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Review

ORGANOPSEUDOHALOSILANES II. AZIDOSILANES[a]

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CONTENTS

I. INTRODUCTION

A survey of the recent literature shows a marked increase in investigations concerned with the preparation and reactions of organoazidosilanes. This review

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[a] Organopseudohalosilanes I: Cyano-, Isocyano- and Isothiocyanato-silanes, R. M. Pike and M. F. Mangano, J. Organometal. Chem. Library, 12 (1981) 53.

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paper discusses the chemistry of this class of organopseudohalosilanes having the C-Si-N_3 linkage. It does not include species such as $(C_2H_5O)_3SiN_3$ or siloxanes containing the Si-N_3 grouping.

The last review on organoazidosilanes was by Peterson in 1974 [1]. Several additional publications have included the chemistry of these compounds as part of the broader aspects of the organopseudohalosilane or organometallic areas. Included in this list are the works of Wannagat [2], Thayer [3], Lappert and Pyszora [4], and Thayer and West [5]. Reviews on synthetic applications of organosilicon compounds have included reactions of trimethylazidosilane [63, 187, 188]. The present review summarizes the work reported on organopseudohalosilanes through 1981.

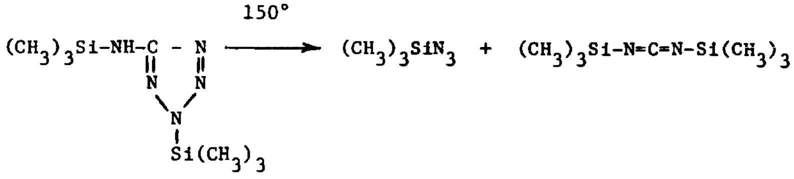
The table containing the known organoazidosilanes includes for each compound listed its molecular formula, structural formula, selected physical properties and references. Compounds are included that have been identified on the basis of spectral evidence. Those organoazidosilanes listed in the tabulations of organosilicon compounds by previous workers [1-5, 6] are included for the sake of completeness.

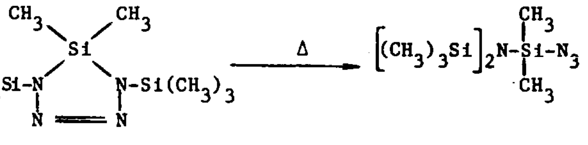
II. METHODS OF PREPARATION

Organoazidosilanes were first reported in 1962 by several groups. Cleavage of the $\equiv$Si-NH- linkage in selected silylamine type compounds was found to lead to the desired $\equiv$Si-N_3 linkage. However, the more general method that developed consists of the reaction of organohalosilanes with metal azides.

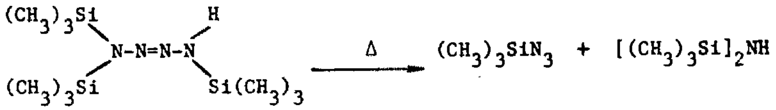
A. CLEAVAGE OF $\equiv$Si-N=

In 1962 Birkofer and co-workers reported the synthesis of an hydrazoic acid derivative containing an organosilicon moiety, $(CH_3)_3SiN_3$, obtained by the pyrolysis of 1-(N-trimethylsilylamino)-3-trimethylsilyltetrazole [7, 8]. Trimethylsilyl substituted silatetrazoles also led to the formation of azidosilane compounds on thermal decomposition [9].

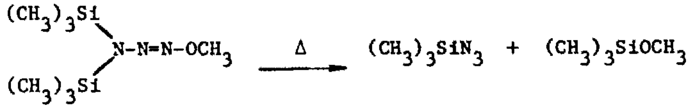




Wiberg and co-workers have shown that pyrolysis of trimethylsilyl substituted triazenes and tetrazenes lead to the generation of trimethylazidosilane [10, 11, 12, 13].



$$[(CH_3)_3Si]_2N\text{-}N{=}N\text{-}N(H)Si(CH_3)_3 \xrightarrow{\Delta} (CH_3)_3SiN_3 + [(CH_3)_3Si]_2NH$$



$$[(CH_3)_3Si]_2N\text{-}N{=}N\text{-}OCH_3 \xrightarrow{\Delta} (CH_3)_3SiN_3 + (CH_3)_3SiOCH_3$$

Reaction of hydrazoic acid with hexamethyldisilazane produces $(CH_3)_3SiN_3$ [7].

$$3\ HN_3 + (CH_3)_3SiNHSi(CH_3)_3 \longrightarrow 2\ (CH_3)_3SiN_3 + NH_4N_3$$

Cleavage of silylamines with organoacylazides also leads to the formation of azidosilanes [14].

$$(CH_3)_3SiNHC_4H_9\text{-}\underline{n} + C_6H_5CON_3 \xrightarrow{AlCl_3} (CH_3)_3SiN_3 + C_6H_5CONHC_4H_9\text{-}\underline{n}$$

B. CLEAVAGE OF $\equiv$Si-X (X = F, Cl, Br)

The major route developed for the synthesis of organoazidosilanes involves the cleavage of the halosilane linkage by reaction with a metal azide. As starting materials, the chlorosilane derivatives have been used extensively with infrequent use of the fluoro- or bromo-silanes.

$$R_nSiX_{4-n} + MN_3 \xrightarrow{\text{solvent}} R_nSi(N_3)_{4-n} + nMX$$

$(n = 1, 2, 3;\ X = F, Cl, Br)$

A wide range of metal azides and solvents have been utilized.

Connolly and Urry prepared $(CH_3)_3SiN_3$ using trimethylchlorosilane and aluminum azide in tetrahydrofuran solvent [16]. This approach was modified by West and Thayer [15, 17, 18] by the use of a sodium azide-aluminum chloride mixture which forms aluminum azide <u>in situ</u>. Sundermeyer used sodium azide in a $ZnCl_2$-KCl melt with good results [19, 20, 39].

Extensive work has been reported on the use of various metal azide-solvent systems. Sodium or lithium azide has been used in tetrahydrofuran [21, 22, 23, 24], pyridine [17, 23, 26, 28], quinoline or 2,4-lutidine [26], and toluene [28, 29]. Weidenbruch and Pesel reported the use of potassium azide in toluene in the presence of 18-crown-6 for the preparation of tri-t-butylazidosilane [30]. A method using potassium azide in absence of a solvent has been patented [28]. Several workers have employed the use of aprotic solvents with alkali metal azides to obtain good yields of the azidosilanes. An Organic Synthesis method employs diethylene glycol dimethyl ether (diglyme) [31], and Washburn and Peterson report that hexamethylphosphortriamide is a superior solvent giving azidosilanes in high yields [32]. However, mixed chlorosilyl azides cannot be prepared with this latter solvent and H-, $(CH_3)_2N$- and CH_2=CH- functionality on silicon is incompatible employing these azide/chloride reaction conditions. Dimethylformamide was also investigated as a solvent with less spectacular results [32]. A patent has been issued covering the use of sodium azide in carboxamide, nitrile and ketone solvents [33]. Elseikh and Sommer report the use of acetonitrile solvent [34]. Reaction of silver azide with $(CH_3)_3SiCl$ in ether solvent is reported to produce $(CH_3)_3SiN_3$ in good yield [18].

C. EXCHANGE REACTIONS

Sundermeyer reported the first preparation of azidosilanes using the exchange technique [19, 39]. This led to the successful preparation of di- and tri-azidoorganosilanes.

$$2\ (CH_3)_3SiN_3 + (CH_3)_2SiCl_2 \xrightarrow{AlCl_3} (CH_3)_2Si(N_3)_2 + 2\ (CH_3)_3SiCl$$

$$C_6H_5SiCl_3 + 3\ (CH_3)_3SiN_3 \longrightarrow C_6H_5Si(N_3)_3 + 3\ (CH_3)_3SiCl$$

Later work by Rühlmann and Ettenhuber extend the utility of the method by providing a route to prepare organoazidosilanes containing the Si-H linkage [22]. Müller and Van Wazer obtained equilibrium constants and ΔG° values for the exchange of azido groups with chloro, methoxy, methylthio and dimethylamino groups on the dimethyl silicon moiety [35]. The results indicate that the azido group acts as a pseudohalide in the exchange reaction. The exchange reaction of Si-N_3 groups with Si-N= units had been previously reported [22].

$$(CH_3)_2Si(N_3)_2 + (\underline{n}\text{-}C_4H_9N)_2Si(CH_3)_2 \longrightarrow 2\ (CH_3)_2Si(N_3)(NC_4H_9\text{-}\underline{n})$$

A method has been patented covering the exchange reaction and includes the exchange of Si-N_3 with Si-CN groups [36].

$$(C_6H_5CH_2)_2Si(N_3)_2 + (C_6H_5\text{-}CH_2)_2Si(CN)_2 \xrightarrow[25°]{\text{xylene}} 2\ (C_6H_5CH_2)_2Si(N_3)(CN)$$

Wiberg and co-workers utilized the reaction of metal salts of hexamethyldisilazane with tosylazide to form the desired organoazidosilane compounds [41].

D. MISCELLANEOUS METHODS

Seyferth and co-workers report the preparation of a Si-N_3 linkage by the opening of the Si-C bond of a substituted silacyclopropyl ring using hydrazoic acid in benzene solvent [37].

Vorbrüggen and Krolikiewicz demonstrated the in situ generation of $(CH_3)_3SiN_3$ using sodium azide, trimethylchlorosilane and the reactive substrate in dimethyl formamide solvent [38]. This technique was successful with aldehydes, ketones or isothiocyanates as the reactive substrate.

