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Trimethylsilylazoles Chemistry*

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Abstract—In the review are summarized and analyzed the data on synthesis, chemical and physico-chemical characteristics of C- and N-trimethylsilylazoles. A special attention is paid to Dondoni reagent (2-trimethylsilylthiazole) extensively used in the asymmetric synthesis.

INTRODUCTION

Azoles** containing trimethylsilyl group are extensively applied to synthetic organic chemistry.

Numerous N-substituted trimethylsilylazoles, especially 1-trimethylsilylimidazole, are convenient trimethylsilylating agents in peptide synthesis. C-trimethylsilylazoles, in particular 2-trimethylsilylthiazoles, are used in asymmetric synthesis for preparation of synthetic analogs of carbohydrates and aminosugars with high stereoselectivity. Although trimethylsilylazoles are widely used in the organic synthesis, the data on these reagents and the ways of their application have not been summarized up till now. This review is intended to fill the gap.

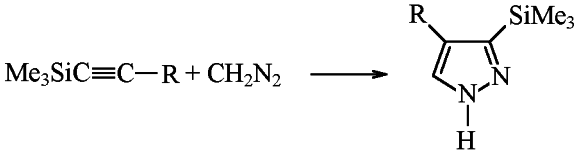
Trimethylsilylazoles may be divided in two large classes: (1) C-Trimethylsilylazoles, substituted azoles and their benzannealed analogs containing a trimethylsilyl group attached to one or several carbon atoms. (2) *N*-Trimethylsilylazoles with one of nitrogens linked to $Si(CH_3)_3$ group.

Since the properties, structure, and especially chemical reactions of C- and N-trimethylsilylazoles are considerably different, they are treated below separately.

I. C-TRIMETHYLSILYLAZOLES

I.1. *Preparation Methods*

C-Trimethylsilylazoles are successfully prepared by classical heterocyclization procedures from appropriate synthons with trimethylsilyl group. For instance, trimethylsilylacetylene reacts with diazomethane to afford 3(5)-trimethylsilylpyrazole in quantitative yield [1–3]. Similarly from the appropriate disubstituted acetylenes were prepared 4-methyl-3(5)-trimethylsilyl- [3], 4-hydroxymethyl-3(5)-trimethylsilyl- [3], 4-fluoro- [5], 3(5)-trimethylsilyl-4-alkoxypyrazole [6] etc.



R = CH_3, CH_2OH, C_6H_5, F, OAlk, $SiMe_3$.

The presence of electron-acceptor substituent at the triple bond (R = CHO [3], $COCH_3$ [1], $COOCH_3$

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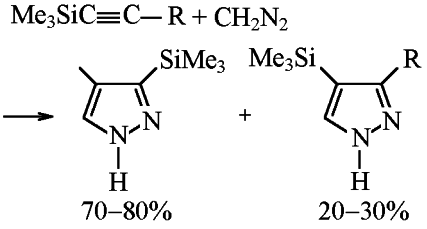
** We regard as azoles five-membered heteroaromatic compounds, also their annealed derivatives, containing no less than two endocyclic heteroatoms with at least one nitrogen among them (pyrazole, imidazole, 1,2,3- and 1,2,4-triazole, oxazole, thiazole, indazole, benzimidazole, benzoxazole, benzothiazole, benzotriazole).

[3, 6] etc.) results in formation of a mixture of 3- and 4-trimethylsilyl derivatives with the former prevailing.



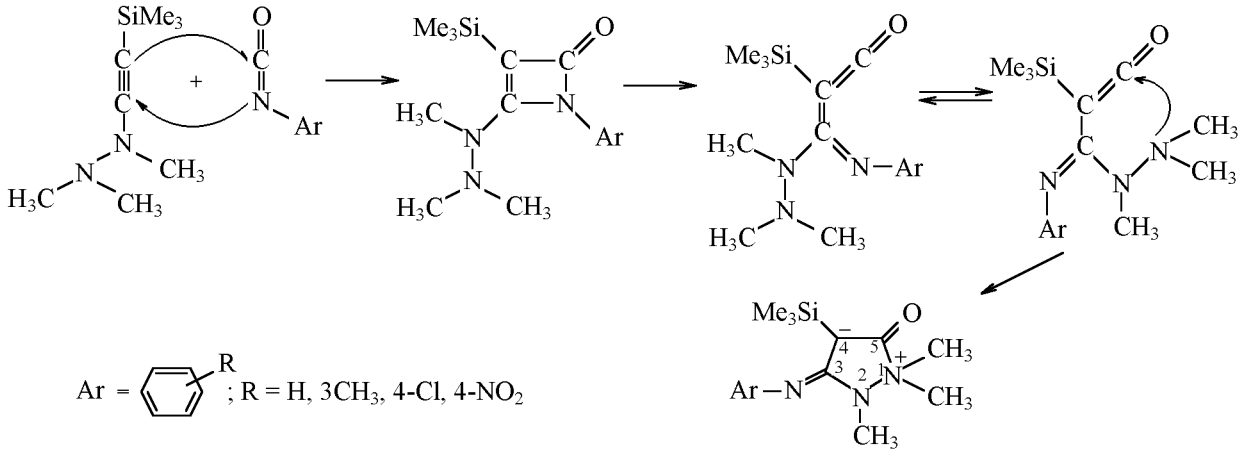
R = CHO, $COCH_3$, $COOCH_3$.

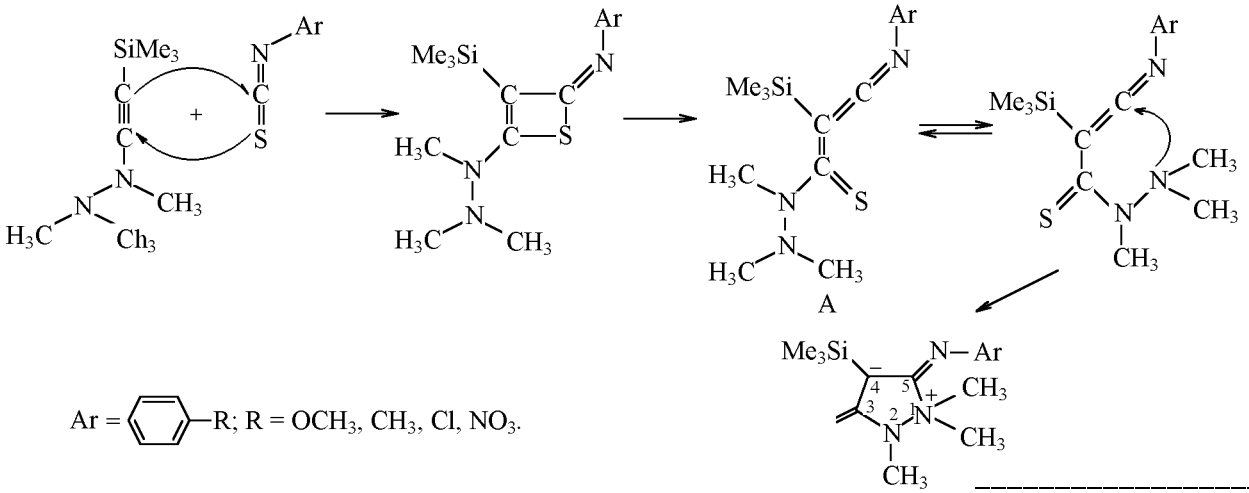
In reaction of diazomethane with 1-trimethylsilyl-2-nitroacetylene was isolated only 4-nitro-3(5)-trimethylsilylpyrazole in ~30% yield [7, 8]. This low yield is due presumably either to loss of the isomeric 3(5)-nitro-4-trimethylsilylpyrazole during separation, or its decomposition at formation. In these reactions the molar ratios of reagents should be rigidly adhered to since the excess diazomethane results in methylation of the pyrazole ring [3].

The bis(trimethylsilyl)acetylene treated with ethyl diazoacetate afforded ethyl 3(5),4-bis(trimethylsilyl)-pyrazole-5(3)-carboxylate [3].

The reaction of 1-trimethylsilyl-2-methoxycarbonylacetylene with 2-diazopropane furnished 3,5-dimethyl-4-methoxycarbonyl-5-trimethylsilylpyrazolenine [3].

In reaction of (trimethylsilylethynyl)trimethylhydrazine with aryl isocyanates or isothiocyanates arise the corresponding betaines (3-arylimino-5-oxo- and 5-arylimino-3-thioxo-1,1,2-trimethyl-4-trimethylsilylpyrazolidinium-4-ide) [9, 10]. Their structures are essentially dissimilar for the reactions take different routes.

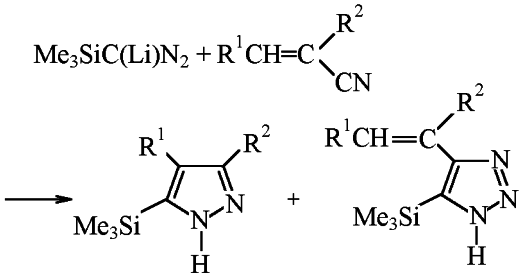




In the first case the betaine arises due to the specific reactivity of the initial hydrazine: a four-membered cycle forms by (2+2)-addition type between the C≡C and C=N bonds followed by rupture of the endocyclic C–N bond to afford amidrazonoketenes that are in a conformational equilibrium. The rotamer in B form cyclizes into 3-arylimino-5-oxo-4-trimethylsilyl-1,1,2-trimethyl-

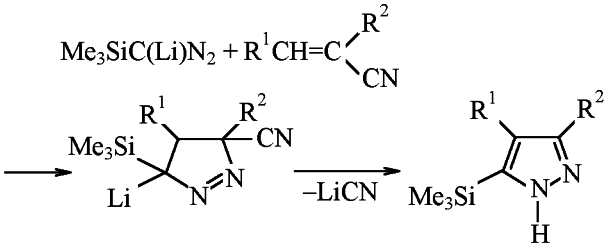
pyrazolidinium-4-ide [9]. Unlike that the products of the second reactions, 2-iminothiethenes, are formed with participation of C=S instead of C=N fragment. The spontaneous opening of the four-membered cycle results in ketene imines that cyclize into 5-arylamino-3-thioxo-1,1,2-trimethyl-4-trimethylsilylpyrazolidinium-4-ide [10].

A good synthon for preparation of C-trimethylsilylazoles is the lithium derivative of trimethylsilyldiazomethane. For instance, its reaction with nitriles of α,β-unsaturated acids gives rise to C-trimethylsilylpyrazoles. With nitriles of the higher acids was observed formation of a side product, the corresponding substituted C-trimethylsilyl-1,2,3-triazole [11].

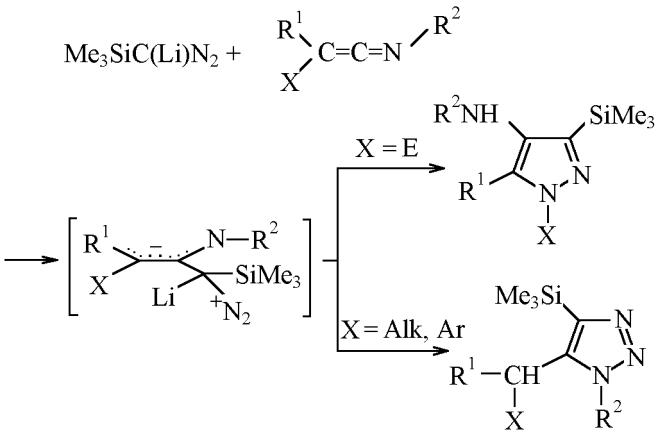


R^1 = H, Alk, Ar; R^2 = H, Alk, CN, CO_2CH_3.

The presumed mechanism of the reaction includes a nucleophilic attack of the diazo component on the carbon in β-position with respect to cyano group followed by cyclization into the corresponding pyrazoline derivative. The latter eliminates subsequently LiCN and transforms into R^1,R^2-substituted 5-trimethylsilylpyrazole [11].



The sulfonates of the α,β-unsaturated acids react with $Me_3SiC(Li)N_2$ in the similar way [12]. Ketene imines with electron-acceptor group (*E*) in reaction with lithiotrimethylsilyldiazomethane undergo cyclization into the corresponding derivatives of 4-amino-3-trimethylsilylpyrazole. Yet the ketene imines with aryl or alkyl group at C^2 atom afford the corresponding 5-substituted 4-trimethylsilyl-1,2,3-triazoles [13].



R^1 = Alk, Ar; R^2 = H, Alk, CN, CO_2CH_3; E = MeCO, EtO_2C, $PhSO_2$, NC, $(EtO)_2PO$.

In some instances the C-trimethylsilylpyrazoles can be obtained from the corresponding pyrazoline derivatives [14].

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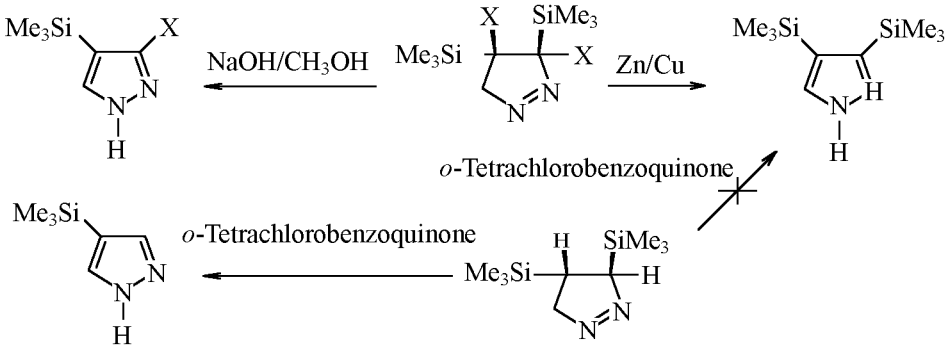
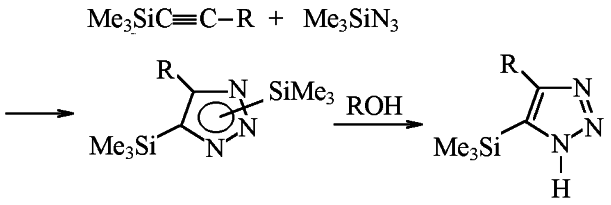


X = Cl, Br.

Allenyltriorganylsilanes in reaction with nitrosonium tetrafluoroborate provide 5-methyl-4-(triorganylsilyl)isoxazoles [15]. Therewith the reaction with dimethyl-*tert*-butylsilane occurs cleanly, but with trimethylsilylallenes the process is accompanied by desilylation.

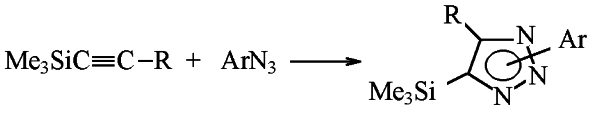
The reaction of bis(trimethylsilyl)acetylene with thiazolyl hydroxamoyl chlorides gives rise to 3-thiazolyl-4,5-bis(trimethylsilyl)isoxazole [16].

The derivatives of trimethylsilylacetylene react with the trimethylsilyl azide to afford the corresponding substituted 5-trimethylsilyl-1,2,3-triazoles [7, 8, 17]. The use in this reaction of organic azides is not recommended due to the explosion hazard.



R = NO_2, C_6H_5, $SiMe_3$.

Nevertheless aryl azides were applied to the synthesis of certain N-aryl-substituted C-trimethylsilyl-1,2,3-triazoles [17, 18].



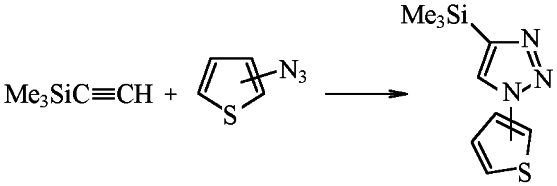
R = H, $COCH_3$, COC_2H_5, CH=NR'.

Bis(trimethylsilyl)butadiyne at 110–130°C reacts with phenyl azide or ethyl diazoacetate giving respectively 1-phenyl-4-trimethylsilyl-5-trimethylsilylethynyl-1,2,3-triazole and 3-ethoxycarbonyl-4-trimethylsilylethynyl-5-trimethylsilylpyrazole. Regiospecificity of this *endo*-cycloaddition is caused by orbital control [19].

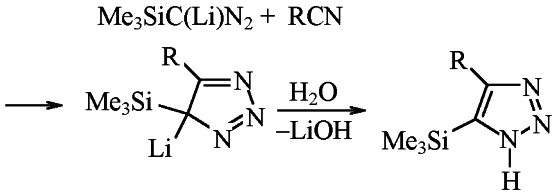
Similarly bis(trimethylsilyl)hexatriyne reacts with 4-nitrophenyl azide affording *endo*-adduct, 1-(4-nitrophenyl)-4-trimethylsilyl-butadiynyl-1,2,3-triazole [19]. The cycloaddition occurs exclusively across the triple bond linked to silicon.

The structure of the compounds obtained was proved by X-ray diffraction analysis (see Table 3) [19].

Isomeric 1-(thienyl-2)- and 1-(thienyl-3)-4-trimethylsilyl-1,2,3-triazoles were prepared from the corresponding 2- and 3-thienyl azides and trimethylsilylacetylene [20].



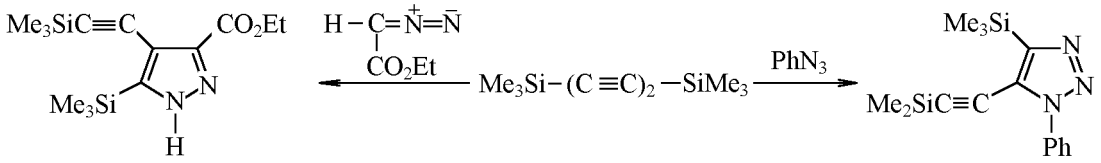
Another convenient way to C-trimethylsilyl-1,2,3-triazoles is the reaction between organic cyanides and lithiated trimethylsilyldiazomethane [21–24].

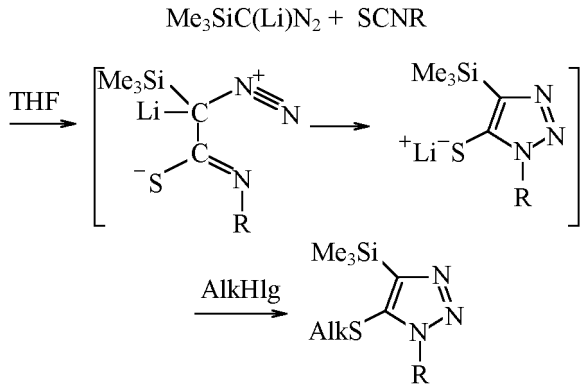


R = Alk, Ar, Ht, AlkS, PhS.

The mechanism of 1,2,3-triazole formation was not studied in detail. Apparently at the beginning of the process either the lithium derivative of trimethylsilyldiazomethane attacks the carbon atom of the cyano group or occurs 1,3-dipolar addition followed by hydrolysis of the intermediate triazolenyne derivative. At the use in this reaction of trimethylsilyl cyanide instead of C,N-bis(trimethylsilyl)-1,2,3-triazole was isolated bis(trimethylsilyl)diazomethane [21].

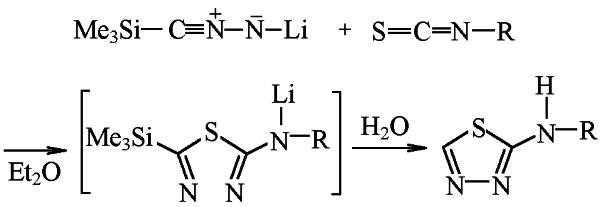
By treating organyl isothiocyanates in THF with lithiotrimethylsilyldiazomethane and alkyl halides were obtained in good yield 1-substituted 4-trimethylsilyl-5-alkylthio-1,2,3-triazoles. The presumable mechanism of the reaction consists in nucleophilic attack of diazomethane on the carbonal atom of the isothiocyanate with subsequent cyclization resulting in 1,2,3-triazole intermediate. The latter at the action of alkyl halides is converted into the corresponding derivatives of 1,2,3-triazole [24, 25].



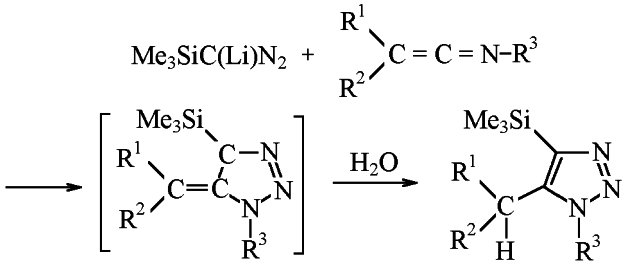


R = Alk, Ph, $PhCH_2$, C_6H_{11}, $CH_2{=}CHCH_2$.

