, *Synlett.*, 333 (**1996**).

4. a) R. N. Ram, K.Varsha, *Tetrahedron Lett.*, **32**, 5829 (1991); b) S. Narayanan and V. S. Srinivasan, *J. Chem. Soc., Perkin Trans 2.*, 1557 (**1986**); c) P. Laszlo and E. Polla, *Synthesis*, 439 (**1985**).

5. a) H. H. Sisler, G. M. Omietanski and B. Rudner, *Chem. Rev.*, **57**, 1021 (1957); b) L. Horner and H. Fernekess, *Chem. Ber.*, **94**, 712 (1961); c) R. E. Erickson, P. J. Jr. Andrulis, J. C. Collins, M. L. Lungle and G. D. Mercer, *J. Org. Chem.*, **34**, 2961 (1969); d) E. J. Corey and S. Knapp, *Tetrahedron Lett.*, 3667 (**1976**); e) A. Kamal, M. Arifuddin and N. V. Rao, *Synth.Commun.*, **28**, 3927 (1998).

6. E. M. Chamberlin and J. Chemerda, *J. Am. Chem. Soc.*, **77**, 1221 (1955).

7. a) A. M. Butler, *J. Chem. Res (S).*, 61 **(1981)**; b) M. Salmon, R. Miranda and E. Angeles, *Synth. Commun.*, **16**, 1827 (1986).

8. a) R. W. Hay, in *Reaction of Co-Ordination Ligands,* P. S. Bratman, ed., Plenum Press, New York, Vol. **2**, 223-364 (1989); b) P. P. Chaloner, *Handbook of Co-Ordination Catalysis in Organic Chemistry,* Butterworths, London, 709-729 **(1986)**.

9. a) A. R. Boate and D. R. Eaten, *Can. J. Chem.*, **55**, 2432 (1977); b) A. C. Dash and S. Preharaj, *J. Chem. Soc. Dalton Trans.*, 2063 **(1981)**; c) T. S. Jin, Y. R. Ma, Z. H. Zhang and T. S. Li, *Org. Prep. Proced. Int.*, **30**, 463 (1998).

10. A. I. Vogel, *A Text Book of Practical Organic Chemistry* , 3rd ed., Longman Group, London, 721 **(1973)**.