Organoazidosilanes containing chloro substitutents may be obtained by reaction of organoazidosilanes having the Si-H functional unit with chlorine in carbon tetrachloride solvent [22].

$$(C_6H_5)_2Si(H)N_3 + Cl_2 \xrightarrow[-15°]{CCl_4} (C_6H_5)_2Si(Cl)N_3 + HCl$$

III. STRUCTURE

Early work demonstrated that the azido group attached to silicon gives rise to an asymmetric stretch near 2100 cm^{-1} and a symmetric stretch near 1300 cm^{-1} [17, 26]. An overtone band for the NNN bending vibration is also observed near 675 cm^{-1} [18]. Triphenylazidosilane exhibits very strong absorption at 2149 cm^{-1} which is higher than predicted. Thayer and West attribute this to dative π-bonding between silicon and nitrogen with the resonance hybrid, A, having increased contribution to the overall structure [17].

A B

Similar results were observed for $(CH_3)_2Si(N_3)_2$ [20] and $(CH_3)_3SiN_3$ [16, 51, 54]. Microwave data for the latter compound indicates the molecule is nonlinear [18]. The infrared assignments for a series of organoazidosilanes including mono-, di-, and tri-functional species has been reported by several groups [23, 45].

Work by Büerger [54] and later a complete vibrational assignment by Durig and co-workers [70] established that for $(CH_3)_3SiN_3$ the SiC_3 antisymmetric deformation band is located at 282 cm^{-1} (gas phase) in the far infrared region. The symmetric SiC_3 stretching mode appears at 627 cm^{-1} as a very strong polarized band in the Raman spectra [70]. This observation indicates that the azido group has C_s molecular symmetry. The NNN out of plane bending and in plane bending modes have been assigned for $(CH_3)_3SiN_3$ at 689 cm^{-1} and 584 cm^{-1}, respectively [70]. It was concluded that this indicates the Si-N-N angle in $(CH_3)_3SiN_3$ is considerably smaller than the corresponding angles in $(CH_3)_3SiNCO$ and $(CH_3)_3SiNCS$. The Raman spectrum for $(CH_3)_3SiN_3$ showed the Si-N= bend for the azido group in both the gas and liquid phase at 102 and 111 cm^{-1}, respectively. The vibrational spectrum indicates that this molecule is permanently bent in the ground vibrational state [70, 76].

Electron diffraction studies with $(CH_3)_3SiN_3$ (gas phase) showed the Si-N= angle to be 128° [71]. It was further concluded that the molecule has neither C_{3v} nor C_s symmetry, but C_1 symmetry. X-ray analysis of solid $(C_6H_5)_3SiN_3$ gave a Si-N-N angle of 120.5° which indicates sp^2 hybridization of the nitrogen atom bonded to silicon [72]. The Si-N bond length was measured as 1.75 A° and the azido group was found to be linear within experimental error (176.6 ±3.0°). The most important resonance contribution to the overall structure of $(C_6H_5)_3SiN_3$ is given as $(C_6H_5)_3Si\text{-}\ddot{N}\text{=}\overset{+}{N}\text{=}\overset{-}{\ddot{N}}\text{:}$, based on the above results.

The ^{14}N NMR spectrum for $(CH_3)_3SiN_3$ has been reported [78]. An attempt to use NMR data to clarify the nature of the bonding in $(C_6H_5)_3SiN_3$ was unsuccessful [72]. The species, m or p-$FC_6H_4(C_6H_5)_2\text{-}SiN_3$ was included in a study of ^{19}F NMR chemical shifts [45]. Schempp and Chao measured the nuclear quadrupole resonance frequencies of ^{14}N in $(CH_3)_3SiN_3$ at 77°K [74]. It was shown that the nitrogen atoms were inequivalent and that the compound can crystallize in two different forms. ^{29}Si NMR spectra have been recorded for $(CH_3)_3SiN_3$, $(CH_3)_2Si(N_3)_2$ and $(C_6H_5)_2Si(N_3)_2$ [77]. A compilation of NMR proton spectra include several organoazidosilanes [75].

Thayer and West report the ultraviolet spectrum of $(CH_3)_3SiN_3$ [18]. Two absorption bands were detected at 396 nm (ε 23) and 472 nm (ε 225) in acetonitrile solvent. The absorptions were assigned $\pi_y \rightarrow \pi_x^*$ and $sp_x \rightarrow \pi_y^*$ transitions, respectively. Small shifts were observed in ether and isooctane solutions.

IV. CHEMISTRY

A. HYDROLYSIS

The organoazidosilanes are susceptible to hydrolysis, the relative rate increasing as the number of organo groups decreases: $R_3SiN_3 < R_2Si(N_3)_2 < RSi(N_3)_3$ [15, 39]. The azido group was found to hydrolyze more slowly than the corresponding chlorides. The hydrolysis reaction was observed to be catalyzed under acidic and basic conditions [15]. The relative rate of hydrolysis was estimated qualitatively in aqueous acetone solutions by formation of the deep-red $[Fe(H_2O)_5N_3]^{++}$ complex [15, 17]. Sundermeyer observed that hydrolysis of $(CH_3)_2Si(N_3)_2$ produced methylpolysiloxane and hydrazoic acid [20]. Although $(CH_3)_3SiN_3$ reacts rapidly with water under all conditions, $(C_6H_5)_3SiN_3$ is relatively stable to water and atmospheric moisture, undergoing hydrolysis slowly. The reaction is much more rapid in mixed organic-aqueous media [15, 18]. The azidosilanes are readily miscible with all organic solvents [15, 23].

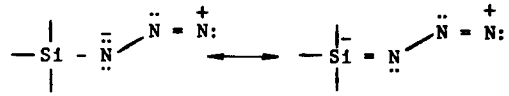
The heat of hydrolysis for $(CH_3)_3SiN_3$ was determined as 6.8 ±2 Kcal/mole employing calorimetric methods [60]. The hydrolysis proceeded as illustrated,

$$(CH_3)_3SiN_3 \quad + \quad 1/2\ H_2O \longrightarrow 1/2[(CH_3)_3Si]_2O \quad + \quad HN_3,$$

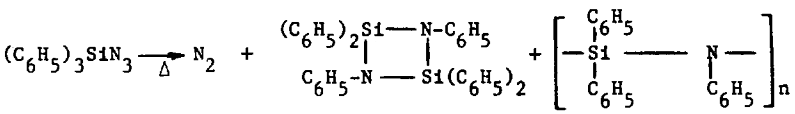
as shown by PMR measurements. From the data, the bond energy of the $Si\text{-}N_3$ linkage was calculated as 76 Kcal/mole [60].

B. THERMOLYSIS

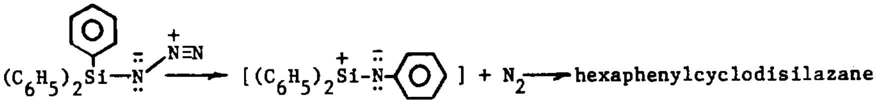
Early workers repeatedly refer to the unusual thermal stability of the organoazidosilanes. Wiberg and co-workers demonstrated that nitrogen gas evolution was not observed over a long period on heating $(CH_3)_3SiN_3$ at 400°C, even in the presence of copper powder [24]. Connoley and Urry reported that $(CH_3)_3SiN_3$ heated at 200° for eight hours was recovered essentially unchanged [16]. Birkoffer and co-workers also remarked on the thermal stability of this material [7]. Sundermeyer commented on the remarkable stability of $(CH_3)_2Si(N_3)_2$, boiling at 143.3°C without decomposition [20]. West and Thayer reported that $(C_6H_5)_3SiN_3$ was only 50% destroyed after 10 hr. at 220° in n-hexadecane solution [15, 17]. They proposed that this unexpected thermal stability is due to strong dative pi bonding from the azido group to silicon.



Reichle observed that the tendency toward stabilization is best effected by phenyl groups bonded to silicon [26]. Whereas $C_6H_5Si(N_3)_3$ decomposed above 325°C, $CH_3Si(N_3)_3$ was stable only to about 180°C. Further work with $(C_6H_5)_3SiN_3$ demonstrated that nitrogen gas was evolved on heating with formation of hexaphenylcyclodisilazane and polymeric silazanes [26].

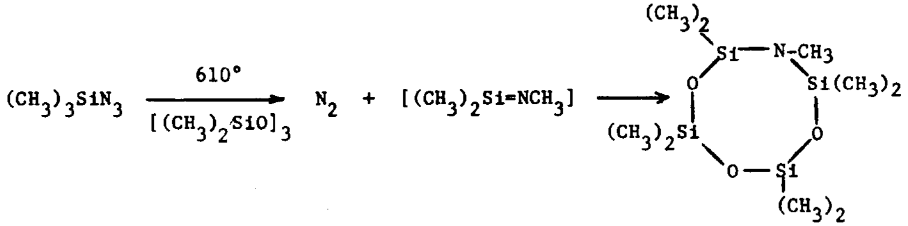


Ettenhuber and Rühlmann isolated cyclodisilazanes from the thermal decomposition of methyldiphenyl- and dimethylphenyl-silanes [22]. Patil and Rao investigated the thermolysis of $(C_6H_5)_3SiN_3$ utilizing DTA and TGA techniques [61]. Both groups visualized the formation of the nitrogen-containing products in terms of formation of an "imidogen-like" intermediate followed by rearrangement of the phenyl group from silicon to nitrogen.

