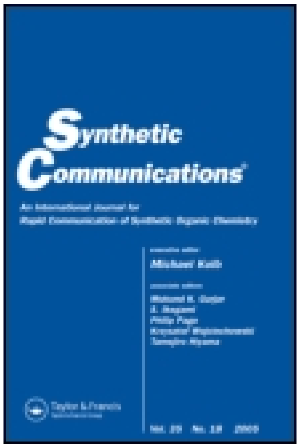

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Silica Chloride/Wet SiO_2 as a Novel Heterogeneous System for Deprotection of Oximes, Hydrazones, and Semicarbazones

F. Shirini [a], M. A. Zolfigol [b], M. Khaleghi [a] & I. Mohammadpour-Baltork [c]
[a] Department of Chemistry, College of Science, Guilan University, Rasht, Iran
[b] Department of Chemistry, College of Science, Bu-Ali Sina University, Hamadan, Iran
[c] Department of Chemistry, Isfahan University, Isfahan, Iran

To cite this article: F. Shirini, M. A. Zolfigol, M. Khaleghi & I. Mohammadpour-Baltork (2003): Silica Chloride/Wet SiO_2 as a Novel Heterogeneous System for Deprotection of Oximes, Hydrazones, and Semicarbazones, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:11, 1839-1844

To link to this article: http://dx.doi.org/10.1081/SCC-120020193

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 11, pp. 1839–1844, 2003

Silica Chloride/Wet SiO_2 as a Novel Heterogeneous System for Deprotection of Oximes, Hydrazones, and Semicarbazones

F. Shirini,[1,*] M. A. Zolfigol,[2] M. Khaleghi,[1] and I. Mohammadpour-Baltork[3]

[1]Department of Chemistry, College of Science,
Guilan University, Rasht, Iran
[2]Department of Chemistry, College of Science,
Bu-Ali Sina University, Hamadan, Iran
[3]Department of Chemistry, Isfahan University,
Isfahan, Iran

ABSTRACT

Oximes, hydrazones, and semicarbazones can be converted to their corresponding carbonyl compounds in good to high yields by a combination of silica chloride and wet SiO_2.

Key Words: Deprotection; Hydrazones; Oximes; Semicarbazones; Silica chloride.

---

*Correspondence: F. Shirini, Department of Chemistry, College of Science, Guilan University, Rasht, Iran; E-mail: shirini@cd.gu.ac.ir.

DOI: 10.1081/SCC-120020193
0039-7911 (Print); 1532-2432 (Online)

Regeneration of carbonyl compounds from stable and readily prepared oximes, hydrazones, and semicarbazones has received attention recent years.[1–7] Since oximes can be prepared from olefins,[8] esters,[9] nitriles,[9] nitro compounds,[10,14–16] nitrites,[11] alcohols,[12] and primary aliphatic amines,[13] the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones. However, many of these methods of generating carbonyl compounds from oximes involve reagents which are either expensive or not readily available.[17–25] Little attention has been paid to the cleavage of carbon–nitrogen double bonds of hydrazones and semicarbazones, and only a few reports are available dealing with the conversion of the derivatives into their corresponding carbonyl compounds.[4–7,26,27]

In continuation of our studies on the application of silica chloride,[28,29] we were interested in using this reagent for regeneration of carbonyl compounds from oximes, hydrazones, and semicarbazones in conjunction with wet SiO_2 in an organic solvent. In this communication we wish to report a simple method for the effective cleavage of carbon–nitrogen double bonds of oximes, hydrazones, and semicarbazones under mild and heterogeneous conditions (Table 1). Our experiments show that oximes, hydrazones, and semicarbazones are converted into their corresponding carbonyl compounds from good to high yields. It should be noted that these deprotection reactions did not proceed using either silica chloride or wet SiO_2 alone, even after prolonged heating. In order to show the ability of this system we have compared some of the results with some of those reported in the literature (Table 2).

In summary silica chloride in the presence of wet SiO_2 can serve as an efficient reagent for the cleavage of carbon–nitrogen double bonds of oximes, hydrazones, and semicarbazones. The yields are almost quantitative and the procedure is simple and convenient. One of the advantages of this method is the conversion of silica chloride to the silca gel during the reaction, which can be used for the regeneration of silica chloride for several times.

