Translated from *Uspekhi Khimii*, **56**, 609-628 (1987) U.D.C. 547.245

New Silylating Agents. Methods of Synthesis and Properties

M.D.Mizhiritskii and Yu.A.Yuzhelevskii

The methods of synthesis and properties of new silylating agents are examined and the results of studies on thier application in organic synthesis and in analytical chemistry are surveyed.
The bibliography includes 223 references.

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I. INTRODUCTION

Organosilicon compounds have found extensive applications in organic[1-13] and analytical[14-16] chemistry. One of the most important fields in which silicon-containing reagents are applied involves their use for silylation. The term "silylation" has come to be understood as the introduction of a triorganylsilyl, usually trimethylsilyl group, into the molecules of organic compounds instead of a mobile ("active") hydrogen atom or the metal atom replacing the latter.[14,17] The triorganylsilyl group is introduced into the organic molecule with the aid of the so called silylating agents, i.e. agents containing an Si–X bond, where X = O, N, S, C, or Hal, which is reactive with respect to a proton donor.

Silylation makes it possible to modify widely the physical and chemical properties of organic and organoelemental compounds: to protect or block certain reaction centres, to increase reactivity, to improve the solubility of substances in non-polar and weakly polar solvents, to reduce or to eliminate the possibility of the formation of hydrogen bonds, and to increase the volatility and stability of compounds.[14,18,19] Silylation is used for the purification of organic and organoelemental substances and also for their identification by physicochemical methods.[14,18,19]

Pierce's monograph[14] contains information about silylating agents and surveys data on the silylation of various classes of organic compounds published up to 1967. Later reviews,[17, 18,20-25], devoted to a different aspect of silylation, also present the characteristics of silylating compounds.

In connection with the synthesis of a series of new effective silylating agents (silyl donors) and also the expansion of their applications, it became necessary to give a systematic account of and to survey data published mainly during the last 10 years. The present review is devoted to this topic.

II. SYNTHESIS AND PROPERTIES OF SILYLATING AGENTS

In recent years silylation has become an increasingly important method in synthetic organic chemistry, simplifying and improving the procedures for the preparation of many complex substances; many silylating agents, such as chlorosilanes and silazanes, are used in the large-scale industrial manufacture of antibiotics,[26,27] organosilicon monomers and polymers,[28] etc. Other silylating agents—silylated amines, amides, urea, sulphonic acids, and certain others—are widely employed in preparative synthesis.

Bearing in mind that silylation takes place with cleavage of the Si–X bond by the proton donor (HY), it is natural to arrange the silylating agents in groups in terms of the character of this bond.

1. Halogenosilanes (R_3Si–Hal)

In this group of silyl donors, chlorotrimethylsilane, which is widely used in industry, is most important.[28] The methods of its synthesis and also its silylating properties have been examined in books[14,28] and reviews.[17,20,21]

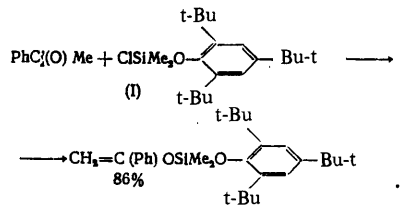
At the same time, the high sensitivity of the Me_3Si–O bond to hydrolysis, to attack by many nucleophiles, and also to hydrogenolysis[29] limits its employment in organic synthesis as a protecting group.[30,31] For this reason, silylating agents with bulkier groups at the silicon atom, for example t-butylchlorodiphenylsilane,[32] chlorotriisopropylsilane,[33,34] and especially t-butylchlorodimethylsilane, first used by Stork and Hudrlik,[35] have come to be employed more frequently in recent times. t-$BuMe_2SiCl$ is synthesised in accordance with the following scheme:[36,37]

$$Me_2SiCl_2 + \text{t-BuLi} \rightarrow \text{t-Bu}Me_2SiCl + LiCl\,.$$

The t-$BuMe_2Si$–O bond is more resistant to hydrolysis than the Me_3Si–O bond (by a factor of 10^4) [38-40] and "withstands" reactions such as hydrogenolysis,[36] mesitylation,[41] phosphorylation,[42] reduction by diisobutylaluminium hydride,[46] oxidation by chromic acid in pyridine[43,44] or by ruthenium tetroxide,[44] and treatment by potassium t-butoxide in dimethylformamide (DMF),[45] Grignard[44] and Wittig[36] reagents, organocopper reagents,[46] and lithium in liquid ammonia.[44] The above group can be readily introduced into the organic molecule in the presence of imidazole,[47,48] *N*-dimethylaminopyridine,[49] or 1,8-diazabicyclo[5.4.0]undec-7-ene [50] as catalysts, after which it can be readily removed with the aid of sources of fluoride ions,[28] for example $Et_3N.HF$,[47] Bu_4NF,[51] KF/18-crown-6 ether,[31] and CsF/diglyme.[47] Bu_4NHSO_4/NaOH is sometimes used instead of tetrabutylammonium fluoride:[52]

$$ROH \xrightarrow[\text{imidazole/DMF}]{\text{t-Bu}_2Me_2SiCl} ROSiMe_2Bu\text{-t} \xrightarrow[THF]{Bu_4NF} ROH\,.$$

The 2,4,6-tri(t-butyl)phenoxydimethylsiloxy-group is even more resistant to the action of acids and bases. It is introduced into the organic molecule by treatment with the corresponding chlorosilane in the presence of sodium iodide and triethylamine in acetonitrile and is removed with the aid of potassium fluoride on celite:[53]



The chlorosilane (I) is a stable crystalline substance. It is obtained in 93% yield by the reaction of dichlorodimethylsilane with 2,4,6-tri(t-butyl)phenol and triethylamine on refluxing in acetonitrile.[53]

Silylation takes place extremely effectively in the presence of lithium sulphide in a polar medium:[54]

$$ROH + ClSiMe_2R' \xrightarrow[25^\circ]{Li_2S/MeCN} \underset{70-95\%}{ROSiMe_2R'} ;$$
$$R' = Me,\ t\text{-}Bu.$$

Bromotrimethyl- and especially iodotrimethyl-silanes are very active silylating agents;[55-58] they are obtained by cleaving the Si–O, Si–C, and other bonds with halogen, hydrogen halides, or the corresponding salts:[59-63]

$$Me_3SiOPh + Br_2 \xrightarrow{cat.} Me_3SiBr ;$$
$$cat. = Zn, Al, Cu, Mg, Sn, Fe ;$$
$$(Me_3Si)_2O \xrightarrow{AlI_3 \text{ or } Al/I_2} Me_3SiI + AlOI ;$$
$$Me_3SiCH_2CH{=}CH_2 \xrightarrow{I_2} Me_3SiI .$$
$$Me_3SiSePh \xrightarrow{I_2} Me_3SiI .$$
$$Me_3SiSiMe_3 \xrightarrow{I_2} Me_3SiI .$$

