SYNLETT Spotlight 363

Phenylsilane

Compiled by Yong-Xiao Li

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

Phenylsilane (PhSiH_3) is an organosilane and has been extensively used in organic synthesis as a mild and environmentally benign reducing agent. It is a clear, colorless, volatile liquid which boils at 120°C .¹ When heated to decomposition it emits acrid smoke and irritating vapors. It reacts violently with water, so the preparation of phenylsilane must be performed in a reaction vessel connected with a vacuum system by a standard ground glass joint. It has been used for the hydrosilylation reduction of ketones and aldehydes to give the corresponding alcohols.² It was also found to be an efficient reagent for selective reduction of quinoline to dihydroquinoline,³ reductive Michael cyclization,⁴ and reductive aldol reaction.⁵ The reductive

coupling of aldimines has been achieved by the use of a combination of PhSiH_3 and titanium isopropoxide $[\text{Ti}(\text{Oi-Pr})_4]$.⁶ Reductions of organic halides to dehalogenated alkanes with the $\text{In}(\text{OAc})_3$ – PhSiH_3 system are readily accomplished.⁷ It can also act as an in situ carboxylic acid activating agent to prepare carboxamides and peptides from carboxylic acids and amines.⁸

Phenylsilane is commercially available now. It can be readily prepared by reduction of phenyltrichlorosilane with lithium aluminum hydride in ether.⁹

Scheme 1

Abstracts

(A) Reduction of Aldehydes, Ketones, Aldimines, and Ketimines:

Matsuoka and Kondo showed that PhSiH_3 can efficiently hydrosilylate aldehydes, ketones, aldimines and ketimines to afford the corresponding reduction products in high yields in the presence of catalytic amounts of Ph_3P and $\text{B}(\text{C}_6\text{F}_5)_3$.¹⁰

(B) Direct Reductive Amination of Aldehydes:

PhSiH_3 can be applied as a mild reducing reagent for direct reductive amination of aldehydes to the corresponding secondary amines catalyzed by oxorhenium complexes¹¹ or molybdenum dioxide dichloride.¹² The protocol tolerates a number of reducible functional groups such as F, Cl, I, OMe, NO_2 , CO_2Me , CN, and double bonds.

(C) Reduction of Sulfoxides to Sulfides:

Cabrita et al. showed that a large variety of aryl, aryl alkyl, and alkyl sulfoxides can be reduced with PhSiH_3 to the corresponding sulfides catalyzed by HReO_4 in THF in high yield.¹³ This system was also highly chemoselective, tolerating several functional groups such as Cl, NO_2 , CO_2R , and double or triple bonds.

(D) Reduction of Azides to Amines:

PhSiH₃ is also used as the hydride source for chemoselective reduction of azides to the corresponding amines catalyzed by dioxobis(*N,N*-diethyldithiocarbamate) molybdenum complex under neutral reaction conditions.¹⁴ This method tolerates a wide variety of reducible functional groups.

(E) 1,4-Reduction and Reductive Aldol Reactions of α -Enones:

Miura et al. found that PhSiH₃ can serve as a mild reducing agent in 1,4-reduction of certain α -enones, and in intermolecular reductive aldol reactions of α -enones with aldehydes in the presence of a catalytic amount of In(OAc)₃ in ethanol at ambient temperature.¹⁵

(F) Dehydration of Amides to Nitriles:

A mild method for the catalytic dehydration of aromatic and aliphatic amides using PhSiH₃ in the presence of catalytic tetrabutylammonium fluoride (TBAF) has been developed.¹⁶

(G) Selective Deiodination of Iodoheterocycles:

Sugimoto et al. reported that nitrogen-containing π -deficient heterocyclic iodides such as iodoquinolines or iodopyridines were deiodinated by treatment with PhSiH₃ in the presence of In(OAc)₃ and 2,6-lutidine to give the corresponding deiodinated heterocycles.¹⁷

(H) Reduction of Aldehydes and Ketones to Symmetric Ethers:

A convenient and practical method for the direct synthesis of symmetric ethers from aldehydes and cyclic ketones using antimony(III) iodide/phenylsilane has been developed.¹⁸ Ketones such as acetone or acetophenone did not give the corresponding dialkyl ethers.

References

- (1) Nebergall, W. H. *J. Am. Chem. Soc.* **1950**, *72*, 4702.
- (2) (a) Addis, D.; Zhou, S. L.; Das, S.; Junge, K.; Kosslick, H.; Harloff, J.; Lund, H.; Schulz, A.; Beller, M. *Chem. Asian J.* **2010**, *5*, 2341. (b) Truong, T. V.; Kastl, E. A.; Du, G. D. *Tetrahedron Lett.* **2011**, *52*, 1670. (c) Mostefai, N.; Sirol, S.; Courmarcel, J.; Riant, O. *Synthesis* **2007**, 1265.
- (3) Voutchkova, A. M.; Gnanamgari, D.; Jakobsche, C. E.; Butler, C.; Miller, S. J.; Parr, J.; Crabtree, R. H. *J. Organomet. Chem.* **2008**, *693*, 1815.
- (4) Oswald, C. L.; Peterson, J. A.; Lam, H. W. *Org. Lett.* **2009**, *11*, 4504.
- (5) Kato, M.; Oki, H.; Ogata, K.; Fukuzawa, S. *Synlett* **2009**, 1299.
- (6) Kumar, A.; Samuelson, A. G. *Eur. J. Org. Chem.* **2011**, 951.
- (7) Miura, K.; Tomita, M.; Yamada, Y.; Hosomi, A. *J. Org. Chem.* **2007**, *72*, 787.
- (8) Ruan, Z. M.; Lawrence, R. M.; Cooper, C. B. *Tetrahedron Lett.* **2006**, *47*, 7649.
- (9) Finholt, A. E.; Bond, A. C.; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692.
- (10) Matsuoka, H.; Kondo, K. *Chin. Chem. Lett.* **2010**, *21*, 1314.
- (11) Sousa, S. C. A.; Fernandes, A. C. *Adv. Synth. Catal.* **2010**, *352*, 2218.
- (12) Smith, C. A.; Cross, L. E.; Hughes, K.; Davis, R. E.; Judd, D. B.; Merritt, A. T. *Tetrahedron Lett.* **2009**, *50*, 4906.
- (13) Cabrita, I.; Sousa, S. C. A.; Fernandes, A. C. *Tetrahedron Lett.* **2010**, *51*, 6132.
- (14) Maddani, M. R.; Moorthy, S. K.; Prabhu, K. R. *Tetrahedron* **2010**, *66*, 329.
- (15) Miura, K.; Yamada, Y.; Tomita, M.; Hosomi, A. *Synlett* **2004**, 1985.
- (16) Zhou, S.; Junge, K.; Addis, D.; Das, S.; Beller, M. *Org. Lett.* **2009**, *11*, 2461.
- (17) Sugimoto, O.; Sugiyama, M.; Tanji, K. *Heterocycles* **2010**, *80*, 601.
- (18) Baek, J. Y.; Lee, S. J.; Han, B. H. *J. Korean Chem. Soc.* **2004**, *48*, 220.