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)

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Introduction

Polymethylhydrosiloxane (PMHS), a silicon industry byproduct 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.

Besides its recognized application in chemoselective as well as regioselective reductions, it finds uses in asymmetric reduction of different species such as acetophenones and benzophenone derivatives, imines, and conjugated double bonds.

In catalytic reduction processes using PMHS in combination with metal catalysts, the catalysts play the role as hydride transferring agents. Some nucleophiles like fluoride 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 as well as carbon–sulfur bonds.

Abstracts

(A) Reduction of Ketones.
Ketones can be reduced directly to alcohols by PMHS and tin(II) triflate/pybox systems with moderate enantioselectivity. This reaction is an excellent way for chemoselective preparation of a-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. Benzophenones can also give chiral alcohols on reduction with chiral diamine–zinc diol complexes and PMHS.

(B) Reduction of Imines.
A number of functionalized imine compounds can be reduced with PMHS and 1:1 mixture of diethylzinc and N,N’-dibenzylethylene-diamine (dbea) to amines. 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.

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(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. In a similar fashion, aryl bromides and iodides can also be hydrodehalogenated selectively with (Ph₂P)₂PdCl₂ with PMHS activated by KF.⁹

(D) Glycals to Dihydropyran Derivatives.
PMHS with molecular iodine promotes the conversion of various glycals 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 glycals.¹²

(E) Synthesis of Ethers.
Various types of symmetrical and unsymmetrical ethers may also be synthesized by using PMHS activated by B(C₆F₅)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