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, pyroles, thiophenes), their cytotoxic and biological properties.

Department of Organic Chemistry, Faculty of Chemistry, University of Łódź, Tamka 12, 91-403 Łódź, Poland
E-mail: agusk@poczta.fm

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 organo-silanes 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.

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. 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 tetra-substituted 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 carbboxaldehyde (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.
(C) A novel straightforward synthetic method for the selective construction of 2,2′-bipyroles and even 2,3′-bipyroles has been developed.\(^1\) An effective oxidative coupling reaction of electron-rich pyrroles was performed using hypervalent iodine(III) reagents, such as phenyliodine bis(trifluoroacetate) (PIFA), and TMSBr. The product 7 was obtained in 75% yield at \(-40^\circ C\).

(D) Loh and co-workers\(^1\) reported an efficient synthesis of 2,6-trans-pyran motifs via Prins 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) Martín, Padrón and co-workers\(^1\) have developed the first iron-hydropyran (F) Spivey\(^1\) and co-workers have reported the diastereoselective (G) Lewkowski and Karpowicz\(^1\) described the isolation of the main two of the three possible isomeric products (\(\text{Et} \)), \(\text{NaphCHO}\) + R, \(\text{Naph CO}_2\text{Me}\). As phenyliodine bis(trifluoroacetate) (PIFA), and TMSBr. The product of 2,6-trans-pyrrole was performed using hypervalent iodine(III) reagents, such as phenyliodine bis(trifluoroacetate) (PIFA), and TMSBr. The product 7 was obtained in 75% yield at \(-40^\circ C\).

(F) Spivey\(^1\) and co-workers have reported the diastereoselective synthesis of 2,3-disubstituted THFs using SnBr\(_2\)-promoted oxonium-Prins cyclizations. (E)-4-Phenylbut-3-en-1-ol (14) as the homallylic alcohol component reacted with 2-naphthyl carboxaldehyde as the aldehyde component, and then converting it into the acid. In this case (17), the formation of only two of the three possible isomeric products (15a and b).

(G) Lewkowski and Karpowicz\(^1\) described the isolation of the main diastereomer of the aminoazaphosphinonic 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 CH\(_2\)Br\(_2\) led to the bromotetrahydropyran 13b in a regioselective and efficient manner.

References