However, Me_3SiBr and Me_3SiI are not often used for silylation because many functional groups are decomposed by them, for example, iodotrimethylsilane cleaves oxirans,[64,65] hydroxycyclanes,[66-68] ethers,[69,70] esters,[71-73] acetals, ketals,[73] etc.[74-78]

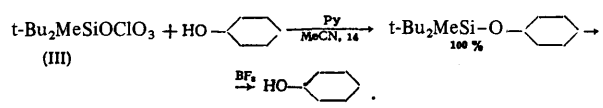
2. Reagents Containing the R_3SiO Group

Among silylating agents containing the Si–O bond, the most readily available compound is hexamethyldisiloxane. It is obtained by the hydrolysis of chlorotrimethylsilane.[28] As early as 1960,[79] it was shown that, in the presence of alkaline or acid catalysts, hexamethyldisiloxane is cleaved by alcohols and phenols, but, until recently it was believed that $(Me_3Si)_2O$ has no significant value as a silylating agent. The results of the study by Pinnick et al.[80] disproved this established view. It was found that the use of the pyridinium salt of toluenesulphonic acid Py.TosOH (II) greatly increases the effectiveness of hexamethylsiloxane as the silyl donor and makes it possible to obtain silyl ethers in yields up to 90%:

$$(Me_3Si)_2O + ROH \xrightarrow[\Delta,\ C_6H_6]{(II)} \underset{70-90\%}{ROSiMe_3} .$$

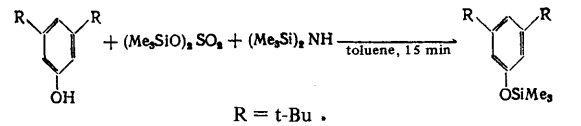
The silyl esters of inorganic acids are sometimes used as silylating agents: silyl perchlorates[13] and bis(trimethylsilyl) sulphate.[19]

Silyl perchlorates, for example compound (III), are obtained from chlorosilane and silver perchlorate[19] and are used to introduce bulky protecting groups [di(t-butyl)methylsilyl groups]:[81]



They are also used as highly selective reagents for the removal of t-butoxycarbonyl groups from peptides.[82]

Bis(trimethylsilyl) sulphate, which is used to silylate OH- and/or NH-containing biologically active compounds, is usually employed in combination with hexamethyldisilazane or *N*-dialkylaminotrimethylsilane:[83]



R = t-Bu .

The interaction of bis(trimethylsilyl) sulphate with urea leads to trimethylsilyl isocyanate as a result of the decomposition of the thermally unstable trimethylsilylurea:[84]

$$(Me_3SiO)_2SO_2 + (NH_2)_2CO \xrightarrow{180^\circ} Me_3SiNCO + (NH_4)_2SO_4 .$$

Silylation of alkali metal nitrates affords trimethylsilyl nitrates:[85]

$$\underset{85\%}{(Me_3SiO)_2SO_2 + KNO_3 \rightarrow Me_3SiONO_2} + K_2SO_4 .$$

It is noteworthy that bis(trimethylsilyl) sulphate is also used as a sulphonating agent. Its interaction with aromatic compounds, pyridine, and thiophen leads to the corresponding sulpho-derivatives,[86,87] for example:

The silyl ethers of enols $R_3SiOC{=}C\langle$ are effective reagents for the silylation of alcohols, carboxylic acids, and certain mercaptans, such as thiophenol:[88-90]

$$\underset{(IV)}{Me_3SiOCR{=}CR'R''} + RXH \rightarrow \underset{86-99\%}{Me_3SiXR} + R'R''CHC(O)R .$$

However, with the aid of silylenols (IV) it is impossible to silylate amides and amines (Schiff bases are formed), ephedrine (oxazolidine is formed), and alkane-thiols (the yield of the trimethylsilyl derivative of 2-mercaptoethanol did not exceed 5%). In addition it has been shown[91] that, in the case of unsaturated alcohols and phenols, another reaction pathway can operate, i.e. the proton donor can add to the double bond of the silylenol:

$$CH_2{=}CHOSiMe_3 + ROH \rightarrow MeCH(OR)OSiMe_3 .$$

An analogous result has been obtained also for acids.[92] Despite the limiting applicability of silylenols in the silylation of NH- and SH-containing compounds, they are widely used in organic synthesis.[1,2,19,93,94] The electrophilic reactions of these compounds make it possible to obtain the vast majority of α-functional derivatives of carbonyl compounds. The oxidation and ozonolysis of silylenols lead to α-hydroxyderivatives.

The reactions of organosilicon ethers of enols (IV) with carbenes lead to the corresponding derivatives of siloxycyclopropane, from which it is possible to obtain in their turn various substituted cyclopropanes and products resulting from the opening or rearrangement of the cyclopropane ring. The C=C–OSiR$_3$ system participates in the [2 + 2]-, [3 + 2]-, and [4 + 2]-cycloaddition reactions with formation of various cyclic adducts, which are important for the synthesis of biologically active substances.[1] The methods of synthesis of silylenols have been surveyed in a number of reviews.[1,2,19,93,94]

The side reactions accompanying silylation with the aid of silylenols can be avoided by employing the *O*-trimethylsilyl *O*-methyl acetal of methylketen, obtained by the successive interaction of ethyl acetate with lithium diisopropylamide and chlorotrimethylsilane:[95,96]

$$MeCOOEt \xrightarrow[2)\ Me_3SiCl]{1)\ iso\text{-}Pr_2NLi} MeCN{=}C(OMe)OSiMe_3 \xrightarrow[MeCN\ or\ CH_2Cl_2,\ 15-50^\circ C]{RXH} RXSiMe_3 ;\quad 95-99\%$$

$$RXH = PhOH,\ PhCH_2OH,\ 3,4,5\text{-}(MeO)_3C_6H_2COOH,\ PhSH,\ PhCH_2SH,\ C(O)C_6H_4C(O)NH$$

The introduction at the oxygen atom of substituents capable of weakening the $(p-d)_\pi$ bonding between the silicon and oxygen atoms and of delocalising the negative charge in the transition state made it possible to obtain a series of new effective silyl donors, among which *N*-alkyl-substituted trimethylsilyl carbamates and trimethylsilyl trifluoromethanesulphonate (trimethylsilyl triflate) are most widely used.