EXPERIMENTAL

General Procedure

A mixture of substrate (1 mmol), silica chloride (2 g), and wet SiO_2[(SiO_2/H_2O: 50% w/w), 1 g] in *n*-hexane was refluxed for the specified time (Table 1). The reaction was monitored by TLC or GLC. After completion of the reaction, the mixture was filtered. Anhydrous

Table 1. Oxime, hydrazone, and semicarbazone deprotection with silica chloride/wet SiO_2 system.

Entry	Substrate	Time (h)	Product[a]	Yield[b] (%)
1	3-Nitrobenzaldoxime	0.5	3-Nitrobenzaldehyde	90
2	2,4′-Dibromoacetophenone oxime	0.25	2,4′-Dibromoacetophenone	85
3	α-Tetralone oxime	0.25	α-Tetralone	85
4	2-Acetylpyridine oxime	0.42	2-Acetylpyridine	90
5	4-Acetylpyridine oxime	0.25	4-Acetylpyridine	80
6	α-Furil dioxime	0.17	Furil	85
7	Cyclohexanone oxime	0.08	Cyclohexanone	85
8	Champhor oxime	0.17	Champhor	90
9	Benzaldehyde-4-nitrophenylhydrazone	1	Benzaldehyde	85
10	2-Nitrobenzaldehyde phenylhydrazone	0.5	2-Nitrobenzaldehyde	87
11	4-Methylbenzaldehyde phenylhydrazone	0.33	4-Methylbenzaldehyde	92
12	4-Chloroacetophenone phenylhydrazone	0.17	4-Chloroacetophenone	90
13	4-Phenylbenzophenone phenylhydrazone	0.67	4-Phenylbenzophenone	95
14	4-Pyridinecarboxaldehyde phenylhydrazone	0.17	4-Pyridinecarboxaldehyde	89
15	3-Acetylpyridine phenylhydrazone	0.25	3-Acetylpyridine	85
16	2-Benzoylpyridine phenylhydrazone	0.25	2-Benzoylpyridine	84
17	4-Methoxybenzaldehyde semicarbazone	0.5	4-Methoxybenzaldehyde	92
18	Benzaldehyde semicarbazone	0.5	Benzaldehyde	94
19	2-Methoxybenzaldehyde semicarbazone	0.5	2-Methoxybenzaldehyde	85
20	Acetophenone semicarbazone	0.5	Acetophenone	90
21	4-Bromoacetophenone semicarbazone	0.5	4-Bromoacetophenone	85

(*continued*)

Table 1. Continued.

Entry	Substrate	Time (h)	Product[a]	Yield[b] (%)
22	Salicyladehyde semicarbazone	0.5	Salicylaldehyde	90
23	Cyclohexanone semicarbazone	0.8	Cyclohexanone	85
24	Cyclopentanone semicarbazone	0.6	Cyclopentanone	82
25	2-Hydroxy-5-nitrobenzaldehyde semicarbazone	0.5	2-Hydroxy-5-nitrobenzaldehyde	90
26	1-Naphthaldehyde semicarbazone	2	1-Naphthaldehyde	92
27	5-Methyl-2-furaldehyde semicarbazone	1	5-Methyl-2-furaldehyde	92
28	α-Tetralone semicarbazone	0.5	α-Tetralone	90
29	3-Acetylpyridine semicarbazone	0.75	3-Acetylpyridine	90

[a] All products were characterized by IR and ^{1}H-NMR spectra and by comparison with authentic samples.

[b] Isolated yield.

Table 2. Comparison of some of the results obtained from silica chloride in the presence of wet SiO_2 (1) with some of those reported with *N*-bromosuccinimide (2),[30] methylammonium chlorochromate adsorbed on alumina (3),[2] and carboxypyridinium chlorochromate (4).[31]

			Time in hour (Yield %)			
Entry	Substrate	Product	1	2	3	4
1	Benzaldehyde-4-nitrophenylhydrazone	Benzaldehyde	1 (90)	—	3 (75)	1.5 (71)
2	Cyclohexanone oxime	Cyclohexanone	0.08 (92)	4 (80)	3.5 (96)	2 (90)
3	Acetophenone semicarbazone	Acetophenone	0.5 (90)	—	—	2.5 (97)

$MgSO_4$ was added to the filtrate and filtered. Evaporation of the solvent, being followed by column chromatography on silica gel, gave the corresponding carbonyl compounds from good to high yields.

