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Organosilicon Derivatives of Monoazaheterocycles

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The literature data and studies in the field of organosilicon derivatives of heterocycles containing one nitrogen atom in the ring have been reviewed. The methods of preparation, physical, chemical, and biological properties, and practical applications of organosilicon nitrogen-containing heterocycles in which the silicon atom is linked directly to a ring carbon or nitrogen atom and also via an oxygen atom or a carbon chain have been examined.
The bibliography includes 350 references.

CONTENTS

I. Introduction 938
II. Compounds containing the Si-C_n-heterocyclic group 938
III. Compounds containing the Si-N bond 944
IV. Compounds containing the Si-O bond 947

I. INTRODUCTION

During recent years, the organosilicon derivatives of nitrogen-containing heterocycles have gained an important place in the chemistry of both organosilicon and heterocyclic compounds. It is sufficient to mention their successful applications in the chromatographic analysis of natural products, their ever increasing use in the syntheses of pyridine, pyrimidine, pteridine, and purine derivatives otherwise difficult to obtain, and also new methods of synthesis of nucleosides and penicillins developed on their basis to demonstrate the important role which organosilicon derivatives of nitrogen-containing heterocycles play in preparative organic chemistry. On the other hand, the study of reactions of organosilicon derivatives with derivatives of nitrogen-containing heterocycles and of the chemical, physical, and physicochemical properties of the products yields valuable information about the structures and reactivities of these heterocycles.

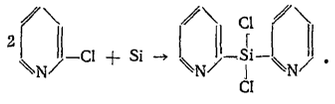
A systematic account of the first data on organosilicon derivatives of nitrogen-containing heterocycles was given in a review[1] which included information about studies published up to 1965. The number of investigations in this field and the wide variety of their subjects have now increased so much that it is desirable to describe them in separate reviews. We felt it necessary to consider in the first place the results of studies on organosilicon derivatives of nitrogen-containing heterocycles with one nitrogen atom in the ring published up to November, 1970.

II. COMPOUNDS CONTAINING THE Si – C_n – HETEROCYCLE GROUP

A. METHODS OF PREPARATION

1. Direct Synthesis

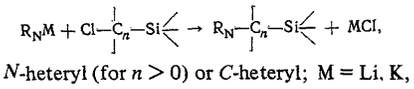
The possibilities of direct synthesis, which is the main industrial method for the preparation of alkyl- and arylchlorosilanes, in the series of nitrogen-containing heterocycles have been hardly investigated. Only two patents indicate that, when 2-chloropyridine is passed over silicon or over a silicon – copper alloy at 350 – 380°C, dichlorobis-(2-pyridyl)silane is formed[2,3]:



2-Bromopyridine reacts similarly. The halogeno-derivatives of other heterocycles have not been used in this reaction.

2. Organometallic Synthesis

The general method for the synthesis of organosilicon derivatives of nitrogen-containing heterocycles in which the silicon atom is linked directly to a ring carbon atom and also to the ring carbon and nitrogen atoms via a carbon chain is based on the interaction of organo-lithium, -potassium, or -magnesium derivatives of heterocycles with R-chlorosilanes ($n = 0$) or R-(chloroalkyl)silanes ($n > 0$)†:



[R_N = *N*-heteryl (for $n > 0$) or *C*-heteryl; M = Li, K, or MgBr]

Using *C*-organolithium derivatives, *N*-methyl-2-pyrrolylsilanes[4], *N*-benzyl-5-indolinylsilanes[5], *N*-alkyl-1-carbazolyl- and *N*-alkyl-3-carbazolylsilanes[6,7], 2-benzothiazolylsilanes[7], 2-pyridylsilanes[8-10], 3-pyridylsilanes[11,12], β-(2-pyridyl)- and β-(4-pyridyl)-ethylsilanes[13,14], 2,3,5,6-tetrachloro-4-pyridylsilanes[15], and 9,10-dihydro-10-methyl-9-acridylsilanes[16] were synthesised in this way. The yields of the trisubstituted pyridylsilanes[8-11] varied from 16 to 50%. (*N*-Alkyl-3-carbazolyl)triphenylsilanes are formed in higher yields than the 1-isomers. For example, whereas 9-ethyl-3-carbazolyl-lithium gives rise to (9-ethyl-3-carbazolyl)triphenylsilane in 64% yield, the yield of the 1-isomer is only 8%. The yield of the latter increases somewhat when bromotriphenylsilane is employed instead

† Unless otherwise stated, R is an organic substituent (Translator).

of the chlorotriphenylsilane[7]. The substitution of the chlorosilane by the bromosilane increases the yield of (2-benzothiazolyl)triphenylsilane from 5 to 19%.[7]

Organic *N*-lithio-derivatives have been used to prepare the piperidides of tri-R-silylacetic acid from their esters[17].

N-Potassio-derivatives of nitrogen-containing heterocycles have been used to synthesise organosilicon phthalimides[18-21] and also tri-R-(*N*-pyrrolylmethyl)silanes[4].

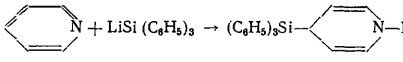
When picolinylpotassium reacts with halogenosilanes, pyridylmethylsilanes are formed[22]. If the initial picolinylpotassium was obtained from potassamide, after its reaction with chlorotrimethylsilane it is possible to isolate from the reaction mixture 2-bis(trimethylsilyl)-methylpyridine in addition to trimethyl-(2-pyridylmethyl)-silane.

Organic *C*-methyl magnesio-derivatives have been used to prepare trialkyl-(2-pyridyl)silanes[11,23], di-R-(2,3,5,6-tetrachloro-4-pyridyl)silanes[15], and tri-R-(8-alkoxy-5-quinolinyl)silanes[24].

Organometallic silyl derivatives, in particular triphenylsilyl-lithium and (tri-R-silyl)-R-lithium, can also be used to prepare *C*-silylated derivatives of nitrogen-containing heterocycles. With halogen-substituted heterocycles, the halogen atom is replaced by the tri-R-silyl-group:

$$R_N{-}Cl + LiSi(C_6H_5)_3 \rightarrow R_N{-}Si(C_6H_5)_3 + LiCl$$

and with unsubstituted heterocycles an addition reaction takes place, for example:



Thus, when triphenylsilyl-lithium reacts with pentachloropyridine in tetrahydrofuran (THF) solution at −70°C, (2,3,5,6-tetrachloro-4-pyridyl)triphenylsilane is formed[25] (together with hexaphenyldisilane and 4,4′-octachlorobipyridyl); (9-alkylcarbazolyl)triphenylsilanes[7,26] and the corresponding (10-ethylphenothiazinyl)triphenylsilane[26] are formed in the reactions with 9-alkyl-2-bromo- and 9-alkyl-3-bromo-carbazoles and with 2-, 3-, and 4-chloro-10-ethylphenothiazines respectively. Triphenylsilyl-lithium cleaves the C–O bond in *N*-alkoxymethylpiperidines with formation of (*N*-piperidinylmethyl)triphenylsilane[27].

Triphenylsilyl-lithium adds to pyridine[28] in the 1,4-positions and to acridine[16,29] in the 9,10-positions. The reaction of acridine with *p*-trimethylsilylphenylmagnesium bromide takes place similarly[30]. On the other hand, in the case of quinoline the addition of *p*-trimethylsilylphenyl-lithium[31] and 2-triphenylsilyl-5-thienyl-lithium[32] takes place in the 1,2-positions.

The addition of trimethylsilylphenyl-lithium to the carbonyl group of phenyl 2-pyridyl ketone leads to the formation of trimethylsilylphenyl-(2-pyridyl)phenylmethanol[33].

3. Amination of Alkenylsilanes

Aziridine[34-42], pyrrolidine[36,37], piperidine[36,37,39,43], and perhydroazepine[44] add to vinylsilanes in the presence of lithium, sodium, potassium, or their amides:

$$\equiv SiCH{=}CH_2 + HN(CH_2)_n \rightarrow \equiv SiCH_2CH_2N(CH_2)_n.$$

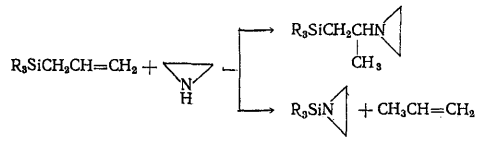
The addition of pyrrolidine and piperidine to triethylvinylsilane in the presence of metallic lithium begins at room temperature and takes place with a spontaneous temperature rise[36,37]. The yields of reaction products after 2 h amount to 70 – 72%. The rate of addition of aziridine is much lower (yield 39%) and pyrrole does not add to triethylvinylsilane under these conditions even after 25 h.[37]

When triethylvinylsilane was heated with aziridine in the presence of sodium for 7 h at 100°C, [2-(*N*-aziridinyl)ethyl]triethylsilane was formed in 90% yield. In the presence of sodamide, the reaction terminates after only 2 h at 50°C. Methyldiphenylvinylsilane readily combines with aziridine even at room temperature.