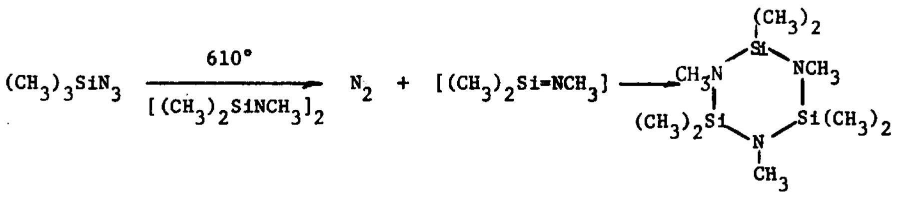


Gaidis and West showed that dimethyl(2-biphenyl)silyl azide decomposes to form 10,10-dimethyl-10,9-silazaphenanthrene, probably by means of a "nitrene" intermediate.

New light was shed on the thermolysis reaction by the work of Parker and Sommer [62]. These workers investigated the high temperature gas-phase pyrolysis of a series of organoazidosilanes, $(CH_3)_3SiN_3$, $C_6H_5(CH_3)_2SiN_3$ and $(C_6H_5)_3SiN_3$, in the presence of a suitable trapping agent. The technique provided a clean reaction and permitted isolation of products in reasonable yields. The evidence obtained established that silaimines, $[R_2Si{=}NR]$, are formed as intermediates.



$$(C_6H_5)_3SiN_3 \xrightarrow[R_2C{=}O]{610°} N_2 + [(C_6H_5)_2Si{=}NC_6H_5] \longrightarrow R_2C{=}NC_6H_5 + [(C_6H_5)_2Si\text{-}O]_3$$



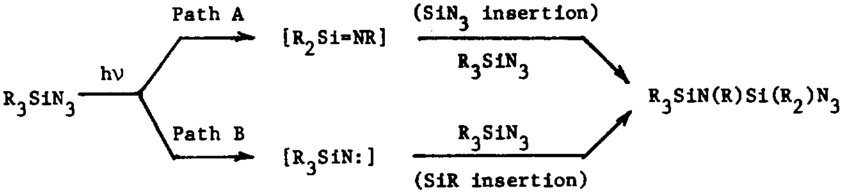
C. PHOTOLYSIS

The first reports on the preparation of azidosilanes included preliminary evidence that these compounds react under photolytic conditions. West and Thayer demonstrated that triphenylazidosilane was completely decomposed by prolonged ultraviolet irradiation at 30° [15]. They proposed that the decomposition occurs through the formation of azene intermediates. Reichle showed that $(C_6H_5)_3SiN_3$ irradiated (2537 Å) in cyclohexane appeared to produce partial decomposition, but a pure species was not isolated [26]. Connolly and Urry found that photolysis of $(CH_3)_3SiN_3$ produces nitrogen, a trace of hydrogen and a non-volatile oil [16].

Photo decomposition of $(CH_3)_3SiN_3$ in a solid argon matrix at 17°K was followed using infrared spectroscopy [66]. The complicated overlapped nature of the spectrum made complete analysis difficult. However, an assignment indicating the formation of $(CH_3)_2(H)Si\text{-}N{=}CH_2$ and not a silaimine such as $(CH_3)_2Si{=}N\text{-}CH_3$, as the intermediate decomposition species was postulated.

Perutz investigated ultraviolet photolysis of trimethylazidosilane in argon, nitrogen and carbon monoxide matrices at 10°K and showed the major product was either $(CH_3)_2(H)Si\text{-}N{=}CH_2$ or $(CH_3)_2(H)Si\text{-}CH{=}NH$ [67, 79]. No evidence for a π-bonded Si=N species was obtained.

A detailed photolytic study using $(CH_3)_3SiN_3$, $\underline{n}\text{-}C_3H_7(CH_3)_2SiN_3$ and $(CH_3)_3SiSi(CH_3)_2N_3$ was reported in 1971 [65]. The reactions were monitored neat or in a 10% benzene solution. The first products of photolysis for each of the azidosilanes was a silazane azide species, $R(CH_3)_2SiN(R)Si(CH_3)_2N_3$ which subsequently reacted to yield cyclosilazane products. The data provided no conclusion as to the nature of the chemical intermediate, but two different mechanistic pathways leading to the observed produces were envisioned [55].



Work by Parker and Sommer [55] produced conclusive evidence for the formation of silaimine intermediates utilizing the technique of a trapping reagent. Photolysis of several azidosilanes in the presence of t-butyl alcohol or hexamethylcyclotrisiloxane produced products, the formation of which, can only be rationalized on the basis of a reactive intermediate containing a pπ-pπ silicon-nitrogen double bond. A polarized double bond structure was proposed for the silaimine, $R_2\overset{\delta+}{Si}{=}\overset{\delta-}{N}R$. Further confirmation was obtained studying the photolysis of triethylazidosilane in the presence of triethoxysilane or trimethoxysilane [68].

$$(C_2H_5)_3SiN_3 \xrightarrow{2537\ \text{Å}} N_2 + [(C_2H_5)_2Si{=}NC_2H_5] \xrightarrow{(C_2H_5O)_3SiH}$$

$$(C_2H_5)_2Si(OC_2H_5)N(C_2H_5)Si(H)(OC_2H_5)_2$$

Photolysis of 1-azido-1-silabicyclo[2·2·1]heptane and 1-azido-1-silabicyclo[2·2·2]octane gave evolution of nitrogen accompanied by rearrangement and ring enlargement [34]. The silaimine intermediates were trapped using methyltriethoxy silane and triethoxy silane.

Ando and co-workers proposed the formation of digonal silicon intermediates such as silacarbodiimides on photolysis of N,N-diazidodiorganosilanes [69]. These species were trapped by use of t-butyl alcohol.

$$(C_6H_5)_2Si(N_3)_2 \xrightarrow{h\nu} [(C_6H_5{-}N{=}Si{=}N{-}C_6H_5] \xrightarrow{t\text{-BuOH}} C_6H_5NHSi(OC_4H_9\text{-}t)_2NHC_6H_5$$

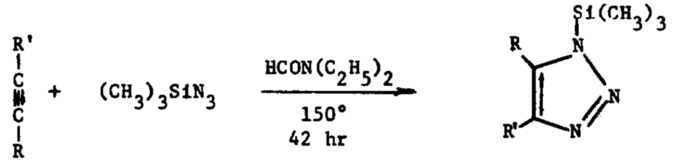
Evidence to date is not sufficient to distinguish between this pathway and that based on the formation of the silaimine intermediate of the type $RSi(N_3){=}NR$.

V. CHEMICAL TRANSFORMATIONS

The organoazidosilanes have been utilized successfully in achieving a wide variety of chemical transformations. The majority of these reactions have employed trimethylazidosilane, $(CH_3)_3SiN_3$, as the reactive species [187, 188]. The scope of the reactivity of organoazidosilanes is summarized.

A. REACTION WITH ALKYNES

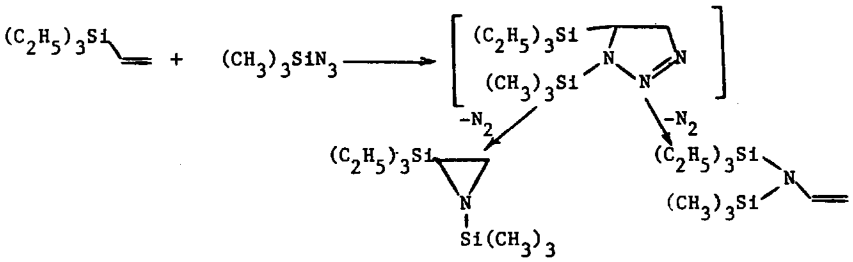
Birkofer and co-workers demonstrated that $(CH_3)_3SiN_3$ undergoes a 1,3-dipolar addition reaction with a variety of alkynes in aprotic solvents to form triazoles in moderate yield [50].



Alkyl and/or aryl mono- and di-substituted alkynes [50], those containing functional groups [8] and diynes were found to react over varying periods of time [80]. Later work showed that the reaction goes poorly with aryl mono-substituted alkynes containing electron-withdrawing substituents [81]. Additional work employing this basic synthesis of triazoles includes work by Wille and Schwab [98], the use of methyl tetrolate [82], and the reaction of beta-D-ribofuranosyl propiolate to produce the corresponding triazole ester [184]. Two patents have been issued utilizing this basis reaction, one a route to anti-inflammatory compounds [83] and the other for the synthesis of anti-wear agents in lubricants [184].

B. REACTION WITH ALKENES

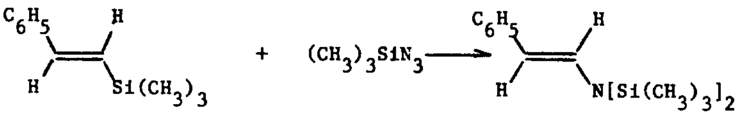
The reaction of cyclohexene and triethylvinylsilane with $(CH_3)_3SiN_3$ was reported by Ettenhuber and Rühlmann to give the corresponding aziridines in yields of 13% and 20%, respectively [22]. Later work by Washburn and MacMillan showed that cyclohexene did not react with $(CH_3)_3SiN_3$ in the absence of dimethylformamide solvent over a two week period [86]. Bassendale and co-workers [122] repeated the reaction of $(C_2H_5)_3SiCH{=}CH_2$ with $(CH_3)_3SiN_3$ under various conditions, including those of the original report [22]. In all cases, the product obtained, whose spectral properties were incompatible with an aziridene (A), was found to be the bis(silyl)enamine, N-triethylsilyl-N-trimethylsilylaminoethene (B).