The important role in this reaction plays the character of the solvent. Thus in ethyl ether the reaction between lithiotrimethylsilyldiazomethane and organyl isothiocyanate results in silylated derivatives of thiadiazole that are further hydrolyzed with water. In this solvent the diazomethane reacts as nitrile isomer $Me_3Si{-}C{\equiv}N^{+}{-}N^{-}{-}Li$ [25].



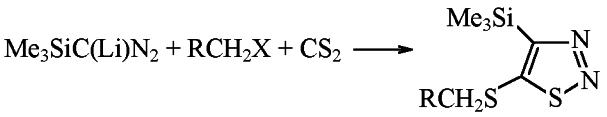
The lithium derivative of trimethylsilyldiazomethane with ketene imines gives rise to 1,5-disubstituted 4-trimethylsilyl-1,2,3-triazoles (yield 67–82%) [26].



R^1, R^2 = Ph, Alk; R^3 = Ar.

The mechanism of the reaction consists in nucleophilic attack on *sp*-hybridized carbon from ketene imine of lithiotrimethylsilyldiazomethane that provides an intermediate which under water treatment yields the corresponding 1,2,3-triazole derivative [26].

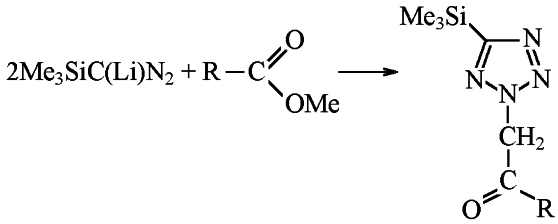
The reaction of lithiotrimethylsilyldiazomethane and a reactive hydrocarbyl halide with carbon disulfide provides 5-hydrocarbyl-4-trimethylsilyl-1,2,3-thiadiazoles [27].



R = H, X = I; R = C_6H_5, X = Br.

The di(*tert*-butyl)thioketone reacts with $Me_3SiC{-}(Li)N_2$ to afford 4-*tert*-butyl-5-trimethylsilyl-1,2,3-thiadiazole (yield 80%). Note that thioketones with less bulky substituents do not enter into this reaction [28].

The lithiotrimethylsilyldiazomethane is also used in preparation of C-trimehylsilyltetrazole. For instance, the carboxylic acids esters treated with this synthon cyclize into the corresponding 2-R-5-trimethylsilyltetrazoles [29].



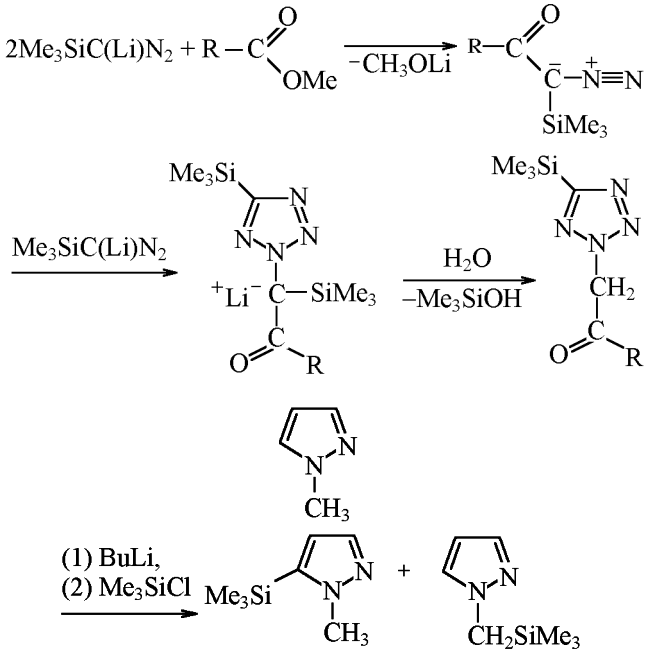
R = C_2H_5, C_6H_5, 4-C_6H_4X, $CH_2C_6H_5$, 3-C_5H_5N;
X = CH_3, Cl, OMe.

The initial stage of the reaction is apparently an attack of the lithiotrimethylsilyldiazomethane on the carbonyl carbon of the ester. The zwitter-ionic ketone thus formed reacts with the second molecule of the lithiotrimethylsilyldiazomethane giving an intermediate cyclic adduct that on hydrolysis furnishes 2-substituted 5-trimethylsilyltetrazole [29].

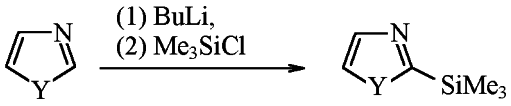
Another common method of C-trimethylsilylazole synthesis is a metallation of heterocycles (usually with butyllitium) followed by treating with trimethylchlorosilane. However this method cannot be used for preparation of azoles and benzazoles with unsubstituted "pyrrole" nitrogen. Nevertheless the azoles with no endocyclic NH moiety fairly cleanly are converted into C-trimethylsilylazoles.

The 1-substituted pyrazoles (1-methyl-, 1-methyl-3-trimethylsilyl-, and 1-methyl-4-trimethylsilylpyrazoles) are usually lithiated in position *5* providing a possibility to convert them into the corresponding 5-trimethylsilyl derivatives [30]. With 1-methylpyrazole and its derivatives the process is ac-

companied by side reaction, a silylation of the methyl group.

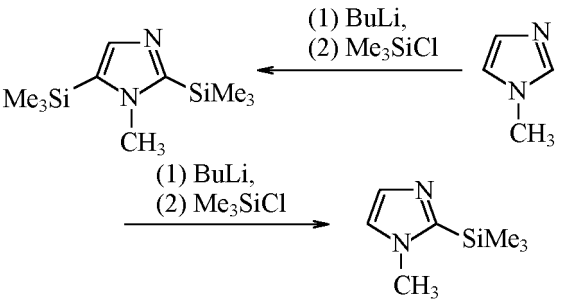


The lithiation and subsequent trimethylsilylation of 1,3-diazoles occurs predominantly into *2* position.



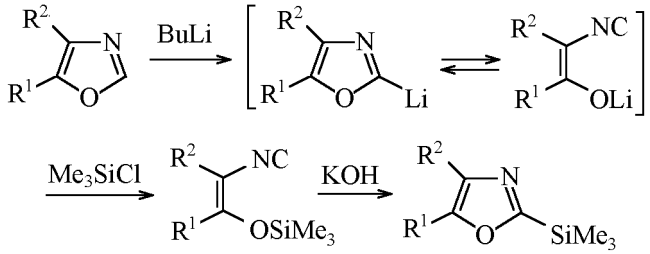
Y = N(CH$_3$), O, S.

For instance, reaction of 1-methylimidazole with 1 equiv of butyllitium affords 1-methyl-2-lithioimidazole that treated with trimethylchlorosilane yields 1-methyl-2-trimethylsilylimidazole [31, 32]. At an excess lithiating agent both carbons in positions *2* and *5* are lithiated, and the subsequent treatment with trimethylchlorosilane results in 1-methyl-2,5-bis(trimethylsilyl)imidazole [32–36]. The preparation conditions for the latter were optimized [33].



Similarly using one or two equiv of butyllithium were successfully obtained both 2-trimethylsilyl- and 2,5-bis(trimethylsilyl)thiazoles [37–39].

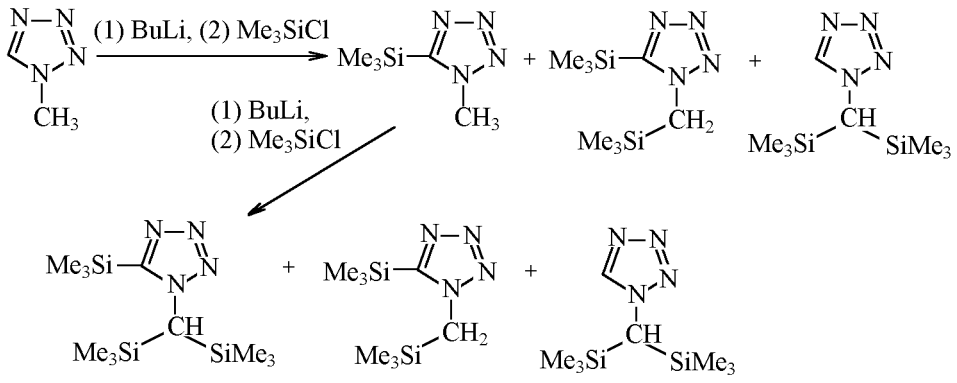
The oxazoles cannot undergo direct lithiation: a heterocycle opening occurs instead, and the subsequent treatment with trimethylchlorosilane affords a derivative of 1-trimethylsiloxy-2-isocyanethylene. Nonetheless the latter under the action of alkali undergoes an untrivial cyclization with Me$_3$Si group transfer yielding the corresponding 2-trimethylsilyloxazole [40, 41].



R^1 = R^2 = Ar; R^1 = H, R^2 = Me.

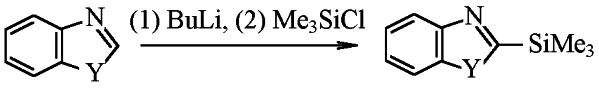
At the same time the β-O-trimethylsilylethyl isocyanide obtained by lithiation and silylation of 4,4-dimethyloxazoline does not undergo cyclization into the corresponding 2-(trimethylsilyl)oxazoline [41].

The main product from reaction of 1-methyltetrazole with butyllithium and trimethylchlorosilane



is 1-methyl-5-trimethylsilyltetrazole. Alongside this compound forms a hard-to-separate mixture of 1-(trimethylsilyl)methyl-5-trimethylsilyl- and 1-(bis(trimethylsilyl)methyltetrazoles [42]. Further lithiation and silylation of 1-methyl-5-trimethylsilyltetrazole provides as the prevailing product 1-bis(trisilylmethyl)methyl-5-trimethylsilyltetrazole in 36% yield [42].

The 1-methylbenzimidazole [31, 32] and the benzothiazole [43–48] when treated with BuLi and further with Me_3SiCl give rise to trimethylsilylbenzazoles.

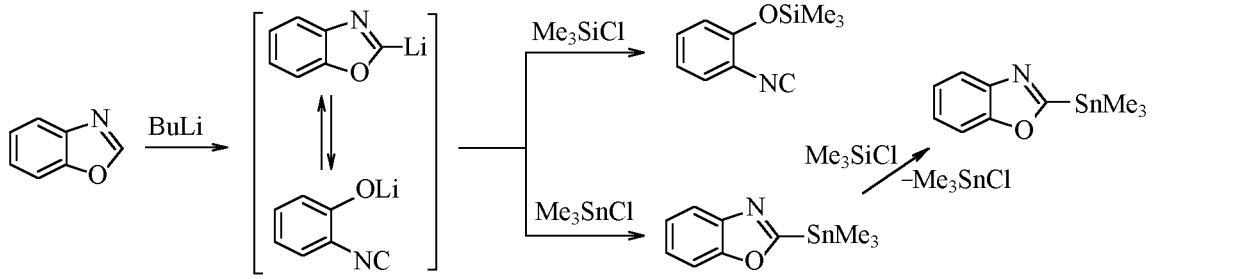


Y = NCH_3, S.

Unlike the above compounds the benzoxazole treated with butyllithium provides an isomeric mixture of two lithium derivatives [49]. At the following treatment with trimethylchlorosilane was separated only 1-trimethylsiloxy-2-isocyanobenzene. On the contrary the reaction of the mixture with trimethylchlorostannane yielded 2-trimethylstannylbenzoxazole [49]. The latter was transformed into 2-trimethylsilylbenzoxazole by the action of trimethylchlorosilane [49].

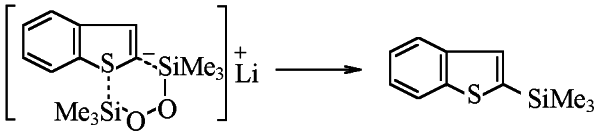
It is presumable that similar to oxazole [40] in the alkaline medium 1-trimethylsiloxy-2-isocyanobenzene would transform into 2-trimethylsilylbenzoxazole; however no attempts to perform this reaction are known.

By treating benzimidazole with butyllithium followed by reaction with trimethylchlorosilane was



obtained in low yield (17%) 2-trimethylsilylbenzimidazole [32]. The latter is apparently a product of silylotropic rearrangement of 1-trimethylsilylbenzimidazole (see further).

In some cases the C-trimethylsilylazoles are prepared through C-bromoazoles. They are converted into C-trimethylsilylazoles by successive treatment with butyllithium and trimethylchlorosilane [37, 38, 50], or by magnesium and trimethylchlorosilane (under conditions of Grignard reaction) [30, 51]. This procedure is commonly used when the trimethylsilyl group should be bonded to a carbon atom that does not form a carbanion center on lithiation. The treatment with bis(trimethylsilyl)peroxide $Me_3SiOOSiMe_3$ of C-lithium derivatives of azoles with a carbanion



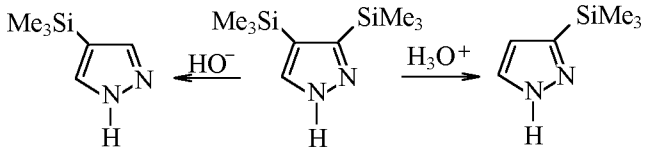
+ $[Me_3SiOOLi]$

center in the α-position with respect to heteroatom (e.g., 2-lithiobenzothiazole) arise solely the corresponding C-trimethylsilyl derivatives. The mechanism of the reaction is presumed to involve intermediate formation of a six-membered transition complex [52].

N-oxides of azoles undergo trimethylsilylation when treated with trimethylsilyl iodide or trimethylsilyl triflate in the presence of diisopropylamine, 1,2,2,6,6-pentamethylpiperidine, or lithiotetramethylpiperidide [53, 54]. The reaction starts by O-silylation of the O ← N group followed by deprotonation of the ring and trimethylsilylation of the arising carbanion.

I.2. *Chemical Properties*

In the chemistry of heterocyclic compounds is extensively used the protodesilylation reaction of C-trimethylsilylazoles. Already in 1972 Birkofer and Franz discovered that in protodesilylation of 3(5),4-bis(trimethylsilyl)pyrazole depending on the reaction condition occurred cleavage of different C–Si bonds.

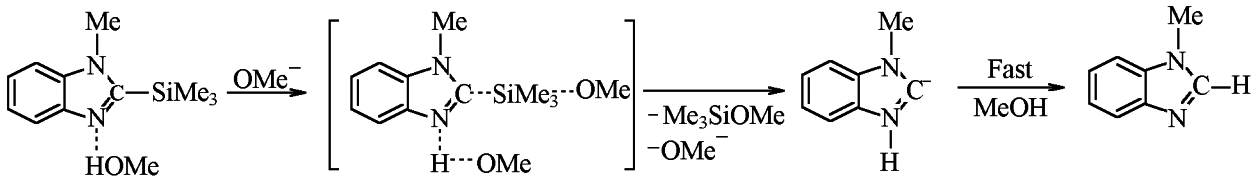


In acidic medium the reaction yields 3(5)-trimethylsilylpyrazole, whereas in alkaline environment the product is 4-trimethylsilylpyrazole [1].

The different regiodirection in desilylation of the 3(5),4-bis(trimethylsilyl)pyrazole when treated with acids or alkali may be rationalized taking into account higher nucleophilicity of the silicon in the 3-trimethylsilyl group facilitating its cleavage under actions of nucleophiles in water medium. In contrast, the trimethylsilyl group in *4* position provides better opportunity to form the corresponding carbanion favoring the electrophilic protodesilylation.

The protodesilylation was successfully applied to preparative problems. Along this process were obtained 3(5)-phenylpyrazole [1], 4-bromopyrazole [4], 4-alkoxypyrazoles [6], 4-organyl-1,2,3-triazoles [17, 21], 1-methyl-5-trimethylsilylimidazoles [32–36], 4- and 5-trimethylsilylthiazoles [38], derivatives of benzothiazole [45] etc. The kinetics and cleavage mechanism of Si–C bond in azoles was investigated [55–57]. The desilylation reaction rate of 1-methyl-2-trimethylsilylbenzimidazole and 2-trimethylsilylbenzothiazole in anhydrous or aqueous methanol in the presence of a base (MeONa) or an acid ($HClO_4$) corresponds to the first order reaction. The cleavage of the Si–C bond in the 1-methyl-2-trimethylsilylbenzimidazole in the presence of a base may be regarded as proton transfer to the nitrogen atom of N=C moiety with simultaneous cleavage of C–$SiMe_3$ bond whereas the rupture of the bond in the 2-trimethylsilylbenzothiazole requires some electrophilic "assistance."

The acid-catalyzed desilylation of benzazole is due to the attack on silicon atom in the benzazole cation by a solvent molecule [55].



The effect of the base nature on the cleavage the Si–C bond in 2-(trimethylsilyl)benzothiazole was studied in the presence of benzaldehyde as electrophilic acceptor of the arising carbanion [57]. A correlation was found between the relative reaction rates and Hammett's σ-constants of substituents. The process starts by attack on the silicon atom followed by dissociation of the pentacoordinated intermediate in the limiting stage of the reaction [40].

The exceptional lability of the Si–C bond in the trimethylsilylazoles is demonstrated in various *ipso*-substitution reactions. For instance, 3(5),4-bis(trimethylsilyl)pyrazole treated with bromine affords 4-bromo-3(5)-trimethylsilylpyrazole or 3(5),4-dibromopyrazole [1]. Similar reaction with bromine or iodine is described for 1-methyl-3,5-bis(trimethylsilyl)pyrazole and 1-methyl-4,5-bis(trimethylsilyl)-pyrazole [30]. The *ipso*-substitution of trimethylsilyl group in trimethylsilylazoles occurs with nitroso [58] and nitro [50] groups.

C-trimethylsilylazoles undergo transsilylation and transmetallation. For instance, 2-trimethylsilylbenzothiazole with 2-(dimethylchlorosilyl)benzothiazole provide dimethyl-bis(benzothiazolyl-2)silane [44, 45, 59].

In a similar way 1-methyl-2-trimethylsilylimidazole reacts with dimethyldichlorosilane to afford dimethyl-bis(1-methylimidazolyl-2)silane [32]. The transmetallation of C-trimethylsilylazoles is also used for preparation of bis(benzazolyl)germanes [59], -stannanes [48], and phosphines [60].

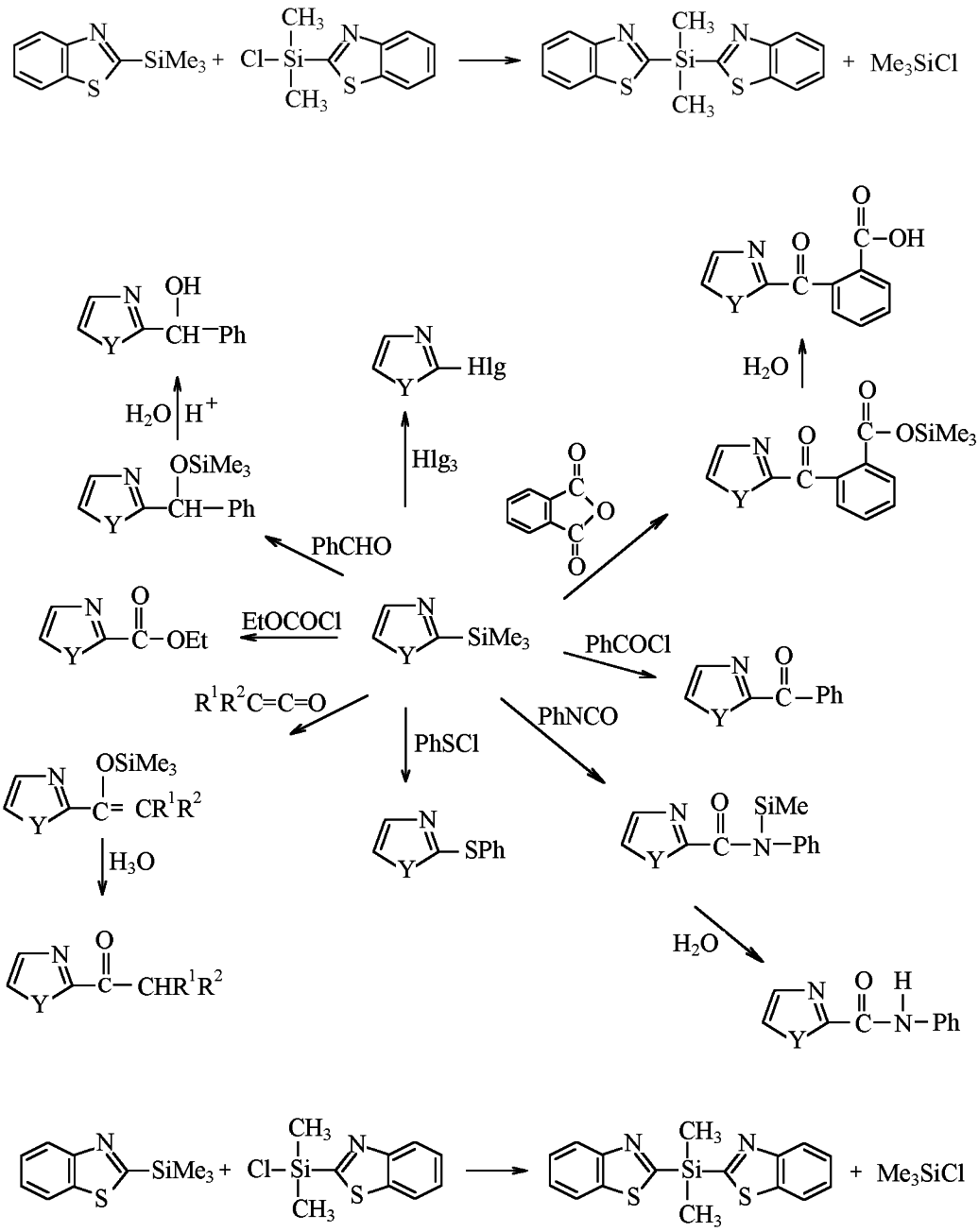
The application of C-trimethylsilylazoles prone to electrophilic substitutions permits introduction of various functional groups into the azole cycle, This may be illustrated with a general scheme.