The rate of addition of piperidine to tri-R-vinylsilanes in the presence of lithium piperidide increases in the following sequence in terms of the organic substituent linked to the silicon atom: ethoxy- < triethyl < trimethyl < dimethylphenyl < methyldiphenyl[39], probably due to the increase in the same sequence of the double bond polarity, which promotes nucleophilic attack. The decrease of the rate of reaction for ethoxy-derivatives can be caused by part of the catalyst being consumed in the cleavage of the $Si-OC_2H_5$ bond[39]. The rate of addition of piperidine to the tri-R-vinylsilanes in THF solution is approximately twice as high as when the reaction is carried out in benzene or heptane[39]. The use of THF also makes it possible sometimes to lower the temperature of the amination reaction and to increase the yield of the reaction products[38].

When R-vinylsilanes with unsubstituted hydrogen atoms react with aziridine in the presence of lithium, dehydrocondensation and addition reactions take place simultaneously, the relative rate of the latter increasing from diethylvinylsilane to diphenylvinylsilane. The introduction of the aziridine group at the silicon atom also increases the rate of the addition reaction[40].

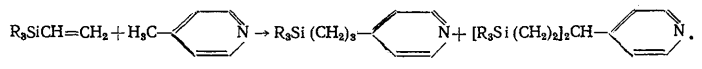
As the double bond is removed further away from the silicon atom in the compounds $R_3Si(CH_2)_nCH{=}CH_2$ (n = 0, 1, or 2), the rate of addition of aziridine decreases. With allylsilanes, addition is frequently accompanied by β-decomposition[34,45]:



(γ-Butenyl)trimethylsilane does not react with aziridine in the presence of $NaNH_2$ even on heating to 100°C. In contrast, *p*-trimethylsilylstyrene readily combines with aziridine[34] even at 50°C.

The addition of piperidine to 1-triethylsilylbuta-1,3-diene in the presence of sodium gives a mixture of 1,4- and 3,4-addition products[46] and the reaction of 1-trimethylsilylbut-3-en-1-yne with piperidyl-lithium gives, apart from the normal product of the addition to the double bond, the corresponding allenic amine[47].

When trimethylvinylsilane is heated with 4-methylpyridine at 55°C in the presence of sodium for 3 – 6 h, mono- (43%) and di-addition (49%) products are formed[48]:

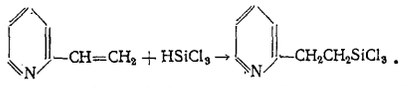


When metallic potassium is employed as a catalyst, the ratio of the products is altered in favour of a higher yield of the disilyl derivative (30 : 60).

4. Hydrosilylation of Heterylalkenes and Heterylalkynes

Trichlorosilane adds to 2-vinylpyridine in the presence of triethylamine and tributylamine giving a high yield

(91% with triethylamine) of trichloro-[β-(2-pyridyl)ethyl]-silane[49]. However, the reaction takes place smoothly also in the presence of other catalysts[49-53]:



High yields of hydrosilylation products are also found in the reaction of trichlorosilane with 4-vinylpyridine and 2,6-dimethyl-4-vinylpyridine[54]. The first stage in this reaction is the formation of a complex $HSiCl_3.nB$ (B = vinylpyridine; $n = 3$ for 4-vinylpyridine and $n = 4$ for 2-vinylpyridine)[55]. The complex of trichlorosilane with 2-vinylpyridine decomposes even at room temperature with evolution of heat and a hydrosilylation product is formed[55].

Alkylchlorosilanes and alkylarylchlorosilanes (both with unsubstituted hydrogen atoms) add to 2-vinylpyridine, 4-vinylpyridine, and 2,6-dimethyl-4-vinylpyridine in the presence of a catalyst (*NNNN'*-tetramethylenediamine and Cu_2Cl_2) with formation of β-adducts[56].

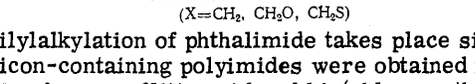
When 2- and 4-vinylpyridines are hydrosilylated with trialkylsilanes in the presence of chloroplatinic acid, a mixture of α- and β- adducts is produced, with the former predominating[51]. Pentamethyldisiloxane[57-59] and *sym*-tetramethyldisiloxane[57] produce α-adducts by this reaction, while heptamethylcyclotetrasiloxane gives a mixture of α- and β-isomers[57].

In the presence of chloroplatinic acid, the hydrosilylation of 2-allyloxypyridine[60,61], *N*-vinyl-lactams[62,63], *N*-vinylsuccinimide[64], and *N*-allyloxymethylphthalimide[65] was achieved.

The hydrosilylation of *N*-propargylpyrrolidine[66], *N*-propargylpiperidine[66,67], and *N*-propargylmorpholine[66] with triethylsilane in the presence of $H_2PtCl_6.6H_2O$ yields γ-adducts with a *trans*-structure. On going from triethylsilane to dibutylmethylsilane and from heptamethyltrisiloxane with three unsubstituted hydrogen atoms to triethoxysilane, there is a gradual increase of the content of the β-adduct in the reaction products and for the last compound the amounts of the γ- and β-adducts are almost equal[67].

5. Amination of Halogenosilanes with Organic Substituents

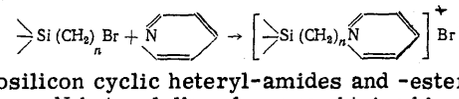
Tri-R-halogenoalkylsilanes silylate the amino-groups of aziridine[42], pyrrolidine[66,68], piperidine[43,68-70], morpholine[44,68,71], thiamorpholine[44], and perhydroazepine[44,72] in the presence of hydrogen halide acceptors (potassium carbonate, triethylamine, excess of heterocyclic base):



(X=CH_2, CH_2O, CH_2S)

N-Silylalkylation of phthalimide takes place similarly[18] and silicon-containing polyimides were obtained from the di-imide of pyromellitic acid and bis(chloromethyl)tetramethyldisiloxane[73].

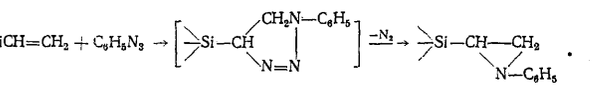
Prolonged heating of halogenoalkylsiloxanes with pyridine gives the corresponding organosilicon pyridinium salts[74-77]:



Organosilicon cyclic heteryl-amides and -esters derived from *N*-heterylalkanols were obtained by the reaction of trimethylsilylbenzoyl and trimethylsilylphenylacetyl chlorides with heterocyclic bases[78,79] and *N*-heterylalkanols[80].

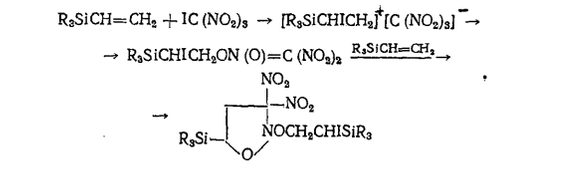
6. Cyclisation Reactions

Organosilicon derivatives of aziridine have been obtained by the reaction of vinylsiloxones with phenyl azide[58,81] at room temperature or with benzyl azide[82] at 60 — 80°C. The first stage of this reaction may be the addition of phenyl azide to the vinyl group with formation of a five-membered ring, which splits off a nitrogen molecule and is converted into an *N*-phenylaziridinyl derivative:



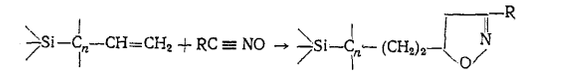
After a 40 day reaction of heptamethylvinylcyclotetrasiloxane and heptamethyl-3-vinyltrisiloxane with phenyl azide, the yields of *C*-aziridinyl derivatives did not exceed 11%. The reaction of allylsiloxanes with phenyl azide is even more difficult[81]. Benzyl azide adds to heptamethyl-3-vinyltrisiloxane somewhat more readily[82]. When the reaction is performed in petroleum ether solution at 30 — 40°C, the yield of product after 10 days was 40.5%.

The addition of iodotrinitromethane to trimethylvinylsilane in carbon tetrachloride solution leads to the formation of an isoxazolidine derivative[83,84]:



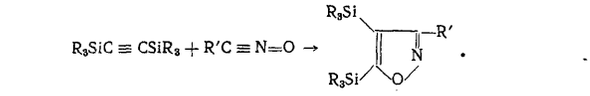
The product of the reaction of allyltrimethylsilane with iodotrinitromethane is *N*-trimethylsiloxy-5-trimethylsilylmethyl-3,3-dinitroisoxazolidine[83].

Organosilicon derivatives of isoxazolidine have been synthesised by the addition of nitrile oxides to vinyl-[85], allyl-[85], and vinylethynyltri-R-silanes[86,87]:

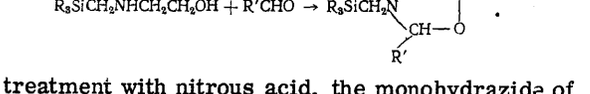


and also by the condensation of vinylsiloxanes with 1,4-dinitrobutane in the presence of phenylene di-isocyanate and triethylamine and by the reaction of alkenylsiloxanes with 1,2-dichloroglyoxime in the presence of triethylamine[88].