(A) (B)

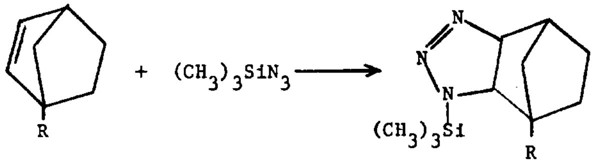
The appropriate triazolene appears to be an intermediate in the sequence of reactions.

Similarly, trans-trimethylsilylphenylethene gave the enamine product.



No reaction occured between trimethylvinylsilane and $(CH_3)_3SiN_3$ at reflux temperature, but in a sealed tube using hexane solvent the desired enamine was formed. Triphenylvinylsilane and trans-triphenylsilylstyrene failed to react.

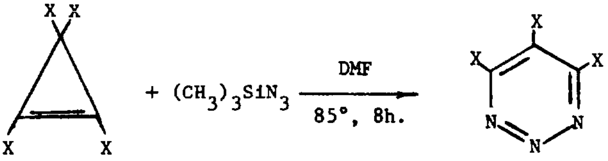
Bridged bicyclo-alkenes were found to undergo a facile 1,3-cycloaddition reaction with trimethylazidosilane [40, 87, 213]. Norbornene and 1-methylnorbornene gave the corresponding triazoline adduct in excellent yield.



(R = H, CH_3)

Dicyclopentadiene produced a mono-adduct, but d,ℓ-alpha-pinene failed to react under similar conditions. The enhanced reactivity of the norbornene systems is attributed to increased ring strain of these bridged alkenes [87].

The reaction of tetrachloro- and tetrabromo-cyclopropene gave the corresponding 1,2,3-triazines [85].



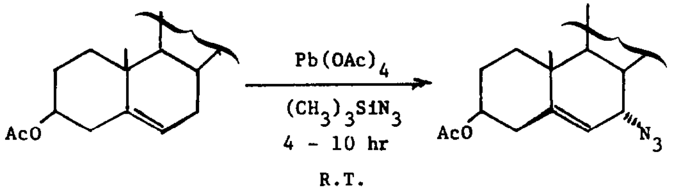
(X = Cl, Br)

The reaction of alkenes and azidosilanes, in the presence of lead tetraacetate as a transfer reagent, has been explored by Zbiral and co-workers [88, 89, 90]. The main products produced in the reaction are 1,2-diazido- and 1-azido-2-acetoxy compounds. A lead azidoacetate species is postulated as the reactive intermediate.

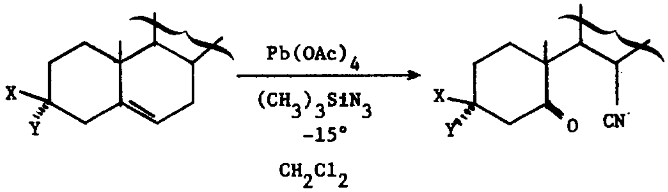
$$Pb(OAc)_4 + (CH_3)_3SiN_3 \longrightarrow [Pb(OAc)_{4-n}(N_3)_n]$$

$$\xrightarrow{RCH=CHR} RCH(N_3)CH(N_3)R + RCH(N_3)CH(OAc)R$$

Steroidal olefins were found to produce α-azidosteroids [21] as did α-pinene [90, 91]. Steroidal dienes were also shown to undergo the reaction [92].

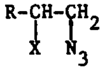


At lower temperatures reaction with unsaturated steroids was found to lead to an opening of the ring containing the double bond to produce a ketonitrile [93].



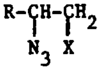
A phenyliododiacetate-trimethylazidosilane reagent has been shown to react readily with a wide range of alkenes to form α-azidocarbonyl compounds. Steroidal Δ^5-olefins are transformed to 5,6-seco-5-oxo-6-oic nitrile derivatives [94]. Alkadienes, cycloalkadienes and cholestadiene systems react similarly [210]. Cyclic olefins and bridged olefins also react readily [95]. The reactive species in these reactions is apparently $C_6H_5I(OAc)_{2-n}(N_3)_n$ [95].

Transfer reactions by means of a thallium triacetate-tri-methylazidosilane system have also been developed by Zbiral and co-workers [96]. Δ^1-olefins, $R{-}CH{=}CH_2$, react with the reagent to give thallium containing adducts which on treatment with iodide, thiocyanate, chloride or bromide ions produces the organoazido compounds I and/or II.



$\mathrm{R{-}\underset{X}{CH}{-}\underset{N_3}{CH_2}}$

I



$\mathrm{R{-}\underset{N_3}{CH}{-}\underset{X}{CH_2}}$

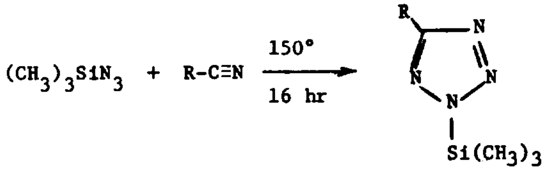
II

where X = I, Cl, Br, SCN

On reaction with HF (40%), the thallium-azidoacetate adduct is transformed into hydroxyazides, I and II (X = OH). Rearrangements were observed in some systems. Reaction of the reagent with methylene cyclohexane [96], cyclohexene [97], and α-pinene [96] were also investigated.

C. REACTION WITH NITRILES

Ettenhuber and Rühlmann investigated the cycloaddition reaction of azidosilanes with nitriles [22]. Aryl and alkyl nitriles were shown to react with $(CH_3)_3SiN_3$ to form the corresponding tetrazoles.



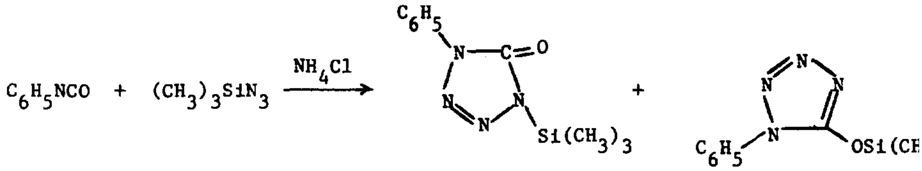
R = C_6H_5-, $C_6H_5CH_2$-, C_2H_5-.

Reichle observed that $(C_6H_5)_3SiN_3$ did not react with benzonitrile (200°, 20 hr.) to yield a tetrazole [26]. However, reaction of $(CH_3)_3SiN_3$ with benzonitrile in the presence of ammonium chloride did lead to the desired tetrazole in low yield [99]. Triethylamine is effective as a catalyst for the reaction of azidosilanes with trihaloacetonitriles [100].

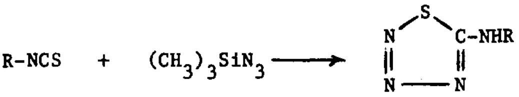
Washburne and Peterson found reaction of a series of organosilylazides and diazides with arylnitriles gives mixtures of tetrazoles, 3,5-diaryl-1,2,4-triazoles and 2,5-diaryl-1,2,4,5-tetrazines [101]. Reaction of cyanoferrocene with $(CH_3)_3SiN_3$ in the presence of aluminum chloride produced 5-ferrocenyl tetrazole [101]. Haloacetonitriles, X_3CCN (X = Cl, F) react with $(CH_3)_3SiN_3$ in the presence of triethylamine to yield the corresponding tetrazoles [186]. The reaction of cyanoformates with organoazidosilanes to produce the corresponding tetrazoles has been utilized in a route to prepare compounds for treatment of allergies [189].

D. REACTION WITH ISOCYANATES AND ISOTHIOCYANATES

The reaction of trimethylazidosilane with phenylisocyanate is reported to be catalyzed by ammonium chloride and to afford a 1:1 adduct that is a mixture of the corresponding tetrazole and tetrazolinone [99].

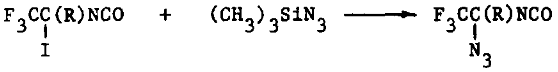


A similar reaction of organoisothiocyanates with $(CH_3)_3SiN_3$ produced 5-anilino-1,2,3,4-thiatriazoles [102].



The $(CH_3)_3SiN_3$ reactant may be generated <u>in situ</u> using $(CH_3)_3SiCl$ and NaN_3 [38].

Substitution can occur on a reactive carbon site in the presence of an isocyanate group [197, 198].

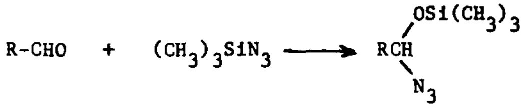


$$F_3C\underset{I}{C}(R)NCO + (CH_3)_3SiN_3 \longrightarrow F_3C\underset{N_3}{C}(R)NCO$$

(R = C_6H_5-, p-CH_3-C_6H_4-, p-F_3C-C_6H_4-)

E. REACTION WITH ALDEHYDES AND KETONES

Birkofer and co-workers investigated the reaction of aldehydes with the azidosilane moiety. Straight and branched chain aldehydes react readily with $(CH_3)_3SiN_3$ in the presence of zinc chloride catalyst to yield the corresponding α-(trimethylsiloxy)alkylazide [103, 104].



$$R\text{-}CHO + (CH_3)_3SiN_3 \longrightarrow RCH(OSi(CH_3)_3)(N_3)$$

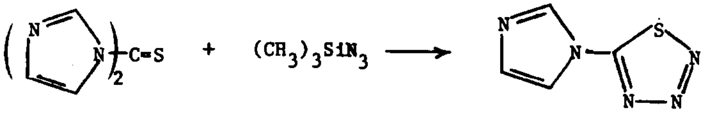
Higher yields and milder conditions resulted when a KN_3-crown ether complex was employed [105].

