

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

Yong-Xiao Li was born in 1986 in Handan, Hebei Province, P. R. of China. She graduated from Hebei University of Science and Technology in 2010 and received her B.Sc degree in Chemistry. Presently, she is working as a postgraduate towards her M.Sc under the supervision of Professor Zhan-Hui Zhang and Qiu-Qing Yang at the Hebei Normal University. Her research interest focuses on the application of nuclear magnetic resonance (NMR) in the Gemini surfactant.

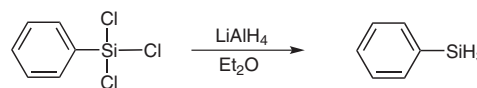
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Introduction

Phenylsilane (PhSiH₃) 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 PhSiH₃ and titanium isopropoxide [Ti(Oi-Pr)₄].⁶ Reductions of organic halides to dehalogenated alkanes with the In(OAc)₃-PhSiH₃ 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

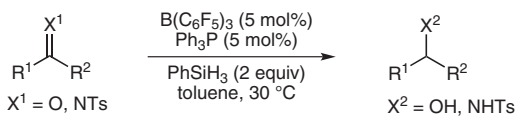


Scheme 1

Abstracts

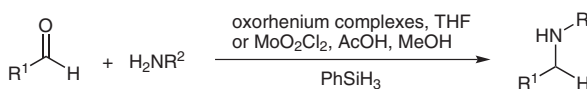
(A) Reduction of Aldehydes, Ketones, Aldimines, and Ketimines:

Matsuoka and Kondo showed that PhSiH₃ can efficiently hydrosilylate aldehydes, ketones, aldimines and ketimines to afford the corresponding reduction products in high yields in the presence of catalytic amounts of Ph₃P and B(C₆F₅)₃.¹⁰



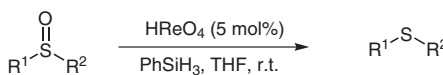
(B) Direct Reductive Amination of Aldehydes:

PhSiH₃ 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, NO₂, CO₂Me, CN, and double bonds.



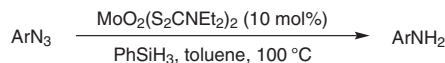
(C) Reduction of Sulfoxides to Sulfides:

Cabrera et al. showed that a large variety of aryl, aryl alkyl, and alkyl sulfoxides can be reduced with PhSiH₃ to the corresponding sulfides catalyzed by HReO₄ in THF in high yield.¹³ This system was also highly chemoselective, tolerating several functional groups such as Cl, NO₂, CO₂R, and double or triple bonds.

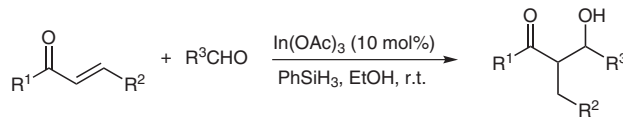


(D) Reduction of Azides to Amines:

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

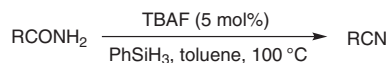
(E) 1,4-Reduction and Reductive Aldol Reactions of α -Enones:

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



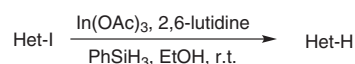
(F) Dehydration of Amides to Nitriles:

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



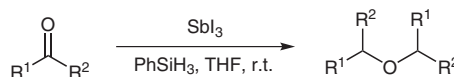
(G) Selective Deiodination of Iodoheterocycles:

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

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