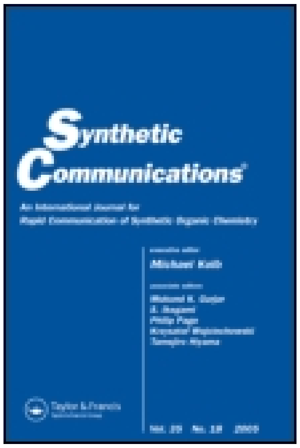


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

$SnCl_2$-SiO_2: A SELECTIVE REAGENT FOR EFFICIENT REGENERATION OF CARBONYLS FROM NITROGENEOUS DERIVATIVES

Nalin B. Das [a], Bhagabat Nanda [a] & Amalendu Nayak [a]
[a] Regional Research Laboratory, Bhubaneswar, 751 013, India

Version of record first published: 16 Aug 2006.

To cite this article: Nalin B. Das, Bhagabat Nanda & Amalendu Nayak (2002): $SnCl_2$-SiO_2: A SELECTIVE REAGENT FOR EFFICIENT REGENERATION OF CARBONYLS FROM NITROGENEOUS DERIVATIVES, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:23, 3647-3651

To link to this article: http://dx.doi.org/10.1081/SCC-120014982

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

SYNTHETIC COMMUNICATIONS
Vol. 32, No. 23, pp. 3647–3651, 2002

$SnCl_2$–SiO_2: A SELECTIVE REAGENT FOR EFFICIENT REGENERATION OF CARBONYLS FROM NITROGENEOUS DERIVATIVES

Nalin B. Das,* Bhagabat Nanda, and Amalendu Nayak

Regional Research Laboratory,
Bhubaneswar-751 013, India

ABSTRACT

Semicarbazones, Phenyl hydrazones, 2,4-DNP and Oxime derivatives are converted into corresponding carbonyl compounds, mostly in quantitative yield by stannous chloride–silica gel. This has general application to various nitrogeneous derivatives.

Nitrogeneous derivatives serve as important synthetic intermediates as they are extensively used[1(a–d)] for purification, characterization and also protection of carbonyl-containing molecules. Regeneration of the parent carbonyl function is an important step in organic synthesis. Most of the reported[2–15] methods for regeneration of carbonyl functions involve

---

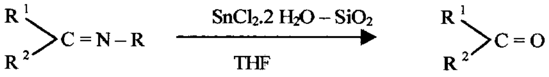
*Corresponding author. E-mail: nbdas@rrlbhu.res.in

DOI: 10.1081/SCC-120014982 0039-7911 (Print); 1532-2432 (Online)

www.dekker.com

strongly, oxidative or reducing, hydrolysis under acidic or basic media or stringent conditions or expensive reagents and or some times longer reaction times. In continuation with our earlier studies on application of metal reagent,[16(a–c)] we now report that $SnCl_2{\cdot}2H_2O–SiO_2$ is an excellent and superior reagent system for the regeneration of carbonyl compounds from their nitrogeneous derivatives in quantitative yields.

We have found that this reagent system has certain advantages over other systems in terms of inexpensive, simple reagent and limited reaction time required, chemoselective regeneration of carbonyl compounds. The semicarbazones, phenyl hydrazones, 2,4-dinitrophenylhydrazones and oximes of aromatic aldehydes and ketones, aliphatic aldehydes and ketones, cyclic ketones and steroidal ketone react smoothly in this reaction condition to give the corresponding aldehydes and ketones. This observation is quite general.



R = –$NHCONH_2$; –NHC_6H_5; –2,4-DNP; –OH

Semicarbazones are tried with $SnCl_2{\cdot}2H_2O$ in THF alone under reflux and the desemicarbazonation occurs in good yield. In contrast, the reaction of phenylhydrazone, 2,4-dnp and oxime derivatives with $SnCl_2{\cdot}2H_2O$/THF does not regenerate the parent carbonyl compounds. The probable mechanism for the reaction of semicarbazones only with stannous chloride, suggests that the stannous (II) ion forms monocyclic chelating complex with semicarbazone through nitrogen and oxygen atoms and hydrolysis favors at the imino bond of the complex to get carbonyl compounds. The regeneration of carbonyl compounds of other nitrogeneous derivatives does not occur, probably the formation of monocyclic chelating complex of stannous (II) ion does not favor in this condition.

Whereas, the addition of SiO_2 to $SnCl_2{\cdot}2H_2O$/THF favors efficiently the selective regeneration of corresponding carbonyl compounds of the semicarbazone, phenylhydrazone, 2,4-dnp and oxime derivatives. However, we speculate that the nitrogeneous compounds get absorbed on the SiO_2 surface and the reactions get facilitated because of SiO_2 acts as an activating agent[18] for the substrates.

In conclusion we have developed an easy and convenient reaction condition with very good yield in less time using in expensive reagents. The results obtained are satisfactory and shows the new reagent system as a valuable addition to the existing findings.