ACKNOWLEDGMENT

Financial support for this work by the research affairs of the Guilan University is acknowledged.

REFERENCES

1. Yang, Y.-T.; Li, T.-S.; Li, Y.-L. Synth. Commun. **1993**, *23*, 1121.
2. Zhang, G.-S.; Yang, D.-H.; Chen, M.-F.; Cai, K. Synth. Commun. **1998**, *28*, 607.
3. Khan, R.H.; Mathur, R.K.; Ghosh, A.C. J. Chem. Res. (S) **1995**, 506.
4. Khurana, J.M.; Ray, A.; Sahoo, P.K. Bull. Chem. Soc. Jpn. **1994**, *67*, 1091.
5. Shirini, F.; Zolfigol, M.A.; Azadbar, M.R. Synth. Commun. **2002**, *32*, 315.
6. Shirini, F.; Azadbar, M.A. Synth. Commun. **2001**, *31*, 3775.
7. Shirini, F.; Zolfigol, M.A.; Mallakpour, B.; Mallakpour, S.E.; Hajipour, A.R.; Mohammadpour-Baltork, I. Tetrahedron Lett. **2002**, *43*, 1555.
8. Kadzyauskas, P.P.; Zefirov, N.S. Russ. Chem. Rev. **1968**, *37*, 543.
9. Touster, O. Org. React. **1953**, *7*, 327.

10. Fujisawa, T.; Kurita, Y.; Sato, T. Chem. Lett. **1983**, 1537.
11. Barton, D.H.R.; Beaton, J.M.; Geller, L.E.; Pechet, M.M. J. Am. Chem. Soc. **1961**, *83*, 4076.
12. Barton, D.H.R.; Beaton, J.M. J. Am. Chem. Soc. **1961**, *83*, 4083.
13. Kahr, K.; Berther, C. Chem. Ber. **1960**, *93*, 132.
14. Stiver, S.; Yates, P. J. Chem. Soc., Chem. Commun. **1983**, *2*, 50.
15. Hanson, J.R.; Organ, T.D. J. Chem. Soc. C **1970**, 1182.
16. Zeilstra, J.J.; Engberts, J.B.F.N. Synthesis **1974**, 49.
17. Depuy, C.H.; Ponder, B.W. J. Am. Chem. Soc. **1959**, *81*, 4629.
18. Chamberlin, E.M.; Chamerda, J.M. J. Am. Chem. Soc. **1955**, *77*, 1221.
19. Vankar, P.; Rathore, R.; Chandrasekaran, S. J. Org. Chem. **1986**, *51*, 3036.
20. Moriarty, R.M.; Praksh, O.; Vivilikolarn, R. Synth. Commun. **1986**, *16*, 1247.
21. Kim, S.B.; Kim, K.; Kim, Y.H. Tetrahedron Lett. **1987**, *28*, 645.
22. Naraya, C.R.; Ramaswamy, O.S.; Wadia, M.S. Chem. Ind. (London) **1977**, 454.
23. Drabowicz, J. Synthesis **1980**, 125.
24. Olah, G.A.; Ho, T.C. Synthesis **1976**, 610.
25. Barton, D.H.R.; Lester, D.J.; Ley, S.V. J. Chem. Soc., Chem. Commun. **1977**, 445.
26. Barton, D.H.R.; Lester, D.J.; Ley, S.V. J. Chem. Soc., Chem. Commun. **1978**, 276.
27. Barton, D.H.R.; Lester, D.J.; Ley, S.V. J. Chem. Soc., Perkin Trans. 1 **1980**, 1212.
28. Zolfigol, M.A.; Shirini, F.; Ghorbani Chogamarani, A. Synth. Commun. **2002**, *32*, 1809.
29. Zolfigol, M.A.; Torabi, M.; Mallakpour, S.E. Tetrahedron **2001**, *57*, 8381.
30. Bandgar, B.P.; Kunde, M.L.B.; Thote, J.L. Synth. Commun. **1997**, *27*, 1149.
31. Mohammadpour-Baltork, I.; Pouranshirvani, S. Synth. Commun. **1996**, *26*, 1.

Received in the Netherlands August 23, 2002