**SYNLETT Spotlight 443**

**Bromotrimethylsilane (TMSBr)**

Compiled by Agnieszka Matusiak

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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 ethers 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, the Hiyama coupling, and the Tamao–Kumada–Fleming oxidation (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 nucleophilic 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 silicones.

**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. 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. 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.

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(C) 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 7 was obtained in 75% yield at –40 °C.

(D) Loh and co-workers reported an efficient synthesis of 2,3-disubstituted THFs using SnBr4-promoted oxonium cyclization using carboalkoxyl allenic alcohol promoted by indium triflate and TMSBr. When the bulky silicon-substituted allenic alcohol 8 was used under these conditions, the reaction proceeded smoothly to afford the 2,6-trans product 10 with excellent diastereoselectivity (>99:1).

(E) Martin, Padrón and co-workers have developed the first iron-promoted oxa- and aza-Prins cyclization of γ,δ-unsaturated alcohols and aminoalcohols using readily available iron salts [FeCl3, Fe(acac)3] and trimethylsilyl halides (TMSCl, TMSBr). The use of a catalytic amount of iron(III) chloride and SnBr4 in CH2Cl2, –78 °C, 4 h led to the formation of only two of the three possible isomeric products (15a and b).

(F) Spivey and co-workers have reported the diastereoselective synthesis of 2,3-disubstituted THFs using SnBr4-promoted oxonium Prins cyclizations. (E)-4-Phenylbut-3-en-1-ol (14) as the homoallylic alcohol component reacted with 2-naphthyl carboxaldehyde as the aldehyde component in the presence of SnBr4 and TMSBr as Lewis acid promoters in CH2Cl2. This reaction led to the formation of only one of the three possible isomeric products (15a and b).

(G) Lewkowski and Karpowicz described the isolation of the main diastereomer of the aminophosphonic acid 17 which was obtained by diastereoselective addition of dialkyl phosphites to the azomethine bond of the chiral Schiff base 16. This method is based on obtaining silylated esters of phosphonic acid in the reaction of TMSBr and then converting it into the acid. In this case (17), the formation of only one diastereomer was observed.

References


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