The readily available trimethylsilyl *NN*-dialkylcarbamates exhibit effective silylating properties especially in relation to alcohols, phenols, and acids,[97] the reactions being autocatalytic:[98]

$$R_2NC(O)OSiMe_3 + R'OH \rightarrow R'OSiMe_3 + R_2NH + CO_2 ;\quad 75-95\%$$

R = Me; R'OH = EtOH, t-$C_5H_{11}OH$, n-$C_7H_{15}OH$, n-$C_{10}H_{21}OH$, cyclo-$C_6H_{11}OH$, $HO(CH_2)_2OH$, PhOH, *m*-MeC_6H_4OH, *m*-HOC_6H_4OH, *p*-HOC_6H_4OH, $MeCO_2H$, $PhCO_2H$.

Silyl *NN*-dialkylcarbamates are obtained by passing carbon dioxide through *NN*-dialkylaminotrimethylsilane[99-106] or through a mixture of dialkylamine and hexamethyldisilazane:[107,108-110]

$$\left.\begin{array}{l} CO_2 + RR'NSiMe_3 \\ CO_2 + RR'NH/(Me_3Si)_2NH \end{array}\right\} \rightarrow RR'NC(O)OSiMe_3 .$$

The interaction of silver carbamates with chlorotrimethylsilane also leads to silylated products:[101,111]

$$RR'NC(O)OAg + Me_3SiCl \xrightarrow{-AgCl} RR'NC(O)OSiMe_3 ;\quad R = R' = H .$$

According to the authors,[97] the most convenient method of synthesis of *N*-alkyl-substituted trimethylsilyl carbamates consists in the interaction of the adduct of an amine and carbon dioxide with chlorotrimethylsilane:

$$2RR'NH + CO_2 \xrightarrow[CH_2Cl_2]{-10-0^\circ} [RR'NC(O)O]^- RR'NHH_2^+ \xrightarrow[CH_2Cl_2;\ -RR'NH\cdot HCl]{Me_3SiCl;\ 0-20^\circ} RR'NC(O)OSiMe_3 ;\quad 85-90\%$$

$$RNH_2 + Et_3N + CO_2 \xrightarrow[CH_2Cl_2]{-10-0^\circ} [RNHC(O)O]^- Et_3NH^+ \rightarrow$$

$$\rightarrow \xrightarrow[CH_2Cl_2;\ -2Et_3N\cdot HCl]{2Me_3SiCl/Et_3N;\ 0-20^\circ} R(Me_3Si)NC(O)OSiMe_3 .\quad > 70\%$$

The trimethylsilyl carbamates obtained can be used not only as silylating agents[97,98] but also for the introduction of the amino-group into the molecules of organic compounds, for example:[97]

$$RR'NC(O)OSiMe_3 \left\{\begin{array}{l} \xrightarrow[20^\circ,\ 15\ min]{R''C(O)Cl} R''C(O)NRR' + CO_2 + Me_3SiCl ;\quad 85-95\% \\ \xrightarrow[80^\circ,\ 2\ h]{PhSO_2Cl} RhSO_2NRR' + CO_2 + Me_3SiCl ; \\ \xrightarrow[CH_2Cl_2]{(R''CO)_2O} R''C(O)NRR' + R''C(O)OSiMe_3 + CO_2 ;\quad 90\% \end{array}\right.$$

$$R'' = Me,\ Ph,\ ClCH_2;\ R, R' = Alk .$$

One of the most active silylating agents is trifluoromethylsilyl trifluoromethanesulphonate (TMS triflate).[1,112-114] It is obtained by heating trifluoromethanesulphonic acid with chlorotrimethylsilane with or without a base[115-118] and also by cleaving aryltrimethylsilanes with this acid:[119]

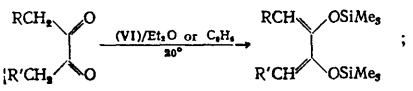
$$CF_3SO_3H \xrightarrow[-ArH]{\begin{array}{c}Me_3SiCl\\ -HCl\\ ArSiMe_3\end{array}} CF_3SO_3OSiMe_3 .\quad (V)$$

Silylation with TMS triflate is usually carried out in the presence of a tertiary amine, triethylamine being the most suitable base, since the salt $CF_3SO_2OH.NEt_3$ is a liquid; it is insoluble in non-polar solvents and can be readily separated from the easily soluble silylated products. The end of reaction is inferred from the formation of the second phase. Triethylamine is also convenient because it is an effective solvent for weak CH acids. The reaction is usually performed in dichloroethane, since in this solvent the reactions are 10^2-10^3 faster than in CCl_4 or Et_2O.

TMS triflate (V) is most important for the silylation of CH acids.[114]

(1) Ketones and aldehydes[120-124] [by treatment with $CF_3.SO_2OSiMe_3/Et_3N$ (VI)]:

$$RC(O)CHR'R'' \xrightarrow{(VI)} RC(OSiMe_3){=}CR'R'' ;$$



$$RR'CHCHO \xrightarrow[0-5^\circ]{(VI)/Et_2O} RR'C{=}CH(OSiMe_3) .$$

It has been shown that TMS triflate induces the isomerisation of the *C*-silylation product to the *O*-silylated compound:[124]

$$Me_3SiCH_2C(O)R \xrightarrow[20^\circ,\ min]{(V)/CCl_4} H_2C{=}C(OSiMe_3)R$$

(2) 1,3-Dicarbonyl compounds:[125]

$$RCH_2C(O)CHR'C(O)R'' \xrightarrow[0^\circ,\ 30\ min]{(VI)} RCH{=}C(OSiMe_3)CR'{=}C(OSiMe_3)R'' ;\quad 50-90\%$$

(3) Carboxylic acid esters:[126-128]

$$RCH_2COOR' \xrightarrow[0\div10^\circ]{(VI)/Et_2O} \left\{\begin{array}{l} \xrightarrow{a} Me_2SiCHRCOOR' ; \\ \xrightarrow{b} RCH{=}C(OR')OSiMe_3 ; \\ \xrightarrow{c} RCH_2C(O)OSiMe_3 ; \end{array}\right.$$

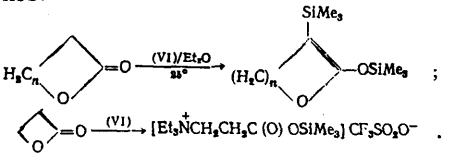
a) R = H, Me, R' = $SiMe_3$, CH_2Ph, Me, Et, iso-Pr; R=R'=Et; R=$SiMe_3$, R'=Et, iso-Pr;

b) R=Me, R'=Ph, $SiMe_3$; R=R'=Et; R=CN, R'=Me, Et; R=$SiMe_3$, R'=Me, Et, iso-Pr, $SiMe_3$, Ph; R=CH_2COOEt, Ph, R'=Et;

c) R' = t-Bu.