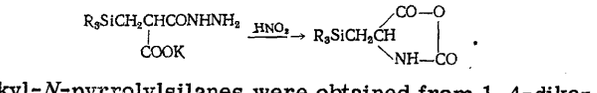
The reaction of ethynylsilanes with nitrile oxides yields isoxazolylsilanes[85]:



Alkyl-*N*-oxazolidinylsilanes were obtained by the condensation of silylaminoalcohols with aldehydes[89]:

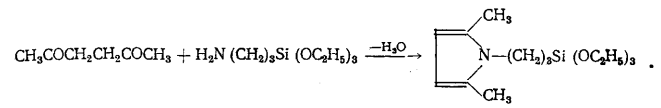


On treatment with nitrous acid, the monohydrazide of trimethylsilylmethylmalonic acid cyclises into an oxazolidinedione derivative[90]:

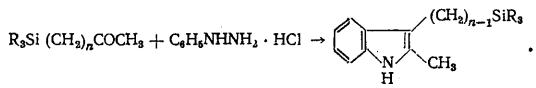


Alkyl-*N*-pyrrolylsilanes were obtained from 1,4-diketones and aminoalkylsilanes[91,92]. Thus triethoxy-γ-(2,5-dimethylpyrrolyl)propylsilane is formed when

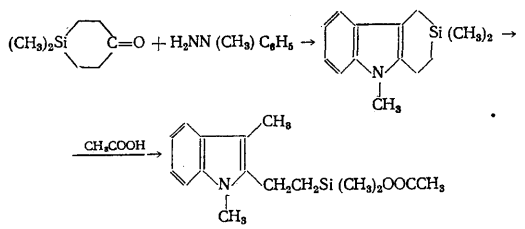
hexane-2,5-dione is heated with γ-aminopropyltriethoxysilane for 1 h at 140—150°C:



The condensation of γ-, δ-, and ε-silylketones with phenylhydrazine hydrochloride at 170—200°C in the presence of copper(I) chloride yielded silyl derivatives of indole[93-95]:

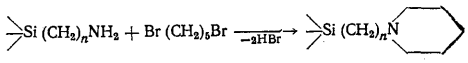


When 4,4-dimethyl-4-silacyclohexanone is refluxed with 1-methyl-1-phenylhydrazine in glacial acetic acid, dimethyltetrahydrosilacarbazole is formed and then converted into indole derivatives[96]:



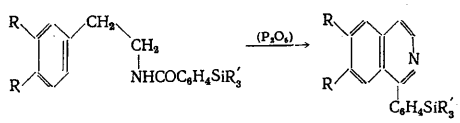
When a solution of *p*-trimethylsilylbenzylamine and itaconic acid is heated to boiling in pyridine, 4-carboxy-*N*-(*p*-trimethylsilylbenzyl)-2-pyrrolidinone is produced[20].

Tri-R-(2-piperidinoethyl)silanes and tri-R-(3-piperidinopropyl)-silanes were synthesised by the reaction of 2- and 3-aminoalkylsilanes with 1,5-dibromopentane[97]:



2,2,4,4-Tetranitropiperidinoalkylsilanes were obtained similarly by the condensation of aminoalkylsilanes with 2,2,4,4-tetranitropentane-1,5-diol[98,99].

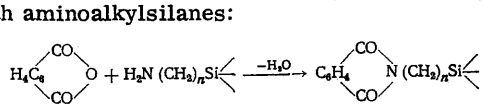
1-Trimethylsilylphenyl- and 1-trimethylsilylbenzyl-derivatives of isoquinoline were synthesised by the cyclisation of β-arylethylamides of the corresponding trimethylsilylarylcarboxylic acids in toluene when acted upon by phosphorus pentoxide or phosphoryl chloride[78]:



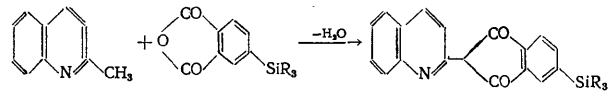
7. Other Methods

The Mannich reaction with piperidine and morpholine has been used for the aminomethylation of tri-R-ethynylsilanes[100] and trimethylsilylmethylacetophenone[101].

Silyl derivatives of succinimide[102,103] and phthalimide[102-105] are formed when dicarboxylic acid anhydrides react with aminoalkylsilanes:

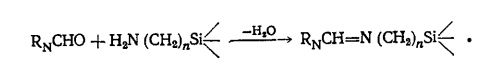


If one employs alkoxyaminoalkylsilanes in this reaction, the hydrolysis of the alkoxy-groups with water liberated on condensation and further polycondensation of phthalimidoalkylsilanols gives rise to polymeric products. Trialkylsilylphthalimides were also obtained by heating the anhydrides of 3- and 4-trimethylsilylphthalic acids with urea at 170°C. The condensation of these anhydrides with quinaldine leads to the formation of the corresponding quinolinophthalones[106]:



N-Heterylsilylalkanols were obtained by the opening of the oxiran ring of alkyloxiranylsilanes with aziridine[107] or phthalimide[104].

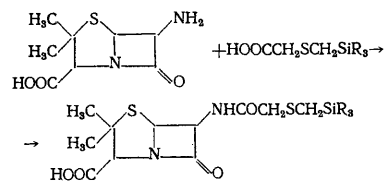
Silylaldimines were obtained by the reaction of heterocyclic aldehydes with aminoalkylsilanes:



The reaction has been used to prepare indole[108], oxazole[108], benzoisoxazole[108,109], thiazole[109], benzoisothiazole[109], pyridine[108], and acridine[108] derivatives.

Organosilicon derivatives of carbazole have been obtained by the reaction of carbazole with trimethylsilylacetyl chloride in the presence of stannic chloride[110]; organosilicon esters of nicotinic acid were obtained by heating alkylchlorosilanes with sodium nicotinate[111]; polymeric alkylsilylpyridylalkylenes were obtained by the copolymerisation of 4-vinylpyridine with methylallylsilacyclobutane[112].

A silicon-containing penicillin was synthesised by the reaction of 6-aminopenicillanic acid with trimethylsilylmethylmercaptoacetic acid in acetone using *NN'*-dicyclohexylcarbodiimide as the condensing agent[113]:



B. PHYSICAL PROPERTIES

Electronic[8,11,114], vibrational[4,15,17,55,66,67,83,86,106,115-118], and ^{1}H NMR[9,10,15,25,46,48,51,57,65,66,86,96,115,119] spectra of organosilicon derivatives of nitrogen-containing heterocycles have been used mainly to confirm the structures of the compounds synthesised.

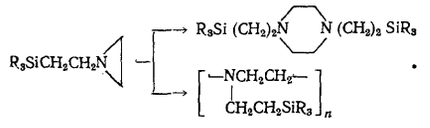
By comparing the calculated and experimental electronic spectra of trimethyl-(2-pyridyl)silane it was suggested that the π electrons of the heterocycle interact with the vacant orbitals of silicon[114]. However, trimethyl-(2-pyridyl)silane is a stronger base than 2-t-butylpyridine (according to potentiometric titration data, the pK_a values are 6.63 and 5.76 respectively). Trimethyl-(4-pyridyl)-silane is a weaker base than 4-t-butylpyridine, the basicity of which is higher than that of the 2-isomer[119].

The changes in the ultraviolet spectra of trialkylpyridylsilanes have been used to investigate the kinetics of their solvolysis[11]. The stereochemistry of this reaction was studied by determining the optical activities of methyl-1-naphthylphenyl-(2-pyridyl)silane and its methanolysis and hydrolysis products[8].

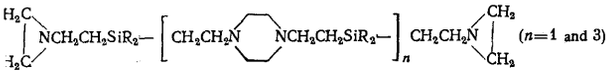
:. CHEMICAL PROPERTIES

. Thermal Reactions

Tri-R-[2-(*N*-aziridinyl)ethyl]silanes remain unchanged fter heating for 5 h at 200°C. An increase of tempera-ıre to 250 — 300°C leads to the formation of considerable mounts of thermal conversion products among which roducts with a high molecular weight are formed ›gether with products of cyclodimerisation to piperazine ›rivatives owing to the opening of the aziridine ng[117,118,120]:



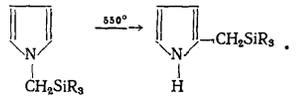
When [2-(*N*-aziridinyl)ethyl]triethylsilane is heated in ə presence of sodium iodide, the only product is the rresponding piperazine derivative, the yield of which ›reases from 22% for a molar reactant ratio of 1 : 0.2 50% for the equimolar ratio[120]. The yield of the poly-›r and the degree of polymerisation depend to a con-lerable degree on the nature of the groups linked to the icon atom. For example, when R = C_2H_5, heating at ›°C leads to the formation of a tetramer in about 7% ld. On the other hand, dimethylphenyl and ethoxy-ıethyl derivatives give 70 — 80% of compounds with 5 — 9.[117] Complexes of alkylaziridinylsilanes with c chloride polymerise at a temperature as low as ›°C to form polymers with $n = 80 - 300$°C.[117] Dialkyldi-[2-(*N*-aziridinyl)ethyl]silanes form linear di-. tetra-mers on heating to 250 — 300°C:[118]



(*n*=1 and 3).