Carbonyl insertion reactions with ketones using organoazidosilanes have also been reported. Birkofer found yields much lower than with aldehydes using $(CH_3)_3SiN_3$ [103]. Ettenhuber and Rühlmann demonstrated that diphenylmethyl- and dimethylphenyl-azidosilane react with benzophenone to give moderate yields of organosilylbenzamides [22]. It has been reported that hexafluoroacetone reacts with $(CH_3)_3SiN_3$ at room temperature to give a substantial yield of the insertion product [106, 108].

$$(CH_3)_3SiN_3 \quad + \quad (CF_3)_2CO \longrightarrow (CH_3)_3SiOC(CF_3)_2N_3$$

The *in situ* technique was used to obtain 1-azido-1-trimethylsiloxycyclohexane. It could not be prepared by direct reaction between cyclohexanone and $(CH_3)_3SiN_3$ [103, 104, 107].

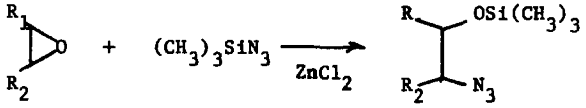
Reaction of trimethyl azidosilane with N,N'-thiocarbonylimidazole gave 5-(1-imidazoyl)-1,2,3,4-thiatriazole in 55% yield [123].



In the presence of thiophosgene a quantitative yield of product was obtained.

F. REACTION WITH EPOXIDES

The reaction of $(CH_3)_3SiN_3$ with epoxides was reported in 1967 [103]. *beta*-Trimethylsiloxyalkylazides are formed.



Cyclohexene oxide produced exclusively *trans*-2-(trimethylsiloxy)-cyclohexyl azide [104]. Styrene oxide readily underwent the ring opening reaction to give 2-phenyl-2-(trimethylsiloxy)ethyl azide. Russian workers have used this addition reaction with epoxides to prepare organoisocyanates [109].

G. REACTION WITH ANHYDRIDES

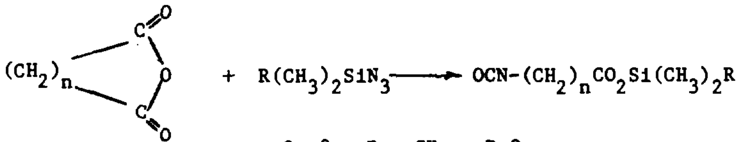
In 1972, Washburne and co-workers in the U.S. [111] and the Kricheldorf group in Germany [110] reported extensive investigations covering the reaction of organic anhydrides with organoazidosilanes.

Reaction of a series of anhydrides of the type $(RCO)_2O$ gave the silylester and corresponding isocyanate in good yield.

$$(RCO)_2O \quad + \quad (CH_3)_3SiN_3 \longrightarrow RNCO \quad + \quad RCO_2Si(CH_3)_3$$

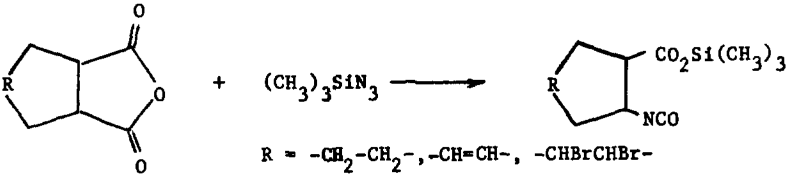
$R = C_2H_5-$, $(CH_3)_2CH-$, $(CH_3)_3C-$, C_6H_5- [110, 116]
$R = C_3H_7-$ [111]

Thus, a method of using $(CH_3)_3SiN_3$ for the conversion of anhydrides to amines with one less carbon atom is available. Cyclic anhydrides, such as succinic anhydride, produced the ω-isocyanatoalkyl silylester [110, 111].



$n = 2, 3 \quad R = CH_3-$, BuO-

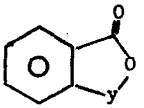
Kricheldorf reported that bicyclic anhydrides also give products containing the isocyanato and silyl ester group [110].



$R = -CH_2-CH_2-$, $-CH=CH-$, $-CHBrCHBr-$

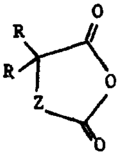
Washburne [111] showed that phthalic and hexahydrophthalic anhydride produced a mixture of the isocyanate product (80%) and an N-trimethylsilyl-N-carboxyanhydride species (20%).

Use of mixed cyclic anhydrides such as



$(y = SO_2, O_2C)$

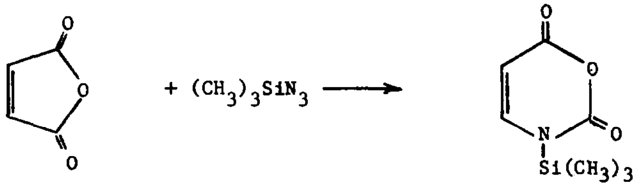
or



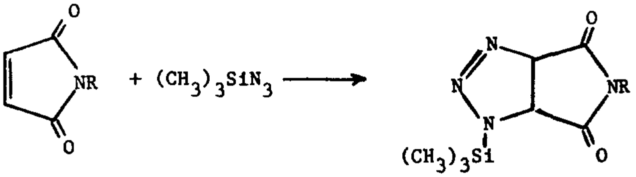
$(R = H, CH_3-; Z = O, NCH_3)$

proceeded with a pyridine catalyst and produced unstable isocyanate products.

Washburne and co-workers discovered that maleic anhydride reacts with $(CH_3)_3SiN_3$ to produce the oxazinedione derivative [111].



An analogous reaction with N-alkyl maleimides forms a triazoline. The use of N-butylisomaleimide gave 3-butyluracil, opening a new route to the pyrimidinedione ring system [111].



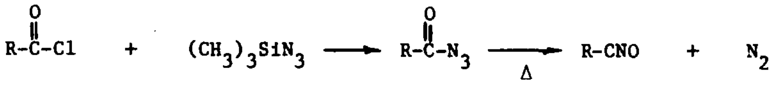
Further work by the Kricheldorf group has included reaction of 1,2-cyclopropane dicarboxylic anhydride [112], use of 5-membered cyclic anhydrides to produce trimethylsilyl-<u>beta</u>-amino acid N-carboxyanhydrides [113], and a series of cyclic anhydrides to produce trimethylsilyl-4-isocyanatocarboxylates [114, 115].

Washburne and co-workers extended the reaction of $(CH_3)_3SiN_3$ with a series of substituted maleic anhydrides to produce a superior route for synthesis of 4-substituted oxazine diones [117, 118, 119]. Reaction of citraconic anhydride with $(CH_3)_3SiN_3$ or $(C_2H_5)_3SiN_3$ produced a mixture of the 4- and 5-methyl-substituted oxazine diones [120]. $(C_6H_5)_3SiN_3$ failed to react. Halo-substituted oxazinedione species have been reported [121].

The reaction of anhydrides with $(CH_3)_3SiN_3$ was utilized in the synthesis of cardiac stimulants [124].

H. REACTION WITH ACID CHLORIDES

In recent years, the reaction of acid chlorides with $(CH_3)_3SiN_3$ has been utilized to prepare carbonyl azides which are intermediates on the route to isocyanates through the well known Curtius Rearrangement [138].



$$R-\overset{\overset{O}{\|}}{C}-Cl \quad + \quad (CH_3)_3SiN_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}-N_3 \xrightarrow[\Delta]{} R-CNO \quad + \quad N_2$$

Acid chlorides such as fluoroacyl chlorides [125, 129, 130], triethylsilylacetyl chloride [126], fatty acid chlorides [127], cyclopropyl-acid chloride [128], 3-(dichlorophosphinyl)propionyl chloride [186], chloroformates [131] and thiochloroformates [132] have been utilized in the reaction. Diisocyanates have been prepared using this method [215].

Reaction of $(CH_3)_3SiN_3$ with di- and tri-substituted chloroiminium chlorides produced tetrazoles in a new Curtius type rearrangement [133, 137].

The reaction has been used in the preparation of herbicides [134], antibacterial compounds [135] and tetrazoles for treatment of allergies [136].

I. REACTION WITH LEWIS ACIDS

Organoazidosilanes undergo reaction with Lewis acids to form fairly stable complexes or enter into exchange reactions. Thayer and West found that $SnCl_4$ and BBr_3 form stable, solid 1:1 adducts with $(C_6H_5)_3SiN_3$ and $(CH_3)_3SiN_3$ [139]. $CH_3(C_6H_5)_2SiN_3$ reacted violently with $SbCl_5$ to give an unidentified black residue [139]. Earlier, Wiberg and Schmid report that $(CH_3)_3SiN_3$ and $(C_6H_5)_3SiN_3$ react with $SbCl_5$ to form the dimer $(Cl_4SbN_3)_2$ and the corresponding chlorosilane, $(CH_3)_3SiCl$ or $(C_6H_5)_3SiCl$, respectively [140, 141]. Under certain conditions the $[Cl_4SbN_3]_2\cdot nSbCl_5$ complex was obtained. These later workers also report that the reaction of $(CH_3)_3SiN_3$ with $SnCl_4$, in methylene chloride solvent forms $Cl_2Sn(N_3)_2$, whereas in pentane solvent $Cl_2Sn(N_3)_2$ and $Cl_3SnN_3\cdot(CH_3)_3SiN_3$ are formed [142].