C-trimethylsilylazoles are fairly readily cleaved with acyl halides [30, 31, 38, 40, 43, 45, 61]. The most reactive are 2-trimethylsilylazoles [31, 38, 43, 45, 61–64]: here the reaction occurs without catalyst. The C-trimethylsilylazoles with the trimethylsilyl group in position *5* undergo the cleavage less easily. Finally, the elimination of the $SiMe_3$ group from the *4* position of the imidazole ring requires the use of Friedel–Krafts catalyst [30].

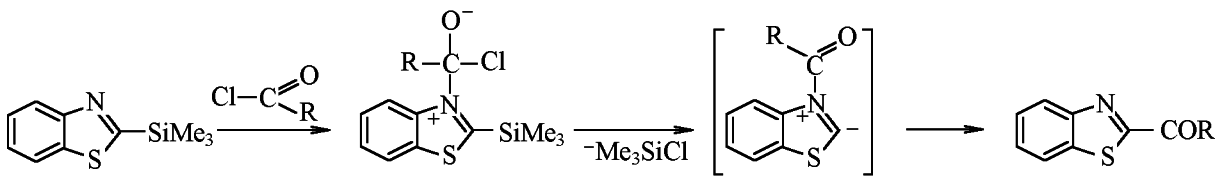
The following mechanism is suggested for substitution of the trimethylsilyl group in 2-trimethylsilylbenzothiazole.

Similarly react the C-trimethylsilylazoles with anhydrides of carboxylic and dicarboxylic acids (in particular, with succinic and phthalic anhydrides) [31, 43, 63]. In their reactions with halogens [30, 65], isocyanates [31], and ketenes [37, 66] occurs *ipso*-substitution of the trimethylsilyl group.

The reaction of C-trimethylsilylazoles with carbonyl compounds, in particular with aldehydes, is well studied [30, 31, 35, 37–41, 43, 61, 65, 67–88]. The most thoroughly investigated in this regard substance is 2-trimethylsilylthiazole (Dondoni



Y = NCH_3, S.



R = CH_3, $CHCl_2$, C_6H_5, 4-$C_6H_4OCH_3$.

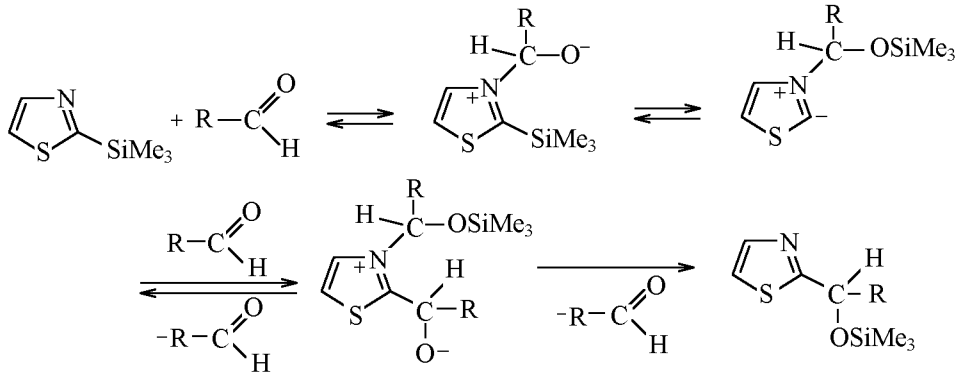
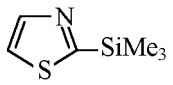
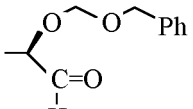
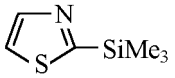
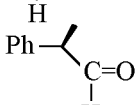
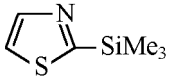
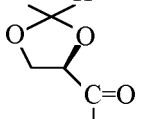
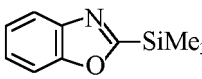
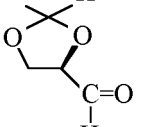
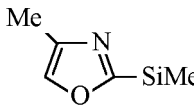
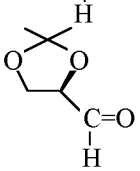
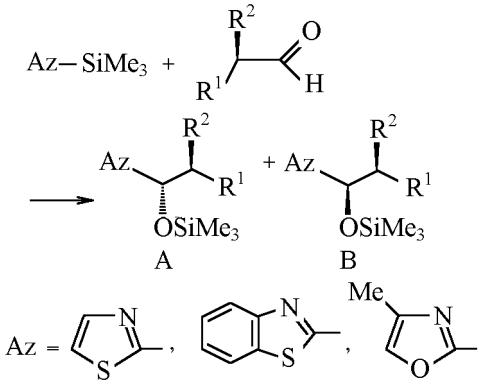


Table 1. Diastereoisomers ratio in the reaction products of 2-trimethylsilylthiazole with α-chiral aldehydes [70]

Azole	Aldehyde	Ratio A : B (yield, %)
		33 : 66 (70)
		73 : 27 (73)
		>95 : <5 (93)
		80 : 20 (65)
		21 : 79 (60)

reagent). The mechanism of its reaction with aldehydes is given in the scheme above [38, 65, 82, 88–90]:

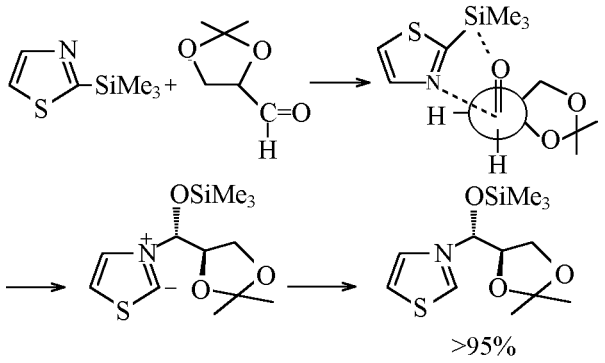
This reaction attracted special interest since the discovery that 2-trimethylsilylthiazole, 2-trimethylsilylbenzothiazole, and 2-trimethylsilyl-4-methyloxazole with α-chiral aldehydes gave rise with high stereoselectivity the insertion products of the aldehydes into the C^2–Si bond.



This reaction was applied to stereoselective homologization of the D-glyceraldehyde [39, 41, 70]. The highest diastereoselectivity (≥95%) was obtained with the 2-trimethylsilylthiazole (Table 1) [70, 72]. This is the reason of the great interest in the latter reagent. In Table 1 is demonstrated the possibility to

control the diastereomeric composition of the final products. The heterocycle nature significantly affects the yield and diastereomer purity of the reaction products.

This high stereoselectivity may be rationalized proceeding from the structure of the transition state in the reaction between the 2-trimethylsilylthiazole and an aldehyde [70, 75, 76].

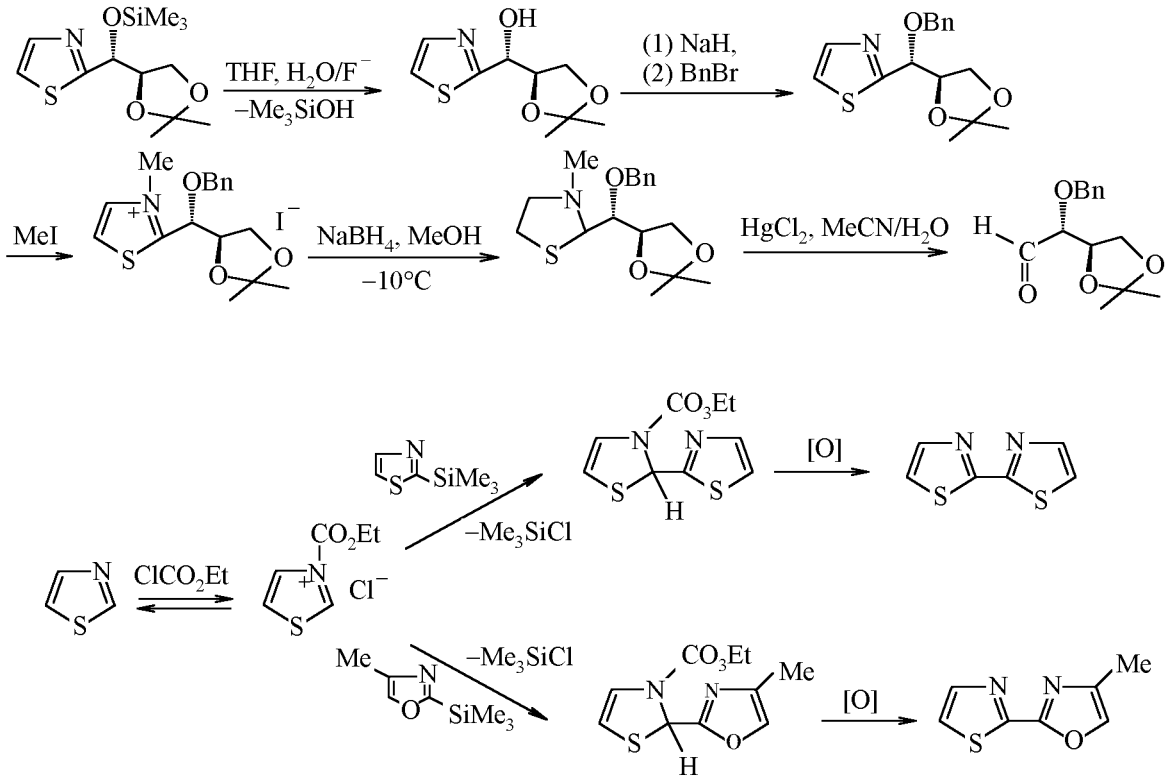


The thiazolyl group can be transformed into an aldehyde group through quaternization followed by reduction and hydrolysis according to the scheme below [38, 39, 65, 70, 72, 76].

Thus arises an opportunity of successive asymmetric synthesis of a homologous series for α-chiral aldehydes. This line of investigation designated as "thiazole way" of asymmetric synthesis is now extensively developed. The application thereof provides a possibility to prepare O-alkoxy-D-tetroses and D-pentoses [80], long-chain aminosugars [73, 74, 78], higher carbohydrates [75, 76], unusual amino-acids [83] and some other chiral compounds. The 2-trimethylsilylthiazole is used in the synthesis of antiphlogistic agents [63], inhibitors of HIV-protease [81, 86, 87], and in particular of a promising drug *Saquinavir Mesylat* [91]. The size of this review does not allow more detailed discussion on the opportunities and promising aspects of the "thiazole way" of asymmetric synthesis, and we recommend to the reader a monograph [92] and the recently published by A. Dondoni review [88].

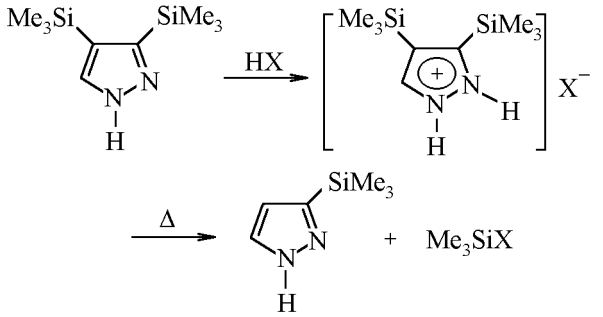
The 2-trimethylsilylthiazole reacts also with ketones affording tertiary alcohols [93, 94]; some among the latter show fungicidal properties [93].

An interesting reaction of 2-trimethylsilylthiazole and 2-trimethylsilyl-4-methyloxazole with a product of thiazole (or pyridine and quinoline) quaternization, ethyl chloroformate, results in adducts that at oxidative deacylation with the o-chloranil give bis-azoles [95].



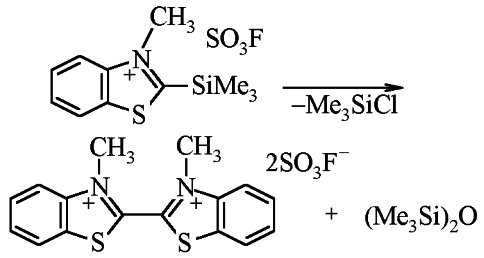
1-Adamantyl halides react with 2-trimethylsilylbenzothiazole in the presence of Lewis acids ($TiCl_4$, $AlCl_3$, $ZnCl_2$) yielding 6-adamantylbenzothiazole [96, 97]

The 3(5),4-bis(trimethylsilyl)pyrazole when treated with concentrated nitric or hydrochloric acid affords the corresponding salts [98]. Thermolysis of the latter with elimination of trimethylsilyl nitrate or trimethylchlorosilane results in 3(5)-trimethylsilylpyrazole.

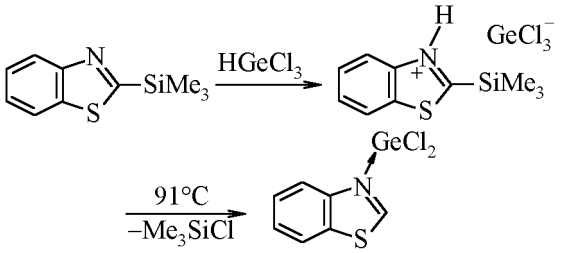


X = ONO_2, Cl.

2-Trimethylsilylazolium ions readily undergo desilylation yielding the corresponding dimers [45, 99] that catalyze the benzoin condensation [99].



The reaction between 2-trimethylsilylbenzothiazole with trichlorogermane first gives 2-trimethylsilylbenzothiazolium trichlorogermanate. On its dehydrosilylation at heating or at dissolution in benzene, chloroform, or ethyl bromide arises a monomeric 3-benzothiazoledichlorogermylene [100, 101]. The structure of the latter was proved by X-ray diffraction analysis [100].



Monocarbonylgold chloride also gives complexes with 2-trimethylsilylbenzothiazole and 1-methyl-2-trimethylsilylbenzimidazole. The Si–C bond in these complexes is considerably less active than in the original compounds [102]. The heating of these complexes results in liberation of elemental gold.

The highly labile Si–C^2 bond in the 2-trimethylsilylbenzothiazole also provides an opportunity to prepare various 2-substituted benzothiazoles [43].

II. *N*-TRIMETHYLSILYLAZOLES

II.1. *Preparation Methods*

The prevailing method for preparation of *N*-trialkylsilylazoles is trialkylsilylation of the corresponding azoles.

This is done mostly with the use of trialkylhalosilanes [103–108] or hexamethyldisilazane [109–129]. The data on N-trimethylsilylazoles prepared by silylation with various silylating agents are listed in Table 2.

In silylation of azoles with trialkylhalosilanes tertiary amines or excess azole are used to bind the hydrogen halide [103–108]. The trimethylsilylation with hexamethyldisilazane is catalyzed with mineral acids [115], ammonium sulfate [113, 126], trimethylhalosilanes [128, 129], or with compounds of XNHY type where at least one of X or Y groups is a strong electron-acceptor [117] (e.g. saccharin [117] or its salt [123]). Sometimes N-trimethylsilylazoles thus prepared are used in further syntheses without additional purification for they form in high yields [127–129].

The trimethylsilylation of azoles with trimethylchlorosilanes and hexamethyldisilazane often occurs in different positions. For instance, the reaction between tetrazole and trimethylchlorosilane affords 1-trimethylsilyltetrazole (see Table 2) whereas with hexamethyldisilazane was isolated only *N*,*N*'-bis(trimethylsilyl)carbodiamide [130].

The reaction of 1,2,3-triazole with trimethylchlorosilane gives rise to 2-trimethylsilyl-1,2,3-triazole [104, 105]. Its reaction with hexamethyldisilazane results in a mixture of 1- and 2-trimethylsilyl-1,2,3-triazoles in 1 : 5 ratio (Table 2, also chapter III) [116].

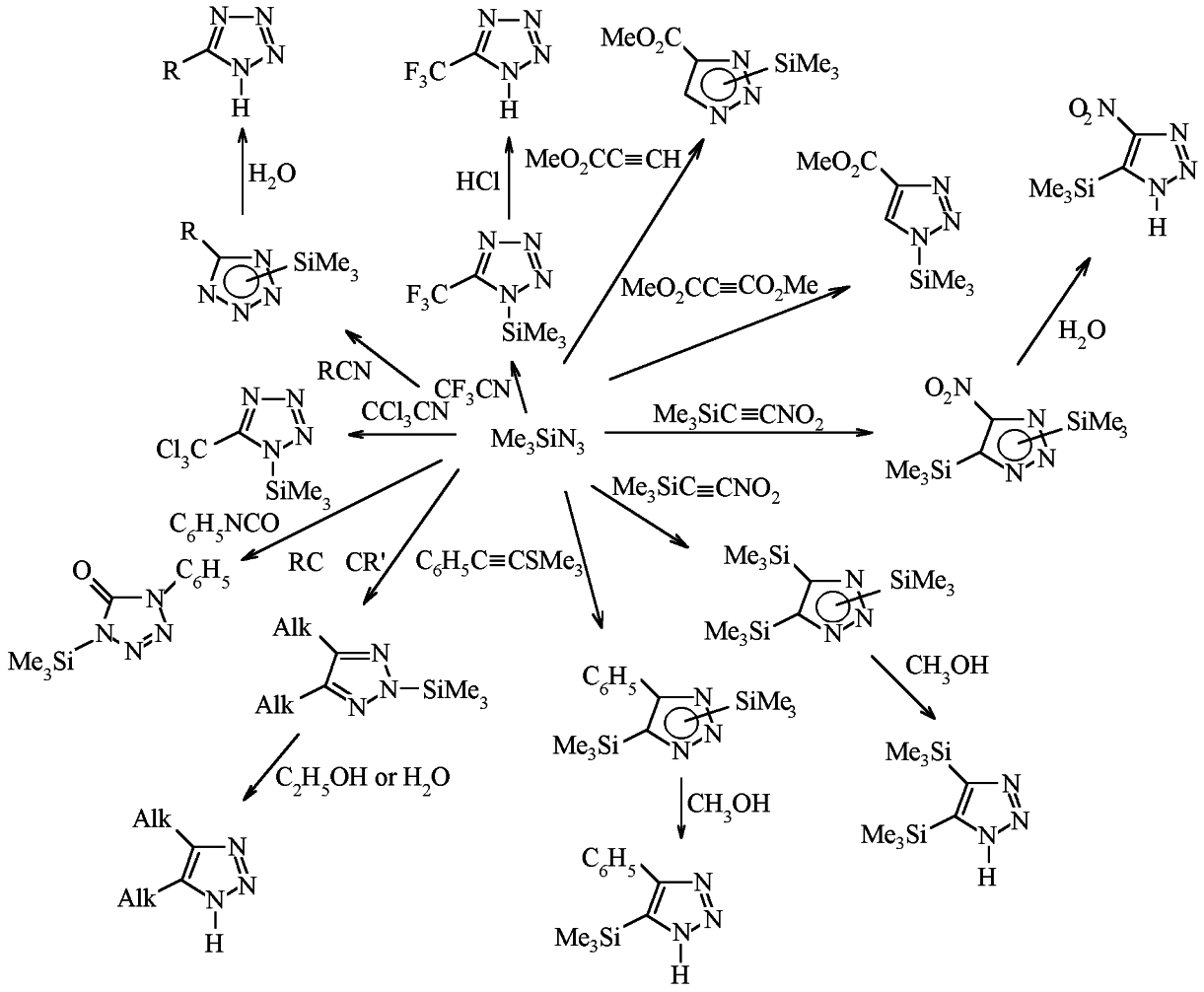
The boiling of 1,2,4-triazole with hexamethyldisilazane affords derivative with trimethylsilyl group in position *1* [109, 112, 120–124]. In a similar reaction with trimethylchlorosilane arises a mixture of 1- and 4-trimethylsilyl-1,2,4-triazoles (Table 2) [103]. The above findings show that the regio-

selectivity of azoles trialkylsilylation with various reagents requires additional investigation.