ırther increase of temperature leads to the formation ross-linked insoluble polymers[118].

When trimethyl-(*N*-pyrrolylmethyl)silane is heated at °C, it isomerises to trimethyl-(2-pyrrolylmethyl)-ne[4]:



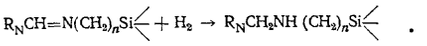
Reduction

he reduction of organosilicon derivatives of nitrogen-ining heterocycles has been used to prepare deriva- with hydrogenated rings and also to modify the func-l groups in the side chain of the heterocycle or ›s linked to the silicon atom.

ıus pyridylsilanes[33] and alkylpyridylsiloxanes[121] were ›rted by catalytic reduction (H_2/PtO_2) into the corre-ling piperidinylsilanes and alkylpiperidinylsiloxanes)-acridinyl)triphenylsilane (reduction with Zn/HCl) :onverted into (9,10-dihydro-9-acridinyl)triphenyl-›[16].

e cyano- and ethoxycarbonyl functional groups of ılsilanes[5], the amide groups of substituted piperi- · and morpholinyl-R-silanes[78], and the alkoxy-groups ylalkoxyaziridinylsilanes[38] were reduced with lithium niumhydride.

Aldimines obtained from heterocyclic aldehydes and silylamines were hydrogenated catalytically to amines:

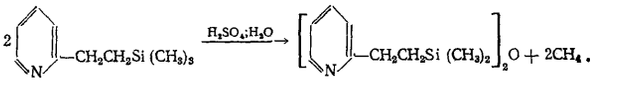


Derivatives of indole[122], oxazole[122], benzoisoxazole[122], pyridine[122], and acridine[122] were obtained in this way.

In the presence of Raney nickel, trimethylsilylmethyl-phenyl piperidinoalkyl ketones were reduced to the corre-sponding carbinols[101].

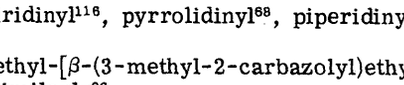
3. The Formation of Siloxanes

When acted upon by concentrated sulphuric acid, tri-methyl-[β-(2-pyridyl)ethyl]silane splits off a methyl group. Subsequent hydrolysis yields tetramethyl-1,3-bis-[β-(2-pyridyl)ethyl]disiloxane which forms copolymers with alkyl- and aryl-polysiloxanes in the presence of KOH:[13,14]



Alkylpiperidyl-[97,121] and alkylcarbazolyl-polysiloxanes[110] were obtained similarly.

Alkaline hydrolysis of dialkylethoxy-(*N*-heterylalkyl)-silanes yields 1,3-bis-(*N*-heterylalkyl)tetramethyldi-siloxanes:



where R_N = aziridinyl[116], pyrrolidinyl[68], piperidinyl[68], and morpholinyl[68].

Acetoxydimethyl-[β-(3-methyl-2-carbazolyl)ethyl]silane is hydrolysed similarly[96].

Alkaline hydrolysis of [2-(*N*-aziridinyl)ethyl]diethoxy-methylsilane results in the formation of a cyclic trimer, while hydrolysis with 95% ethanol leads to a linear tri-siloxane with terminal ethoxy-groups. Hydrolysis with an excess of water yields a polysiloxane oil which solidifies on standing[116].

Polysiloxanes were obtained by the hydrolysis of dichloromethyl-(2-succinimidoethyl)silane[64], triethoxy-(3-succinimidopropyl)silane[102,103], triethoxy-(3-phthal-imidopropyl)silane[102,103], and diethoxymethyl-[γ-(2-pyridyl-oxy)propyl]silane[61]. Polysiloxane resins obtained by the hydrolysis of trichloro-[β-(2-pyridyl)ethyl]silane and its 4-analogue do not lose their solubility in inert solvents even after heating to 105°C for 24 h.[49,50,54]

4. Desilylation

The Si — C bond between the silicon atom and the hetero-cycle in (9-ethyl-3-carbazolyl)triphenylsilane and (9-ethyl-1-carbazolyl)triphenylsilane is readily cleaved by hydrogen chloride in glacial acetic acid[7]. The process also involves a partial cleavage of the Si — C_6H_5 bond.

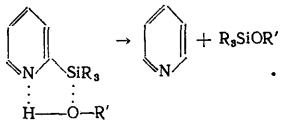
In the combined protonation and desilylation by perchlo-ric acid in aqueous methanol, (9-ethyl-3-carbazolyl)tri-methylsilane is more reactive than the corresponding dibenzofuran and dibenzothiophen derivatives[6].

(9-Ethyl-1-carbazolyl)triphenylsilane is cleaved by a solution of alkali in aqueous dioxan or ethanol but with appreciably greater difficulty than the corresponding dibenzofuran and dibenzothiophen derivatives. Under the above conditions, (9-ethyl-3-carbazolyl)triphenylsilane is stable[7].

Trimethyl-(2-pyrrolylmethyl)silane is cleaved by alcoholic alkali with much greater difficulty than benzyltrimethylsilane[4].

The Si — CH_2CO bond in the piperidide of diethylmethylsilylacetic acid[17] is cleaved quantitatively by 5% hydrochloric acid even at 0°C.

In contrast to the 3- and 4-isomers, trimethyl-(2-pyridyl)silane readily reacts with water, methanol, or ethanol to form pyridine and trimethylsilanol or alkoxytrimethylsilane[11,123]. The relative rates of desilylation at 50°C in water, methanol, and ethanol are 740 : 120 : 1. Higher alcohols do not enter into this reaction. The desilylation of trimethyl-(2-pyridyl)silane by water is inhibited by acids, while alkalies do not alter its rate. The reaction is of first order with respect to silane, has a high negative entropy of activation, and does not show an isotope effect. On the basis of these data, one may suppose that the desilylation proceeds via a five-membered cyclic complex[11]:

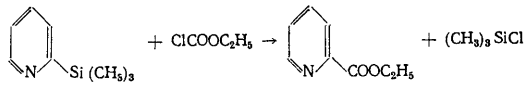


The above mechanism is confirmed by the finding that the hydrolysis and methanolysis of the optically active methyl-1-naphthylphenyl-(2-pyridyl)silane takes place with retention of its configuration[8].

Trimethyl-(2-pyridyl)silane is hydrolysed much faster than trimethyl-(2-pyridyl)germane but more slowly than trimethyl-(2-pyridyl)stannane[124]. The relative rates of hydrolysis of the silicon, germanium, and tin derivatives are $1 : 10^{-4} : 22$.

The rate of methanolysis of trialkyl-(2-pyridyl)silanes as a function of the groups linked to the silicon atom decreases in the following sequence: dimethyl > trimethyl > triphenyl > triethyl[10]. The rate of cleavage of the Si — C bond in methyl-substituted 2-trimethylsilylpyridines, $2\text{-}(CH_3)_3Si(C_5H_3N)R$, by water decreases in the following sequence as a function of the position of the methyl group[9,125] (the positions of the methyl group R and the relative rates of desilylation at 30.2°C are quoted): 4-methyl-(1.70)- > 6-methyl-(1.59) > 3-methyl-(1.58) > H(1) > 5-methyl-(0.71). The same sequence is largely followed also in methanolysis. The only exception is trimethyl-(3-methyl-2-pyridyl)silane which is least reactive in this case[9,125].

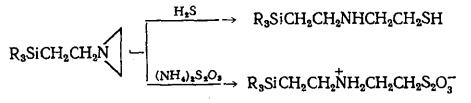
Trimethyl-(2-pyridyl)silane is readily desilylated by carboxylic acid chlorides and chlorocarbonic esters[126]:



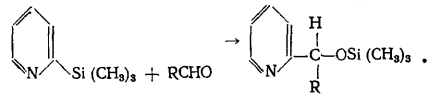
The Si — C bond in trimethyl-(2-pyridylmethyl)silane is cleaved by 95% aqueous ethanol with formation of hexamethyldisiloxane. However, in contrast to trimethyl-(2-pyridyl)silane, this requires prolonged heating and the reaction is catalysed by alkalies and especially by acids[22]. The rate of reaction decreases in the sequence trimethyl-(4-pyridylmethyl)silane > trimethyl-(2-pyridylmethyl)-silane > methyl-2-bis(trimethylsilyl)pyridine. There is a particularly marked difference between the rates of hydrolysis in an acid medium of the last two compounds, probably owing to steric factors which impede the protonation of the nitrogen atom preceding the attack on the silicon atom.