Table 1. Regeneration of Carbonyl Compounds from Nitrogeneous Derivatives with $SnCl_2 \cdot 2H_2O$–SiO_2

Entry	Substrate[a]	Time (min)	Carbonyl Compounds Yield (%)[b]
	Semicarbazones of		
1	Benzaldehyde	45	86[c]
2	*p*-Chlorobenzaldehyde	60	82[d]
3	Acetophenone	30	92[c]
4	Benzophenone	30	81[d]
5	Cyclohexanone	30	85[c]
6	Dihydrocarvone	45	64[c]
7	2-Octanone	30	78[c]
8	Hexanal	45	84[c]
	2,4-Dinitrophenyl hydrazones of		
9	Acetophenone	60	80[c]
10	Benzophenone	60	78[d]
11	Hexanal	60	84[c]
12	Cyclohexanone	90	82[c]
13	5α-Cholestan-3-one	90	90[d]
	Phenylhydrazone of		
14	Benzaldehyde	45	88[c]
15	*p*-Chlorobenzaldehyde	45	90[d]
16	Benzophenone	30	76[d]
17	Heptanal	45	80[c]
	Oxime of		
18	Benzophenone	60	78[d]
19	Cyclohexanone	75	80[c]
20	Heptanal	60	70[c]
21	5α–Cholestan-3-one	90	86[d]

[a] Nitrogeneous derivatives of different carbonyl compounds; [b] Yield refers to parent carbonyl compounds; [c] Purification by distillation; [d] Purification by preparative column chromatography (E.A. and P.E.) and crystallization from ethanol.

EXPERIMENTAL

Nitrogeneous derivatives are prepared[17] from the carbonyl compounds. The products are characterized by m.p., b.p., spectral data and by direct comparison with the authentic samples.

General Procedure

Tin (II) chloride dihydrate (3 mmol) and silica gel (mesh 60–120) (200 mg) were added separately to a solution of nitrogeneous derivatives (1 mmol) in THF (10 mL) and the mixture was heated under reflux on a water bath. The reaction was monitored by TLC for completion, Table 1. The reaction mixture was filtered after cooling and filtrate was extracted with dichloromethane. The extract was washed with water and brine and dried (anhydrous Na_2SO_4). Evaporation of solvent under reduced pressure furnished the crude product which, on purification by distillation and chromatography, yielded the carbonyl compounds (Entries 1–21) in 64–92% yields.

ACKNOWLEDGMENT

We thank Dr. V.N. Misra, Director and Dr. Y. R. Rao, Head, F & M Division, Regional Research Laboratory for their valuable suggestions and for providing the necessary facilities for this work.

REFERENCES

1. (a) Shapiro, R.H.; Heart, M.J. J. Am. Chem. Soc. **1967**, *89*, 5734; (b) Reese, C.B. In *Protective Group in Organic Chemistry*; Mc Omie, J.F., Ed.; Plenum Press: New York, 1973; (c) Kabalka, G.W.; Summers, S.T. J. Org. Chem. **1981**, *46*, 1217; (d) Rosini, G.; Ballini, R. Synthesis **1983**, 228 and references cited therein.
2. Hershber, E.B. J. Org. Chem. **1948**, *13*, 542.
3. Barton, D.H.R.; Lester, D.J.; Ley, S.V. J. Chem. Soc. Chem. Commun. **1977**, 445.
4. Ballini, R.; Petrini, M. J. Chem. Soc. Perkin Trans. I **1988**, 2563.
5. Laszlo, P.; Polla, E. Synthesis **1985**, 439.
6. Butler, R.N.; Morris; O' Donohue, A.M. J. Chem. Res. (S) **1981**, 61.
7. McKillop, A.; Hunt, J.D.; Naylor, R.D.; Taylor, E.C. J. Am. Chem. Soc. **1971**, *93*, 4918.
8. Khan, R.H.; Mathur, R.K.; Ghosh, A.C. J. Chem. Res. (S) **1995**, 506.
9. Rao, C.G.; Radhkrishima, A.S.; Singh, R.B. Synthesis **1983**, 808.
10. Depuy, C.H.; Ponder, B.W. J. Am. Chem. Soc. **1959**, *81*, 4629.
11. Fleisher, G.A.; Kendall, E.C. J. Org. Chem. **1951**, *16*, 556.
12. Mc Murry, J.E.; Silvestri, M. J. Org. Chem. **1975**, *40*, 1502.
13. Shim, S.B.; Kim, K.; Kim, Y.H. Tetrahedron Lett. **1987**, *28*, 645.

14. Bird, J.W.; Diaper, D.G.M. Can. J. Chem. **1969**, *47*, 145.
15. Kim, Y.H.; Lee, H.K.; Chang, H.S. Tetrahedron Lett. **1987**, 4285.
16. (a) Singhal, G.M.; Das, N.B.; Sharma, R.P. J. Chem. Soc. Chem. Commun. **1990**, 498; (b) Das, N.B.; Sharma, J.C.; Sharma, R.P.; Bordoloi, M. Tetrahedron Lett. **1993**, *34*, 869; (c) Sarangi, C.; Das, N.B.; Nanda, B.; Nayak, A.; Sharma, R.P. J. Chem. Res. (S) **1997**, 378 and references cited therein.
17. Vogel, A.I. *Textbook of Practical Organic Chemistry*, 5th. Edn.; Longman: London, 1989, p. 1258.
18. (a) Mc Killop, A.; Young, D.W. Synthesis **1979**, 401; (b) Nishiguchi, T.; Machida, N.; Yamamoto, E. Tetrahedron Lett. **1987**, *28*(39), 4565 and references cited therein.

Received in the UK July 13, 2001

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