Trialkylsilylation of azoles with the other silylating agents {trimethyl(dialkylamino)silane [121, 122, 131, 132], trimethylsilyldiphenylcarbamide [122], and *N*,*O*-bis-trimethylsilylacetylindol [121, 122]} is used more seldom.

Since the *N*-trimethylsilylazoles are used in important applied positions a patent was taken on semicommercial installation for silylation process [107].

A trimethylsilyl azide is widely applied to the synthesis of *N*-trimethylsilyl azides [8, 17, 130, 133–138].



R = Me, Ph, 4-pyridyl-5-ferrocenyl.

Since the handling of trimethylsilyl azide is significantly less hazardous than free hydrazoic acid, and the N-trimethylsilyl group easily undergoes protolytic elimination, this method is widely applied to preparation of the corresponding 1,2,3-triazoles and tetrazoles. The other trialkylsilyl azides react in the same way [138]. Sometimes the trimethylsilyl azide can be generated in situ. In this case is used a mixture of trimethylhalosilane and sodium azide in acetonitrile medium [138]. In a number of publications the exact place where the trimethylsilyl group is linked to heterocycle is not indicated or is described without any proofs [133, 136, 137]. An irreversible migration of the trimethylsilyl group in the N-trimethylsilyl-1,2,3-triazole into *2* position should be mentioned [8, 17].

The addition product of reaction between trimethylsilyl azide and norbornadiene decomposes under synthesis conditions yielding 2-trimethylsilyl-

Table 2. Products of azoles trimethylsilylation with various silylating agents

Original azoles	Reagents[a]	Reaction products	bp, °C (*p*, mm Hg)	n_D^{20}	Yield	References
Pyrazole	A	1-Trimethylsilylpyrazole	153 (760)	1.4599	34–90	109–112
	B		40 (0.5)	1.4599	100	103
	C		69 (30)	1.4598	80	131
4-Chloropyrazole	A	1-Trimethylsilyl-4-chloropyrazole	59–61 (5)	1.4750	85	114
4-Bromopyrazole	A	4-Bromo-1-trimethylsilylpyrazole	48–49 (1)	1.4965	90	114
4-Iodopyrazole	A	4-Iodo-1-trimethylsilylpyrazole	78–79 (1)	–	95	114
3(5)-Methylpyrazole	A	3(5)-Methyl-1-trimethylsilylpyrazole	167–168	1.4655	94.4	115
	A		37–38 (1.5)	1.4620[b]	85.5	116
4-Methylpyrazole	A	4-Methyl-1-trimethylsilylpyrazole	50–51 (5)	1.4635[b]	66.7	116
3-Trimethylsilylpyrazole	A	1,3-Bis(trimethylsilyl)pyrazole	47–48 (1.5)	1.4592[b]	96.2	116
4-Trimethylsilylpyrazole	A	1,4-Bis(trimethylsilyl)pyrazole	64–65 (1.5)	1.4640[b]	98.5	116
3(5),4-Bis(trimethylsilyl)-pyrazole	A	1,3,4-Tris(trimethylsilyl)pyrazole	80–81 (1.0)	1.4710[b]	95.7	116
3-Ethoxycarbonylpyrazole	A	1-Trimethylsilyl-3-ethoxycarbonylpyrazole				113
3,5-Dimethylpyrazole	A	3,5-Dimethyl-1-trimethylsilylpyrazole	73 (12)	1.4708	59	109
	A		185–186		61	110, 111
	C		84 (18)		80	132
3,5-Bis(trifluoromethyl)-pyrazole	A	1-Trimethylsilyl-3,5-bis(trifluoromethyl)pyrazole	135–136		85	110
3,4,5-Trimethylpyrazole	A	1-Trimethylsilyl-3,4,5-trimethylpyrazole	204–205	–	70	110
Imidazole	A	1-Trimethylsilylimidazole	91 (12)	1.4756	72–88	135, 109 112, 117
	B		50 (15)	1.4756	95	103
2-Methylimidazole	A	2-Methyl-1-trimethylsilylimidazole	40 (0.4)	–	64	112
			47–50 (0.1)	–	34	118
	B				85	108
Imidazolin-2-one	A	1-Trimethylsilyl-2-(trimemethylsilyloxi)imidazole	T.subl. 105 (15)	–	78	119
1,2,4-Triazole	A	1-Trimethylsilyl-1,2,4-triazole	74 (12)	1.4604	81	109
			80 (15)	–	85	112, 120
			78–79 (12)	–	80	121, 122
			72–74 (11)	–	96	123
			20–70 (1.5)	–	56	124
	B	1-Trimethylsilyl-1,2,4-triazole + 4-Trimethylsilyl-1,2,4-triazole	70–200 (1.5)		11	103
3-Chloro-1,2,4-triazole	A, C, D	1-Trimethylsilyl-3-Chloro-1,2,4-triazole	59–60 (1.5)	–	80	121, 122

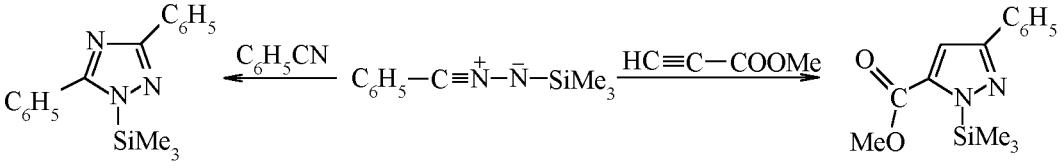
Table 2. (Contd.)

Original azoles	Reagents[a]	Reaction products	bp, °C (*p*, mm Hg)	n_D^{20}	Yield	References
3-Methyl-1,2,4-triazole	A	3-Methyl-1-trimethylsilyl-1,2,4-triazole	41–42 (1)	–	93–95	121, 122
3-Bromo-1,2,4-triazole	A	3-Bromo-1-trimethylsilyl-1,2,4-triazole	73–74 (2)	–	88	122
3-Nitro-1,2,4-triazole	A, C, D	3-Nitro-1-trimethylsilyl-1,2,4-triazole	107–108 (0.8)	–	93	122
1,2,3-Triazole	A	1-Trimethylsilyl-1,2,3-triazole + 2-Trimethylsilyl-1,2,3-triazole (1 : 5)	147–148			116
	C	2-Trimethylsilyl-1,2,3-triazole	80–81 (90)	1.4490[b]	81–96	104
4-Methyl-1,2,3-triazole	B	4-Methyl-2-trimethylsilyl-1,2,3-triazole	83–84 (55)	1.4523	81–96	104
Tetrazole	B	1-Trimethylsilyltetrazole	110 (0.1)		70	130, 103
5-Phenyltetrazole	A	2-Trimethylsilyl-5-phenyltetrazole	104–105 (0.05) mp 25		88	130
Indazole	A	1-Trimethylsilylindazole	132 (18)	1.5445	79	109, 113
Benzimidazole	A	1-Trimethylsilylbenzimid-azole	112 (0.3) mp 66–67		89	109
			103–104 (2)	1.5455	92.7	115
			155 (4)		73	125
			mp 60–65		92	126
Benzoxazol-2-one	B	N-$SiMe_3$-Benzoxazole[c]	85 (1.33)	1.5240	94	106
Benzotriazole	A	1-Trimethylsilylbenzo-triazole	100–110 (0.2)	–	95	118

[a] A, $(Me_3Si)_2NH$, B, Me_3SiCl, C, Me_3SiNMe_2, D, $Me_3SiN{=}C(Me)OSiMe_3$. [b] Determined at 25°C. [c] See chapter III.

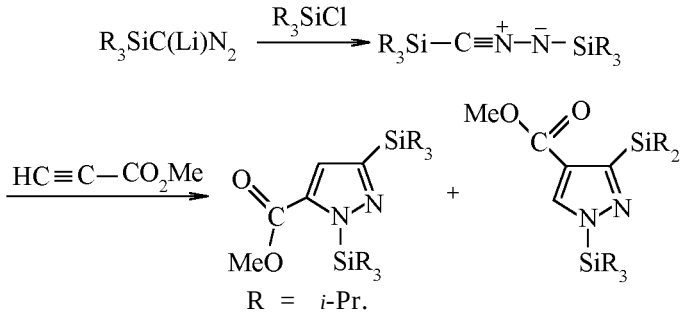
1,2,3-triazole and a little of bis-triazoline adduct [139].

Trimethylsilyl nitrile imines arising on thermolysis of 5-substituted 2-trimethylsilyltetrazoles also can be used in the synthesis of *N*-trimethylsilylpyrazoles and -1,2,3-triazoles [140, 141]. For instance, the reaction of C-phenyl-*N*-trimethylsilylnitrile imine with aromatic nitriles [136] or with methyl propiolate [141] results respectively in 3,5-diphenyl-1-trimethylsilyl-1,2,4-triazole and 5-methoxycarbonyl-1-trimethylsilyl-3-phenylpyrazole.



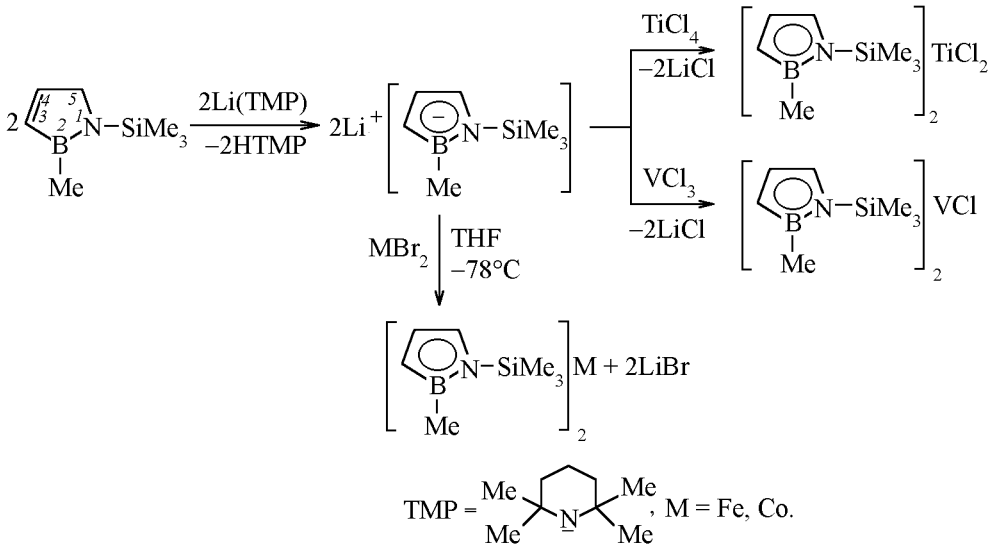
Trimethylsilylnitrile imines can be prepared by reaction of trialkylsilyllithiodiazomethanes with trialkylhalosilanes [142]. Thus was obtained *C*,*N*-bis-(triisopropylsilyl)nitrile imine. By treating with methyl propiolate it was converted into a mixture of 4-methoxycarbonyl- and 5-methoxycarbonyl-1,3-bis (triisopropylsilyl)pyrazoles in 52 : 48 ratio [142].

Pyrazoline analog, 2-methyl-1-(trimethylsilyl)-1,2-azaborolinyllithium obtained in reaction of 2-methyl-



R = *i*-Pr.

1-(trimethylsilyl)-Δ^3-1,2-azaboroline with 1-lithio-2,2,6,6-tetramethylpiperidine, reacts with $TiCl_4$, VCl_3 [143], $FeBr_2$, and $CoBr_2$ [144] giving rise to the corresponding sandwich complexes of bis[2-methyl-1-(trimethylsilyl)-ν^5-1,2-azoborolinyl] including interplane fragments $TiCl_2$, VCl, Fe, and Co.



The data of X-ray diffraction study and ^{11}B NMR spectra show that in the first two complexes occurs interaction between boron and chlorine atoms (interatomic distance B...Cl in the first one is 2.978 and 2.954 Å, in the second 2.984 Å). This is due to the absence of coordination between the central metal atom (Ti, V) and the endocyclic boron atom [143].

Similar complexes with V, Fe, and Co were obtained by reaction of 2-methyl-1-trimethylsilyl-Δ^3-1,2-azaboroline with appropriate metal atoms in a vacuum of 10^{-4} mm Hg at −130°C. The structure of the complexes was also proved by ^{11}B NMR spectra and X-ray diffraction analysis [145, 146].

The reaction of 1-ethyl and 1-vinylimidazole with triethyliodosilane apparently yields the corresponding iodides of 1-organyl-3-(trimethylsilyl)imidazolium that are fluids stable at distillation in a vacuum [147]. The above structure may be assigned thereto since the trimethyliodosilane with trialkylamines gives rise to trialkyl(trialkylsilyl)ammonium iodides $R_3(R'_3Si)N^+ I^-$ [148]. Unlike that the reaction of these 1-organylimidazoles with triethylbromosilane results in adducts of 2:1 composition that also are fluids stable at distillation in a vacuum [147]. For the compounds were investigated IR and ^1H NMR spectra. It is presumable that if these 2:1 complexes the silicon is hexacoordinate, and they possess octahedric structure. The coordination of the central atom could have been revealed by ^{29}Si NMR spectra but they regretfully were not measured. It should be noted that similar complexes of 1-ethyl- and 1-vinylimidazole are formed with trialkylhalostannanes and -plumbanes [149–153].

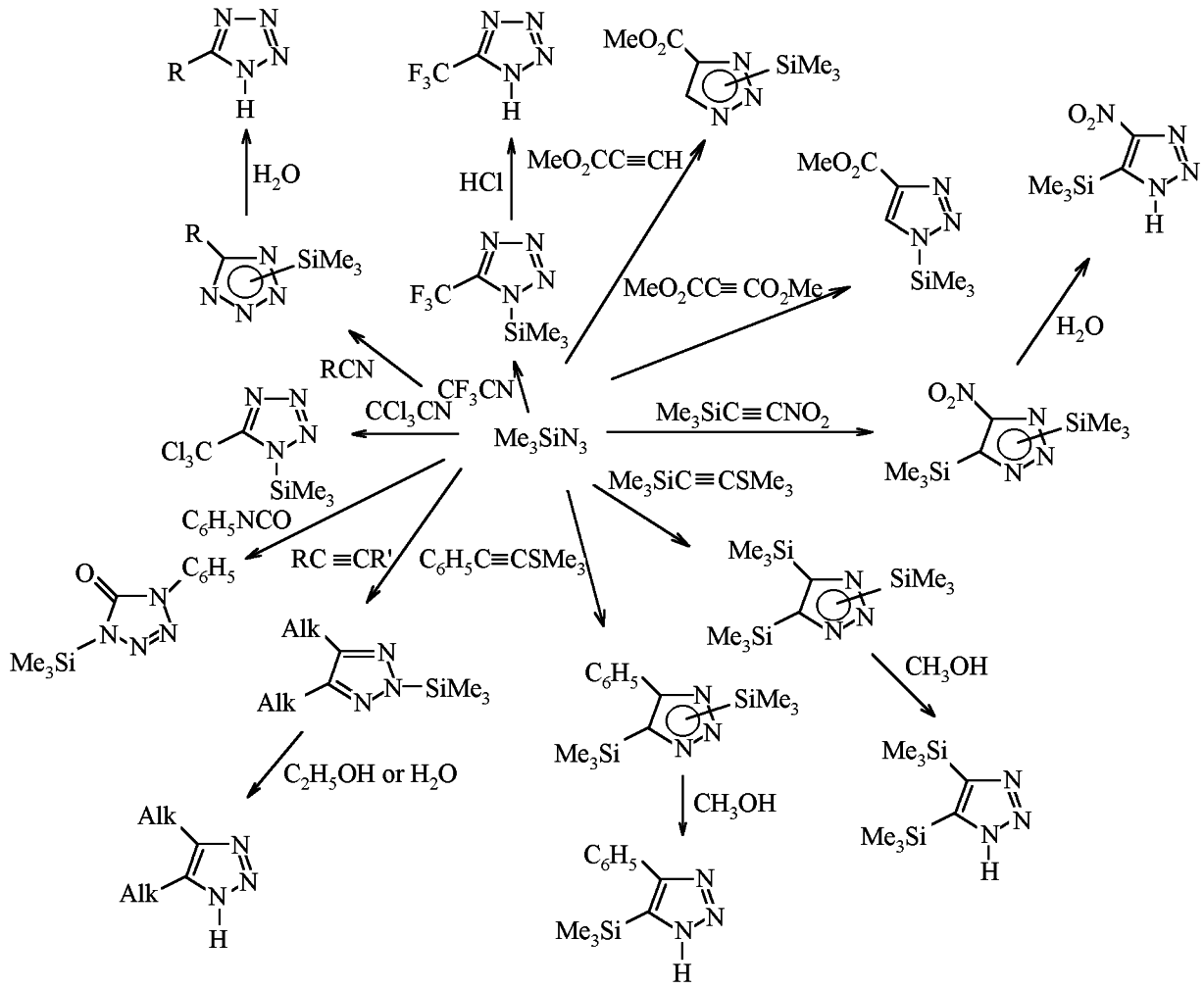
II.2. *Chemical Properties*

N-Trimethylsilylazoles, first of all 1-trimethylsilylimidazole and 1-trimethylsilyl-1,2,4-triazole, are extensively used in organic synthesis for hydroxy group protection [154–158]. They turned out to be very useful silylating agents in the fine organic synthesis [154, 159–162]. Recently in the synthesis of optically active compounds found successful application 1-(*tert*-butyldimethylsilyl)imidazole [163, 164].

N-Trimethylsilylazoles are widely applied as reagents in the peptide synthesis [165], and also in preparation of composite membranes for selective separation of gases [166].

1-Trimethylsilylimidazole is used for hydroxy groups protection in hydrocortisone at its quantitative determination by GLC in culture medium [167]. It is also used in monosaccharide analysis [168], also in milk [169, 170].

In the organic synthesis *N*-trimethylsilylazoles are used for introduction of various functional groups to a heterocyclic nitrogen atom.



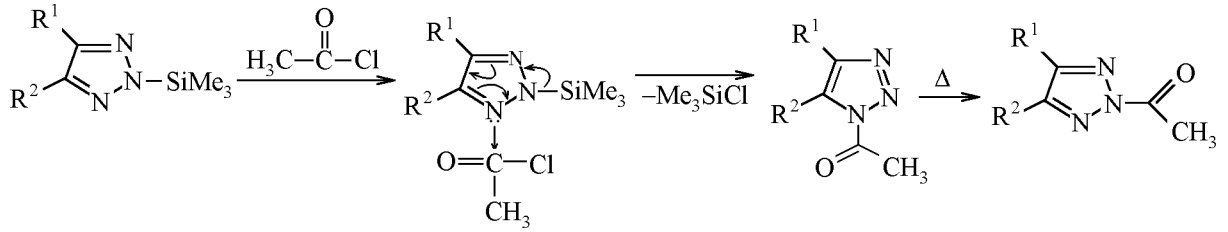
X = CH, N; Y = Hlg, N_3; *n* = 0–2.

To butoxycarbonyl protection of aminoacids is applied 1-*tert*-butoxycarbonyl-1,2,4-triazole that is prepared by reactions of 1-trimethylsilyl-1,2,4-triazole with *tert*-butyl chloroformate or azide of *tert*-butyl carbonate [171].

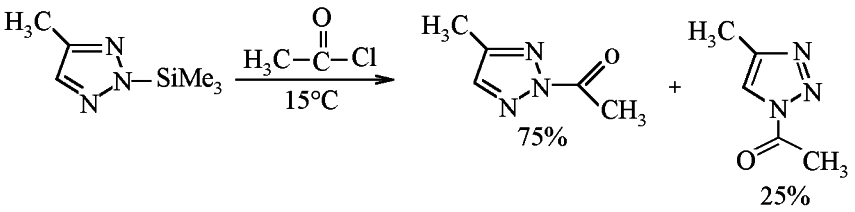
At the action of acyl chlorides on the *N*-trimethylsilylazoles form the corresponding N-acyl derivatives of the azole with trimethylchlorosilane elimination [120, 172, 173, etc.].