5. Other Reactions

The aziridine ring in [2-(*N*-aziridinyl)ethyl]trimethylsilane and [3-(*N*-aziridinyl)propyl]trimethylsilane is opened by hydrogen sulphide or ammonium thiosulphate with formation of the corresponding silyl derivatives of 2-aminoethanethiol and 2-aminoethanethiosulphuric acid[42]:



Trimethyl-(2-pyridyl)silane adds to aldehydes via the mechanism[127,128]:



A number of the usual reactions involving the functional groups linked to the heterocycle have also been carried out. These include the transformation CN → $CONH_2$ → NH_2 → OH in 2- and 4-substituted trimethyl-(3-pyridyl)-silanes[12], alkylation[96] and vinylation[129,130] of the NH group in trialkylsilylindoles, transamination of 3-dimethylaminomethyl-5-trimethylsilylindole with piperidine[5], the conversion of phthalimidoalkylsilanes into aminoalkylsilanes by treatment with hydrazine hydrate[18,20,21], and the formation of trimethylsilyl-substituted derivatives of indigo[131].

D. BIOLOGICAL PROPERTIES

The toxicity of trialkyl(piperidinylmethyl)silanes to white mice depends little on the nature of the alkyl groups linked to the silicon atom and varies in the range from 45 to 90 mg kg^{-1}.[132,133] Trialkyl-(3-piperidinopropyl)-silanes are somewhat more toxic than 2-piperidinylethyl and piperidinylmethyl derivatives[132-134]. Triethyl-(3-piperidinylpropyn-1-yl)silane (LD_{50} = 195 mg kg^{-1}) is less toxic than the corresponding vinyl and ethyl derivatives[64,132]. The toxicity of diethoxy-[3-(*N*-heteryl)propyl] methylsilanes decreases from the piperidine derivative to morpholine and thiamorpholine derivatives[135,136].

The hydrochlorides of diethylmethyl-(2-piperidinylethyl)silane and triethyl-(3-piperidinylpropyl)silane impair the coordination of the movement of white mice when administered in doses smaller by a factor of 8.2 and 7.3 respectively than the median lethal doses[132].

Trialkyl-(3-piperidinylpropyl)silanes exhibit a fungistatic activity in relation to the pathogenic fungi *Candida albicans*, *Epidermophyton* Kaufmann-Wolf, and *Trychophyton gypseum*. The minimum concentration of the compound inhibiting the growth of *Epidermophyton* Kaufmann-Wolf 41 decreases in the following sequence as a function of the groups linked to the silicon atom: diethylmethyl, methyldipropyl > methyldipentyl > dibutylmethyl, amounting to 12.5 μg ml^{-1} for the last silane.

E. PRACTICAL APPLICATIONS

Alkylpyrrolylsiloxanes and alkylpiperidinylsiloxanes are used as lubricating oils[97,121] and as modifying agents in various oils and resins[121]. Pyridylsiloxanes[121] and (pyridylalkyl)siloxanes[47] are used to synthesise ion-exchange resins.

The products of the joint hydrolysis of diethoxymethyl-[β-(4-pyridyl)ethyl]silane and dichlorodimethylsilane[55] and alkyl-(2-pyridyloxy)polysiloxanes[60] have been used to prepare elastomers. Polysiloxane elastomers based on alkylpyrrolylsiloxanes[92], alkyloxopyrrolidinylsiloxanes[62], and alkylsuccinimidosiloxanes[64] exhibit a high resistance to oils. Alkoxyalkylaziridinylsiloxanes form coatings on the surface of various materials which are resistant to the action of organic solvents[107].

Alkylpyrrolylsilanes have been suggested as antioxidants[137] and the addition of ethoxydimethyl(piperidinylmethyl)silane accelerates the formation of polyurethane foam plastics[68].

Alkylpyridylpolysiloxane salts are used as emulsifying agents[23,76] and also to impart hydrophobic properties to textiles[74,75,79] and to increase their fire resistance[75].

III. COMPOUNDS CONTAINING THE Si—N BOND

A. METHODS OF PREPARATION

1. Reaction of Halogenosilanes with Heterocyclic Bases

A general method for the preparation of organosilicon derivatives of nitrogen-containing heterocycles with an Si—N bond is the reaction of heterocyclic bases with halogenosilanes. Heterocycles with an unsubstituted N—H bond give rise to *N*-silylheterocycles and tertiary heterocyclic bases give rise to complexes or the reaction does not occur at all, depending on the structure of the halogenosilane.

The *N*-silylation of nitrogen-containing heterocycles may be represented by the general mechanism

$$R_NNH + Cl{-}Si\lessgtr \xrightarrow{+B} R_NN{-}Si\lessgtr + B{\cdot}HCl,$$

where R_NNH = aziridine[138-142], pyrrolidine[143-147], succinimide[148], the anhydrides of *N*-carboxy-α-aminoacids[149], phthalimide[65,150], piperidine[43,143,146,151-155], morpholine[152,155-159], perhydroazepine[156], and ε-caprolactam[160,161].

Ammonia[138], triethylamine[138,140,143,149,150,156,160,161], pyridine[65,138], or an excess of the heterocyclic base itself[139,141,146,147,153,154,159] are used as the acceptors (B) of the hydrogen halide liberated. The reaction can be achieved without a solvent[153] or in solution in ethyl ether[151,161], pentane[140,144], benzene[138,139,142,143,154,159], THF,[149] or dimethylformamide (DMF).[150] *N*-Silylpyrrolidine and *N*-silylpiperidine were obtained from iodosilane and the corresponding bases in the gas phase[146].

Tri-R-(*N*-heteryl)silanes and di-R-bis-(*N*-heteryl)-silanes can be obtained in this way readily and rapidly.

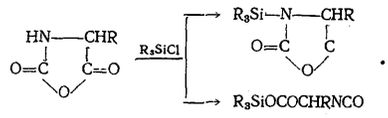
The rate of reaction of di-R-dichlorosilanes with ε-caprolactam decreases in the following sequence as a function of the organic substituent linked to the silicon atom[161]:

$$(CH_3)_2SiCl_2 > CH_3C_2H_5SiCl_2 > CH_3(i\text{—}C_4H_9)SiCl_2 > CH_3C_6H_5SiCl_2 > (C_6H_5)_2SiCl_2 .$$

To obtain a high yield of R-tris-(*N*-heteryl)silanes, prolonged heating of the reactants is often necessary[154,156]. Tetrapyrrolidinylsilane was obtained in 50% yield by heating silicon tetrachloride with an excess of pyrrolidine[147]. A similar reaction with piperidine in ethereal solution yielded a mixture of trichloropiperidinylsilane, dichloropiperidinylsilane, and chlorotripiperidinylsilane[151]. To obtain tetrapiperidinylsilane, chlorotripiperidinylsilane must be heated with piperidine for 12 h at 250—270°C.[151] The reaction of morpholine with silicon tetrachloride yielded only chlorotrimorpholinylsilane[159].

A study of the stereochemistry of the reaction of chloromethyl-1-naphthylphenylsilane with pyrrolidine showed that it proceeds with inversion of configuration[144].

In certain cases, when *N*-heterylsilanes are synthesised from chlorosilanes, side reactions reduce their yield. For example, in the reaction of chlorosilanes with aziridine, silylation is accompanied also by the opening of the aziridine ring, which in the absence of hydrogen chloride acceptors becomes the main process[139,146]. Two products are formed in the silylation of the anhydrides of *N*-carboxy-α-aminoacids with chlorotrimethylsilane at 0°C in the presence of triethylamine[149]:



An increase of reaction temperature promotes the formation of an acyclic product polymerisation[149].

Depending on their structure, halogenosilanes react with pyridine to form both ionic and molecular complexes. Bromosilane[162,163], iodosilane[162-164], dibromosilane[162,163], di-iodosilane[162,163], and silicon tetraiodide[163,165,168] form complexes with pyridine which conduct electricity in acetone solutions and to which the following structures have been attributed: $[2C_5H_5N.SiH_3]^+X^-$, $[4C_5H_5N.SiH_2]^{2+}2X^-$, and $[4C_5H_5N.SiI_2]^{2+}2I^-$. In the presence of pyridine, dichlorosilane and chlorosilane form a current-conducting complex $H_2SiCl_2.2C_5H_5N$.[162,163] Fluorosilane and difluorosilane are decomposed by pyridine[163]. Silicon tetrafluoride[162,167-172], silicon tetrachloride[162,165,167,170,172-178], and silicon tetrabromide[162,165,167,170,179] form with pyridine, quinoline, and isoquinoline complexes of the type $SiX_4.2L$ (X = F, Cl, or Br; L = pyridine, quinoline, or isoquinoline). Data concerning the formation of complexes with a different structure[166,177,180-182] were not confirmed[162,168,170,178,183].

The acceptor capacity of tetrahalogenosilanes in relation to pyridine decreases in the sequence $SiCl_4 \sim SiBr_4 > SiF_4$, since the heats of formation $-\Delta H$ of complexes of the type $SiX_4.2C_5H_5N$ also decrease on passing from the chloro- (27.7 kcal mole^{-1}) and bromo- derivatives (26.8 kcal mole^{-1}) to the fluoro-derivative (17.9 kcal mole^{-1})[167,184,185]. The values of $-\Delta H$ quoted in other studies[170,186] are clearly too high.