Tellurium tetrachloride was found to react with $(CH_3)_3SiN_3$ to form Cl_3TeN_3, $Cl_2Te(N_3)_2$ and $(CH_3)_3SiCl$, while SCl_4 and $SeCl_4$ underwent reduction [143].

$$SCl_4 + 2\,(CH_3)_3SiN_3 \longrightarrow SCl_2 + 3\,N_2 + 2\,(CH_3)_3SiCl$$

$$SeCl_4 + 3\,(CH_3)_3SiN_3 \longrightarrow \text{"SeCl"} + 4.5\,N_2 + 3\,(CH_3)_3SiCl$$

Tellurium tetrabromide gave no reaction under similar conditions [143].

Organogermanium halides react with $(CH_3)_3SiN_3$ to form mainly the corresponding organoazidogermanes [144]. Triphenylsilicon, germanium and tin hydrides undergo reaction with $(C_6H_5)_3SiN_3$ to form the corresponding silazane or silylamine derivatives [145].

$$(C_6H_5)_3SiN_3 + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_3SiNHSi(C_6H_5)_3 + N_2$$

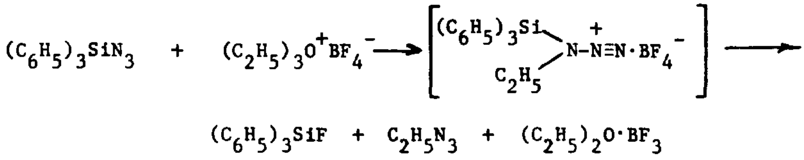
$$(C_6H_5)_3SiN_3 + (C_6H_5)_3GeH \longrightarrow (C_6H_5)_3SiNHGe(C_6H_5)_3 + N_2$$

$$(C_6H_5)_3SiN_3 + 2(C_6H_5)_3SnH \longrightarrow (C_6H_5)_3SiNH_2 + (C_6H_5)_6Sn_2 + N_2$$

Group II halides, $BeCl_2$, MgX_2(X = Cl, Br, I), and group III halides, BX'_3 (X' = F, Cl, Br) and $AlCl_3$ all react with $(CH_3)_3SiN_3$ in methylene chloride or ether solvent to form $[BeClN_3\cdot O(Et)_2]_2$ and polymeric $Be(N_3)_2$, $Mg(N_3)_2$ and polymeric $MgXN_3$, $[BX'_2N_3]_3$ and $AlCl_2N_3$ and polymeric $AlCl(N_3)_2$, respectively [146].

The titanium complexes, $[Ti(\eta^5-C_5H_5)Cl_2(N_3)]$, $[Ti(\eta^5-C_5H_5)_2Cl(N_3)]$, $TiCl(N_3)(S_2NEt_2)_2$ and $Ti(N_3)(S_2CNEt_2)_3]$ have been prepared by reactions of the corresponding metal halide with $(CH_3)_3SiN_3$ [147].

Reaction of triethyloxonium tetrafluoroborate with $(C_6H_5)_3SiN_3$ did not give the expected N-diazonium salt, but triphenylfluorosilane [148].



$$(C_6H_5)_3SiN_3 + (C_2H_5)_3O^+BF_4^- \longrightarrow \left[\begin{matrix} (C_6H_5)_3Si \\ C_2H_5 \end{matrix} \!\!>\! \overset{+}{N}-N{\equiv}N \cdot BF_4^- \right] \longrightarrow$$

$$(C_6H_5)_3SiF + C_2H_5N_3 + (C_2H_5)_2O \cdot BF_3$$

J. REACTION WITH PHOSPHINES, PHOSPHITES AND PHOSPHINE IMIDES

Early workers investigating the reactions of organoazidosilanes found that triorganophosphines readily converted the azidosilanes to the corresponding phosphine imines [8, 15, 17, 18, 23, 27, 155, 156, 157].

$$R_3P + R'_3SiN_3 \longrightarrow R_3P{=}NSiR'_3 + N_2$$

Later work has shown this to be a general reaction for a wide variety of triorganophosphines [149, 159, 161, 162], tetraorganodiphosphines [158, 160], triorganophosphites [151-154], and phosphine imides [152, 153, 163, 164, 165, 214].

$$(C_6H_5)_2PP(C_6H_5)_2 + (C_6H_5)_3SiN_3 \longrightarrow (C_6H_5)_3SiN{=}P(C_6H_5)_2P(C_6H_5)_2{=}NSi(C_6H_5)_3$$

$$[(C_2H_5)_2N]_3P + (CH_3)_3SiN_3 \longrightarrow [(C_2H_5)_2N]_3P{=}NSi(CH_3)_3$$

The reaction of diphenylphosphine with triphenylazido silane was observed to proceed through an intermediate stage to form a compound wherein phosphorus is in a pentavalent state [160].

$$(C_6H_5)_2PH + (C_6H_5)_3SiN_3 \longrightarrow (C_6H_5)_3SiNHP(C_6H_5)_2 \longrightarrow$$

$$(C_6H_5)_3SiNHP(C_6H_5)_2{=}NSi(C_6H_5)_3$$

Diazidodisilanes undergo the reaction [166] as do $\underline{\alpha}$, $\underline{\omega}$-polymethylene triphosphines [167].

$$2\ R_3P + N_3Si(CH_3)_2Si(CH_3)_2N_3 \longrightarrow R_3P{=}NSi(CH_3)_2Si(CH_3)_2N{=}PR_3$$

$$(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2 + (CH_3)_3SiN_3 \longrightarrow$$

$$(n = 1-3)$$

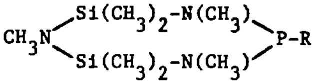
$$(CH_3)_3SiN{=}P(C_6H_5)_2-(CH_2)_nP(C_6H_5)_2{=}NSi(CH_3)_3$$

$(CH_3)_2Si(N_3)_2$ also undergoes the latter reaction to yield linear and cyclic products. The reaction of organoazidosilanes with substituted phosphines has been used to prepare heat resistant polymers [168, 169].

It is noted that the organoazidosilanes react with phosphine imines to yield diphosphazenes [170, 171, 173].

$$(CH_3)_3P{=}NP[C(CH_3)_3]_2 \; + \; (CH_3)_3SiN_3 \longrightarrow (CH_3)_3P{=}NP[C(CH_3)_3]_2{=}NSi(CH_3)_3$$

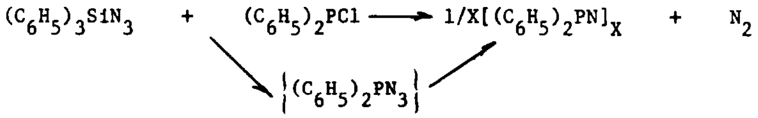
Wannagat and co-workers observed that oxidative addition of the $-NSi(CH_3)_3$ group to the P atom occurs when $(CH_3)_3SiN_3$ reacts with



$(R = CH_3-, C_6H_5-)$ [172].

K. REACTION WITH CHLOROPHOSPHINES

The reaction of organoazidosilanes with chlorophosphines leads to the formation of azidophosphine intermediates by an exchange reaction. These intermediates decompose to yield phosphonitrilic materials plus nitrogen [174].



$$(C_6H_5)_3SiN_3 \; + \; (C_6H_5)_2PCl \longrightarrow 1/X[(C_6H_5)_2PN]_X \; + \; N_2$$
$$\{(C_6H_5)_2PN_3\}$$

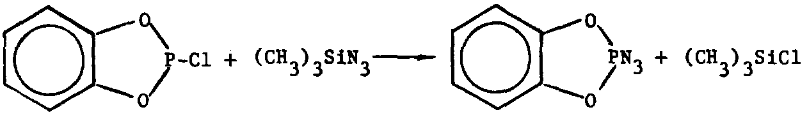
The course of the reaction is dependent on solvent, temperature, and to some extent concentration. The rate of exchange of Cl on P with the N_3 group increases with the extent of C_6H_5- substitution on the trivalent P atom:

$$PCl_3 < C_6H_5PCl_2 < (C_6H_5)_2PCl.$$

Azidophosphorus compounds are formed when chlorophosphine imides react with $(CH_3)_3SiN_3$ [175, 176].

$$\left[[(CH_3)_2CH]_2N\right]_2PCl \; + \; (CH_3)_3SiN_3 \longrightarrow \left[[(CH_3)_2CH]_2N\right]_2PN_3$$

The reaction of pyrocatechol chlorophosphite with $(CH_3)_3SiN_3$ gives the corresponding azidophosphorus compound [177]. Chlorophosphanes of this type containing single or double catechol bidentate ligands were shown to react with $(CH_3)_3SiN_3$ through the formation of hexacoordinated phosphorus complexes [178].



It is possible to obtain the phosphonitrilic trimer as the product, under suitable conditions [179].

