Bromotrimethylsilane (TMSBr)

Compiled by Agnieszka Matusiak

Agnieszka Matusiak was born in Łęczyca, Poland in 1986. She graduated from the University of Łódź, Poland in 2010 working in the group of Professor Jarosław Lewkowski. Currently, she is pursuing her Ph.D. in the same group. Her current research is focused on new aminophosphonates, which include heterocyclic aromatic five-membered rings (furans, pyrroles, thiophenes), their cytotoxic and biological properties.

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Introduction

Bromotrimethylsilane (TMSBr) is an organosilicon compound, a silyl halide with the formula C₃H₉SiBr. Under standard conditions, it is a colorless liquid, which is stable in the absence of water. It is used as a powerful silylating agent and as a catalyst for the cleavage of ethers¹ and phosphonic/phosphoric acid alkyl esters.

Carbon–Silicon bonds (186 pm) are longer and weaker than carbon–carbon bonds (154 pm), with bond dissociation energies of 451 kJ/mol (C–Si) vs. 607 kJ/mol (C–C). The C–Si bond is polarized towards carbon due to the lower electronegativity of silicon (Si 1.90 vs. C 2.55). Some examples using the bond polarization of organosilanes are the Hosomi–Sakurai reaction,² the Hiyama coupling,³ and the Tamao–Kumada–Fleming oxidation⁴,⁵,⁶ (certain alkyl silanes can be oxidized to alcohols).

Preparation

TMSBr can be prepared from silicon tetrabromide by nucleophilic substitution of three of the bromide groups with a nucleophillic methyl source such as methyllithium. Another method uses consecutive Grignard reactions with metal alkyl halides. These are particularly important reactions due to the use in the production of organosilicon compounds, which can be converted into siloxanes.⁷

Scheme 1 The Grignard reaction used to prepare TMSBr

Abstracts

(A) The chemoselective and efficient deprotection of (primary, secondary and aromatic) silyl ethers using catalytic amounts of TMSBr in various solvents has been reported.⁸ The best results were obtained using methanol as the solvent. A bis-[tert-butyldimethylsilyl (TBS)] ether 1 was effectively cleaved to afford the corresponding diol 2 in 92% yield.

(B) An efficient Prins cyclization reaction to construct tetrasubstituted 2,6-cis-4,5-dibromo tetrahydropyran (THP) rings with high stereoselectivity in good yields has been developed.⁹ The cyclization of γ-brominated homoallylic alcohol (Z)-3 and cyclohexane carboxaldehyde (4) proceeded smoothly with 1.2 equivalents of TMSBr to afford 5 in 95% yield as a single isomer. THP product 5 was selected to perform a series functionalizations, such as debromination and further epoxidation or hydroxylation.¹⁰–¹²

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A novel straightforward synthetic method for the selective construction of 2,2′-bipyroles and even 2,3′-bipyroles has been developed. An effective oxidative coupling reaction of electron-rich pyroles was performed using hypervalent iodine(III) reagents, such as phenyliodine bis(trifluoroacetate) (PIFA), and TMSBr. The product was obtained in 75% yield at −40 °C.

Loh and co-workers reported an efficient synthesis of 2,3-disubstituted THFs using SnBr4-promoted oxonium-hydropyran. Spivey and co-workers have reported the diastereoselective synthesis of the aminophosphonic acid by diastereoselective addition of dialkyl phosphites to the azomethine bond of the chiral Schiff base, and then converting it into the acid. In this case, the bulky silicon-substituted allenic alcohol promoted by indium triflate and TMSBr. The use of a combination of FeCl3, TMSBr, and CH2Br2 led to the bromotetrahydropyran in a regioselective and efficient manner.

Martin, Padrón and co-workers have developed the first iron-promoted oxa- and aza-Prins cyclization of γ,δ-unsaturated alcohols and amides using readily available iron salts [FeBr3, FeCl3 or Fe(acac)3] and trimethylsilyl halides (TMSCl, TMSBr). The reaction proceeded smoothly to afford the trans product with excellent diastereoselectivity (>99:1).

References