# SYNLETT Spotlight 363

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

## Phenylsilane

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## Introduction

Phenylsilane (PhSiH<sub>3</sub>) 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.<sup>1</sup> 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.<sup>2</sup> It was also found to be an efficient reagent for selective reduction of quinoline to dihydroquinoline,<sup>3</sup> reductive Michael cyclization,<sup>4</sup> and reductive aldol reaction.<sup>5</sup> The reductive coupling of aldimines has been achieved by the use of a combination of  $PhSiH_3$  and titanium isopropoxide  $[Ti(Oi-Pr)_4]$ .<sup>6</sup> Reductions of organic halides to dehalogenated alkanes with the  $In(OAc)_3$ – $PhSiH_3$  system are readily accomplished.<sup>7</sup> It can also act as an in situ carboxylic acid activating agent to prepare carboxamides and peptides from carboxylic acids and amines.<sup>8</sup>

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





## 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  $B(C_6F_5)_3$ .<sup>10</sup>

(B) Direct Reductive Amination of Aldehydes:

PhSiH<sub>3</sub> can be applied as a mild reducing reagent for direct reductive amination of aldehydes to the corresponding secondary amines catalyzed by oxorhenium complexes<sup>11</sup> or molybdenum dioxide dichloride.<sup>12</sup> The protocol tolerates a number of reducible functional groups such as F, Cl, I, OMe, NO<sub>2</sub>, CO<sub>2</sub>Me, 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<sub>3</sub> to the corresponding sulfides catalyzed by HReO<sub>4</sub> in THF in high yield.<sup>13</sup> This system was also highly chemoselective, tolerating several functional groups such as Cl, NO<sub>2</sub>, CO<sub>2</sub>R, and double or triple bonds.

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#### (D) Reduction of Azides to Amines:

PhSiH<sub>3</sub> is also used as the hydride source for chemoselective reduction of azides to the corresponding amines catalyzed by dioxobis(N,N,-diethyldithiocarbamato) molybdenum complex under neutral reaction conditions.<sup>14</sup> This method tolerates a wide variety of reducible functional groups.

(E) 1,4-Reduction and Reductive Aldol Reactions of  $\alpha$ -Enones: Miura et al. found that PhSiH<sub>3</sub> can serve as a mild reducing agent in 1,4-reduction of certain  $\alpha$ -enones, and in intermolecular reductive aldol reactions of  $\alpha$ -enones with aldehydes in the presence of a catalytic amount of In(OAc)<sub>3</sub> in ethanol at ambient temperature.<sup>15</sup>

(F) Dehydration of Amides to Nitriles:

A mild method for the catalytic dehydration of aromatic and aliphatic amides using  $PhSiH_3$  in the presence of catalytic tetrabutylammonium fluoride (TBAF) has been developed.<sup>16</sup>

(G) Selective Deiodination of Iodoheterocycles:

Sugimoto et al. reported that nitrogen-containing  $\pi$ -deficient heterocyclic iodides such as iodoquinolines or iodopyridines were deiodinated by treatment with PhSiH<sub>3</sub> in the presence of In(OAc)<sub>3</sub> and 2,6lutidine to give the corresponding deiodinated heterocycles.<sup>17</sup>

(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.<sup>18</sup> Ketones such as acetone or acetophenone did not give the corresponding dialkyl ethers.

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ΩН

ArN<sub>3</sub>  $\xrightarrow{MoO_2(S_2CNEt_2)_2 (10 \text{ mol}\%)}{PhSiH_3, \text{ toluene, } 100 ^{\circ}C} ArNH_2$ 



RCONH<sub>2</sub> TBAF (5 mol%) PhSiH<sub>3</sub>, toluene, 100 °C RCN



