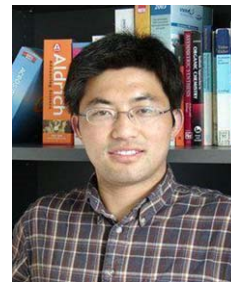


# SYNLETT Spotlight 247

## Trichlorosilane (HSiCl<sub>3</sub>) – A Cheap and Convenient Reducing Agent

Compiled by Zhiguo Zhang



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

Zhiguo Zhang was born in Henan Province, P. R. of China in 1977. He obtained his B.Sc. in English Pharmacy and M.Sc. in Pharmaceutical Chemistry from China Pharmaceutical University, Nanjing. Financed by the DAAD, he commenced his Ph.D. studies at the Justus-Liebig-Universität Giessen, Germany under the supervision of Prof. Dr. Peter R. Schreiner. His research interests focus on the development of novel non-covalent organocatalysts and their application to the synthesis of biologically active molecules.

Institut für Organische Chemie, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, 35392 Gießen, Germany  
E-mail: zhiguo.zhang@org.chemie.uni-giessen.de

Dedicated to my research advisor Prof. Dr. Peter R. Schreiner

### Introduction

Trichlorosilane (HSiCl<sub>3</sub>) is a cheap, stable, and commercially available reagent, which has been widely used as stoichiometric reductant. In general, activators are necessary for HSiCl<sub>3</sub> to reduce efficiently C=C, C=O, C=N, and P=O functionalities. The currently most successful methodologies are based on transition-metal-centered catalyzed hydrosilylation; however, recent advances in the field of organocatalysis have also provided a series of small organic molecules as efficient alternative catalysts

for asymmetric reductions of ketones or imines with HSiCl<sub>3</sub>. In this paper, reductions using HSiCl<sub>3</sub> are summarized.

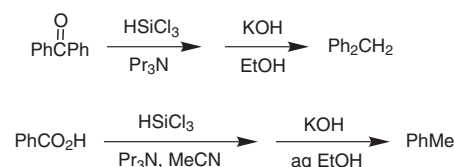
A number of methods are available for the preparation of trichlorosilane in the laboratory, for example, by the reaction of dry HCl gas with silicon (Scheme 1)<sup>1</sup> or with metallic silicides.<sup>2</sup> The title compound is also an abundant byproduct of the industrial Rochow process.<sup>3</sup>



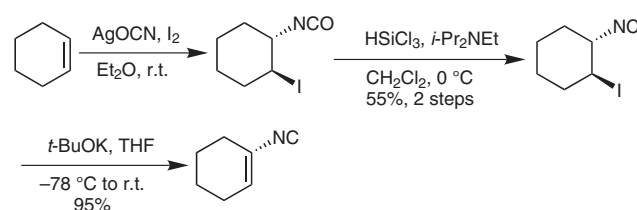
Scheme 1

### Abstracts

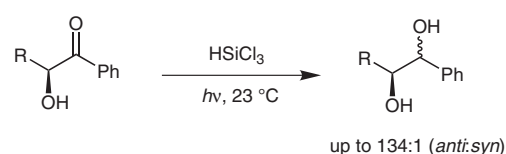
(A) Trichlorosilane has often been used together with tertiary amines to reduce carbonyl groups of aromatic aldehydes, ketones, acids, amides, acid chlorides, and anhydrides to give the corresponding benzylic trichlorosilanes. This transformation was termed a 'reductive silylation' for the replacement of a carbonyl oxygen with H and SiCl<sub>3</sub>.<sup>4</sup> This method provides a new way to form silicon-carbon bonds, and the benzylic trichlorosilane products can be further transformed to toluenes by base treatment.



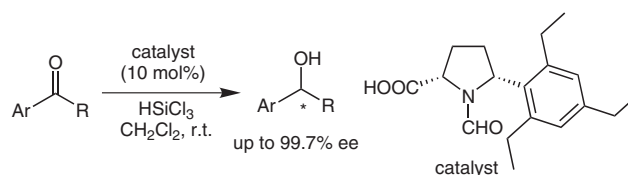
(B) Reduction of isocyanates with HSiCl<sub>3</sub> gives the corresponding isocyanides in high yield under mild conditions.<sup>5</sup> This provides a relatively simple method for the synthesis of vinyl isocyanides from alkenes.<sup>6</sup>



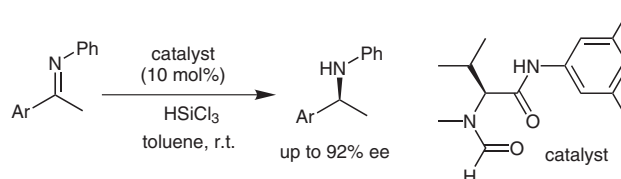
(C) Highly diastereoselective reduction of  $\alpha$ -hydroxy ketones can be achieved using HSiCl<sub>3</sub> as the reductant under neutral free-radical conditions.<sup>7</sup> This reduction provides a diastereoselective, mild, one-electron alternative to the established two-electron methods that employ hydride reagents.



