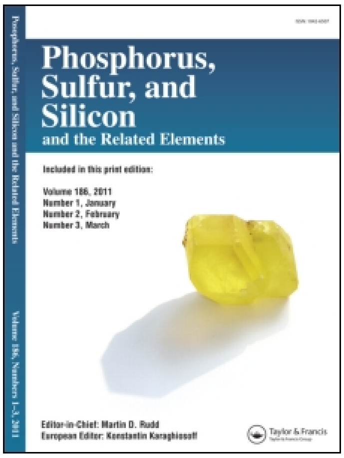

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Deprotection of Semicarbazones Using Bismuth(III)nitrate Pentahydrate Supported onto Silica Gel

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DEPROTECTION OF SEMICARBAZONES USING BISMUTH(III)NITRATE PENTAHYDRATE SUPPORTED ONTO SILICA GEL

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Semicarbazones undergo facile and high yielding deprotection in acetone in the presence of $Bi(NO_3)_3{\cdot}5H_2O$ *supported onto silica gel.*

Keywords: Bismuth nitrate; carbonyl compounds; desemicarbazonation; nonaqueous condition; supported reagent

INTRODUCTION

Semicarbazones frequently are used to protect, purify, and isolate carbonyl compounds[1,2] and hence considerable attention has been paid to develop methods for their deprotection. Regeneration of carbonyl compounds from their semicarbazones has been accomplished by several reagents such as phthalic anhydride,[3] pyruvic acid,[4] nitrous acid in acetic acid, concentrated hydrochloric acid,[5] cation exchange resins,[6] thallium nitrate,[7] titanium chloride,[8] chlorotrimethylsilane-sodium nitrate,[9] supported bis (trimethylsilyl) chromate[10] supported cerium ammonium nitrate,[11] and hexamethylene tetramine.[12] Many of these regents are strong oxidizing agents, and some of are toxic and produce waste that persists in the environment. Due to environmental concerns, there is an increasing need and interest in developing processes that minimize production of toxic waste; therefore, there is emphasis on the use and design of environmental friendly solid acid-base catalysis.[13]

Bismuth compounds are attractive candidates for use in green chemistry because bismuth is the less toxic of the heavy metals.[14] The

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biochemistry,[15] toxicology,[16] and environmental effects[17] of bismuth compounds have been well documented.

Reagents supported by inorganic solids display modified reactivity and selectivity. Added bonuses are easy work-up and isolation, enhanced selectivity, milder reaction conditions, and associated ease of manipulation.[18]

RESULTS AND DISCUSSION

Bismuth(III)nitrate recently has been used as an oxidizing agent.[19] Bismuth(III)nitrate supported onto montmorillonite K-10 along with $Cu(OAc)_2$ in a mixture of acetone-water has been reported as a nontoxic and inexpensive reagent for deprotection of ketoximes.[20]

Here we wish to report that $Bi(NO_3)_3 \cdot 5H_2O$ supported onto silica gel is an efficient reagent for the regeneration of carbonyl compounds from their semicarbazones.

The supported reagent was prepared by mixing 0.5 mmol of bismuth nitrate pentahydrate with silica gel (0.1 g) using pestle and mortar. The use of silica gel gave a better yield of products through desemicarbazonation relative to its absence; most probably silica gel acts as a carrier to increase the surface of heterogeneous reaction. When deprotection was carried out in the absences of silica gel, in the same

TABLE I Regeneration of Aldehydes and Ketones from Their Semicarbazones[a]

Entry	Aldehyde/ketone[d]	Reaction time (h)	Yield (%)
1	Benzaldehyde	1/2	98[b]
2	4-Nitrobenzaldehyde	1/2	98[c]
3	4-Methylbenzaldehyde	3	97[b]
4	Salicyl aldehyde	1/4	98[c]
5	Cinnamaldehyde	2	99[b]
6	Crotonaldehyde	3.5	90[b]
7	2-Butanone	3/4	98[c]
8	Cyclohexanone	1.5	86[b]
9	Acetophenone	1/4	99[b]
10	Camphor	3.5	56[b]

[a] All semicarbazones have been prepared by a known literature procedure.[21]

[b] Refers to yield determined by GC.

[c] Refers to yield of isolated product.

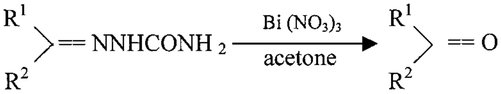
[d] All products were identified by comparison of their physical and spectroscopic data with those of authentic samples.

condition a considerable amount of semicarbazone was detected unchanged. However when the supported reagent was heated under reflux with semicarbazones in acetone the protection occurred in good to high yields (Table I). No over-oxidation to carboxylic acid was observed with this reagent.

