Azidotrimethylsilane

Compiled by Bao-Le Li

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Introduction

Azidotrimethylsilane (TMSN₃) is a clear, colorless, quite stable organosilane reagent and decomposes slowly even at 200 °C. It is considered a very convenient and safer replacement for hydrazoic acid as an azide source in many reactions.¹ It has been used for the synthesis of aryl 1,2,3-triazoles,²⁻⁵ tetrazoles,⁶⁻⁷ functionalized bicyclic triazoles,⁸ azides,⁹⁻¹⁵ and N-tetrazolated diamine derivative.¹⁶ In addition, azidotrimethylsilane has been employed for the preparation of proline-derived chiral aminotriazole ligands.¹⁷ It was found to be a useful reagent for the aziridine ring opening to obtain azidomethyl-substituted pyrrole precursors,¹⁸ or kinetic resolution of monosubstituted epoxide for the synthesis of optically pure 1-azido-2-trimethylsiloxyalkanes.¹⁹

Abstracts

(A) One-Pot Rearrangement of Carboxylic Acids to Carbamates:
Augustine and co-workers have developed a simple and efficient procedure for a one-pot conversion of carboxylic acids into carbamates through the Curtius rearrangement by employing propylphosphonic anhydride (T3P®) and azidotrimethylsilane in the presence of an alcohol.²⁰

(B) Preparation of α-Azido Oximes:
Sukhorokov and co-workers reported that α-azido oximes could be obtained from aliphatic nitro compounds via interaction of N,N-bis(silyloxy) enamines with trimethylsilylazide.²¹

(C) Synthesis of Chiral Terminal 1,2-Diamines:
A regioselective ring opening of aziridines with TMSN₃ has been developed and the azido group and the double bond were reduced by LiAlH₄ to give chiral terminal 1,2-diamines in high yields.²²

(D) Synthesis of Fullereryl Azide:
In the presence of a Lewis acid, the first fullereryl azide compound has been synthesized via addition of azidotrimethylsilane effectively to a cage-opened fullerene derivative.²³
(E) Synthesis of Tetrazoles:
Direct conversion of 1,3-diarylprop-1-ones into tetrazole was demonstrated in the presence of azidotrimethylsilane and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) using CuI as the catalyst at 80 °C in MeCN.24

(F) Synthesis of Triazolothiadiazepine-1,1-dioxides:
Recently, a one-pot synthesis of triazolothiadiazepine-1,1-dioxides via copper-catalyzed [3+2] cycloaddition has been achieved in the presence of azidotrimethylsilane and Hüning’s base (DIPEA).25

(G) Azidation of Hemiketals:
Azidotrimethylsilane is also used as an efficient azide source of reaction oxidative azidation of aldehydes (H)

(D) Oxidative Azidation of Aldehydes:
In addition to the above cases, azidotrimethylsilane can also be applied as an azide source of reaction oxidative azidation of aldehydes in the presence of 1,3-dimethyltriazolium iodide, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 3,3,5,5-tetramethyl-2-pyrrolidinedione-quinone.27

References