Phosphinyl azides may be prepared by reaction of the corresponding chloro compound with organoazidosilanes [180].

$$R_2P(O)Cl \quad + \quad R_3SiN_3 \longrightarrow R_2P(O)N_3 \quad + \quad R_3SiCl$$

L. REACTION WITH MISCELLANEOUS REAGENTS

(a) LITHIUM AND MAGNESIUM COMPOUNDS

Wiberg and co-workers investigated the reaction of organoazidosilanes with respect to Grignard and organolithium reagents [181]. Based on conditions, both substitution and addition reactions were observed.

$$\begin{tikzcd}
& & R_3SiR' + MN_3 \\
R_3SiN_3 + R'\text{-}M \arrow[urr, "\text{substitution}"] \arrow[drr, "\text{addition}"'] & & \\
& & R_3SiN(R')M + N_2
\end{tikzcd}$$

$(M = Li, MgR', MgX)$

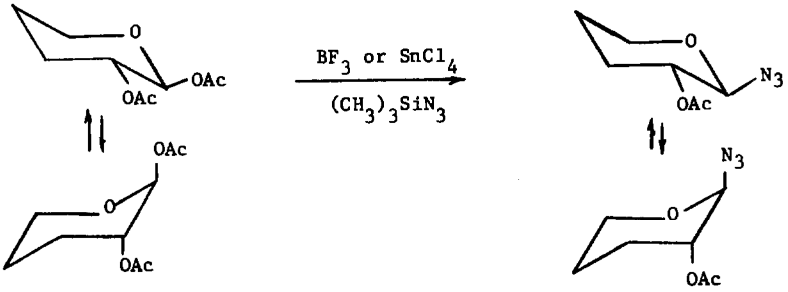
The addition reaction opens a route for converting aromatic halides to aromatic amines.

$$R_3SiN(R')M \xrightarrow{H_2O} R_3SiN(R')H \xrightarrow{H^+} H_2NR'$$

The monomeric form of the Grignard reagent, R'MgX, was shown to act as a Lewis base toward the azidosilanes [182]. The reaction is visioned as a nucleophilic substitution. The dimeric form, $(R'MgX)_2$, acts as a Lewis acid forming a complex, $R_3SiN_3 \cdot R'MgX$, which is thermally unstable. This route produces products through the addition sequence illustrated above. Employing ^{15}N NMR, the Grignard complex was shown to have an N-diazonium group. This complex can decompose thermally via two pathways [183].

(b) CARBOHYDRATES

A series of tetra(penta)-O-acetyl-aldopento(hexo) pyranoses give with $(CH_3)_3SiN_3$, in the presence of BF_3 or $SnCl_4$, the corresponding glycosyl azides [185]. Only the anomeric glycosyl azide having the azido group trans to the 2-acetoxy group is obtained in each case.



(c) TRANSITION METAL COMPOUNDS

The reaction of $Ru(CO)_{12}$, $\pi\text{-}C_5H_5Co(CO)_2$ and $(\pi\text{-}C_5H_5Rh)_3(CO)_2$ with $(CH_3)_3SiN_3$ leads to the formation of the corresponding μ_3-trimethylsilylimido complexes [190]. Dicyclopentadienyl vanadium, $(C_5H_5)_2V$, reacts with R_3SiN_3 ($R = CH_3$-, C_6H_5-) to give $[(C_5H_5)_2V]_2NSi(CH_3)_3$ and $(C_5H_5)_2VNSi(C_6H_5)_3$, respectively [191]. Chatt and co-workers found $(CH_3)_3SiN_3$ to be a convenient reagent for the preparation of Mo(VI) and Mo(V) nitrido complexes [192-195]. The thionitrosyl complexes of molybdenum, rhenium and osmium were also reported.

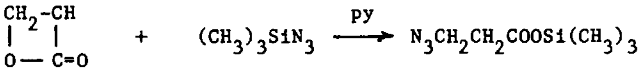
(d) DIAZONIUM SALTS

Aromatic azides are readily prepared by reaction of $(CH_3)_3SiN_3$ with the corresponding diazonium salts [196].

$$\underline{m}\text{-}H_2N\text{-}C_6H_4COOH \xrightarrow[2.\ (CH_3)_3SiN_3]{1.\ HCl,\ NaNO_2,\ 0°} \underline{m}\text{-}N_3\text{-}C_6H_4\text{-}COOH \qquad (82\%)$$

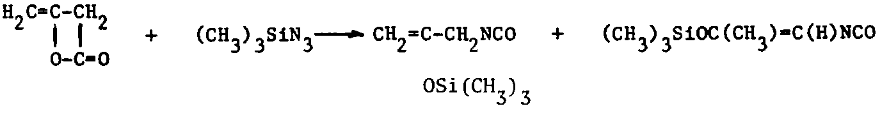
(e) LACTONES

Kricheldorf found that reaction of beta-propiolactone with $(CH_3)_3SiN_3$ in the presence of pyridine catalyst gave the 3-azido isomer of the silylester [207].



$$\begin{array}{l} CH_2\text{-}CH \\ |\quad\ \ | \\ O\text{—}C{=}O \end{array} + (CH_3)_3SiN_3 \xrightarrow{py} N_3CH_2CH_2COOSi(CH_3)_3$$

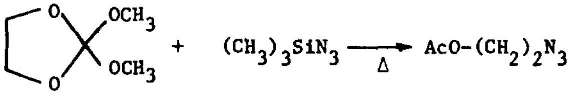
Strongly activated carbonyl esters, RCOOR', produced the carbonyl azide which decomposed to the corresponding isocyanate RNCO. Reaction of diketene with $(CH_3)_3SiN_3$ produced isomeric isocyanates [206].



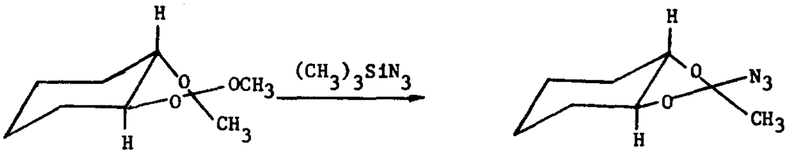
$$\begin{array}{l} H_2C{=}C\text{-}CH_2 \\ \quad\ \ |\quad | \\ \quad\ O\text{-}C{=}O \end{array} + (CH_3)_3SiN_3 \longrightarrow CH_2{=}\underset{OSi(CH_3)_3}{C}\text{-}CH_2NCO + (CH_3)_3SiOC(CH_3){=}C(H)NCO$$

(f) ORTHOESTERS

Hartmann and co-workers observed that reaction of 1,2-glycol cyclic orthoesters with $(CH_3)_3SiN_3$ produce the corresponding azidohydrin [199, 200].



Threo and *erythro* isomers are obtained with substituted dioxolane starting materials. Becsi and Zbiral demonstrated that cyclic orthoesters of *trans*-1,2 cyclohexanediol, and related systems in the steroidal series, give the corresponding azido compound [201].



(g) ZWITTER IONS, SO_3, $(CH_3)_3Al$ and S

The reaction of $(CH_3)_3SiN_3$ with zwitter ions of the diazaphosphonialuminatacyclobutane type has been investigated [206].

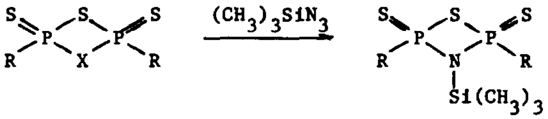
The insertion of SO_3 into $(CH_3)_3SiN_3$ gives $N_3SO_2OSi(CH_3)_3$ as product [207]. $(C_6H_5)_2Si(N_3)_2$ gave the disubstituted compound.

$$2\ SO_3 \quad + \quad (C_6H_5)_2Si(N_3)_2 \longrightarrow (C_6H_5)_2Si(OSO_2N_3)_2$$

Azido complexes of elements of group IIIA and IVA were investigated [208].

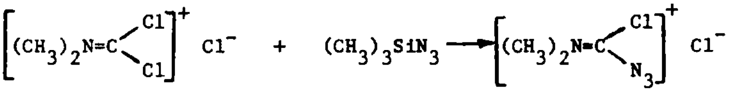
$$(CH_3)_3SiN_3 \quad + \quad (CH_3)_3Al \longrightarrow (CH_3)_3SiN_3 \cdot Al(CH_3)_3$$

Reaction of sulfur with $(CH_3)_3SiN_3$ gave S_7NH and traces of $S_6(NH)_2$ isomers [209]. Cyclic alkyldithiophosphonic anhydrides on reaction with $(CH_3)_3SiN_3$ led to the insertion of the $-NSi(CH_3)_3$ group [211].



(R = CH_3-, C_2H_5-; X = S)

Dichloroimine compounds react with $(CH_3)_3SiN_3$ [212].



$$\left[(CH_3)_2N{=}C\begin{smallmatrix}Cl\\Cl\end{smallmatrix}\right]^+ Cl^- + (CH_3)_3SiN_3 \longrightarrow \left[(CH_3)_2N{=}C\begin{smallmatrix}Cl\\N_3\end{smallmatrix}\right]^+ Cl^-$$

M. APPLICATIONS - POLYMER FORMATION

Washburn and Baldwin in a series of patents covered the reactions of diorganodiazidosilanes with organo phosphines, arsines and stibines to yield fairly high molecular weight silylimido-phosporanes, -arsanes and -stilbanes, respectively [202]. $(C_6H_5)_2Si(N_3)_2$ treated in bulk or in solution with phosphines or arsines of the structure $(C_6H_5)_2Z(CH_2)_nZ'(C_6H_5)_2$ (Z, Z' = P, As; n = 0-2) produced oligomers having a Si-N=Z linkage [203]. Reaction of chloromethylated divinyl benzene-styrene copolymers with $(CH_3)_3SiN_3$ produced the corresponding azidomethyl substituent which on reaction with $(C_2H_5O)_3P$, $[(C_2H_5)_2N]_3P$ or $(C_2H_5)_3P$ gave polymers containing $-CH_2N{=}P(OEt)_3$, $-CH_2N{=}P[(N(C_2H_5)_2]_3$ or $-CH_2N{=}P(C_2H_5)_3$ units [204].

Si_3N_4 coatings for insulation, protection or reduction of reflections at the surface of semiconductive devices are deposited by exposing a substrate to a plasma discharge in a vapor of $(CH_3)_3SiN_3$ [205].