The primary product of 2-trimethylsilyl-1,2,3-triazole reaction with acetyl chloride is a 1-acetyl derivative that at heating isomerizes into 2-acetyl-1,2,3-triazole [104, 134].

The process is significantly affected by the size of substituents attached to carbon atom in position *5*. The acylation of 2-trimethylsilyl-4-methyl-1,2,3-triazole affords 1-acetyl-4-methyl-1,2,3-triazole (75%) and 1-acetyl-5-methyl-1,2,3-triazole (25%) [104].



R^1, R^2 = H, Alk.



The reaction between *N*-trimethylsilylazoles with phosgene is well investigated [115, 124, 174, 175]. It is interesting since it provides an easy way to *N*,*N*'-carbonyl-bis(azoles), in particular, the corresponding pyrazole, imidazole, and 1,2,4-triazole derivatives. These compounds found application to organic and especially peptide synthesis. In the latter case the aminoacids racemization either does not occur or is quite insignificant [176].

In a similar way by reaction of 1-trimethylsilylazoles with thiophosgene were obtained *N*,*N*'-thiocarbonyl-bis(azoles) [174, 177, 178]. These compounds are convenient thiocarbonylating reagents.

Similarly mono -and diazoles are formed in reactions of *N*-trimethylsilylazoles with thiobenzoyl chloride [118], trichloromethylsulfinyl chloride [118], SCl_2 [125, 174], S_2Cl_2 [174], $SOCl_2$ [174, 179, 180, 181], SO_2Cl_2 [174, 177]. Some of these compounds show interesting biological activity [177, 179].

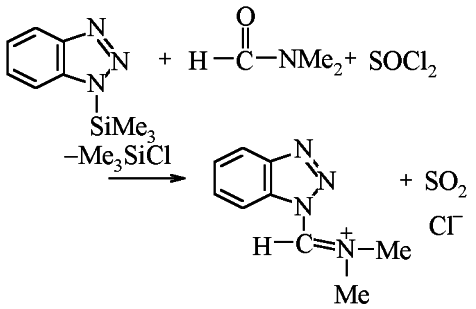
$$Az{-}SiMe_3 + RCl \rightarrow AzR + Me_3SiCl$$

$$R = CCl(SC_6H_5),\ SCCl;$$

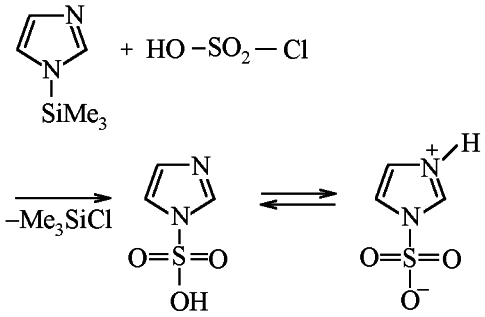
$$2\ Az{-}SiMe_3 + Cl_2Y \rightarrow Az{-}Y{-}Az + 2\ Me_3SiCl$$

$Y = S,\ S_2,\ SO,\ SO_2$; Az = pyrazole, imidazole, 1,2,4-triazole, benzimidazole, benzotriazole.

The reaction between 1-trimethylsilylbenzotriazole with *N*,*N*-dimethylformamide in the presence of thionyl chloride gives rise to *N*,*N*-dimethylbenzotriazolylmethyleniminium chloride [181, 182].

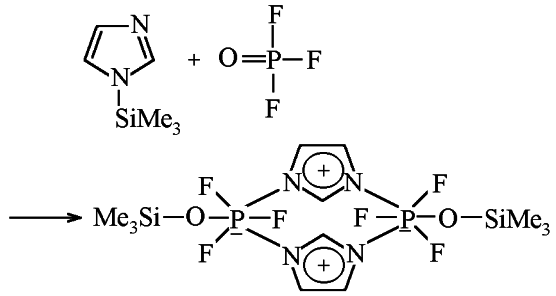


The treatment of 1-trimethylsilylimidazole with the chlorosulfonic acid affords 1-imidazolylsulfonic acid that exists as a mixture of two tautomers [183, 184]. This compound was erroneously regarded formerly as a charge-transfer complex [185].



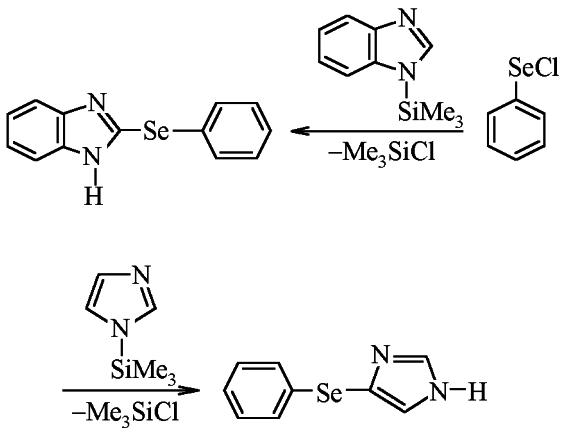
The $SiMe_3$ group is also eliminated from *N*-trimethylsilylazoles under the action of phosphorus acids chlorides [131, 184, 186–190].

The reactions of 1-trimethylsilylpyrazole, -imidazole, and -1,2,4-triazole with phosphoryl trifluoride take dissimilar routes [187]. The treatment of 1-trimethylsilylpyrazole or -1,2,4-triazole with POF_3 results in the corresponding 1-difluorophosphoryl-azoles, whereas a similar reaction with 1-trimethylsilylimidazole affords an adduct of 1 : 1 composition [187].



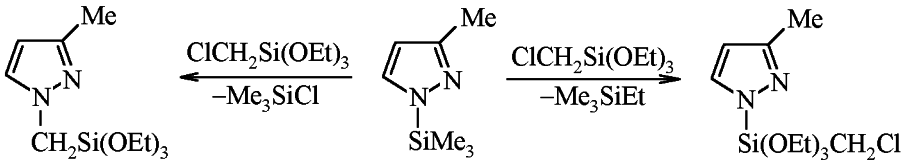
The substitution of trimethylsilyl group in 1-trimethylsilylimidazole or -benzimidazole under the action of arylselenyl chloride proceeds in an uncommon way: instead of replacement of the trimethylsilyl group it migrates into *4* (*5*) position of the imidazole ring or into *2* position of the benzimidazole ring [191]. The sequence of reaction stages is not clear: whether occurs selenation of the endocyclic

carbon, or first forms an N-seleno derivative that further rearranges into the more stable compound.



The alkylation of *N*-trimethylsilylazoles with alkyl halides yields the corresponding *N*-alkylazoles [173].

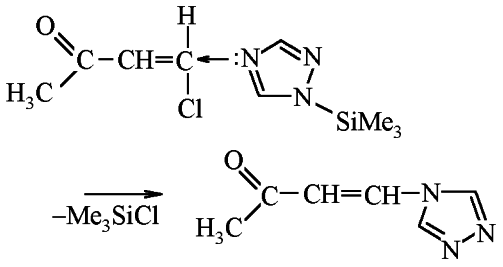
The reaction of 1-trimethylsilylpyrazole with chloromethyltriethoxysilane takes two parallel routes:



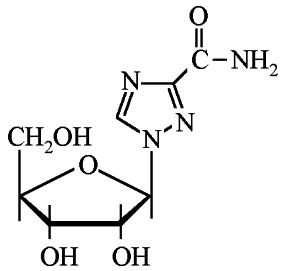
The alkylation of *N*-trimethylsilylazoles became especially important because of an attractive prospect of a synthesis of azole analogs of nucleosides, promising antiviral preparations. Thus in reaction of 1-trimethylsilylbenzimidazole with 2,3,5-tri-*O*-benzoyl-1-bromo-1-desoxyribofuranose was obtained 1-(2,3,5-tri-*O*-benzoyl-*D*-ribofuranosyl)benzimidazole [126].

The reaction of 1-trimethylsilyl-5(6)-chloro-2-methylbenzimidazole with α-acetobromoglucose occurs analogously [127]. Cyclic analogs of nucleosides were prepared by reaction of 1-trimethylsilylbenzimidazole and -benzothiazole with 1-acetoxy-4-chloro-3-oxobutane in the presence of tin tetrachloride [128]. In the same way were obtained nucleosides of 1,2,4-triazole series [196, 197]. Since the brominated sugars were relatively hard to obtain they were replaced by acylated sugars. In this case were used as catalysts tin tetrachloride [119, 128, 198–203], trimethylsilyl triflate [129, 204] and some siloalkylation and transsilylaion with the first one prevailing (85 : 15) [192].

A special attention drew the reaction between 1-trimethylsilylazoles with methyl β-chlorovinyl ketone [193–195] due to uncommon direction of the process with the participation of 1-trimethylsilyl-1,2,4-triazole. The usual way of the 1-trimethylsilylazoles reaction with $CH_3COCH{=}CHCl$ results in 1-(β-acetylvinyl)azoles. The same reaction with 1-trimethylsilyl-1,2,4-triazole yields 4-(β-acetylvinyl)-1,2,4-triazole [193]. Apparently the process consists in an attack of the azole on the double bond at the β-carbon of the methyl β-chlorovinyl ketone followed by elimination of the trimethylchlorosilane.



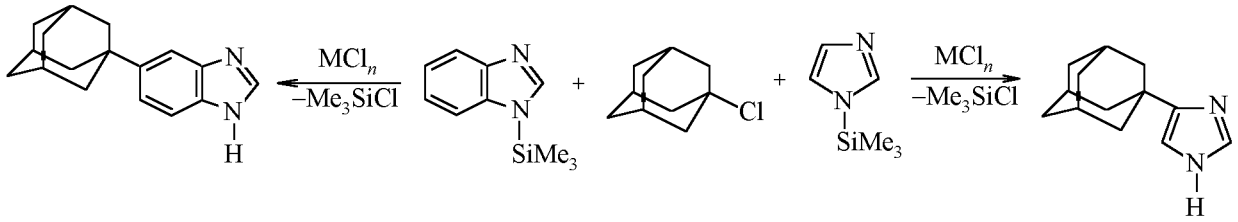
other compounds [204, 205]. A synthetic nucleoside prepared from *N*-trimethylsilyl-1,2,4-triazole, 1-β-D-ribofuranosyl-1,2,4-triazole-3-carboxamide (virazole, ribamidyl), found wide application due to its antiviral activity [196].



The medicine passes through cell membranes and enters into metabolism by transformation into mono- and triphosphate. This substance is a competing inhibitor of dehydrogenase inosinemonophosphate

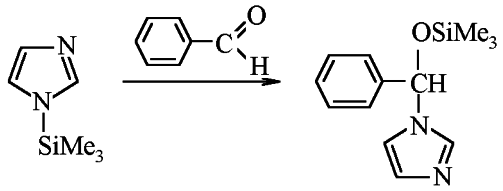
and thus retards the synthesis of viral RNA and DNA not affecting the host cells [206].

The reaction of 1-adamantyl chloride with 1-trimethylsilylimidazole and -benzimidazole in the presence of Lewis acids ($AlCl_3$, $TiCl_4$, $ZnCl_2$) proceeds unusually: Instead of the common replacement of the trimethylsilyl group in position *1* a 4(5)-adamantylimidazole or 5(6)adamantylbenzimidazole is formed [96, 97].



Quite a number of *N*-trimethylsilylazoles, 1-trimethylsilyl-3,5-dimethylpyrazole among them, react with gaseous formaldehyde with N–Si bond rupture to furnish 1-trimethylsilyloxymethyl-3,5-dimethylpyrazole [207].

Aromatic aldehydes also insert into the N–Si bond of 1-trimethylsilylazoles yielding the corresponding derivatives. For instance, 1-trimethylsilylimidazole and benzoic aldehyde afford *N*-(α-trimethylsilyloxybenzyl)imidazole [208].

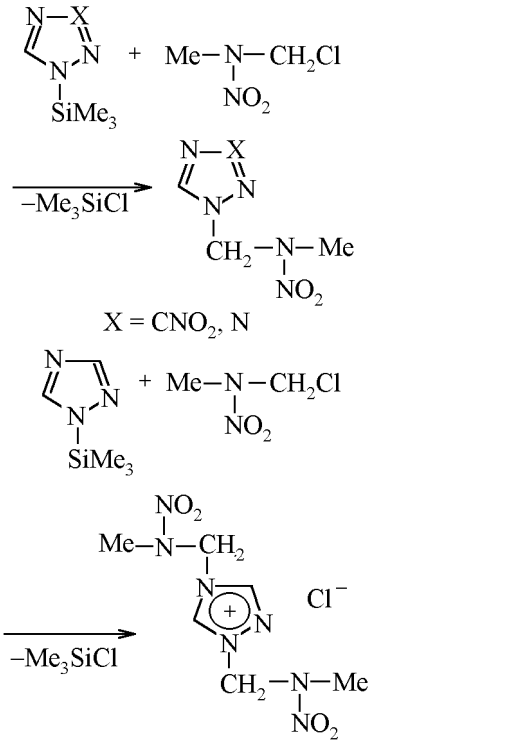


To insert the cyclohexanone into the Si–N bond of *N*-trimethylsilylazoles was used as catalyst trimethylsilyl triflate [209].

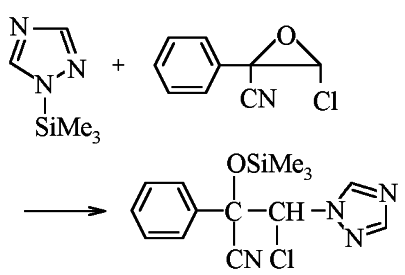
Apparently the insertion of carbonyl compounds into the Si–N bond of *N*-trimethylsilylazoles is a general process although it is not sufficiently investigated.

Dimethyl(trimethylsiloxymethyl)amine reacts with 1-trimethylsilylazoles with hexamethyldisiloxane liberation forming 1-dimethylaminomethylazoles [210, 211].

2-Nitro-1-trimethylsiloxy-2-azapropane does not react with the *N*-trimethylsilyl derivatives of 1,2,4-triazole, 3-nitro-1,2,4-triazole, and tetrazole. Therewith 2-nitro-1-chloro-2-azapropane reacts with the compounds to afford the corresponding nitraminomethyl derivatives of azoles. With 1-trimethylsilyl-1,2,4-triazole bis-nitraminomethylation occurred to yield quaternary salt [212].



The reaction between *N*-trimethylsilylazoles with epoxides was not systematically investigated. It was only mentioned that 3-chloro-2-cyano-2-phenyloxirane alkylated 1-trimethylsilyl-1,2,4-triazole to afford the corresponding trimethylsiloxy derivative (yield 71%) [213].

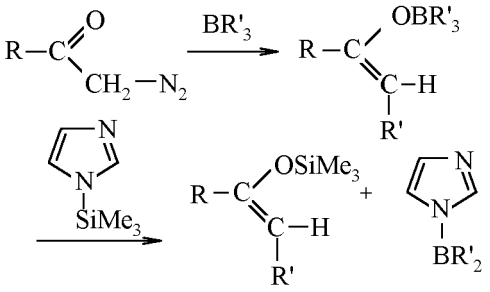


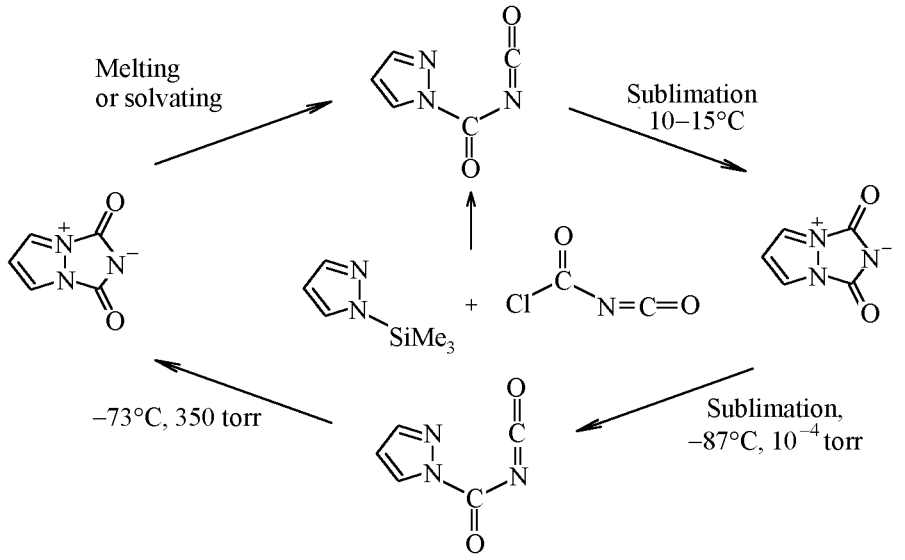
The reaction of aryl isocyanates with 1-trimethylsilylimidazole yields 1-(arylaminocarbonyl)imidazoles [214].

The reaction product from 1-trimethylsilylpyrazole and chlorocarbonyl isocyanate exists both as 1-pyrazolylcarbonyl isocyanate and bipolar heterocyclic compound [111].

Alkane- and arenethioles in the presence of trimethylsilyl triflate eliminate $SiMe_3$ group from *N*-trimethylsilylazoles to give a free azole and the corresponding trimethylorganylthiosilane; the latter can react in situ with aldehydes or ketones providing in high yield OS-organylmonothioacetals [209].

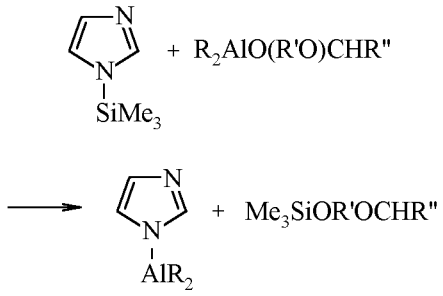
N-Trimethylsilylazoles can be used for preparation of trimethylsilyl enol ethers that are important synthons for the organic synthesis [215, 216]. For instance, trimethylsilyl enol ethers (exclusively





E-isomers) are obtained when treating with 1-trimethylsilylimidazole enol boranes that have been prepared from diazoketones and trialkyl boranes [215].

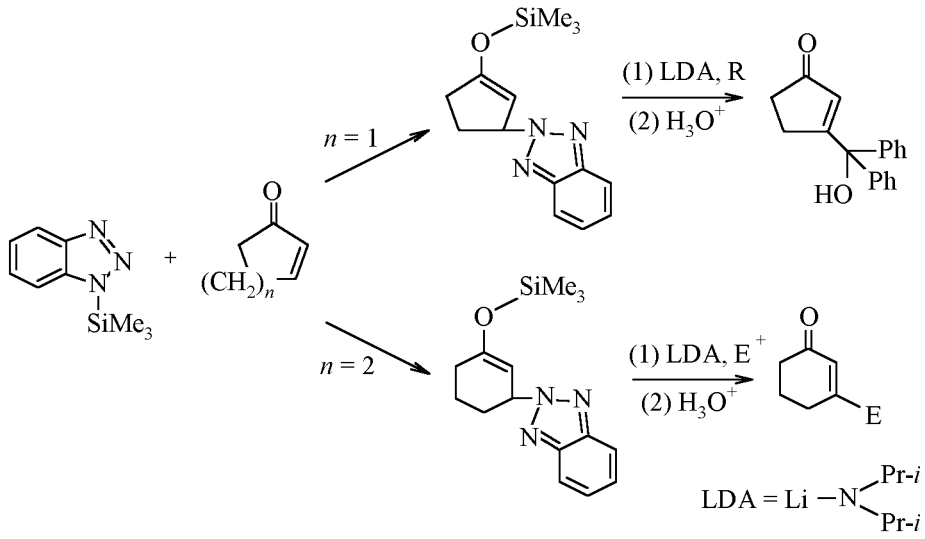
N-Trimethylsilylimidazole is able to trap thermally unstable aluminoxyacetals (intermediates identified by ^1H NMR spectroscopy) affording relatively stable monotrimethylsilylacetals [217].



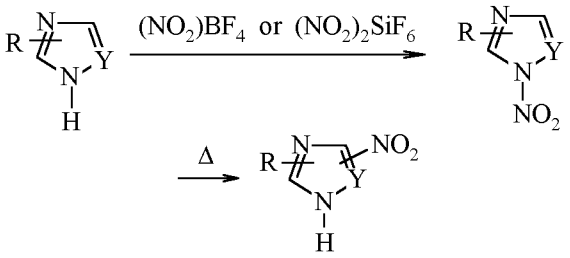
An elegant method was developed for converting 2-cycloalkenones into 3-substituted cycloalkenones including the use of 1-trimethylsilylbenzotriazole according to the scheme show on the next page [181, 218].

The nitration of 1-trimethylsilylimidazoles and 1-trimethylsilyl-1,2,4-triazoles with nitronium tetrafluoroborate or hexafluorosilicate results in the unstable N-nitroazoles. On heating they rearrange into C-nitroderivatives [121, 122, 219].

