

SYNLETT Spotlight 129

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

Polymethylhydrosiloxane (PMHS)

Compiled by Kula Kamal Senapati

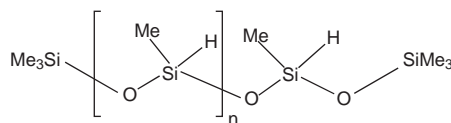
Kula Kamal Senapati was born in Assam, India. He received his first degree in Chemistry from N.N.S. College, Titabar and obtained his Master degree in Chemistry from Gauhati University, Guwahati, Assam, India in 2002. Then he joined in Tocklai Tea Research Association (TRA), India as research fellow. After 2 years experience as analyst in TRA, he moved to Tezpur University in 2004. He is currently pursuing research under the supervision of Dr. A. J. Thakur, faculty of the Department of Chemical Sciences, Tezpur University, Assam, India in the area of synthetic organic chemistry. His research interest is in the area of synthesis of bioactive heterocycles with a greener approach.

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Introduction

Polymethylhydrosiloxane (PMHS), a silicon industry by-product¹ incorporating with various catalysts including Sn, Ti, Pd, Zn, Zr and Cu, is found to be effective as an excellent alternative reducing agent in organic synthesis. It is inexpensive, commercially available, non-toxic, biodegradable and stable to air and moisture, which makes it an attractive reagent of choice. The reagent is of low viscosity and soluble in most organic solvents.²



Besides its recognized application in chemoselective as well as regioselective³ reductions, it finds uses in asymmetric reduction of different species such as acetophenones⁴ and benzophenone derivatives,⁵ imines,⁶ and conjugated double bonds.^{7a,b}

In catalytic reduction processes using PMHS in combination with metal catalysts, the catalysts play the role as hydride transferring agents.^{2,8} Some nucleophiles like fluoride^{1,8,9} also act as catalyst in addition to metals.

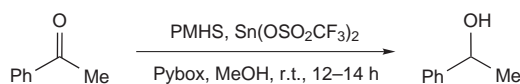
Being a convenient chemoselective reagent for different ketones, imines and phosphine oxides, it has also been used in reductive cleavage of carbon–halogen^{1,9} as well as carbon–sulfur bonds.¹

Abstracts

(A) Reduction of Ketones.

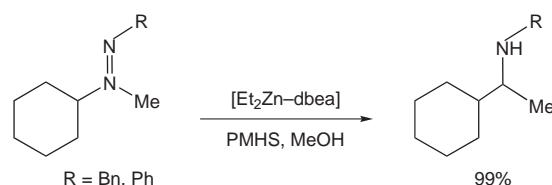
Ketones can be reduced directly to alcohols by PMHS and tin(II) triflate/pybox systems with moderate enantioselectivity.¹⁰ This reaction is an excellent way for chemoselective preparation of α -hydroxy esters from α -keto esters.

Chelucci et al. have developed a number of tin(II) complexes with different pyridine derivatives to be used as chiral catalyst with PMHS for effective reduction of acetophenone to chiral alcohol under the same reaction conditions.⁴ Benzophenones can also give chiral alcohols on reduction with chiral diamine–zincdiol complexes and PMHS.⁵



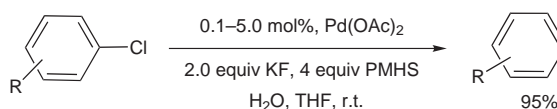
(B) Reduction of Imines.

A number of functionalized imine compounds can be reduced with PMHS and 1:1 mixture of diethylzinc and *N,N'*-dibenzylethylenediamine (dbee) to amines.¹¹ Recently, a very useful method has been reported that a number of catalyst–chiral ligand combinations and PMHS convert imines into chiral amines in good yields.⁶

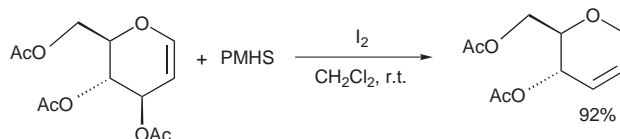


(C) *Hydrodehalogenation of Aryl Chlorides.*

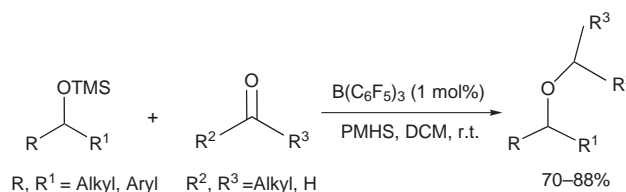
PMHS is an attractive alternative for hydrodehalogenation of aryl chlorides. Using catalytic amounts of Pd(II) acetate with PMHS and aqueous KF, a variety of chloroarenes can be reduced rapidly at room temperature with high yield. The reaction is chemoselective towards ketones, amides, esters, nitriles, ethers and amines, fluorides and borate esters.⁸ In a similar fashion, aryl bromides and iodides can also be hydrodehalogenated selectively with $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ with PMHS activated by KF.⁹

(D) *Glycols to Dihydropyran Derivatives.*

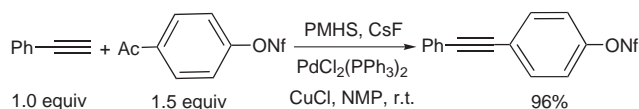
PMHS with molecular iodine promotes the conversion of various glycols to their corresponding dihydropyran derivatives in good yields and rates. Mechanistically, iodine first reacts with PMHS to give trimethylsilyl iodide and an unstable reducing agent and the latter can reduce the glycols.¹²

(E) *Synthesis of Ethers.*

Various types of symmetrical and unsymmetrical ethers may also be synthesized by using PMHS activated by $\text{B}(\text{C}_6\text{F}_5)_3$ catalyst. The reaction occurs through the reductive coupling of various TMS ethers and carbonyl compounds.¹

(F) *Sonogashira Couplings.*

An important synthetic utility of PMHS is in the Sonogashira coupling reaction.¹³ These are facilitated by the use of four reagents namely PMHS, CsF, CuX and palladium catalyst under mild, relatively neutral, amine-free conditions. In a typical reaction an alkyne is treated with 1.5 equivalents of nonaflate or triflate, PMHS (2 equiv), CsF (5 equiv), CuCl or CuTC (5 mol%) and bis(triphenylphosphine)palladium dichloride (5 mol%). Compared to traditional Sonogashira reaction, this reaction gives superior results with no homocoupled dialkynes being formed.



References

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