When mixed silicon tetrahalides were allowed to react with pyridine, the complexes $SiCl_3Br_3.2C_5H_5N$, $SiCl_3Br.2C_5H_5N$, $SiCl_3I.3C_5H_5N$, and $SiCl_2I_2.4C_5H_5N$ were formed[187]. Ionic structures were attributed to the last two compounds[187,188]: $[3C_5H_5N.SiCl_3]^+I^-$ and $[4C_5H_5N.SiCl_2]^{2+}2I^-$.

Trichlorosilane forms a 1 : 2 complex with pyridine[162,167,168], a 1 : 3 complex with 4-vinylpyridine[55], and a 1 : 4 complex with 2-vinylpyridine[55]. Trifluorosilane and tribromosilane form 1 : 4 complexes with pyridine[163]. When bromomethylsilane and iodomethylsilane react with pyridine, 1 : 2 complexes are formed, while chloromethylsilane undergoes quantitative disproportionation under these conditions to methylsilane and dichloromethylsilane[189]. The latter forms with pyridine an extremely unstable complex of unknown composition. The greatest influence of halogenosilanes on the stoichiometry of pyridine complex has been observed with iodosilanes. Thus, whereas iodomethylsilane forms with pyridine a 1 : 2 complex, di-iodomethylsilane forms a 1 : 4 complex and di-iododimethylsilane and iodotrimethylsilane give rise to 1 : 1 complexes[163,189]. Bromotrimethylsilane forms with pyridine an unstable product of unknown

composition[163]. Fluorotrimethylsilane, chlorotrimethylsilane, dichlorodimethylsilane, and trichloromethylsilane do not interact with pyridine[163,167,173,189]. The claims of successful reactions of this type[190,191] were not confirmed in this respect.

Complexes of halogenosilanes with pyridine *N*-oxide[192], picoline[167,168], 2-hexylpyridine[164], 2,4-dimethylpyridine[166], 2,2-bipyridyl[164,165,182,193-204], and phenanthroline[187,196,204] have also been obtained.

Iodotriphenylsilane combines with 2,2′-bipyridyl to form a complex which dissociates in dichloromethane solution into an iodide anion and a triphenyl(bipyridylyl)-siliconium cation in which both nitrogen atoms form coordinate bonds with the silicon atom[193]. The reaction is more difficult with bromotriphenylsilane and does not occur at all with chlorotriphenylsilane.

The reactions of hexachlorodisilane and hexabromodisilane with pyridine involve the cleavage of the Si — Si bond[187]:

$$Cl_3SiSiCl_3 + 3C_5H_5N \rightarrow 2C_5H_5N \cdot SiCl_4 + 1/n\,(C_5H_5N \cdot SiCl_2)_n .$$

Tetrapropylammonium pentafluorosilicate forms an unstable complex with pyridine[205].

Pyridine complexes, similar to those of halogenosilanes, are formed also by a series of other organosilicon compounds: silicon tetraisothiocyanate[206], tetranitrate[207], and oxalate[208], silyltetracarbonylcobalt, and silylpentacarbonylmanganese[209-211]. Poly-(2-vinylpyridine *N*-oxide) (PVPO) forms a complex with silicic acid[212]. Possibly such complex formation is in fact responsible for the increase of the resistance of macrophages to the action of quartz dust under the influence of PVPO.[213,214]

2. Organometallic Synthesis

In the synthesis of Si — N derivatives, *N*-organometallic derivatives of the heterocyclic base are allowed to react with chlorosilanes instead of the base itself:

$$R_NNM + ClSi\lessgtr \rightarrow R_NN{-}Si\lessgtr + MCl$$

M=Li, Na, K, MgBr

Using *N*-lithium-substituted heterocycles, *N*-R-silyl derivatives of pyrrole[215,216] and pyrrolidine[144] were obtained in this way. The reaction of chloromethyl-1-naphthylphenylsilanes with pyrrolidinyl-lithium takes place with inversion of configuration[144].

The reaction of 9-carbazolylsodium with silicon tetrachloride in benzene solution yielded di-(9-carbazolyl)dichlorosilane[217].

N-Pyrrolylsilanes[143,218-220] (and not *C*-pyrrolylsilanes as believed previously), succinimidosilanes[221], phthalimidosilanes[63,221], and *N*-indolylsilanes[143] have been synthesised on the basis of *N*-potassium-substituted heterocycles. The reaction of indolylpotassium with chlorotrimethylsilane is more difficult than the reaction of pyrrolylpotassium[143].

N-Pyrrolylsilanes were also obtained from pyrrolylmagnesium bromide and R-chlorosilanes[215,216,218,222,223]. Pyrrolidinyl-, piperidinyl-, and morpholinyl-silanes were obtained similarly via organomagnesium derivatives[224].

Triphenylsilyl-lithium silylates piperidine with formation of triphenylpiperidinylsilane[225]:

$$(C_6H_5)_3SiLi + HN\bigcirc \rightarrow (C_6H_5)_3SiN\bigcirc + LiH .$$

The reaction of bis(trimethylsilyl)mercury with pyridine leads to the formation of 1,1′-bis(trimethylsilyl)-1,1′,4,4′-tetrahydro-4,4′-bipyridyl[226]:

$$R_3SiHgSiR_3 + 2N\bigcirc \rightarrow R_3SiN\bigcirc\!\!-\!\!\bigcirc NSiR_3 + Hg .$$

2-Methylpyridine and 4-methylpyridine react similarly.

1,4-Bis(trimethylsilyl)-1,4-dihydropyridine was obtained by the reaction of pyridine with chlorotrimethylsilane in the presence of alkali metals[227]:

$$N\bigcirc + 2M + 2ClSiR_3 \xrightarrow{-2MCl} R_3Si{-}\bigcirc NSiR_3 .$$

3. Silylation with Aminosilanes and Silazanes

When aminotriethylsilane is heated to boiling with pyrrolidine over a period of 6 h, triethylpyrrolidinylsilane is formed in 95% yield[143]:

$$(C_2H_5)_3SiNH_2 + HN\square \rightarrow (C_2H_5)_3SiN\square + NH_3 .$$

Piperidine enters into this reaction with somewhat greater difficulty. The yield of triethylpiperidinylsilane reaches 89% only after refluxing the reaction mixture for 10 h.[143] 2-Aminothiazole reacts similarly[228].

Dialkylaminotrimethylsilanes were used instead of aminotrialkylsilanes for the *N*-trimethylsilylation of piperidine[42], perhydroazepine[156], morpholine[156], 2-aminothiazole and 2-aminobenzothiazole[229], δ- and ϵ-caprolactams[160], and also proline and tryptophan esters[230].

Hexamethyldisilazane silylates the NH group of heterocycles with much greater difficulty than do aminotrialkylsilanes. Frequently catalytic amounts of ammonium sulphate[218,231] or chloride[231] are essential for the occurrence of this reaction. Thus after pyrrole has been refluxed for 12 h with hexamethyldisilazane, no reaction was observed. On the other hand, in the presence of ammonium sulphate the yield of trimethyl-(*N*-pyrrolyl)silane reached 50% after only 2 h.[231] Indole was found to be somewhat more reactive than pyrrole[231].

After refluxing for 3 h a mixture of piperidine and hexamethyldisilazane without a catalyst, the yield of trimethylpiperidinosilane reached only 16%, but in the presence of chlorotrimethylsilane it increased to 35%. The addition of ammonium chloride or sulphate increased the yield further to 52 — 55%.[230] The yield of the silylation product depends also on the nature of the solvent and is a maximum when the reaction is carried out in quinoline (61%). Toluene (54%) and decalin (54%) are also satisfactory solvents. In ethyl ether, trimethylpiperidinosilane is not formed at all[230].

The reaction of nitrogen-containing heterocycles with hexamethyldisilazane has also been used to synthesise *N*-trimethylsilylpyrrolidinone[232], *N*-trimethylsilylsuccinimide[221], and *N*-trimethylsilylindoline[231].

4. Silylation with Silanes containing Unsubstituted Hydrogen Atoms

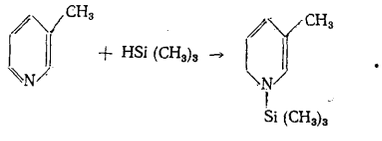
In the presence of alkali metals or Pd/C, silanes with unsubstituted hydrogen atoms enter into dehydrocondensation reactions with heterocyclic compounds containing the N — H bond:

$$R_NNH + H{-}Si\lessgtr \rightarrow R_NN{-}Si\lessgtr + H_2 .$$

Aziridine[35,39,233,234], 2-substituted aziridines[235], pyrrolidine[236], and piperidine[237] were silylated in this way. The reaction with aziridine proceeds more readily than with secondary aliphatic amines and piperidine and may be catalysed by potassium, sodium, and lithium. Aziridine is silylated at the maximum rate by tri-R-silanes containing phenyl and benzyl groups. Trialkylsilanes react more slowly and with alkoxysilanes the rate of dehydrocondensation is lowest. When aziridine reacts with vinylsilanes, the dehydrocondensation process competes with the addition of aziridine to the vinyl group[39]. 2,2-Dimethylaziridine reacts with greater difficulty than 2-methyl- and 2-phenyl-aziridines[235].