The reaction of 1-trimethylsilylbenzotriazoles with azomethines and Grignard reagents gives rise to secondary amines [181, 220, 221].

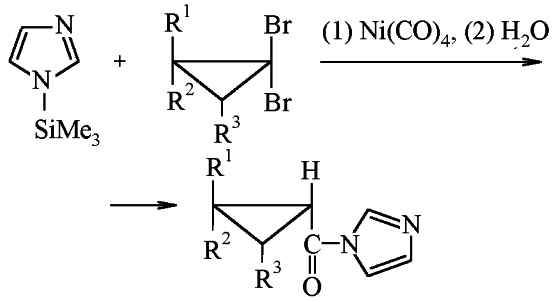


n = 1, R = Ph_2CO; *n* = 2, E = $C_{10}H_{21}$, 3,5-$Me_2C_6H_3CH_2$, 4-ClC_6H_4NHCS, $PhCH_2$, PhCO, CHOH, Ph_2COH, PhNHCS.



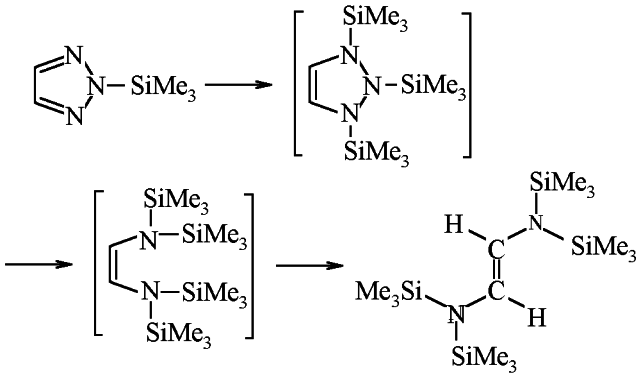
Y = CH, N; R = H, Alk, Cl.

1-Trimethylsilylimidazole with 1,1-dibromo-2,2,3-R_3-cyclopropanes and tetracarbonylnickel affords imidazolides of cyclopropanecarboxylic acids [222]. In this case one C–Br bond is carbonylated, and the other one reduced.



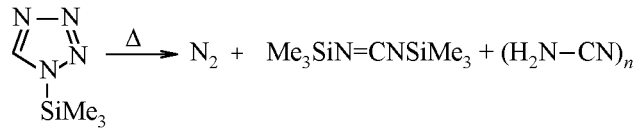
R^1 = H, Alk, Ph, COOMe, Me_3Si, Me_3SiCH_2; R^2 = H, Alk; R^3 = H, Alk.

At reductive silylation of 2-trimethylsilyl-1,2,3-triazole with a system Me_3SiCl/K initially arises an intermediate 1,2,3-tris(trimethylsilyl)-1,2,3-triazoline that is quickly reduced and trimethylsilylated into *E*-1,1,4,4-tetrakis(trimethylsilyl)-1,4-diazabutene-2 [223]. The data of photoelectron spectroscopy, NMR, and ESR show that the compound is not planar unlike its tetrazene analog.

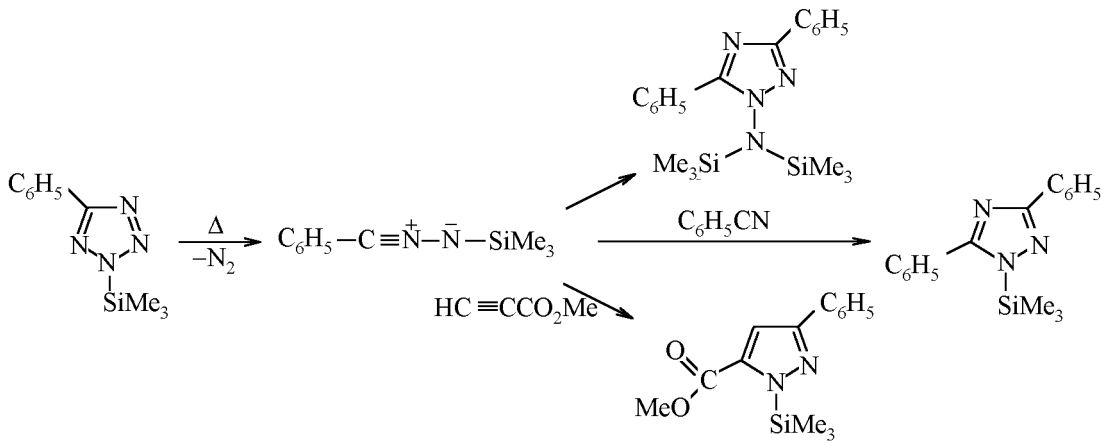


1-Trimethylsilylimidazole and its benzannelated analog behave differently when oxidized with molibdenum peroxides. *N*-Trimethylsilylimidazole when treated with oxodiperoxomolibdenum (**VI**) in DMF is converted into imidazole in a nearly quantitative yield. 1-Trimethylsilylbenzimidazole under similar conditions affords benzimidazol-1-oxide in 10% yield [224].

Thermolysis of *N*-trimethylsilyltetrazoles and their C-substituted derivatives is studied in detail [130, 136, 140, 141, 225]. The main products of 1-trimethylsilyltetrazole thermolysis are *N*,*N*'-bis(trimethylsilyl)carbodiimide, polycyanimides, and nitrogen [130].

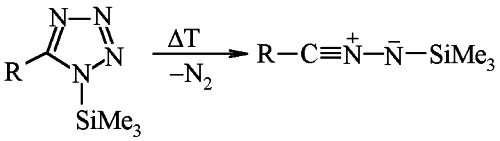


The thermolysis of 2-trimethylsilyl-5-phenyltetrazole first gives C-phenyl-*N*-trisilylmethylnitrile imine. This intermediate spontaneously undergoes cyclization into 1-bis(trimethylsilyl)amino-3,5-diphenyl-1,2,4-triazole [130].



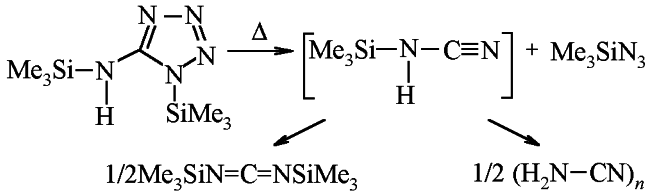
On passing the gaseous pyrolysis products through a solution of nitrile or methyl ester of acetylenecarboxylic acid arises 1-trimethylsilyl-3,5-diphenyl-1,2,4-triazole [136] or 5-methoxycarbonyl-3-phenyl-1-trimethylsilylpyrazole [141] respectively.

Photoelectron spectroscopy provided a possibility to optimize the conditions of vacuum flash-pyrolysis of 5-methyl- and 5-phenyl-1-trimethylsilyltetrazole providing trimethylsilylnitrile imines that could serve as synthons for preparation of five-membered heterocycle, in particular azoles [225].



R = CH_3, C_6H_5.

At thermolysis of 5-trimethylsilylamino-1-trimethylsilyltetrazole arise trimethylsilyl azide, *N*,*N*'-bis(trimethylsilyl)carbodiimide, and polycyanamides [130].

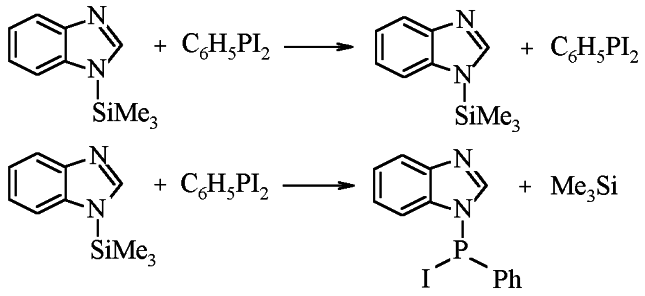


N-Trimethylsilylazoles were used in the synthesis of herbicides [226], as components of initiating systems for polymerization [227], and for stabilization of polyoxymethylene [228].

The hydrolysis of 1-trimethylsilylimidazole and its 2-methyl-substituted derivative is catalyzed with bases, e.g. with triethylamine [108]. The bases also catalyze the intermolecular exchange of trimethylsilyl group of the *N*-trimethylsilylimidazoles with the free imidazoles. However organic bases (triethylamine) retard this intermolecular silylotropic process. A mechanism is suggested for the base catalysis of these reactions [108].

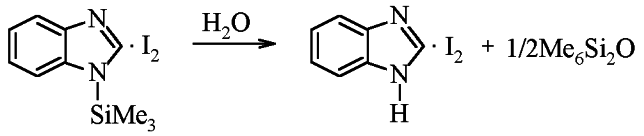
1-Trimethylsilyl- and 2-methyl-1-trimethylsilylimidazole give covalent imidazolates with compounds of copper, nickel, palladium, iridium, and platinum [229–232]. These complexes are soluble in certain organic solvents, and are monomeric in solutions.

In reaction of 1-trimethylsilylbenzimidazole with $PhPI_4$ arises a complex of the imidazole with iodine



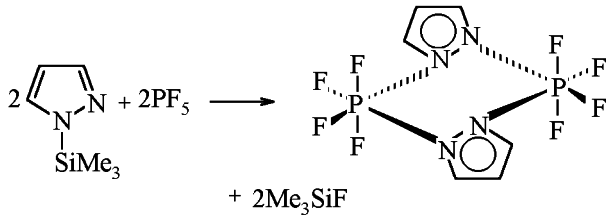
and phenyldiiodophosphine. Further reaction of the latter with 1-trimethylsilylbenzimidazole affords phenyl(*N*-benzimidazolyl)iodophosphine [233].

The complex of 1-trimethylsilylbenzimidazole with iodine is readily desilylated by treating with water to afford a complex of benzimidazole with iodine [233].

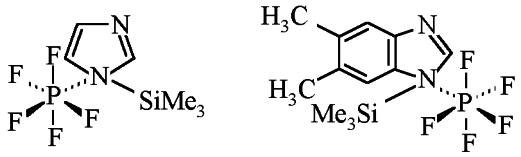


1-Trimethylsilylimidazole and -pyrazole form complexes with borane, trimethyl- and triethylborane [234]. The complex of 1-trimethylsilylimidazole with POF_3 was already mentioned earlier (see p. 166) [187].

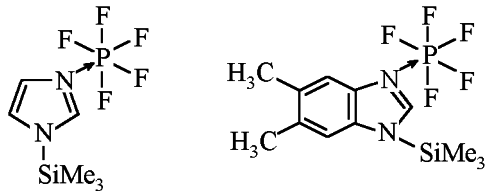
Reactions of *N*-trimethylsilyl derivatives of pyrazole, imidazole, 5,6-dimethylimidazole, and 1,2,4-triazole with a pentafluorophosphorane were systematically investigated [235]. 1-Trimethylsilylpyrazole reacts with PF_5 to afford bis(1-pyrazolo-2-azonia)tetrafluorophosphate; its structure was proved by X-ray diffraction study [235].



1-Trimethylsilylimidazole and 1-trimethylsilyl-5,6-dimethylbenzimidazole give with PF_5 adducts of 1 : 1 composition which are assigned the following structure [235]:

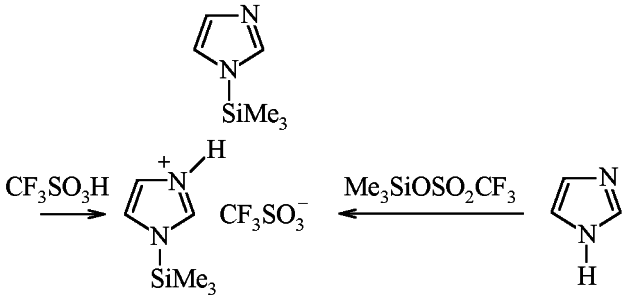


It is regretful that the structure of the complexes was not confirmed. It is just based on an assumption that the sp^3-hybridized nitrogen atom in azoles is more basic than the sp^2-hybridized one. It cannot be true since the "pyrrole" nitrogen atom (sp^3) is notably less basic than "pyridine" (sp^2) one [236–238]. The presumable structure of these complexes would be as follows:

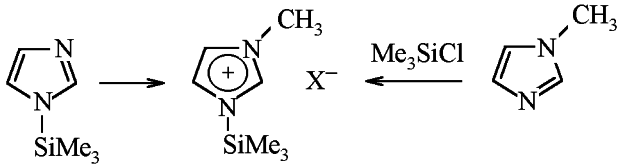


The structure of reaction product of PF_5 with 1-trimethylsilyl-1,2,4-triazole was not determined [235].

The reaction between 1-trimethylsilylimidazole with CF_3SO_3H resulted in high yield (96%) of trimethylsilylimidazolium triflate [239]. This compound obviously forms also in reaction of imidazole with trimethylsilyl triflate.



The halides of 3-methyl-1-trimethylsilylimidazole were obtained by treating *N*-methyl- [240] or *N*-trimethylsilylimidazole [234] respectively with Me_3SiCl or methyl iodide.



X = Cl, I.

N-Trimethylsilylazoles react with tris(dimethylamino)sulfonium difluoromethylsilicate giving tris(dimethylamino)sulfonates of azoles [241].

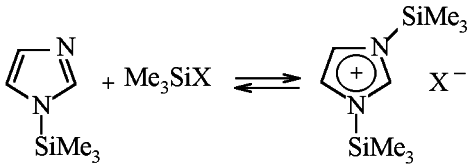
$$Az{-}SiMe_3 + [(Me2_N)3S]^+[Me3SiF2]^- \rightarrow [(Me_2N)3S]^+[Az]^- + 2\ Me_3SiF$$

Az = pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole.

Bis(trimethylsilyl)azolium salts were described only for pyrazole [114] and imidazole[242, 243]. Silylotropic transformations of *N*-trimethylsilylpyrazole are catalyzed with halogens or trimethylhalosilanes via an intermediate formation of *N*,*N*'-bis(trimethylsilyl)pyrasolium halides [114].

The influence of halogens on trimethylsilyl group migration apparently involves the formation of trimethylhalosilane with its subsequent reaction with the substrate [114]. The addition of catalytic quantity of trimethylbromo- or trimethyliodosilane to 1-trimethylsilylpyrazole results in coalescence in the NMR spectra of the proton signals of pyrazole ring from H^3 and H^5 (see chapter III). It is apparently caused by fast degenerate exchange between the initial *N*-trimethylsilylpyrazole and the formed *N*,*N*'-bis-(trimethylsilyl)pyrasolium halide. The equilibrium is considerably shifted in the direction of the salt formation.

The exchange rate between the salts of *N*,*N*'-bis-(trimethylsilyl)imidazolium and electrophilic silanes decreases in the following series of X: Cl > Br > CF_3SO_3 > I, ClO_4. The equilibrium formation constants for these salts decrease virtually in the opposite order: ClO_4 > OSO_2CF_3 > I > Br > Cl [243].

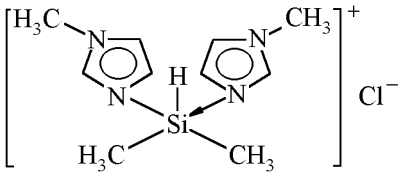


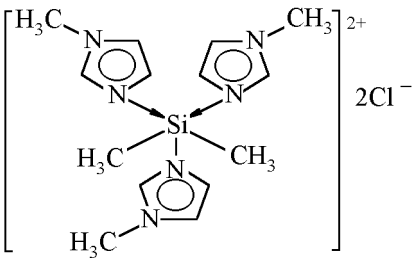
X = Cl, Br, I, OSO_2CF_3, $OClO_3$.

The data of X-ray diffraction analysis showed that the 1 : 1 crystalline adduct obtained from *N*-trimethylsilylimidazole and Me_3SiI was *N*,*N*'-bis(trimethylsilyl)imidazolium iodide [244].

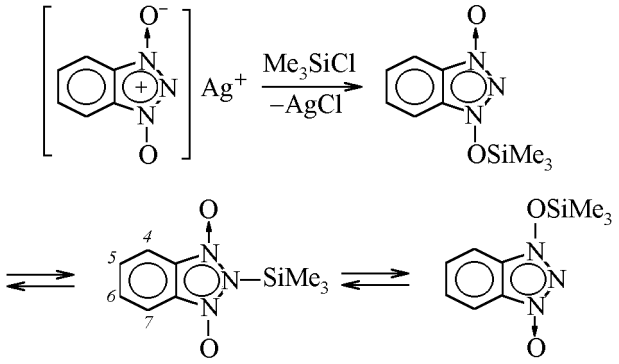
With dimethylchlorosilane and dimethyldichlorosilane *N*-methylimidazole gave rise to the derivatives of pentacoordinated silicon [240].

In the former molecule the two Si–N bond lengths are virtually equal (2.005 and 2.034 Å). In the latter compound two Si–N bonds (1.983 and 2.023 Å) are considerably longer than the third one (1.817 Å). Thus the longer bonds are coordinate bonds.



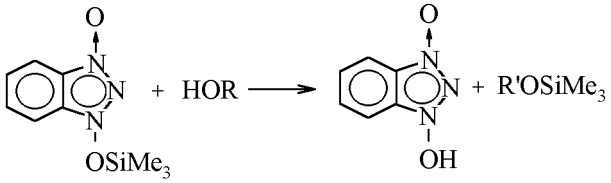


The treating of 1-hydroxybenzotriazole-3-oxide silver salt with trimethylchlorosilane was isolated 1-trimethylsiloxybenzotriazole-3-oxide [245].



The number of signals in the NMR spectrum of this compound, their multiplicity and broadening evidence an equilibrium of two structures with respective positions of $OSiMe_3$ groups *1* and *3*. 1,3-O,O-shift of $SiMe_3$ group was regarded as two successive 1,2-O,N- and 2,3-N,O-shifts [245]. The reaction mechanism was not proved. It is quite possible that the traces of trimethylchlorosilane remaining in the system catalyze the process, and the intermediate compound is 2-trimethylsilyl-1-trimethylsiloxybenzotriazolium-3-oxide chloride.

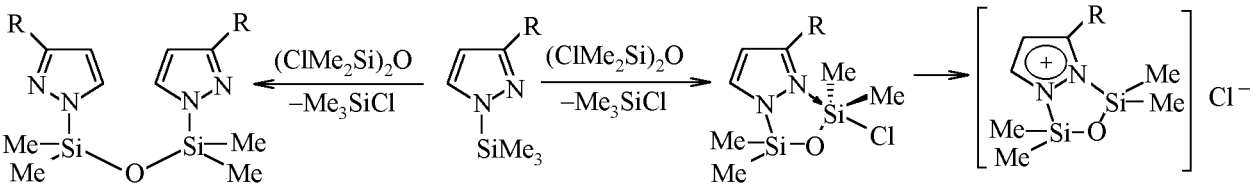
The ready hydrolysis and methanolysis of the 1-trimethylsiloxybenzotriazolium-3-oxide results in 1-hydroxy derivative [245].



R = H, Me_3Si, Me; R1 = Me_3Si, Me.

1-Trimethylsiloxybenzotriazolium-3-oxide does not react with nitroethane, i.e. it does not silylate this typical C–H acid [245].

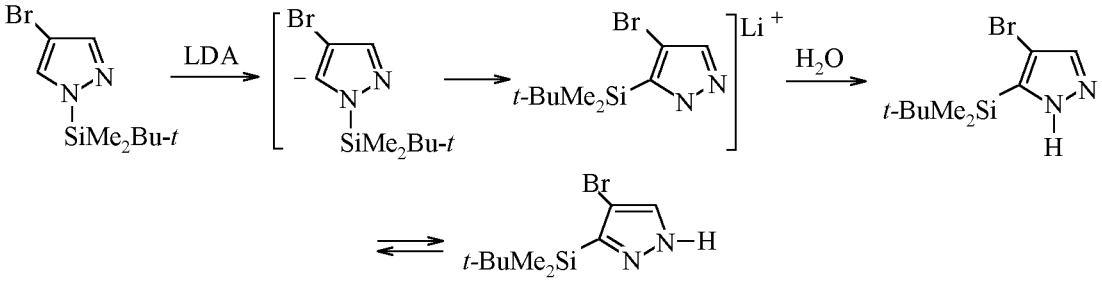
In the study of reaction between 1-trimethylsilylpyrazole, its 3-methyl derivative and $(ClMe_2Si)_2O$ was expected that the reaction would afford either the corresponding compounds of pentacoordinated silicon, or pyrazolium chlorides, or the products of bimolecular condensation [246].



R = H, CH_3.

