Hexamethyldisilane

Compiled by Audrey Giros

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Introduction

Hexamethyldisilane (Me₃SiSiMe₃, CAS: 1450-14-2) is a hygroscopic colorless and odorless liquid which absorbs in the far UV region.¹ In organic chemistry it is often used as an alternative of chlorotrimethylsilane or hexamethyldisilazane silylating agents. Hexamethyldisilane also promotes reduction and can act as a co-catalyst. It was recently revealed to be a key reagent in the anomerization of carbohydrates. Additionally, hexamethyldisilane can be a valuable starting material for the synthesis of sila-substituted organic and biologically active molecules. In the semiconductor industry this oligoorganosilane is employed as a precursor in the Chemical Vapor Deposition process.² Hexamethyldisilane is commercially available, but it can be easily synthesized by reaction of chlorotrimethylsilane with an alkali metal in organic solvents (Scheme 1).³ This method is particularly efficient and cheap.⁴

Scheme 1 Efficient preparation of hexamethyldisilane in laboratory

Abstracts

(A) Hexamethyldisilane as a Source of Trimethylsilylanion:
In the stereoselective synthesis of 3-trimethylsilyldihydrocarvone developed by Blay et al., hexamethyldisilane is used as a precursor of the nucleophilic species 1.⁵ The Michael addition of Me₃SiLi on (R)-(–)-carvone 2 proceeds in a very high yield (91%). This optimized procedure for the cleavage of a Si–Si bond is carried out under inert atmosphere, using hexamethylphosphoric triamide (HMPA) in a specific proportion with three temperature ranges.⁶

(B) New C–C and C–Bond Activation:
Rhodium-catalyzed silylation of the C–CN bond from aryl nitrides⁷ and palladium-catalyzed allylic C–H silylation⁸ have been performed with hexamethyldisilane assistance. From the allylic substrates 1, excellent regio- and good stereoselectivities were observed with a high level of functional group tolerance.
A Useful Allylic C–OH Activation:
Szabó and co-workers described an inexpensive procedure for the regioselective synthesis of allylsilanes from allylic alcohols under palladium catalysis. With hexamethyldisilane, the silylation proceeds smoothly under mild conditions (50–60 °C, without an inert atmosphere, no addition of acid or additive). Diverse functional groups (hydroxy-, methoxy- and nitrophenyl, ether and ester) and cyclic scaffolds like 1 are tolerated.

Hexamethyldisilane as a Silicon Backbone:
Starting from hexamethyldisilane, Tacke and co-workers build silicon analogues of biologically active molecules. The odorant 1,2,3-trisilaindane 3 is synthesized via a multistep procedure including a chloromethylation step by ring opening of a silylated carbohydrate intermediate. It is noteworthy the trisila-phantolide derivative 3 displays a creamy-lactonic odor in contrast with the musk odor of its carbon analogue.

Hexamethyldisilane/I₂ as a Precursor of TMSI:
Malik et al. demonstrated that the hexamethyldisilane–iodine system mediated anomerization of alkyl glycoside in quantitative yield. Indeed the in situ formation of Me₃Si– species leads to the anomerization step by ring opening of a silylated carbohydrate intermediate.

Hexamethyldisilane as Co-Catalyst:
Hexamethyldisilane promotes reduction of alkynes and enones, desulfonation and Mizoroki–Heck-type coupling of arylnitriles to vinylsilanes. In these metal-catalyzed reactions, the disilane acts as a ‘counterattack reagent’ by successive nucleophilic attacks of the resulting Me₃Si– and Me₃SiO– species. Bis(trimethylsilyl)ether is generated as side product. For instance, N-(phenylethylidene)hydroxylamine 2 is formed in good yield (73%).

Hexamethyldisilane as a Reducing Agent:
Under mild conditions nitroalkanes can be mono-deoxygenated to ketoximes by treatment of the corresponding nitronate anions with hexamethyldisilane. The cleaved disilane reacts as a ‘counterattack reagent’ by successive nucleophilic attacks of the resulting Me₃Si– and Me₃SiO– species. Bis(trimethylsilyl)ether is generated as side product. For instance, N-(phenylethylidene)hydroxylamine 2 is formed in good yield (73%).

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References
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