The scheme indicates the dominant reaction pathways for various substituents. Thus the product ratio *a*/*b* is 9 : 1 for CH_3COOPh and 19 : 81 for CH_3CH_2COOPh.[127]

(4) Lactones:[114]

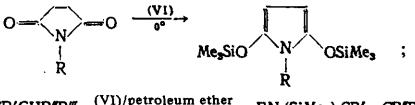


(5) Thiocarboxylic acid esters:[129]

$$RR'CHC(O)SR'' \xrightarrow[0-20^\circ]{(VI)/CH_2Cl_2} RR'C{=}C(OSiMe_3)SR'' .\quad 75-81\%$$

(6) Amides,[114] imides,[114], imines,[130] and iminoesters:[114]

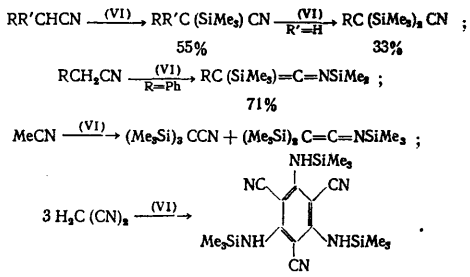
$$RR'CHC(O)NR''_2 \xrightarrow[0^\circ]{(VI)/CH_2Cl_2} RR'C{=}C(OSiMe_3)NR''_2 ;$$



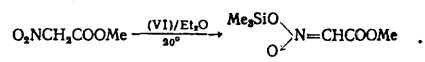
$$RN{=}CR'CHR''R''' \xrightarrow[0\div20^\circ]{(VI)/petroleum\ ether} RN(SiMe_3)CR'{=}CR''R''' ;$$

$$MeC(OMe){=}NR \xrightarrow{(VI)} MeC(O)N(SiMe_3)R .$$

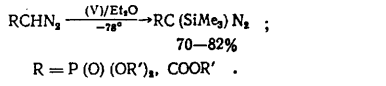
(7) Nitriles:[114,131]



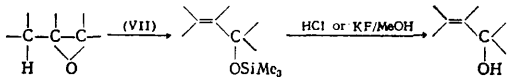
(8) Nitroalkanes:[132]



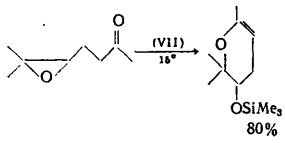
(9) Diazo-compounds:[133]



Oxirans are silylated by TMS triflate with ring opening,[112,114] which is used widely in preparative chemistry. The reaction proceeds under the influence of CF_3SO_2OSiMe/1,8-diazabicyclo[5.4.0]undec-7-ene (VII):



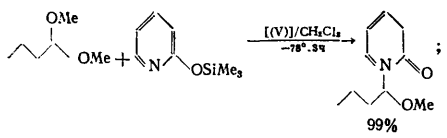
For example, according to this scheme the following reactions take place:[112,134]

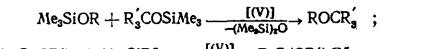


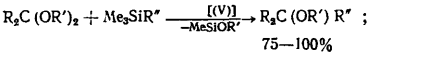
It has been found that tetrahydrofuran (THF) is also cleaved in accordance with this scheme, while ethers do not react with silylated sulphonic acids.

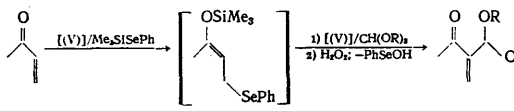
In addition TMS triflate can be used to obtain carbenes.[135]

New methods of organic synthesis involving the employment of TMS triflate as the catalyst of exchange and addition reactions have come to be widely used recently:[112,128,136–140]

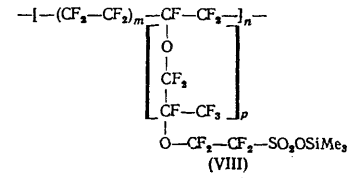






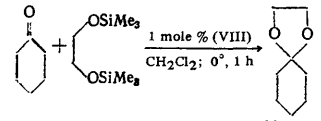


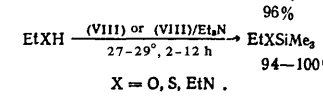
Bearing in mind that in the course of these reactions TMS triflate is lost irreversibly and also taking into account its high relative cost compared with other silylating agents, it has been suggested that TMS triflate be immobilised on a polymer base, which yielded in this way the immobilised catalyst (VIII):[141]



(VIII)

Compound (VIII) can be used both as a catalyst and as a silylating agent,[141] for example:





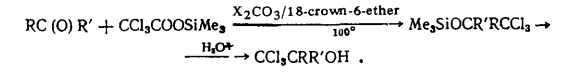
X = O, S, EtN .

Trimethylsilyl trichloroacetate has been recently proposed[142] as a reagent for the silylation of alcohols, phenols, carboxylic acids, amides, acetylenes, and β-ketoesters. The interaction takes place in the presence of potassium carbonate and 18-crown-6 ether on heating for 1–2 h. The chloroform obtained in the reaction promotes the latter:

$$CCl_3COOSiMe_3 + XH \rightarrow XSiMe_3 + CO_2 + CHCl_3 \ ;$$

X = PhO (88%); 3-MeC_6H_4O (90%); $PhCO_2$ (88%); 4-BrC_6H_4S (91%); $PhC{\equiv}C$ (88%) etc.

Trimethylsilyl trichloracetate reacts with aldehydes and ketones to form the silyl ether of trichloromethylmethanol, whose acid hydrolysis affords the free alcohol:



3. Compounds Containing the Si–N Bond

Compounds containing the Si–N bond are very powerful silylating agents especially for the silylation of OH groups, since in this instance the stronger Si–O bond is formed instead of the comparatively weak Si–N bond. The reaction is also promoted by the protonation of the nitrogen atom of the silyl donor, which decreases or eliminates the $(p-d)_\pi$ interaction between the silicon and nitrogen atoms and facilitates the removal of the leaving group in the form of a neutral molecule.