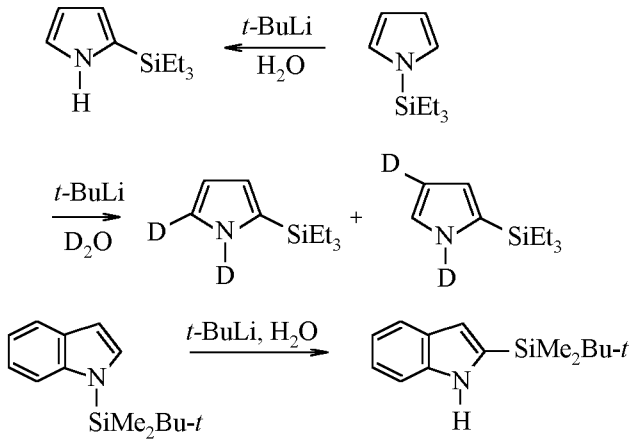
The NMR spectra of the reaction products evidence formation of tetramethyl-1,3-bis(1-pyrazolyl)disiloxane or the respective methylated analog. Therewith for compounds with R = H in the ^1H and ^{13}C NMR spectra the chemical shifts of CH moieties in *3* and *5* positions of the pyrazole fragments are equivalent. This fact is presumably due to a fast silylotropic exchange of the siloxane fragment between the nitrogen atoms of the ring under catalysis with the traces of Me_3SiCl [246].

In 4-bromo-1-*tert*-butyldimethylsilylpyrazole that was easily obtained with a good yield from dimethyl-*tert*-butylchlorosilane and 4-bromopyrazole was observed an irreversible migration of the trialkylsilyl group from a nitrogen to a carbon atom. This compound treated with lithium derivative of diisopropylamine (LDA) gives the corresponding C-centered anion that undergoes fast isomerization into more stable N-centered anion. The latter reacting with water affords 4-bromo-3(5)*tert*-butyldimethylsilylpyrazole [247].



R = H, CH_3.

Similar irreversible migration of a trialkylsilyl group occurs at lithiation of *N*-triethylsilylpyrrole [248, 249] and *N*-dimethyl-*tert*-butylsilylindole [250].



It was presumed that the N→C migration of a trialkylsilyl group was an intramolecular process [249]. This helped to elucidate the early studies of reactions between trimethylchlorosilane and N-lithium derivatives of benzimidazole [32] and pyrrole [251, 252]. In both cases the corresponding C-trimethylsilyl derivatives were obtained.

On the contrary 2-trimethylsilylpyrrol was described to isomerize slowly into *N*-trimethylsilylpyrrol already at room temperature [252].

The irreversible migration of a trimethylsilyl group was observed in the synthesis of *N*-trimethylsilyl-1,2,3-triazole from acetylene and trimethylsilyl azide [116].

The reversible silylotropic rearrangements of trimethylsilylazoles are fairly well studied. The N→N'

migration of a $SiMe_3$ group was described for trimethylsilyl derivatives of pyrazole [110, 114, 116, 253, 254], imidazole [108, 111, 253, 255], 1,2,4-triazole [253], benzimidazole [255, 256], and benzoxazolone [106]. In particular, this $N \rightarrow N'$ migration in the trimethylsilyl derivatives of pyrazole and 1,2,4-triazole occurs intramolecularly. However, with *N*-trimethylsilylimidazole [108, 111] and -benzimidazole [256] the process proceeds intermolecularly.

III. PHYSICO-CHEMICAL CHARACTERISTICS OF C- AND N-TRIMETHYLSILYLAZOLES

The dipole moments and the pK_{BH+} values were determined for N-trimethylsilyl-substituted pyrazoles, imidazoles, and benzimidazoles [257]. Here was revealed that the basicity of the heteroaromatic compounds studied remained practically unchanged on incorporating a trimethylsilyl substituent into their molecules. This fact shows that the Me_3Si group weakly affects the lone electron pair of nitrogen not involved in the aromatic sextet. The dipole moments of azoles grow because of *N*-trimethylsilylation due to a significant contribution from the + *I*-effect of trimethylsilyl group to the heteroaromatic system through the Si–N bond [257]. The experimental data obtained are consistent with the quantum-chemical calculations by CNDO method [258].

Some structures of trimethylsilyl derivatives of azoles were determined by X-ray diffraction analysis [8, 9, 10, 19, 138, 143–146, 240, 244, 259–273]. According to X-ray diffraction study the addition product of *N*-methylimidazole and Me_3SiCl is 1-methyl-3-trimethylsilylimidazolium chloride (Table 3) [240].

Table 3. Interatomic distances Si–N, Si–C_{az} and Si–CH_3 in the molecules *C*- and *N*-trimethylsilylazoles

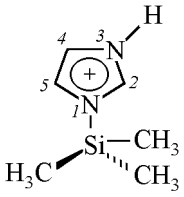
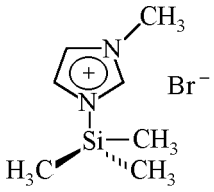
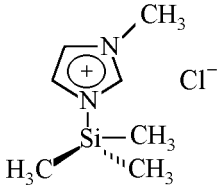
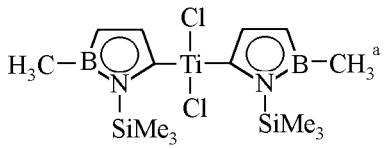
Compound	Bond length, Å		References
	Si–N (Si–C_{az})	Si–CH_3	
	1.840	1.849 1.850 1.853	259
	1.819	1.842 1.859 1.870	260
	1.821	1.844 1.845 1.837	240
	1.825 1.832	1.839 1.856 1.851 1.845 1.838 1.841	261

Table 3. (Contd.)

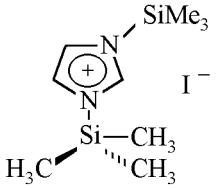
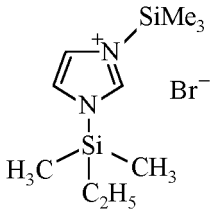
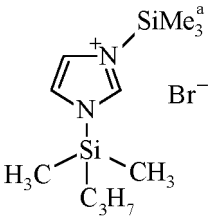
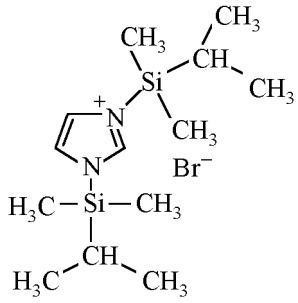
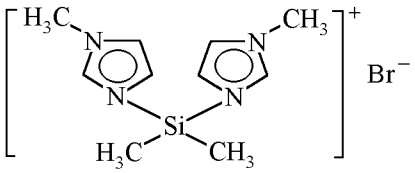
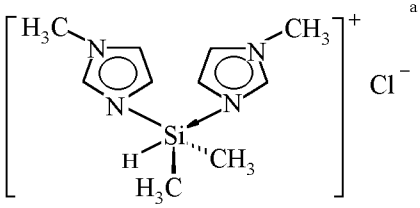
Compound	Bond length, Å		References
	Si–N (Si–C_{az})	Si–CH_3	
	1.772	1.870 1.832 1.829	244
	1.826 Si–N[1] 1.834 Si–N[3]	1.845 1.865 1.848 1.832 1.842 1.847	261
	1.811 Si–N[1] 1.823 Si–N[3] 1.824 Si–N[1] 1.794 Si–N[3]	1.833 | 1.810 1.833 | 1.848 1.841 | 1.843 1.819 | 1.843 1.839 | 1.817 1.834 | 1.852	261
	1.827 1.827	1.846 1.814 1.882 1.846 1.814 1.882	261
	1.791 1.791	1.822 1.808	262
	1.982 2.042 2.034 2.005	1.842 Si–C[1] 1.851 Si–C[2] 1.843 Si–C[1] 1.851 Si–C[2]	240

Table 3. (Contd.).

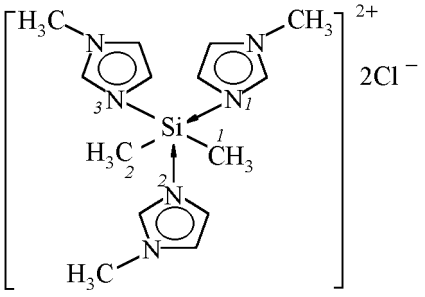
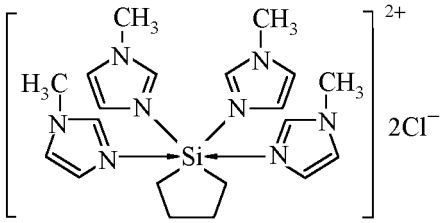
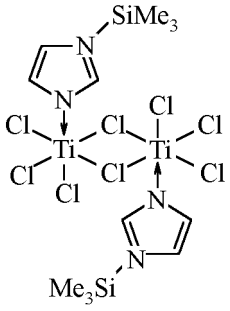
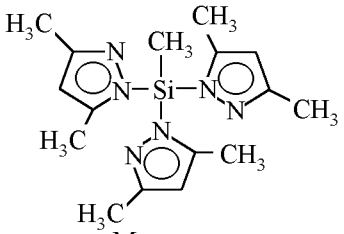
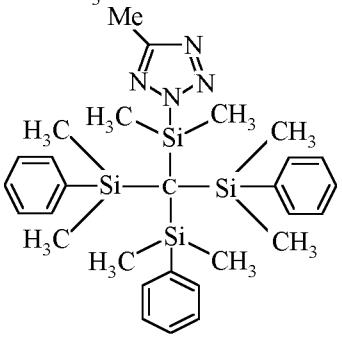
Compound	Bond length, Å		References
	Si–N (Si–C_{az})	Si–CH_3	
	1.983 Si–N[1] 2.023 Si–N[2] 1.817 Si–N[3]	1.854 Si–C[1] 1.861 Si–C[2]	240
	1.995 2.005 2.005	1.930 Si–CH_2 1.950 Si–CH_2	263
	1.806	1.836 1.844 1.845	264
	1.744 1.744 1.745	1.836	265
	1.984	1.864 1.907	138

Table 3. (Contd.).

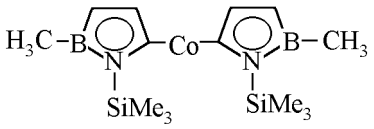
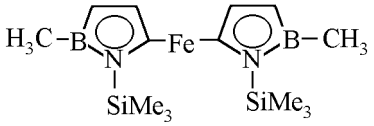
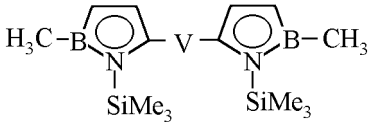
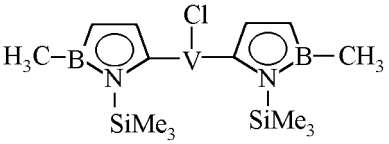
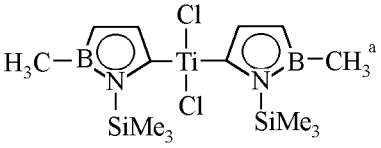
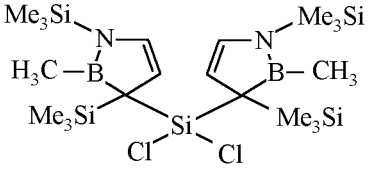
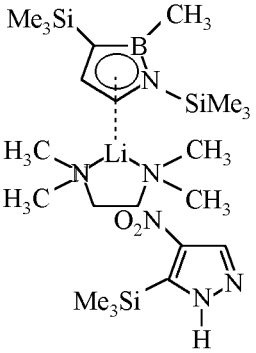
Compound	Bond length, Å		References
	Si–N (Si–C_{az})	Si–CH_3	
	1.781	1.813 1.822 1.871	144, 145
	1.799	1.834 1.841 1.858	144, 145
	1.777	1.825 1.850 1.851	146
	1.768	1.828 1.843 1.844	143
	1.784 1.792	1.845 | 1.823 1.852 | 1.849 1.864 | 1.864	143
	1.760 1.759 N–Si (1.917) (1.911) (C–Si) (1.845) (1.848) (C–SiCl)	1.833 | 1.858 1.841 | 1.862 1.846 | 1.862 1.839 | 1.862 1.840 | 1.864 1.852 | 1.864	266
	1.771 (1.764) (1.895)	1.867 | 1.869 1.870 | 1.872 1.876 | 1.872 1.848 1.850 1.856	266 8

Table 3. (Contd.)

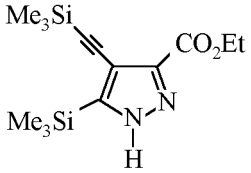
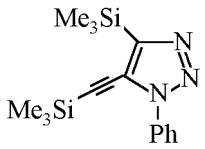
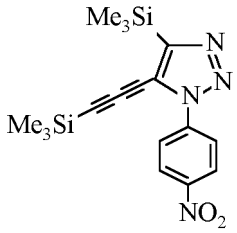
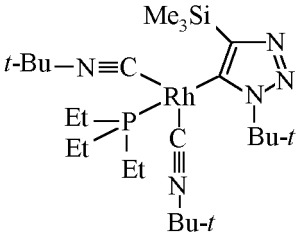
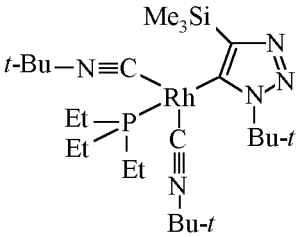
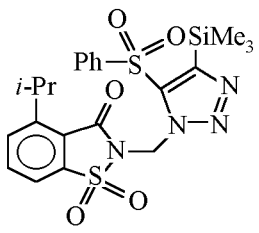
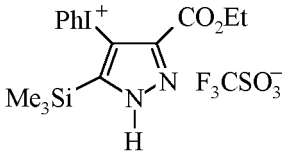
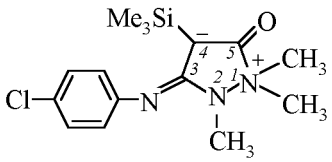
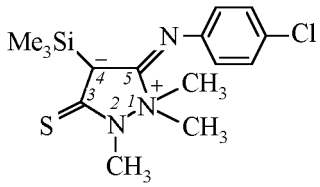
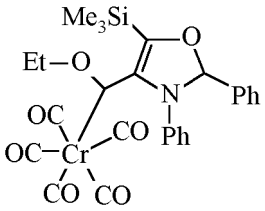
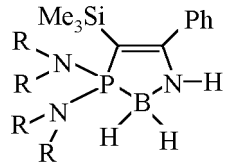
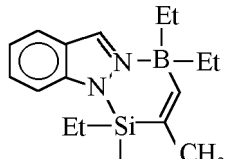
Compound	Bond length, Å		References
	Si–N (Si–C_{az})	Si–CH_3	
	(1.755)C[5] (1.755)	1.941 1.952 1.961	19
	(1.860) (1.862)	1.819 1.827 1.817 1.771 1.727 1.814	19
	(1.874)	1.859 1.867 1.863	19
	(1.745)	1.830 1.779 1.785	267
 60°C	(1.784)	1.815 1.816 1.792	268
	(1.904)	1.850 1.859 1.866	269

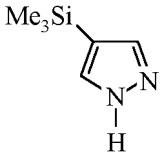
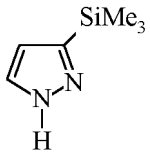
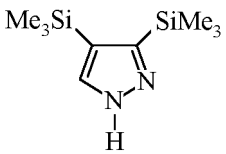
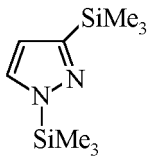
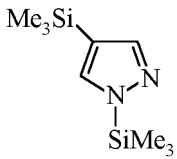
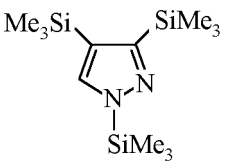
Table 3. (Contd.)

Compound	Bond length, Å		References
	Si–N (Si–C_{az})	Si–CH_3	
	(1.892)	1.823 1.838 1.813	270
	(1.846)	1.828 1.834 1.842	10
	(1.881)		9
	(1.892)	1.844 1.851 1.863	271
	(1.868)	1.873 1.875 1.880	272
	1.791	1.849 Si–CH_2 1.851 Si–CH_2 1.828 Si–C	273

[a] Two independent molecules in the unit cell.

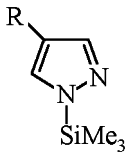
In the silicon derivatives of azoles containing penta- [240] or hexacoordinated [263] silicon the Si–N bond is notably longer (1.98–2.04 Å) than the valence bond in compounds of the tetracoordinated silicon (1.74–1.80 Å). In cations of the trimethylsilylazoles the Si–N bond (1.77–1.84 Å) is longer than in a neutral molecules, and this bond length varies within wide limits (cf. [244]). The Si–N bond in the 1,3,-bis(trimethylsilyl)imidazolium iodide (1.772 Å) [244] is considerably shorter than in the analogous bromide (1.832 Å) [261]. In the unit cell of a crystal of 1-trimethylsilyl-3-propyldimethylsilylimidazolium bromide are located two molecules with different Si–N bond lengths (1.794 and 1.823 Å)

Table 4. Chemical shifts in ^{1}H, ^{13}C and ^{29}Si NMR spectra of C-trimethylsilylpyrazoles (ppm)

No.	Compound	$\delta^{1}H$					$\delta^{13}C$				$\delta^{29}Si$	Solvent
		H^3	H^4	H^5	$Si(CH_3)_3$	NH	C^3	C^4	C^5	$Si(CH_3)_3$		
1[a]		7.58 7.57 7.70 7.50[b]		7.58 7.57 7.56 7.50[b]	0.21 0.21 0.21 0.22[b]	12.97 14.78[b]	138.23	113.58	138.23	–0.22	–10.35	$CDCl_3$ CD_3OD CD_3OD (–90°C)
2			6.40, 6.37[b]	7.64 7.62[b]	0.28 0.30[b]	12.99 13.78[b]	142.39	112.09	138.49	–1.06	–10.1	$CDCl_3$
3				7.66 7.60[c]	0.27, 0.39 C–Si, N–Si 0.30[c], 0.35[c]	10.88 12.60[c]	146.39	120.09	145.38	0.95, –0.15	–9.3, –10.3	$CDCl_3$
4			6.40	7.58	0.26, 0.44 C–Si, N–Si		156.76	112.22	133.55	–0.48, –0.80 C–Si, N–Si	–9.3, 13.92 C–Si, N–Si	$CDCl_3$
5		7.73 7.63		7.55 7.60	0.21, 0.46 C–Si, N–Si 0.17, 0.37		147.59 148.01	114.88 115.04	138.55 139.04	–0.28, –0.87 C–Si, N–Si –0.06, 0.72	–10.7, 14.5 C–Si, N–Si –11.1, 13.4	$CDCl_3$ Neat fluid
6				7.56	0.25, 0.31, 0.43		160.60	120.80	140.44	1.08, 0.30, –0.35	–11.0 –8.2, 13.6 C–Si, N–Si	$CDCl_3$

[a] $G_c^{\#}$ 11.9 kcal mol^{-1} (t_c –44°C, $\Delta\nu$ 8.5 Hz, CD_3OD). [b] In CCl_4 [1]. [c] In CCl_4 [4].

Table 5. Parameters of ^{1}H, ^{13}C and ^{29}Si NMR spectra of 4-substituted 1-trimethylsilylpyrazoles (neat fluids)



R	$\delta^{1}H$, ppm			$\delta^{13}C$, ppm				$\delta^{29}Si$, ppm	$\Delta G_c^{\#}$, kcal mol^{-1}	T_c, K	Reference
	H^3	H^5	$Si(C\underline{H}_3)_3$	C^3	C^4	C^5	$Si(\underline{C}H_3)_3$				
CH_3	7.53	7.39	0.40	144.82	116.86	132.86	–0.26	13.1	22.3	433	[a]
H	7.73[b]	7.56	0.44	142.85	105.71	133.29	–1.20	14.6	>24	>458	114
	7.65[c]	7.55	0.37	143.00	106.30	133.64	–0.85	14.2	>24	>458	114
	7.68[d]	7.56[d]							23.1[d]	438[d]	110
	7.80[e]	7.65[e]	0.50[e]	143.5[f]	106.3[f]	134.0[f]					255
Cl	7.59	7.54	0.38	141.77	110.88	131.69	–1.1	17.1	24.0	438	114
Br	7.60	7.56	0.39	143.60	94.1	133.80	–1.10	17.0	23.8	432	114
I	7.68	7.63	0.40	147.36	57.68	137.86	–1.20	17.0	[g]		114
NO_2	8.41	8.15	0.56	138.78	137.61	133.96	–1.37	22.1	>24	>458	[a]

[a] Data of this article.
[b] In $CDCl_3$, $\delta^{1}H^4$ 6.28 ppm.
[c] $\delta^{1}H^4$ 6.22.
[d] Registered at 60 MHz; $\delta^{1}H^4$ 6.22.
[e] [112], in CCl_4, $\delta^{1}H^4$ 6.40.
[f] In $CDCl_3$.
[g] $\Delta G_c^{\#}$ 12.2 kcal mol^{-1}, $\Delta\nu$ 4 Hz, T_c 227 K (CD_2Cl_2).