The dehydrocondensation of optically active methyl-1-naphthylphenylsilane with pyrrolidine in the presence of palladium and charcoal takes place with inversion of configuration[236].

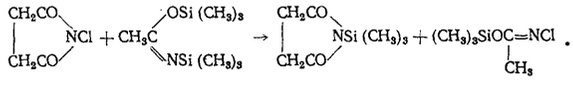
Trimethylsilane reacts with pyrridine in the presence of palladium on charcoal to form *N*-trimethylsilyl-1,2-dihydropyridine (yield about 25% after 25 h at 30°C), *N*-trimethylsilyl-1,4-dihydropyridine (35%), *NN'*-bis(trimethylsilyl)-1,1'-dihydro-4,4'-bipyridyl (25%), *N*-trimethylsilyl-1,2,3,6-tetrahydropyridine (12%), and many other trimethylsilylhydropyridines[238-240]. Pd/C is a more active catalyst than Rd/C, palladium(II) chloride, platinum, and Ru/C. However, Rd/C is more selective, driving the process mainly towards the formation of *N*-trimethylsilyl-1,4-dihydropyridine[239]. With 3-methylpyridine, trimethylsilane adds quantitatively to the 1,4-positions in the presence of Pd/C:[239]



4-Methylpyridine reacts four times as slowly as pyridine and it proved altogether impossible to add trimethylsilane to 2-methylpyridine[239].

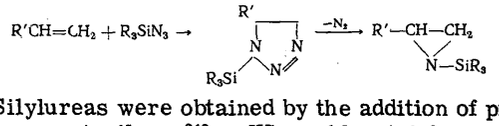
5. Other Methods

N-Trimethylsilylsuccinimide was obtained by the reaction of *N*-chlorosuccinimide with bis(trimethylsilyl)-acetamide[241,242]:



The same compound is formed when *N*-bromosuccinimide reacts with ethyl trimethylsilylacetate[242], bromotrimethylsilane in the presence of styrene[243], and hexa-alkyldisilanes[244,245]. Phthalimide and homodihydrocarbostyril are silylated by bis(trimethylsilyl)acetamide like succinimide[246,247].

Trimethyl-(2-R-*N*-aziridinyl)silanes were obtained by the thermal decomposition of *N*-trimethylsilyl derivatives of dihydro-1,2,3-triazole, which is formed as an intermediate when azidotrimethylsilane adds to alkenes[248]:



N-R-Silylureas were obtained by the addition of piperidine to isocyanatosilanes[249]. When chlorotriphenoxysilane was allowed to react with hexamethylenediamine, the formation of triphenoxy-(*N*-perhydroazepinyl)silane was observed, probably as a result of the cyclisation of (6-aminohexylamino)triphenoxysilane formed initially[250].

B. PHYSICAL PROPERTIES

Electronic[198,222,239], vibration[55,146,147,156,159,161,168,188,196,205,206,209,210,218,234,239,243,251-254], and ^{1}H NMR [140,147,156,239,243,247,255] spectra of *N*-heterylsilanes were not investigated systematically. In both cases spectroscopic data were used only to confirm the structures of the compounds synthesised.

In a number of instances, an attempt was made to assign the bands in the infrared absorption spectra to the corresponding Si — N stretching vibrations. The absorption bands at 695 cm^{-1} for pyrrolidinylsilane[146,253], at 705 cm^{-1} for piperidinylsilane[146], at 910 cm^{-1} for iodopiperidinylsilane[254], at 932 cm^{-1} for chloropiperidinylsilane[254], at 945 — 950 cm^{-1} for R-piperidinylsilanes[156], at 960 cm^{-1} for R-morpholinylsilanes[156], at 975 cm^{-1} for chlorotrimorpholinylsilane[159], and at about 1057 cm^{-1} for trimethyl-(*N*-pyrrolyl)silane[218] were assigned to $\nu_{as}(S-N)$.

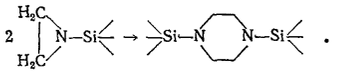
Quantum-chemical calculations have been made for (*N*-pyrrolyl)silanes on the basis of spectroscopic data and it has been concluded that $p_\pi - d_\pi$ interaction takes place in their molecules[222,223]. ^{1}H NMR spectra confirmed the occurrence of such interaction also in the (*N*-aziridinyl)-trimethylsilane molecule[255].

X-Ray diffraction analysis[256] established that the complex $2C_5H_5N.SiF_4$ has a centrosymmetric *trans*-configuration with an Si — N distance of 1.93 Å.

C. CHEMICAL PROPERTIES

1. Thermal Reactions

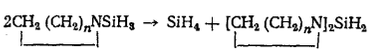
On heating to 250°C, tri-R-(*N*-aziridinyl)silanes are converted into piperazine derivatives[257]:



When platinised charcoal is introduced into the reaction mixture, the yields of products are unaffected. The addition of azobisisobutyronitrile makes it possible to obtain higher yields even when the reaction temperature is reduced to 200°C.

The nature of the organic groups linked to the silicon atom in the tri-R-(*N*-aziridinyl)silane molecule has a considerable influence on its reactivity. Thus, whereas the yield of *NN'*-bis(trimethylsilane)piperazine is only 25% after heating (*N*-aziridinyl)triethylsilane for 5 h at 250°C, in the case of the diethylphenyl derivative the yield of the piperazine derivative reaches 40%, while (*N*-aziridinyl)-diethoxyethylsilane does not undergo any changes under these conditions[257].

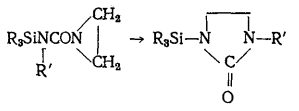
On heating in a sealed tube at 260°C, *N*-silylpyrrolidine and *N*-silylpiperidine disproportionate[146]:



In contrast, trialkyl-(*N*-pyrrolyl)silanes remain unchanged on heating to 260°C for 12 h.[218]

Urea derivatives obtained by the reaction of R-(*N*-aziridinyl)silanes with isocyanates rearrange to

2-imidazolidinone derivatives at a temperature as low as 140°C:[140]



2. Desilylation

The Si — N bond in *N*-heterylsilanes dissociates with elimination of the silyl group under the influence of various reagents: hydrogen chloride[144,146,258], sulphur halides[143], phosphorus[229,259], boron[270], acyl halides[155], carboxylic acid *N*-halogenoamides[242], water[144,155,156,159,168,174,216,218], alcohols[168,218,238-240,261], hydrogen sulphide[258], oxygen compounds of sulphur[258], ammonia[218,230,258], *NN'*-dialkylureas[247,262,263], and lithium aluminiumhydride[144,145].

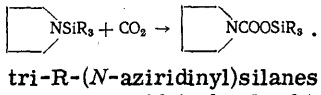
This reaction has been used both for the synthesis of heterocyclic compounds (for example, 1,4-dihydropyridine[238-240]) and their derivatives (for example, *N*-pyrrolylphosphines[259] and di-*N*-piperidinyl sulphide[143]) and for the silylation of compounds containing an active hydrogen atom (for example, *N*-hydroxymethyl-*N*-methylformamide[261] and *NN'*-dialkylureas[247,262,263]).

A study of the stereochemistry of the hydrolysis[144] and cleavage of optically active methyl-(1-naphthyl)phenylpyrrolidinylsilane with boron trifluoride[260] established that these reactions take place with inversion of configuration, while in the cleavage by hydrogen chloride and in the reduction by lithium aluminium hydride the configuration is retained[144].

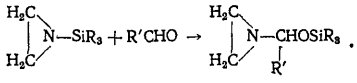
Many reactions which involve the dissociation of the Si — N bond at room temperature can lead to the formation of adducts with retention of this bond at a lower temperature. For example, at −88°C pyrrolidinylsilane and piperidinylsilane form hydrogen chloride complexes of the type $C_5H_{10}NSiH_3 \cdot 2HCl$, which decompose with dissociation of the Si — N bond when the temperature is raised[146]. At −46°C piperidinylsilane and pyrrolidinylsilane form 1:1 adducts with iodosilane[146,254].

3. Addition to Carbonyl Compounds

Tri-R-(*N*-heteryl)silanes add to carbon dioxide and also to carbon disulphide according to the mechanism[264]

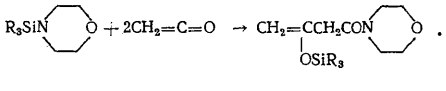


The reactions of tri-R-(*N*-aziridinyl)silanes with aliphatic, aromatic, and heterocyclic aldehydes lead to the formation of tri-R-(*N*-aziridinylalkoxy)silanes[265,266]:

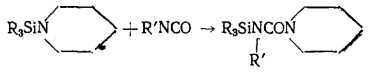


The addition of *N*-trimethylsilylpyrrolidinone[261,267] and *N*-trimethylsilylsuccinimide[261] to benzaldehyde and of trimethylpyrrolidinylsilane and trimethylpiperidinylsilane to chloral[268] takes place similarly.