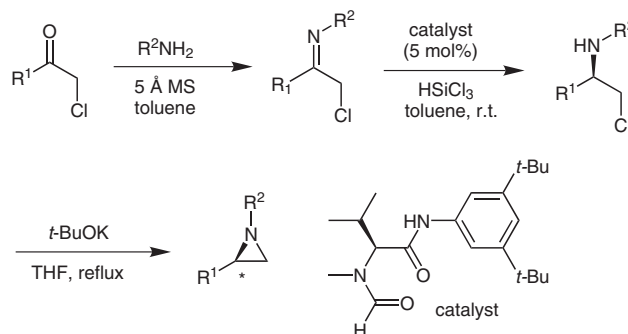
(D) The catalytic enantioselective reduction of aryl ketones by  $\text{HSiCl}_3$  gives the corresponding alcohols with excellent enantioselectivity in the presence of catalytic amounts of *N*-formyl- $\alpha'$ -(2,4,6-triethylphenyl)-L-proline as activator.<sup>8</sup>



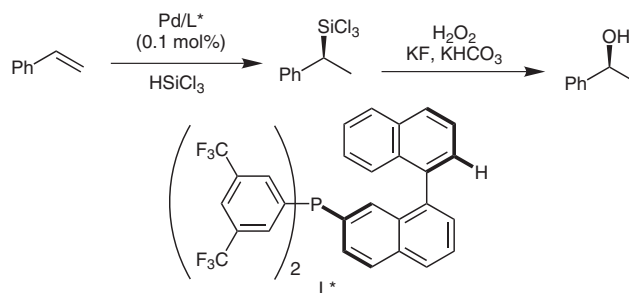
(E) Asymmetric reduction of ketimines with trichlorosilane can be catalyzed by a new *N*-methyl-L-valine derived Lewis basic organo-catalyst, affording the respective secondary amines with high enantioselectivity.<sup>9</sup>



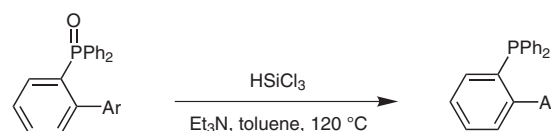
(F) The *N*-methylvaline derived Lewis basic formamide catalyzed reductive amination of  $\alpha$ -chloroketones is a key step in the enantioselective synthesis of 1,2-diarylaziridines that had not been prepared previously as pure enantiomers.<sup>10</sup> This provides an efficient and environmentally friendly methodology for the preparation of enantiopure aziridines.



(G) The preparation of optically active alcohols from prochiral styrenes can be realized by the palladium-MOP complex catalyzed asymmetric hydrosilylation of styrenes with trichlorosilane.<sup>11</sup>



(H) Trichlorosilane is an often-used reducing agent for converting phosphine oxides to phosphines, which play an extremely important role as ligands in homogeneous catalysis.<sup>10</sup>



## References

- (1) (a) Friedel, C.; Ladenburg, A. *Justus Liebigs Ann. Chem.* **1867**, *143*, 118. (b) Buff, H.; Wöhler, F. *Justus Liebigs Ann. Chem.* **1857**, *104*, 94.
- (2) (a) Taylor, A. G.; Walden, G. *J. Am. Chem. Soc.* **1944**, *66*, 842. (b) Ruff, O.; Albert, K. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 2222. (c) Warren, F. *Ber. Dtsch. Chem. Ges.* **1889**, *22*, 657. (d) Gattermann, L. *Ber. Dtsch. Chem. Ges.* **1889**, *22*, 190.
- (3) Rochow, E. G. *J. Am. Chem. Soc.* **1945**, *67*, 963.
- (4) Benkeser, R. A. *Acc. Chem. Res.* **1971**, *4*, 94.
- (5) Brooks, C. J. W.; Ekhatto, I. V. *J. Chem. Soc., Chem. Commun.* **1982**, 942.
- (6) Baldwin, J. E.; Yamaguchi, Y. *Tetrahedron Lett.* **1989**, *30*, 3335.
- (7) Enholm, E. J.; Schulte, J. P. *J. Org. Chem.* **1999**, *64*, 2610.
- (8) Matsumura, Y.; Ogura, K.; Kouchi, Y.; Iwasaki, F.; Onomura, O. *Org. Lett.* **2006**, *8*, 3789.
- (9) Malkov, A. V.; Mariani, A.; MacDougall, K. N.; Kočovský, P. *Org. Lett.* **2004**, *6*, 2253.
- (10) Malkov, A. V.; Stončius, S.; Kočovský, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 3722.
- (11) Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozumi, Y. *J. Org. Chem.* **2001**, *66*, 1441.