The most widely used Si–N containing silyl donor is hexamethyldisilazane, which is obtained by the reaction of Me_3SiCl with ammonia[19] (p.128). This reagent is widely employed in the pharmaceutical and chemical industries for the introduction of a temporary protecting group in various organic syntheses and also in chromatography for the modification of the surfaces of solid carriers.

At the same time, hexamethyldisilazane belongs to the group of "mild" silylating agents, i.e. it can be used even with very acid proton donors such as alcohols and phenols. Heating or the presence of a catalyst are necessary for the completion of the reaction. Inorganic acids, ammonium salts, sodium bisulphate, and chlorotrimethylsilane are used as catalysts.[14] The silylation method, the essential feature of which is the employment of an equimolar $(Me_3Si)_2NH/Me_3SiCl$ mixture, proved to be extremely fruitful.[143] This procedure made it possible to intensity appreciably the silylation reaction with the aid of hexamethyldisilazane, to increase the yield, and to reduce the reaction time. The role of $(Me_3Si)_2NH$

then consists in accepting the hydrogen chloride and in generating chlorotrimethylsilane:[144–147]

$$ROH + Me_3SiCl \rightarrow ROSiMe_3 + HCl\ ;$$
$$HCl + (Me_3Si)_2NH \rightarrow Me_3SiCl + NH_4Cl\ .$$

Apart from the intensification process, it has been possible to expand greatly the synthetic possibilities of this reaction, extending it to classes of compounds (such as, for example, mercaptans and siloxanols) whose silylation by both Me_3SiCl and $(Me_3Si)_2NH$ (each separately) is relatively ineffective.[143–147]

Compounds containing the $\equiv Si-\underset{|}{N}-C(O)$ group (silylureas and silylamides) are more active silylating agents than silazanes and silylamines.[14,17] Although the majority of trimethylsilylureas can function as effective silyl donors, two representatives of this class have come to be most widely used recently: *NN'*-bis(trimethylsilyl)urea and *NN'*-diphenyl-*N*-trimethylsilylureas. The main advantage of the disilylated urea consists in the ease of its synthesis from widely distributed cheap starting materials: urea and hexamethyldisilazane.[148] The interaction of *N*- and *NN'*-substituted ureas with hexamethyldisilazane leads to isocyanates as a result of the thermal decomposition of unstable reaction intermediates. For this reason, silylureas are synthesised by the reaction of metallated ureas with chlorotrimethylsilane, of *N*-alkyl(aryl)ureas with *NO*-bis(trimethylsilyl)-acetamide, and of organoaminosilanes and organosilazanes with organic isocyanates,[149] which reduces their availability and increases their cost compared with *NN'*-bis(trimethylsilyl)ureas.

NN'-Bis(trimethylsilyl)urea is a convenient reagent for the silylation of alcohols and carboxylic acids.[150] The interaction is usually carried out in methylene chloride for 2–3 h, which ensures a high yield of the silylated derivatives (84 to 96%):

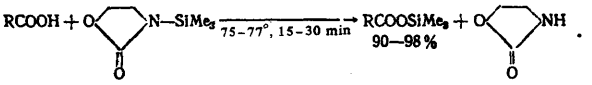
$$ROH + (Me_3SiNH)_2C{=}O \xrightarrow[20-40^\circ]{CH_2Cl_2} ROSiMe_3 + (H_2N)_2C{=}O\ ;$$
$$R = C_9H_{19},\ \text{cyclo-}C_6H_{11},\ p\text{-}MeC_6H_4,\ p\text{-}ClC_6H_4;$$
$$R'COOH + (Me_3SiNH)_2C{=}O \xrightarrow[40^\circ]{CH_2Cl_2} R'COOSiMe_3 + (H_2N)_2C{=}O\ ;$$
$$R' = Ph,\ C_5H_{11},\ ClCH_2,\ H_2C{=}C(Me),\ MeCH(OH),\ HOOCCH{=}CH-\ .$$

NN'-Diphenyl-*N*-trimethylsilylureas, which silylates not only alcohols and acids but also nitromethane, malononitrile, thiourea, guanidine, β-diketones, oxindole, *NN'*-dialkylurea, and other compounds, is a more effective silyl donor.[151] *NN'*-Diphenyl-*N*-trimethylsilylurea is more reactive not only compared with other silylureas but also compared with silyl donors such as *N*-silylamines and hexamethyldisilazane. For example,[151] its interaction with *NN'*-dimethylurea leads to a 100% yield of the silylated product only 2 min after mixing the initial compounds, in silylation with the aid of *N*-trimethylsilylaniline the product is formed in only 3% yield after 3 h, while in the reaction involving *N*-trimethylsilylpiperidine the yield is 10% after 3 days. The reaction with hexamethyldisilazane does not take place at all.

Trimethylsilyl derivatives of diphenylurea are obtained by the reaction of *N*-trimethylsilylaniline with phenyl isocyanate.[151] This compound is a convenient silylating agent, because diphenylurea formed in the reaction is insoluble in most organic solvents and can be readily removed from the reaction mixture by filtration. The insolubility of diphenylurea is apparently the reason why the silyl–proton exchange equilibrium is in this case almost wholly displaced to the right:

$$Me_3SiN(Ph)C(O)NHPh + (H_2N)_2C{=}S \xrightarrow[30-35^\circ,\ 2\ h]{MeCN} \underset{82\%}{(Me_3SiNH)_2C{=}S} + (PhNH)_2CO\ .$$

In many instances *N*-trimethylsilyl-2-oxazolidinone[152] or silylated hydantoins [153,154] are conveniently used for the silylation of carboxylic acids and certain biologically active compounds (penicillins, steroids, etc.):



However, the commonest silylating agents containing the N–C(O) group are silylamides: *NO*-bis(trimethylsilyl)-acetamide,[155] *NO*-bis(trimethylsilyl)trifluoroacetamide,[156] *N*-methyl-*N*-trimethylsilyltrifluoroacetamide,[157] and *N*-(t-butyldimethylsilyl)-*N*-methyltrifluoroacetamide.[158] The reaction of the corresponding amide with chlorotrimethylsilane in triethylamines constitutes a preparative method for the synthesis of the above silylamides, for example:[159,160]

$$RC(O)NH_2 + 2Me_3SiCl + 2Et_3N \xrightarrow[-2Et_3N.HCl]{r_b,\ 8-15\ h} \underset{\sim 80\%}{RC(OSiMe_3){=}NSiMe_3}\ .$$