Trimethylmorpholinylsilane reacts with keten at room temperature to form the morpholide of β-(trimethylsiloxy)vinylacetic acid[269,270]:

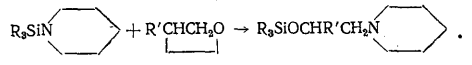


The addition of tri-R-(*N*-aziridinyl)silane[140] and tri-R-piperidinylsilanes[271] to organic isocyanates leads to the formation of *N*-tri-R-silyl-substituted ureas:



4. Reactions with Oxirans and Lactones

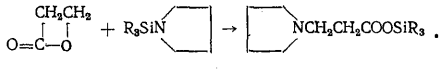
The reaction of trimethylpiperidinylsilane with R'-oxirans at 80°C takes place with the opening of the oxiran ring via the mechanism[272,273]



A necessary condition for the occurrence of this reaction is the presence of powerful electro-accepting substituents in the group R' of the oxiran. For example, when trimethylpiperidinylsilane reacts with trichloromethyloxiran, the yield of (1-trichloromethyl-2-piperidinylethoxy)trimethylsilane is 89% after only 1.3 h, while with chloromethyloxiran the yield of the reaction product does not exceed 45% even after heating for 22 h and methyloxiran and trimethylpiperidinylsilane do not react at all in a sealed tube at 80°C.

The reaction of substituted oxirans with *N*-trimethylsilylpyrrolidinone takes place via a similar mechanism[274,275].

Trimethylpyrrolidinylsilane, trimethylpiperidinylsilane, and trimethylmorpholinylsilane react with β-propiolactone on heating to 80°C with formation of trimethylsilyl esters of β-(*N*-heteryl)propionic acid[224,276,277]:



Trimethylpyrrolidinylsilane reacts faster than the corresponding piperidinyl- and diethylamino-silanes[276].

D. PRACTICAL APPLICATIONS

Trialkylpiperidinylsilanes and trialkylmorpholinylsilanes are used as catalysts for the hydrosilylation of acrylonitrile with trichlorosilane which promote the formation of the β-isomer[152,157,158,278].

Trimethylmorpholinylsilane and methylphenyldipyrrolidinylsilane are used in the preparation of organosilicon polymers[279].

Dihydropyridylsilanes inhibit the oxidation of various polymers and increase their resistance to the action of light[240].

Organosilicon derivatives of aziridine have been used to prepare water- and oil-repellent fabrics[138,142].

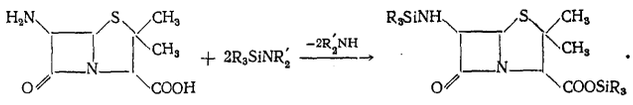
IV. COMPOUNDS CONTAINING THE Si — O BOND

A. METHODS OF PREPARATION

A number of general methods for the silylation of the hydroxy-group have been used to synthesise organosilicon derivatives of nitrogen-containing heterocycles with the Si — O bond. In the presence of tertiary amines, chlorosilanes were used to silylate *N*-hydroxymethylphthalimide[150,280], 2-hydroxypyridine[281-283] (Ismail[283] claims that

the *N*-silylation product was obtained), 2- and 4-pyridylalkanols[284], 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxide[285-289], *N*-carboxyanhydrides of hydroxy-α-amino acids[290], proline[291], and picolinic[292], nicotinic[293] and 6-aminopenicillanic[294-296] acids.

The trimethylsilyl ester of 6-trimethylsilylaminopenicillanic acid forms in 29% yield when a suspension of calcium 6-aminopenicillanate is heated with chlorotrimethylsilane in the presence of triethylamine for 3 h to 60°C. When the sodium salt is used instead of the calcium salt, the yield of product falls to 25%.[294] The same compound is formed in 98.5% yield when 6-aminopenicillanic acid reacts with (diethylamino)trimethylsilane at 80 – 150°C with simultaneous distillation of the diethylamine evolved in the process[294]:



The trimethylsilyl ester of 7-trimethylsilylaminocephalosporanic acid is obtained similarly[297].

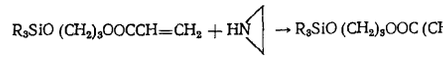
When 6-aminopenicillanic acid is heated with hexamethyldisilazane in nitrogen at 120°C for 3 h, the trimethylsilyl ester of 6-trimethylsilylaminopenicillanic acid is formed in 64.5% yield[294,298].

Silazanes have also been used to silylate penicillins[299-301], lincomycin[302,303], hydroxyproline[304,305], tryptophan[304], pyridylalkanols[306,307], piperidinylalkanols[307,308], morpholinylalkanols[309], and 8-hydroxyquinoline[310].

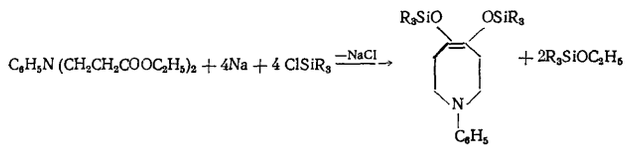
Oxindole and tryptophan have been silylated with bis(trimethylsilyl)acetamide[246,247].

Many reactions leading to the formation of derivatives of nitrogen-containing heterocycles with the Si – O bond were already considered above in the discussion of the chemical properties of compounds with Si – C and Si – N bonds. These include the reactions of trialkyl-(2-pyridyl)silanes with aldehydes[127,128] and the reactions of *N*-heterylsilanes with aldehydes[261,264-268], oxirans[272-275], keten[269,270], and lactones[224,276,277].

Aziridine, azetidine, and pyrrolidine add to the double bonds of trialkylvinyloxysilanes and 3-(trimethylsiloxy)-propyl acrylates with formation of the corresponding 2-(*N*-heteryl)ethoxysilanes and 3-(trimethylsiloxy)propyl β-(*N*-heteryl)propionates[311]:



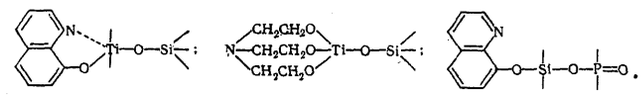
When *NN*-bis-(β-ethoxycarbonylethyl)aniline is heated with sodium and chlorotrimethylsilane in toluene solution, it is cyclised and silylated with formation of 4,5-bis(trimethylsiloxy)-1-phenyl-3,2,6,7-tetrahydroazepine[312]:



Tri-R-silanols[313] and 1,1,3,3-tetra-R-disiloxane-1,3-diols[314-317] form complexes with piperidine, picoline, and quinoline.

When 2-hydroxypyridine *N*-oxide was allowed to react with silicic acid, a complex was formed, which was characterised by conversion into its chloride, hexachlorostannate, and tetrachloroferrate[318] and resolved into optical isomers with the aid of the disodium salt of dibenzoyl-L-tartrate[319].

Oxinatotitanosiloxans[320-341], cyclic nitriloethylene tri-R-siloxytitanates[342], and dioxinatosilicon bisphosphorodichloridate[343] are obtained by the general methods used for the formation of the Ti – O – Si [344] and P – O – Si [345] groups:



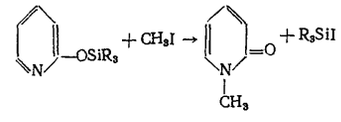
B. PHYSICAL, CHEMICAL, AND BIOLOGICAL PROPERTIES

Studies of the ultraviolet spectra of oxinatosilanes showed that dioxinatodiphenylsilane (λ_{max} = 370 nm) has a chelate structure with a hexacovalent silicon atom, in contrast to trimethyloxinatosilane and dimethyldioxinatosilane[310].

A high inversion frequency of the nitrogen atom in the trialkyl[α-(*N*-aziridinyl)alkoxy]silane molecule was demonstrated by ^{1}H NMR.[346] ^{1}H NMR [272,346,347] and ESR [286,287] spectra were also used to confirm the structures of the compounds synthesised.

The majority of organosilicon derivatives of nitrogen-containing heterocycles with the Si – O bond are readily hydrolysed by water[224,273,283,310,312]. Their Si – O bond is cleaved by methanol[272] and acetic acid[272].

Pyridyloxysilanes readily react with alkyl halides[281,283]. Thus, in contrast to α-pyridone which reacts with methyl iodide only at 100°C under pressure, 2-(trimethylsiloxy)-pyridine reacts with methyl iodide after only brief heating on a water bath with formation of a high yield of *N*-methyl-α-pyridone[281]:



2-(Trimethylsiloxy)pyridine interacts with 2,3,4,6-tetra-acetyl-1-bromoglucose in the presence of $AgClO_4$ even at room temperature, forming *N*-(2,3,4,6-tetra-acetylglucosido)-α-pyridone[281].

Trimethylsilyl esters of 6-trimethylsilylaminopenicillanic acid react with carboxylic acid anhydrides or chlorides and are converted into trimethylsilyl esters of penicillins, which give high yields of the corresponding penicillin on hydrolysis with water[294-296,298,299,348,349]. Cephalosporins are obtained similarly[297].

The complex of benzylpenicillin and potassium methylsiliconate proved to be effective in the treatment of myxomatosis (a virus disease), which is not susceptible to the action of either potassium methylsiliconate or benzylpenicillin separately[350]. Thus it has been shown that the spectrum of the activity of penicillin can be extended by employing its complex with potassium methylsiliconate.

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