When semicarbazone of cinnamaldehyde was examined, only cinnamaldehyde was obtained and no benzaldehyde was formed showing the reagent could not cleave carbon-carbon double bond. However, the semicarbazone of camphor gave a moderate yield of deprotected compound most probably due to steric hindrance.

Deprotection worked very well for a variety of semicarbazones. The experimental procedure is very simple and involves the heating of semicarbazones with the supported reagent in acetone. The isolation of product due to the advantage of supported reagent is easy. Acetone was found to be the best solvent for this deprotection.

In summary, this work demonstrates the use of bismuth(III)nitrate pentahydrate for the selective deprotection of semicarbazones of aldehydes, conjugated aldehydes and ketones. Bismuth(III)nitrate is relatively nontoxic, it is easy to handle, insensitive to air, and inexpensive. These features coupled with the use of a relatively non-toxic and inexpensive solvent (acetone) make this method even more attractive.



EXPERIMENTAL

Deprotection of Semicarbazones Using $Bi(NO_3)_3{\cdot}5H_2O$ Supported onto Silica Gel

General Procedure

A solution of an appropriate semicarbazone (1 mmol) was refluxed with a mixture of $Bi(NO_3)_3{\cdot}5H_2O$ (0.25 g, 0.5 mmol) and silica gel (0.1 g) in acetone (2 ml) for the specified time (Table I). The progress of reaction was monitored by TLC, using petroleum ether/EtOAc, 8:2. The mixture was filtered and the filtrate was evaporated to dryness to give the corresponding carbonyl compound (Table I).

REFERENCES

[1] A. E. Gillman and T. F. West, *J. Chem. Soc.*, 95 (1945).
[2] D. N. Kirk and C. F. Stade, *Tetrahedron Lett.*, **21,** 651 (1980).

[3] E. B. Hershberg, *J. Org. Chem.*, **13,** 542 (1948).
[4] T. Goldsmidt and W. L. C. Veer, *Recl. Trav., Chim. Pays-Bas.*, **65,** 796 (1916).
[5] C. Ranu and C. C. Sarkar, *J. Org. Chem.*, **53,** 878 (1988).
[6] R. Ballini and M. Petrini, *J. Chem. Soc.*, *Perkin Trans.*, **1,** 2563 (1988).
[7] A. McKillop, J. D. Hunt, E. D. Naylor, and E. C. Taylor, *J. Am. Chem. Soc.*, **93,** 4918 (1971).
[8] V. V. Vakatkar, J. G. Tatake, and S. V. Sunthanker, *Chem. Ind.*, (London), **17,** 742 (1977).
[9] R. H. Khan, R. K. Mathur, and A. C. Ghosh, *J. Chem. Res.*, 506 (1995).
[10] M. M. Heravi, M. Tajbakhsh, H. Bakooie, and D. Ajami, *Monatsh, Chem.*, **130,** 933 (1999).
[11] K. Aghapoor, M. M. Heravi, M. A. Nooshabadi, and M. Ghassemzadeh, *Monatsh, Chem.*, **133,** 107 (2002).
[12] M. A. Nooshabadi, K. Aghapoor, M. Tajbakhsh, and M. M. Heravi, *J. Sci.*, *I. R. Iran*, **12,** 33 (2001).
[13] C. B. Khour, J. A. Lalenger, and M. E. Davis, *J. Catal.*, **149,** 195 (1994).
[14] N. Irwing-Sax, R. Bewis, J. “Dangerous Properties of Industrial Materials,” Van. Nostrand Reinghuld: New York, 283 (1989).
[15] K. Dill, E. L. McGown, *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*, edited by S. Patai (John Wiley, New York, 1994), p. 715.
[16] J. Reglinski, *The Chemistry of Arsenic, Antimony and Bismuth*, edited by N. C. Norman (Blackie. Academic and Professional, New York, 1998), pp. 403–440.
[17] W. Rigby, *J. Chem. Soc.*, 793 (1953).
[18] M. M. Heravi, D. Ajami, and M. Ghassemzadeh, *Synthesis*, **3,** 393 (1999).
[19] a) S. T. Tymoko, B. A. Natties, and R. S. Mohan, *Tetrahedron Lett.*, **40,** 7656 (1999); b) K. J. Eash, M. S. Pulia, L. C. Wieland, and R. S. Mohan, *J. Org. Chem.*, **65,** 8399 (2000).
[20] B. A. Nattiers, K. J. Eash, and R. S. Mohan, *Synthesis* (in press).
[21] A. I. Vogel, *Textbook of Practical Organic Chemistry* (Longman, London, 1989), p. 1258.