Another method of synthesis of *NO*-bis(trimethylsilyl)amide is provided by the reaction of carboxylic acid halides with sodium bis(trimethylsilyl)amide:[161]

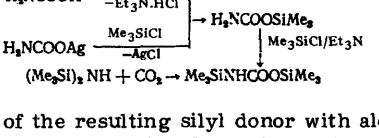
$$RC(O)Cl + NaN(SiMe_3)_2 \xrightarrow{-NaCl} RC(OSiMe_3){=}NSiMe_3\ ;$$
$$R = Ph,\ C_6H_4N,\ t\text{-}Bu\ .$$

NO-Bis(trimethylsilyl)amides belong to the class of the strongest silyl donors. Alcohols, acids, phenols, amines, mercaptans, amides, ureas, enols, CH acids etc. are silylated with their acid. The silylation is usually carried out in a solvent (benzene, ether, CCl_4, $CHCl_3$, acetonitrile, pyridine, and DMF), which is taken in threefold excess relative to the mass of the initial reactants.[162] Comparison of the silylating properties of *N*-(t-butyldimethylsilyl)-*N*-methyltrifluoroacetamides with those of the $t\text{-}BuMe_2SiCl$/imidazole/DMF system showed that the given silylamide is more effective as the silyl donor[163] and the reaction proceeds in acetonitrile at 20 °C:

$$CF_3C(O)NRSiMe_2Bu\text{-}t + XH \rightarrow \underset{92-100\%}{XSiMe_2Bu\text{-}t};$$
$$XH = HO(CH_2)_3OH,\ PhOH,\ PrSH,\ PhCH_2NHMe;\ R = H,\ Me\ .$$

For the analysis of organic derivatives by gas–liquid chromatography (GLC), it is more convenient to silylate them by fluorinated silylamides, since fluorinated derivatives are more volatile compared with their non-fluorinated analogues.[14,157]

It has been shown[164] that in the presence of carbon dioxide the silylation of thiazoles by hexamethyldisilazane is accelerated by a factor of 2–3, probably owing to the formation of *NO*-bis(trimethylsilyl) carbamate. It has been suggested that this compound be used as a silylating agent.[101] It can also be synthesised by silylating carbamic acid or its silver salt with chlorotrimethylsilane:



The interaction of the resulting silyl donor with alcohols and acids takes place on heating for 1–2 h and the yield of silylated derivatives reaches 96%:

$$Me_3SiNHCOOSiMe_3 + HX \rightarrow Me_3SiX + CO_2 + NH_3\ ;$$
$$HX = MeOH\ (95\%);\ MeCOOH\ (91\%)\ .$$

NO-Bis(trimethylsilyl) sulphamate has a structure similar to that of the bis(silyl) carbamate and is obtained by means of analogous reactions:[165–170]

$$\left.\begin{array}{l} NH_2SO_3NH_4 + (Me_3Si)_2NH \xrightarrow{-NH_3} \\ NH_2SO_3Ag + Me_3SiCl \xrightarrow{-AgCl} \end{array}\right\} \rightarrow Me_3SiNHSO_2OSiMe_3 .$$

However, *NO*-bis(trimethylsilyl) sulphamate is a much more powerful silyl donor than the bis(silyl) carbamate and many common silylating agents such as hexamethyldisilazane, *N*-trimethylsilyldiethylamine, *N*-trimethylsilylimidazole, and *NO*-bis(trimethylsilyl)acetamide.[167] Alcohols, phenols, acids, organosilicon compounds, and biologically active substances have been silylated with the aid of *NO*-bis(trimethylsilyl) sulphamate.[168–170] Excellent yields (in excess of 90%) of the trimethylsilyl derivatives were obtained in all cases after 30 min at 30 °C. The sulphamic acid liberated as a result of the reaction is insoluble in most organic solvents and can be readily removed by filtration:

$$BuOH + Me_3SiNHSO_2OSiMe_3 \rightarrow \underset{93\%}{BuOSiMe_3} + H_2NSO_3H .$$

4. Compounds Containing the Si–S Bond

Since the Si–S bond is weaker (63 kcal mol^{-1}) than the Si–O (108 kcal mol^{-1}) and Si–N (77 kcal mol^{-1}) bonds and is more readily polarisable, it is evident that thiosilanes should be more reactive in relation to proton donors than the corresponding oxygen- and nitrogen-containing organosilicon reagents.

Alkylthiosilanes are readily obtained by the reaction of chlorotrimethylsilane with alkylthiomagnesium iodide[19] or with dialkyl disulphide and sodium in ether.[171] However, their reaction with proton donors leads to the evolution of toxic merceptans with an unpleasant smell, which are in addition not always indifferent to the reaction products. These factors limit the application of alkylthiosilanes as silyl donors.

Among the compounds containing the Si–S bond, hexamethyldisilthiane meets the requirements imposed on silylating agents to the greatest extent. It can be obtained from chlorotrimethylsilane and sodium sulphide at 250 °C or by passing chlorotrimethylsilane vapour through a melt of the eutectic mixture of lithium and potassium chlorides containing 25% of potassium sulphide at 400 °C.[19] Hexamethyldisilthiane is also formed when hydrogen sulphide is silylated by chlorotrimethylsilane in the presence of tertiary amines,[19,172] organosilylamines,[19] including *N*-trimethylsilylimidazole,[19] hexamethyldisilazane,[173–175] *N*-phenyl-*N*-silylacetamide,[176] and cyanotrimethylsilane[177] and by the interaction of iodotrimethylsilane with silver[172] and mercury[172,178,179] sulphides.

The reaction of chlorotrimethylsilane with ammonium hydrogen sulphide is an extremely effective method of synthesis of hexamethyldisilthiane:[180]

$$Me_3SiCl + NH_4SH \rightarrow (Me_3Si)_2S + NH_4Cl + H_2S .$$

However, the easiest and most promising method of synthesis of hexamethyldisilthiane involves the cothiolysis of *N*-trimethylsilyldiethylamine or hexamethyldisilazane with chlorotrimethylsilane:[181,182]

$$Me_3SiNEt_2 + Me_3SiCl + H_2S \rightarrow (Me_3Si)_2S + Et_2NH\cdot HCl ;$$
$$(Me_3Si)_2NH + Me_3SiCl + H_2S \rightarrow (Me_3Si)_2S + NH_4Cl .$$

The reaction takes place with a small exothermic effect at 20–50 °C in a neutral solvent or without a solvent. The hexamethyldisilthiane formed in this process is 99.95% pure according to GLC data.