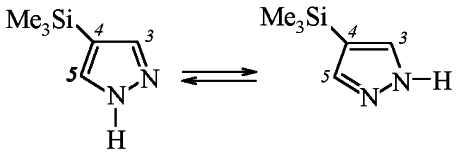
[261]. There are no steric factors that might induce this bond lengths difference. The wide range of bond length for the Si–N bonds apparently evidences its lability, in particular in the treimethylsilylimidazole derivatives. This fact allows understanding of easy formation of intermolecular complexes and also the uncommonly low barrier to intermolecular migration of thetrimethylsilyl group in trimethylsilylimidazoles in solution (NMR data, see below).

Virtually in all C-trimethylsilylazoles the bond length between the silicon atom and the endocyclic carbon (Si–C_{az}) is within 1.84–1.90 Å range. The only exception is 5-rhodium derivative of 1-*tert*-butyl-4-trimethylsilyl-1.2.3-triazole where the bond length for Si–C_{az} at 20°C [267] and –60°C [268] equals respectively to 1.745 and 1.748 Å (Table 3). Sharply differ the bond lengths of Si–C_{az} in the molecules of 3-ethoxycarbonyl-4-trimethylsilyl-ethynyl-5-trimethylsilylpyrazole and 1-phenyl-4-trimethylsilyl-5-trimethylsilylethynyl-1,2,3-triazole (1.755 and 1.860 Å respectively [19]. The charge state of the molecule (neutral molecule, internal salt betaine, azolyl cation) virtually does not affect the length of the Si–C_{az} bond. The bond length for Si–CH_3 both in N- and C-trimethylsilylazoles lies in 1.82–1.87 Å range. Only in the above rhodium derivative of 1,2,3-triazole this bond is shortened (1.78, 1.79 Å) (Table 3) [267, 268].

The most extensive study with NMR technique was performed on the derivetives of trimethylsilylpyrazole [14, 110, 114, 116, 253 etc] and -imidazole [108, 242, 243, 253]. The parameters of ^{1}H, ^{13}C, and ^{29}Si NMR spectra of C- and N-trimethylsilylpyrazole derivatives are listed in Tables 4 and 5 [114, 116]. The proton resonances of the C-trimethylsilyl group vary vithin 0.21–0.39 ppm whereas for the *N*-trimethylsilyl group this interval is 0.40–0.46 ppm. Chemical shifts of the ring protons is practically unchanged on introduction of Me_3Si group and is weakly affected by its location in the cycle.

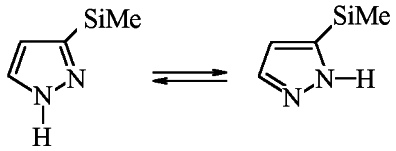
The chemical shifts in the ^{29}Si NMR spectra of C-and N-trimethylsilyl groups are essentially different. In the first case δ ^{29}Si is shifted upfield, its value is negative and varies within –8.2 to –11.1 ppm range (Table 4). The chemical shifts of *N*-trimethylsilyl groups in the ^{29}Si spectra are positive and change

within 13.1–22.1 ppm limits (Table 5). It is curious that in compounds 1 and 2 the chemichal shift δ ^{29}Si of the C–Me_3Si groups is practically the same whereas in the corresponding compounds 4 and 5 (containing additionally N–$SiMe_3$ group) the chemical shift of these moieties differs by over 1 ppm (Table 4). We for the first time studied the prototropic tautomerism in 4-trimethylsilylpyrazole (Table 4) [116].



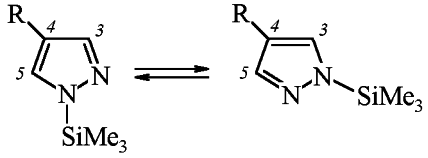
At the room temperature the compound is in tautomeric equilibrium as show the single resonance (7.57 ppm) in the ^{1}H NMR spectrum; the signal corresponds both to protons in *3* and *5* positions in the pyrazole ring. At low temperature (–90°C) in its spectrum appear two narrow signals (7.70 and 7.56 ppm) belonging respectively to protons C^3–H and C^5–H. This temperature transformation of the spectrum reveals the dynamic exchange of N–H proton between the nitrogens of the pyrazole ring. The barrier to proton migration ($\Delta G_c^{\#}$) between N^1* and N^2* in this compound (at 0.2 mol l^{-1}) equals to 11.9 kcal mol^{-1} (Table 4) [116].

The cooling of 3(5)-trimethylsilylpyrazole solution in CD_3OD to –90°C did not result in transformation of its NMR spectra unlike those of its methylated analog.



This finding may be due either to very low barrier to the prototropic exchange in the 3(5)trimethylsilylpyrazole or to the existence of a single isomer of the compound. Quantum-chemical calculations (AM1, MNDO, PM3) of formation heats for 3- and 5-trimethylsilylpyrazole indicate the prevalence of 3-tautomer in the gas phase (Table 6) [116].

The values of free activation energy ($\Delta G_c^{\#}$) of the silylotropic process in 4-substituted *N*-trimethylsilylpyrazoles measured by dynamic NMR technique are weakly sensitive to the substituent character in *4* position (22–24 kcal mol^{-1}) (Table 5) [116].

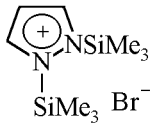


R = $SiMe_3$, CH_3, H, Cl, Br, I, NO_2.

Table 6. Quantum-chemical calculation of formation heats (ΔH) of 3(5)-trimethylsilylpyrazole

Method	ΔH, kcal mol^{-1}	
	3-tautomer	5-tautomer
AM1	17.207	18.990
PM3	2.692	0.072
MNDO	–13.459	–11.718

Table 7. Chemical shifts in the ^{1}H, ^{13}C, and ^{29}Si spectra of *N*,*N*'-bis(trimethylsilyl)pyrazolium bromide (ppm, $CDCl_3$)



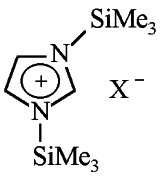
δ^{1}H			δ^{13}C			δ^{29}Si
$H^{3,5}$	H^4	$SiMe_3$	$C^{3,5}$	C^4	$SiMe_3$	
7.84	6.48	0.59	136.76	136.76	2.34	24.3

Yet the ^{29}Si in *N*-trimethylsilylazoles is sensitive to the effect of 4-substituent: At increasing electron-acceptor properties of the substituent the shielding of the silicon nucleus is reduced.

The silylotropic exchange processes are known to be slow in the NMR time scale. The migration of Me_3Si group is observable only at higer temperatures. On heating over 100°C of 4-iodo-1-trimethylsilylpyrazole arises the treimethyliodosilane that catalytically accelerates the exchange of trimethylsilyl groyp between nitrogen atoms. This is evidenced by coalescence of NMR signals belonging to protons H^3 and H^5 that remains at cooling to the room temperature. As seen from Table 5, the value of the silylotropic exchange in the $\Delta G_c^{\#}$ 4-iodo-trimethylsilylpyrazole is considerably less and amounts to 12.2 kcal mol^{-1} (t_c –45°C) [114].

With ^{1}H, ^{13}C, and ^{29}Si NMR was studied the catalyzed silylotropy in the 4-substituted *N*-trimethyl-

Table 8. Chemical shifts in ^1H, ^{13}C and ^{29}Si NMR spectra of the *N*,*N*'-bis(trimethylsilyl)imidazolium (ppm, CD_2Cl_2) [242]

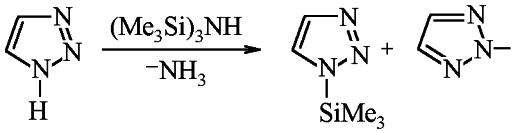


X	δ^1H			$\delta^{13}C$			$\delta^{29}Si$
	H^2	$H^{4,5}$	$Si(C\underline{H}_3)_3$	C^2	$C^{4,5}$	$Si(\underline{C}H_3)_3$	
Br	9.79	7.48	0.72	144.1	124.5	0.0	26.3
I	9.34	7.52	0.75	143.0	124.5	0.0	26.9
CF_3SO_3	8.63	7.42	0.64	141.0	124.1	–0.8	26.9
ClO_4	8.52	7.39	0.64	143.3	124.9	–0.69	26.1

silylpyrazoles. In the presence of halogen (X_2) or trimethylhalosilane (Me_3SiX, X = I, Br, Cl) as was already mentioned the catalyzed migration of the trimethylsilyl group occurred with intermediate formation of *N*,*N*'-bis(trimethylsilyl)pyrazolium halide [114]. On adding to 1-trimethylsilylpyrazole a catalytic quantity of either Me_3SiBr or Me_3SiI the signals in the ^1H NMR spectrum of protons of the pyrazole ring H^3 and H^5 coalesce. It is caused apparently by a fast degenerate exchange between the original *N*-trimethylsilylpyrazole and the arising *N*,*N*'-bis(trimethylsilyl)pyrazolium halide. The ^1H, ^{13}C, and ^{29}Si NMR spectra of the *N*,*N*'-bis(trimethylsilyl)pyrazolium bromide are presented in Table 7.

The similar bis-1,3-imidazolium salts were studied by NMR method (Table 8) [242, 243], conductometric titration [242], and X-ray diffraction analysis (Table 3) [244]. The electrical conductance of their solutions as measured by conductometric titration grows in the following series of anions X: Cl < Br < I < OSO_2CF_3 [241]. The upfield shift of the ^1H and ^{13}C NMR signals from protons abd carbons in *2* position of the imidazole ring grows in the same order of anions X, whereas the ^{29}Si is virtually independent of the anion character (Table 8).

The ^1H, ^{13}C, and ^{29}Si NMR was used in the study of the trimethylsilylation products of 1,2,3-triazole with hexamethyldisilazane. As mentioned previously, it was a mixture of 1- and 2-trimethylsilyl-1,2,3-triazoles in 1 : 5 ratio (Table 9).



The isomers ratio was determined from ^{13}C NMR spectra by NNE procedure (with proton decoupling but without Overhauser effect) [116].

The ^1H, ^{13}C, and ^{29}Si NMR spectra of the bispyrazolyl compound (R = H) evidence the chemical equivalence of the CH groups in the *3* and *5* positions of the pyrazole ring (see chapter II.2) (Table 10) [246]. This is apparently due to the fast silylotropic exchange of the siloxane fragment between the nitrogen atoms of the ring catalyzed with traces of Me_3SiCl.

In the *N*-trimethylsilylimidazole and the *N*-trimethylsilylbenzimidazole the barrier to trimethylsilyl group migration is lower than in the other *N*-trimethylsilylazoles [255]. The broadening of signals is observed at room temperature from C^4 and C^4 in the

Table 9. Chemical shifts in the ^1H, ^{13}C and ^{29}Si NMR spectra of 1-trimethylsilyl- and 2-trimethylsilyl-1,2,3-triazole in $CDCl_3$ and in the neat fluid (the numbers in parentheses) (ppm) [116]

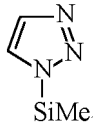
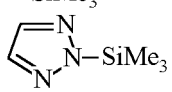
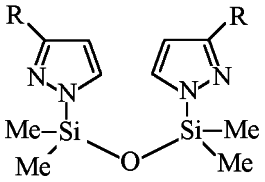
Compound	δ^1H			$\delta^{13}C$			$\delta^{29}Si$
	H^4	H^5	$Si(CH_3)_3$	C^4	C^5	$Si(CH_3)_3$	
	7.92 (7.07)	7.92 (6.98)	0.58 (0.25)	132.70	126.59	–1.10	20.2
	7.82 (7.40)	7.82 (7.40)	0.58 (0.21)	135.65	135.62	–1.32	22.0

Table 10. Chemical shifts in the ^1H and ^{29}Si NMR spectra of tetramethyl-1,3-bis(3-R-pyrazolyl-1)-disiloxane (ppm) (data of this study)



R	δ¹H			δ²⁹Si	Solvent
	H^{3,5}	H^4	Si(CH$_3$)$_3$		
H	7.64	6.23	0.41	–6.4	Neat
	7.69	6.32	0.48	–6.8	fluid
					$CDCl_3$
CH_3	7.47	6.02	0.39	–5.5	$CDCl_3$

N-trimethylsilylimidazole (Table 11) and from C^5, C^6 and C^4, C^7 in the analogous benzimidazole (Table 12). In the latter the silylotropy is not observed in the solid state: In the ^{13}C NMR spectra of a solid sample the carbon atoms appear as separate signals [255, 256]. The ^1H (Table 11) [112] and ^{14}N NMR data [234] also confirm the relatively fast silylotropic process in the *N*-trimethylsilylimidazole:

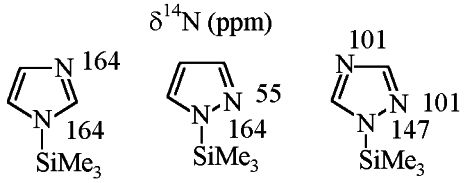
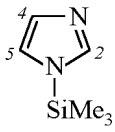
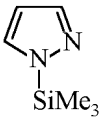
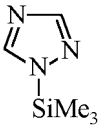
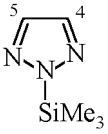
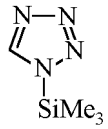


Table 11. Chemical shifts in the ^{13}C and ^{29}Si NMR spectra (δ, ppm) and coupling constants (*J*, Hz) of *N*-trimethylsilylazoles

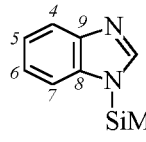
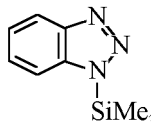
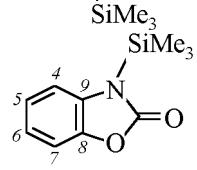
Compound	δ¹³C[a] (δ¹H[b])			δ²⁹Si[c]
	C^3 (H^3)	C^4 (H^4)	C^5 (H^5)	
		129.9[d] (7.10)	120.7[d] (7.10)	13.16
	143.5 ^1J 183.2 ^2J 7.3 ^3J 7.3 (7.80)	106.3 ^1J 175.6 ^2J 9.4 ^2J 11.7 (6.40)	134.0 ^1J 183.1 ^2J 9.2 ^3J 4.6 (7.65)	14.39
	154.2 (8.2)		148.4 (7.9)	17.05
		135.9 ^1J 191.7 ^2J 13.8 (7.82[e])		22.0[e]
			147.5 ^1J 212.3	

[a] [255]. [b] [112]. [c] [274].

[d] The signals of C^4 and C^5 are broadened at room temperature (25 MHz), δ^{3}C (C^2) 139.7, δ^{1}H (H^2) 7.60.

[e] [116].

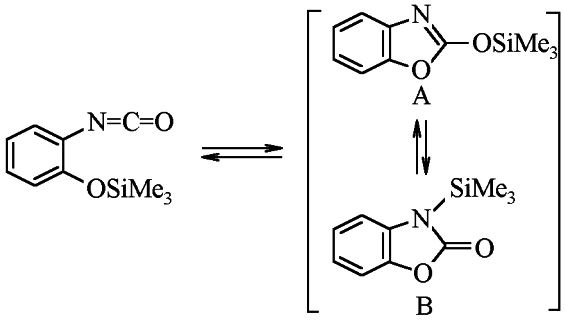
Table 12. Chemical shifts in ^{13}C and ^{29}Si NMR spectra of *N*-trimethylsilylbenzazoles (ppm)

Compound	δ¹³C [255]						δ²⁹Si
	C^4	C^5	C^6	C^7	C^8	C^9	
	115.8[a]	122.0[b]	122.0[b]	115.8[a]	139.2[a]	139.2[a]	12.80 [274]
	119.8	123.4	126.0	111.1	137.8	146.6	18.18 [274]
	111.5	122.3	123.5	109.5	145.3	133.7	16.8 [106]

[a] Broad signals. [b] ^1J 191.7, ^2J 13.8 Hz.

The ^{29}Si shift from the Me_3Si group in the trimethylsilylazoles moves upfield with the growing number of heteroatoms in the azole cycle (Tables 11 and 12) [274].

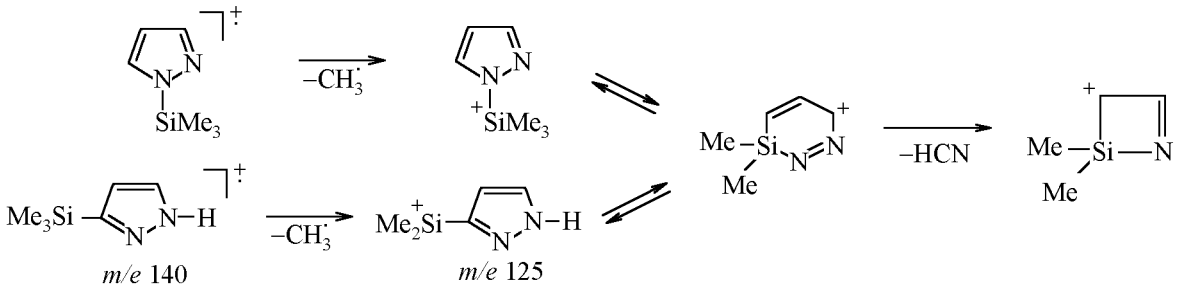
With the use of NMR spectroscopy was studied lactim-lactam tautomerism (A ⇄ B) in trimethylsilylbenzoxazolone that occurred alongside the ring-chain tautomerism (Table 12) [106].



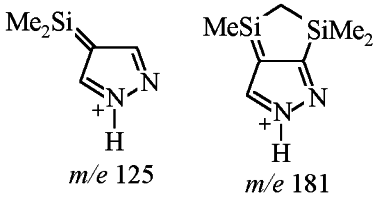
Kuznetsova *et al.* [106] assigned the $\delta^{29}Si$ 16.8 ppm to O–$SiMe_3$ moiety and thus assumed that the tautomeric form A prevailed. However this value fits better to $NSiMe_3$ group (see data of [274–276], and therefore the B form is the dominant (see Table 12).

Mass spectra were studied for some C- and *N*-trimethylsilylpyrazoles [277, 278]. The most probable fragmentation pattern of 1- and 3(5)-trimethylsilylpyrazole is as follows [278].

The rupture of a methyl group from Me_3Si is accompanied by cycle expansion to form 1,3-diaza-2-cilacyclohexa-3,5-diene structure. The formation of a stable allyl type cation and of additional Si–N bond recompense the energy loss due to destruction of the cycle aromaticity. The ejection of HCN molecule from this structure occurs along the mechanism of retrodiene decomposition. The main distinction between the mass spectra of 1- and 3(5)-trimethylsilylpyrazole is in the different intensity ratio of the molecular ion and that with *m/e* 125 (1.2 and 0.56, respectively).



In the case of 4-trimethylsilylpyrazole to the ion $[M–CH_3]^+$ (*m/e* 125) was ascribed a fulvene-like structure:



The fragmentation of 3,4-bis(trimethylsilylpyrazole at the electron impact is unlike that of the above compounds only due to the presence in its mass spectrum of relatively intense ion peak (6%) with *m/e* 181 [278].

IV. CONCLUSION

In the synthetic organic chemistry the *N*-trimethylsilylazoles are used as synthons, trimethylsilylating agents, and also for introduction of various functional groups to a heterocyclic nitrogen atom. Starting from the *N*-trimethylsilylazoles were prepared azole analogs of nucleosides. The most widely applied are the nucleosides of the 1,2,4-triazole series, for instance, 1-β-D-ribofuranosyl-1,2,4-triazole-3-carboxamide (virazole, ribamidyl), that retards the synthesis of viral RNA and DNA not affecting the host cells. N-Trimethylsilylazoles are widely applied as reagents in the peptide synthesis and also in preparation of composite membranes for selective separation of gases. 1-Trimethylsilylimidazole is used for hydroxy groups protection in hydrocortisone at its

quantitative determination by GLC in culture medium [167]. It is also used in monosaccharide quantitative analysis, also in milk.

C-Trimethylsilylazoles, in particular, Dondoni reagent (2-trimethylsilythiazole), turned out to be very useful for asymmetric synthesis. Proceeding from this reagents was obtained a promising inhibitor of HIV-protease *Saquinavir Mesylat.* Alongside further development of this field we expect that also the other C-trimethylsilylazoles would be applied to the asymmetric synthesis.

It is presumable that the studies of silylotropy in the other N-trimethylsilylazoles would be carried out, and the summing up reviews on this topic will appear, also those considering the effect of the character of endocyclic heteroatoms on the thermodynamics of the process.

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