Acknowledgement

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VI. TABLE

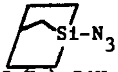
ORGANOAZIDOSILANES

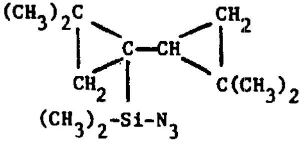
In the table under the column I*, the symbols used are: IR = infrared spectroscopy, MS = mass spectroscopy, NMR = nuclear magnetic resonance, and R = Raman spectroscopy.

The density and refractive index values are at 20° unless otherwise noted.

TABLE I

ORGANOAZIDOSILANES

Molecular Formula	Structural Formula	bp(°C)(Torr)	mp(°C)	n_D^{20}	d_4^{20}	I*	References
CH_3ClN_6Si	$CH_3(Cl)Si(N_3)_2$	47(20)	-	-	-	MS	21,39,42
$CH_3Cl_2N_3Si$	$CH_3(Cl)_2SiN_3$	100.5	-	-	-	-	21,39,43
CH_3N_9Si	$CH_3Si(N_3)_3$	70-73(20)	-	-	-	MS	26,39,44
$C_2H_6ClN_3Si$	$(CH_3)_2ClSiN_3$	120	-	-	-	-	39,43,44
$C_2H_6FN_3Si$	$(CH_3)_2FSiN_3$	-	-	-	-	NMR	35
$C_2H_6N_6Si$	$(CH_3)_2Si(N_3)_2$	144.3	-	1.4579	1.0845	IR	14,20,26,39
$C_3H_9N_3Si$	$(CH_3)_3SiN_3$	94	-95	1.4161	0.8763	IR,UV,Ra	8,16,26,46
$C_3H_9N_3OSi$	$(CH_3)_2Si(N_3)OCH_3$	-	-	-	-	NMR	35
$C_3H_9N_3SSi$	$(CH_3)_2Si(N_3)SCH_3$	-	-	-	-	NMR	35
$C_4H_{11}N_3OSi$	$(CH_3)_2(C_2H_5O)SiN_3$	36(18)	-	1.4046	-	IR	22
$C_4H_{12}N_4Si$	$(CH_3)_2Si(N_3)N(CH_3)_2$	-	-	-	-	NMR	35
$C_5H_{13}N_3Si$	$(CH_3)_2(\underline{n}C_3H_7)SiN_3$	143	-	-	-	IR,NMR	65
$C_5H_{15}N_3Si_2$	$(CH_3)_3SiSi(CH_3)_2N_3$	47-49(10)	-	1.4572	-	IR,NMR,MS	22
$C_6H_4N_{18}Si_2$	$1,4-(N_3)_3SiC_6H_4-Si(N_3)_3$	-	-	-	-	-	28
$C_6H_5N_9Si$	$C_6H_5Si(N_3)_3$	63(0.01)	-	-	-	-	18,26,39,44
$C_6H_{11}N_3Si$		-	-	-	-	IR,NMR,MS	34
$C_6H_{15}N_3Si$	$(C_2H_5)_3SiN_3$	39(5)	-	1.4424	-	-	23,53
$C_6H_{15}N_3Si$	$(CH_3)_3C(CH_3)_2SiN_3$	-	-	-	-	IR,NMR,MS	55
$C_6H_{15}N_3OSi$	$(\underline{n}-C_4H_9O)(CH_3)_2SiN_3$	-	-	-	-	-	110

Molecular Formula	Structural Formula	bp(°C)(Torr)	mp(°C)	n_D^{20}	d_4^{20}	I*	References
$C_6H_{16}N_4Si$	$(CH_3)_2(\underline{n}\text{-}C_4H_9NH)SiN_3$	75(20)	-	1.4409	-	IR	22,47
$C_6H_{18}N_4Si_2$	$(CH_3)_3SiN(CH_3)Si(CH_3)_2N_3$	-	-	-	-	IR,NMR	65
$C_7H_8N_6Si$	$CH_3(C_6H_5)Si(N_3)_2$	120-122(22)	-	1.5368(19)	-	NMR	21,32
$C_7H_9N_3Si$	$CH_3(C_6H_5)(H)SiN_3$	95(15)		1.5182	-	IR	22
$C_7H_{13}N_3Si$		-	-	-	-	IR,NMR,MS	34
$C_8H_{11}N_3Si$	$(CH_3)_2(C_6H_5)SiN_3$	89(11)	-	1.5189	-	-	15,22,28,47
$C_8H_{24}N_4Si_3$	$[(CH_3)_3Si]_2NSi(CH_3)_2N_3$	50-52(vac)	-	-	-	IR,NMR	9
$C_9H_{21}N_3Si$	$(\underline{n}\text{-}C_3H_7)_3SiN_3$	7(13)	-	1.4468(23)	-	IR	21
$C_9H_{27}N_5Si_3$	$(CH_3)_3Si(NCH_3)Si(CH_3)_2(NCH_3)Si(CH_3)_2N_3$	-	-	-	-	IR,NMR	65
$C_{10}H_{26}N_4Si_2$	$\underline{n}\text{-}C_3H_7Si(CH_3)_2N(C_3H_7\text{-}\underline{n})Si(CH_3)_2N_3$	-	-	-	-	IR,NMR	65
$C_{10}H_{26}N_4Si_2$	$\underline{n}\text{-}C_3H_7Si(CH_3)_2N(CH_3)Si(CH_3)(C_3H_7\text{-}n)N_3$	-	-	-	-	IR,NMR	65
$C_{10}H_{30}N_4Si_4$	$(CH_3)_3Si(CH_3)_2SiN[Si(CH_3)_3]Si(CH_3)_2N_3$	-	-	-	-	IR,NMR	65
$C_{11}H_{17}N_3Si$	$(CH_3)(\underline{n}\text{-}C_4H_9)(C_6H_5)SiN_3$	98-94(1.5)	-	1.5009(27.8)	-	-	21
$C_{11}H_{18}ON_3Si$	$CH_3(C_6H_5NH)Si[OC(CH_3)_3]N_3$	-	-	-	-	-	69
$C_{12}H_{10}ClN_3Si$	$(C_6H_5)_2ClSiN_3$	134-5(0.5)	-	1.5838	-	IR	22
$C_{12}H_{10}N_6Si$	$(C_6H_5)_2Si(N_3)_2$	121-3(0.1)	-	1.5887	-	IR,NMR	26,39,47,52
$C_{12}H_{11}N_3Si$	$(C_6H_5)_2(H)SiN_3$	139(2)	-	1.5885	-	IR	22
$C_{12}H_{19}N_3Si$	$CH_3(C_5H_{11})(C_6H_5)SiN_3$	111-113(1.0)	-	1.4978(27.8)	-	IR	21
$C_{12}H_{23}N_3Si$		41-43(0.01)	-	1.4850(25)	-	NMR	37

Molecular Formula	Structural Formula	bp(°C)(Torr)	mp(°C)	n_D^{20}	d_4^{20}	I*	References
$C_{12}H_{27}N_3Si$	$(\underline{n}\text{-}C_4H_9)_3SiN_3$	88(0.001)	-	1.4522(22)	-	IR	23,53
$C_{12}H_{27}N_3Si$	$(\underline{t}\text{-}C_4H_9)_3SiN_3$	-	114-16	-	-	IR,NMR,MS	56
$C_{13}H_{13}N_3Si$	$(C_6H_5)_2(CH_3)SiN_3$	196-8(47)	-	1.5799	-	IR	22,39,47,48,57
$C_{14}H_{14}N_6Si$	$(C_6H_5CH_2)_2Si(N_3)_2$	-	-	-	-	-	36
$C_{14}H_{15}N_3Si$	$2\text{-}C_6H_5\text{-}C_6H_4Si(CH_3)_2N_3$	152(6.5)	-	1.5745(25)	-	-	29
$C_{15}H_{14}N_4Si$	$(C_6H_5CH_2)_2(CN)SiN_3$	-	-	-	-	-	36
$C_{18}H_{14}FN_3Si$	$\underline{p}\text{-}F\text{-}C_6H_4(C_6H_5)_2SiN_3$	-	67.5-68.5	-	-	NMR	45
$C_{18}H_{14}FN_3Si$	$\underline{m}\text{-}F\text{-}C_6H_4(C_6H_5)_2SiN_3$	-	59.5-60	-	-	NMR	45
$C_{18}H_{15}N_3Si$	$(C_6H_5)_3SiN_3$	100-5(0.001)	81	-	-	IR	15,17,22,59
$C_{18}H_{22}N_6Si$	$[2,4,6\text{-}(CH_3)_3C_6H_2]_2Si(N_3)_2$	-	87.5	-	-	IR	23
$C_{19}H_{25}N_3Si$	$[2,4,6\text{-}(CH_3)_3C_6H_2]_2CH_3SiN_3$	-	68.5	-	-	IR	23,53
$C_{19}H_{17}N_3OSi$	$\underline{p}\text{-}CH_3O\text{-}C_6H_4\text{-}(C_6H_5)_2SiN_3$	170(0.01)	-	-	-	-	45
$C_{19}H_{17}N_3OSi$	$\underline{m}\text{-}CH_3OC_6H_4(C_6H_5)_2SiN_3$	180(0.05)	-	-	-	-	45
$C_{29}H_{30}N_6Si_2$	$N_3Si(C_6H_5)_2(CH_2)_5Si(C_6H_5)_2N_3$	-	-	-	-	-	28
$C_{36}H_{37}N_4PSi$	$[2,4,6\text{-}(CH_3)_3C_6H_2]_2[(C_6H_5)_3PN]SiN_3$	-	189	-	-	-	23

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