Hexamethyldisilthiane is a highly effective reagent for the silylation of alcohols,[19,183–191] aminoalcohols,[187] phosphorylated alcohols,[192] phenols,[194–195] inorganic and carboxylic acids,[194,195,197,198] enols,[199,200] arylmercaptans,[199,200] oximes,[199,200] and also certain organoelemental compounds,[199,201] including organosilicon[202] and organophosphorus compounds:[199,201]

$$(Me_3Si)_2S + 2RXH \rightarrow 2Me_3SiXR + H_2S ;$$
$$RXH = AlkOH, ArOH, HO(CH_2)_nOH, H_3BO_3, H_2SO_4,$$
$$HHal, H_2N(CH_2)_nOH, ArSH, R'C(O)CH_2C(O)R'', R'R'' = NOH,$$
$$Ph_2Si(OH)_2, (RO)_2POOH \text{ etc.}$$

One of the main advantages of hexamethyldisilthiane compared with other silyl donors is the simplicity of the silylation reaction, which is achieved by mixing and heating the initial reactants (at 30–120 °C) for a short time (0.5–3 h), ensuring a high yield (70–98%) of the silyl derivatives. The course of the reaction can be conveniently followed volumetrically from the amount of hydrogen sulphide formed. The reaction does not require the use of catalysts and solvents. Furthermore, hexamethyldisilthiane ensures the selective silylation of proton donors containing two and more active groups in the molecule.[199]

5. Compounds Containing Si–C Bonds

Reagents with the Si–C bond are much more resistant to the action of proton donors than the silyl donors with the Si–Hal, Si–O, Si–N, and Si–S bonds examined above. However, in the presence of catalysts certain compounds containing electron-accepting groups such as C_6F_5, CN, etc. can act as effective silyl donors. Thus, in the presence of strong acids (toluene-*p*-sulphonic[203] or trifluoromethanesulphonic[204] acids), allylsilane silylates alcohols and acids in accordance with the following scheme:

$$CH_2=CHCH_2SiMe_3 + ROH \xrightarrow[MeCN]{TosOH} \underset{87–99\%}{ROSiMe_3} + CH_3{=}CHMe .$$

The catalytic action of the above acids consist in the ready cleavage by the latter of the silicon–allyl bond with the intermediate formation of powerful silyl donors—the trimethylsilyl esters of sulphonic acids.[205] Further interaction of these intermediates with proton donors leads to silylated products with regeneration of the acid:[204]

$$CH_2{=}CHCH_2SiMe_3 + CF_3SO_2OH \xrightarrow[20–25°]{CH_2Cl_2} CF_3SO_2OSiMe_3 + CH_2{=}CHMe ;$$
$$CF_3SO_2OSiMe_3 + RCO_2H \rightarrow RCO_2SiMe_3 + CF_3SO_2OH .$$

In the presence of $Bu_4N.3H_2O$ as the catalyst, alkyl trimethylsilylacetates can be used to silylate compounds containing a comparatively acid hydrogen atom, for example:[206]

$$Me_3SiCH_2COOR + XH \rightarrow \underset{88–92\%}{Me_3SiX} + MeCOOR ;$$
$$R = Me, Et; X = Ph(CH_2)_3O, Ph(\text{isoferrocene})_2CO, 4\text{-}MeC_6H_4O, Me(CH_2)_5S,$$
$$PhCH_2S, \text{l-menthyloxy}, Me_3CS, PhC{\equiv}C, EtCOO ;$$
$$Me_3SiCH_2COOMe + HO(CH_2)_2SH \rightarrow \underset{83\%}{Me_3SiO(CH_2)_2SSiMe_3} + MeCOOMe .$$

When the silicon atom is linked to the trichloromethyl group, the cleavage of this bond can take place also in the absence of the catalyst, for example:[207–209]

$$Me_3SiCCl_3 + Bu_2NH \xrightarrow[3–4\ h]{120–140°} \underset{85\%}{Me_3SiNBu_2} + CHCl_3 .$$

The use of (trichloromethyl)trimethylsilane is convenient also because chloroform formed as a side product can serve simultaneously as the solvent for the reaction product.

(Trichloromethyl)trimethylsilane can be obtained by the reaction of phosphorus acid amides with chlorotrimethylsilane in the presence of CCl_4 [210] and by the decarboxylation of the trimethylsilyl ester of trichloroacetic acid in the presence of triethylamine:[211]

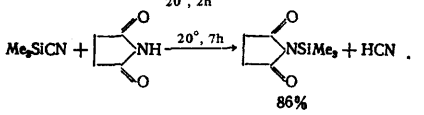
$$(R_2N)_3P + CCl_4 + Me_3SiCl \xrightarrow{Et_2O} (R_2N)_3PCl_2 + Me_3SiCCl_3 ;$$

$$CCl_3COOSiMe_3 \xrightarrow[66°,\ 4h]{Et_3N,\ THF} Me_3SiCCl_3 + CO_2 \quad (79\%) .$$

In recent years there has been a growth of interest in cyanotrimethylsilane not only as a reagent which makes it possible to introduce the cyano-group readily into the molecules of organic and organoelemental compounds[1,2] but also as a silyl donor. It has been found[177] that Me_3SiCN readily reacts with compounds containing SH and NH bonds:

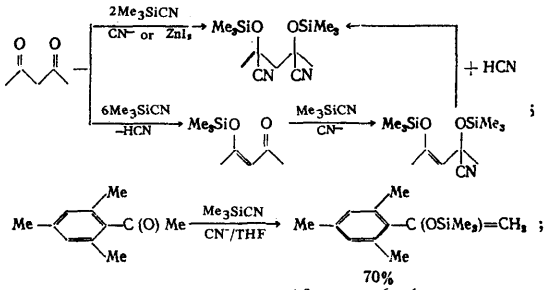
$$Me_3SiCN + H_2S \xrightarrow[80°;\ 3,5h]{} (Me_3Si)_2S + HCN \quad (86\%) ;$$

$$Me_3SiCN + 2Et_2NH \xrightarrow[20°,\ 2h]{} Me_3SiNEt_2 + Et_2NH\cdot HCN ;$$



(86%)

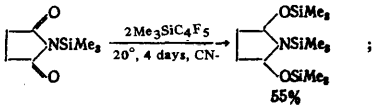
The interaction of Me_3SiCN with carbonyl compounds is unusual; depending on the conditions and the catalyst, both silylation and addition to the carbonyl group can take place:[212–215]

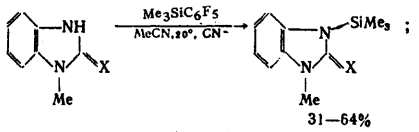


CN^- = KCN/18-crown-6-ether.

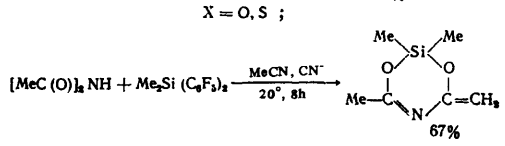
Thus cyanotrimethylsilane can be used to convert a ketone into a cyanohydrin with the simultaneous protection of the hydroxy-group, which has been used in the synthesis of prostaglandin.[2,216]

The successful selection of the catalyst for the silylation of carbonyl compounds (KCN/18-crown-6 ether) made it possible to employ also (pentafluorophenyl)trimethylsilane as the silyl donor. This resulted in the formation of silyl derivatives which are either difficult or impossible to obtain by another method, for example:[212,215,217–222]





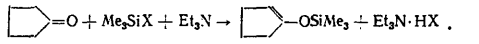
X = O, S ;



III. COMPARATIVE CHARACTERISTICS OF SILYLATING AGENTS

Evidently factors weakening the Si–X bond in the silyl donor R_3SiX increase the rate of silylation. The effect of various factors, including the nature of the leaving group X, the substituents R, the acidity of the proton donor, and the influence of the medium and the catalyst on the efficiency of the silylation, have been described in reviews,[14–24] silyl donors of one class being usually compared. Studies in which a quantitative comparison has been made of the silylating agents with Si–X bonds of different character are more important.

The activity of silyl donors is determined either by measuring the rate of reaction of various silyl donors with the relatively inactive proton donor or the yield of the product of the silylation of this proton donor after a specific time interval is determined. For example, the activities of silyl donors of the type Me_3SiX, where X = Cl, $MeSO_3$, 4-$MeC_6H_4SO_3$, $PbSO_3$, Me_3SiOSO_3, 4-$BrC_6H_4SO_3$, $CF_3CH_2SO_3$, Br, CF_3SO_3, or I, in relation to cyclopentanone and diisopropyl ketone, have been investigated.[223] The reactions proceed in the presence of triethylamine in accordance with the following mechanism:



The rate of reaction was determined by ^1H NMR. The extremum values of the standardised rate constants (at 23 °C) and the relative rate constants for the given silylation reactions were calculated. The silylating activity scale was obtained in this way (the reactivity of Me_3SiCl was adopted as unity); the highest reactivity is shown by Me_3SiI:[223]

X	Cl	$MeSO_3$	$PhSO_3$	Me_3SiOSO_3	Br	CF_3SO_3	I
k_{rel}	1	40	160	270	$7{,}9\cdot10^4$	$6{,}7\cdot10^8$	$7\cdot10^9$

In another study[167] the authors claim that *NO*-bis(trimethylsilyl) sulphamate is more effective as a silylating agent than the majority of silyl donors. To confirm this, they compared the efficiency of the most frequently used silylating agents in relation to the silylation with sterically hindered 2,6-di-s-butylphenol; the yield of the silylated product was determined by GLC.

In another investigation[199] the interaction of dodecyl alcohol with a series of silyl donors [chlorotrimethylsilane, hexamethyldisilazane, the equimolar mixture of chlorotrimethylsilane and hexamethyldisilazane, *N*-trimethylsilyldiethylamine, *NO*-bis(trimethylsilyl)acetamide, and hexamethyldisilthiane] was chosen as the model reaction. It was shown by GLC that the reactivities of *NO*-bis(trimethylsilyl)acetamide and hexamethyldisilthiane in relation to the above alcohol are approximately the same and exceed appreciably the reactivities of the remaining silyl donors.

The available data permit the conclusion that the most active silyl donors are trimethylsilyl trifluoromethanesulphonate, iodotrimethylsilane, *NO*-bis(trimethylsilyl) sulphamate, *NO*-bis(trimethylsilyl)acetamide, and *NO*-bis(trimethylsilyl)trifluoroacetamide. Hexamethyldisilthiane and *N*-trimethylsilylimidazole are extremely active in relation to compounds containing OH groups; on the other hand, they are less suitable for silylation of NH and SH bonds.

In recent years there has been a growth of interest in catalytic silylation of proton donors by compounds containing the Si–C bond, although this method has not so far come to be sufficiently widely used.

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Thus, efforts to create new silylating agents or to apply known reagents to silylation have been made in five directions: (1) the synthesis of silyl donors containing groups which would promote easier elimination of the silyl group (trimethylsilyl triflate and trifluoromethyl-containing amides); (2) the synthesis of silyl donors which do not form deposits, during the silylation process, hindering the isolation and purification of silylated products (hexamethyldisilthiane and silyl carbamates); (3) the synthesis of reagents forming in the course of the reaction substances which are indifferent to the reaction products and which liquefy the reaction mass, promoting a higher degree of completion of the process [trimethylsilyl trichloroacetate, alkyl trimethylsilylacetate, (trichloromethyl)trimethylsilane]; (4) the use of catalytic systems which convert known reagents into effective silyl donors (allyltrimethylsilane, hexamethyldisiloxane in the presence of the KCN/18-crown-6 ether complex); (5) the use of reagents which serve simultaneously for the introduction of protecting (silyl) groups as well as other reactive groups (cyanotrimethylsilane). We suggest that the synthetic possibilities of the first two procedures have been virtually exhausted and the main effort will therefore probably be concentrated on the last three procedures, especially that involving the creation of catalytic silylation systems.

In conclusion one should note that the usefulness of a particular silyl donor is determined both by the nature of the compound silylated and by the aim of the investigator. For example, analytical chemistry (GLC, mass spectroscopy) requires highly effective reagents such as trimethylsilyl trifluoromethanesulphonate, which silylate rapidly and quantitatively, although they are usually expensive and scarce. Since the analytical chemist deals with small amounts of substances to be analysed the cost of the silyl donor does not play a significant role for his purposes. On the other hand, in the development of the technology for the large-scale synthesis of organic substances, it is more useful to select a cheaper, albeit a less active silyl donor, such as organochlorosilane or hexamethyldisilazane. In selecting a suitable silylating agent, the synthetic chemist must take into account primarily the structure of the proton donor and the synthetic possibilities of the different silyl donors, information about which is available in monographs,[1,14] original articles,[15–24] and in the present review.

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Lebedev All-Union Synthetic Rubber Institute, Leningrad