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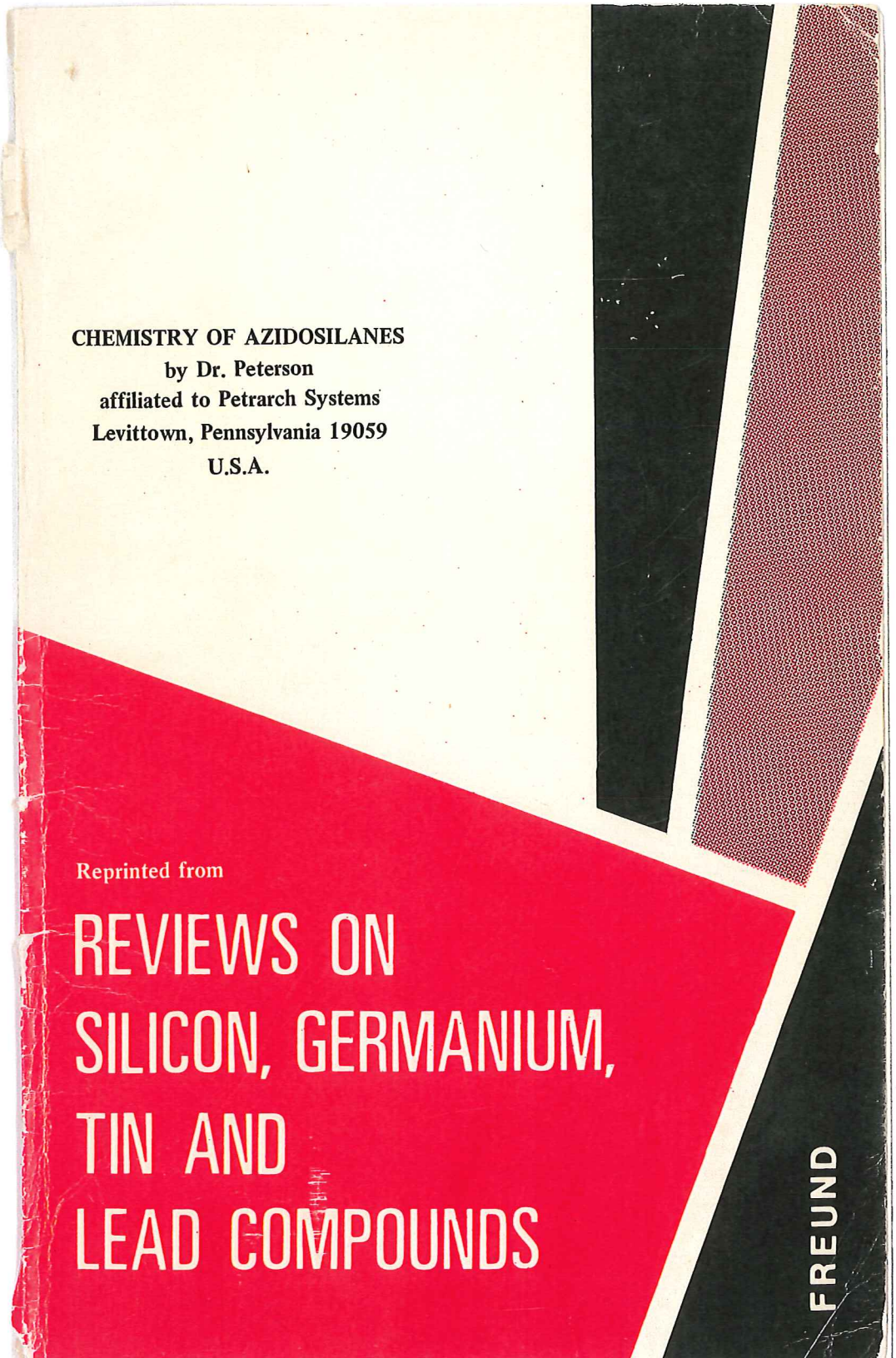

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REVIEWS

ON

SILICON, GERMANIUM, TIN AND LEAD COMPOUNDS

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A QUARTERLY REVIEW

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CHEMISTRY OF ORGANOAZIDOSILANES

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INTRODUCTION

The preparation of silicon tetraazide in 1954 marked the first reported synthesis of an azide bonded directly to a silicon. This white, crystalline material was reported[1] shock sensitive and so thermally unstable it decomposed violently on warming. Traditionally, azide derivatives of organometallic compounds, especially those containing heavy metals, have been notoriously treacherous. Compounds even such as $MeZnN_3$ have been reported to explode not only by shock and heat, but also through addition of water [2]. Trepidations of this nature probably deterred further investigations until 1962 when more adventuresome researchers reported the first syntheses of organosilicon azides.

Surprisingly, these materials were found to possess remarkable thermal stability and resistance to detonation by shock. Since that time a great deal of research has gone into studies concerning syntheses, reactions and molecular structures of these interesting and novel compounds.

Organoazidosilanes are volatile, colorless, water-white liquids or white, crystalline, low melting solids. As opposed to ionic azides which contain the N_3^- ion and possess salt-like properties, organoazidosilanes are covalent materials in which the azide group is bonded to the silicon by a single σ-bond. They exhibit properties and reactions more similar to that of organic azides than to most other organometallic azides, as reviews of the former by Boyer and Cantor [2], Evans, Yoffe and Gray[3] and recently by L'Abbe[4] illustrate. The similitude of organo and silyl azides is exemplified *via* IR spectroscopy in the asymetric stretching band of the azide (both silyl and organic azides being at higher frequency than in ionic azides) [5,6], in reactions with organic phosphines to form phosphineimines[7] and in thermolyses which occur through internal cleavage of the azide group with loss of nitrogen. Both classes of azides are soluble in non-polar solvents and hydrolyze rapidly with water, the organosilicon derivatives being particularly noteworthy in that they also react rapidly with protic solvents and in some instances enolizeable solvents such as acetone. The more volatile, lower molecular weight derivatives hydrolyze on contact with moisture in the air, liberating poisonous hydrazoic acid. Respiratory contact with trace quantities produces a burning sensation of the mucous membranes, increased respiration, heart beat and a flushed feeling of the face and neck. The general long term effect is very much like that of a bad hangover [8].

METHODS OF PREPARATION

A number of synthetic methods for the preparation of organoazidosilanes have been devised. The known methods, reflecting originality through their diversity, are listed below.

Halosilane, ionic azide, organic solvent, $AlCl_3$

Of the two general methods available for synthesis of organometallic azides, the method of Luijten[9] involving treatment of etheral solutions

of organometallic halides or hydroxides with aqueous solutions of sodium azide was incompatible with azidosilane synthesis due to the hydrolytic sensitivity of the silicon-azide bond. Alternatively, a procedure developed by Wiburg and Michaud[1] for preparation of moisture sensitive inorganic silicon azides was modified by West and Thayer[10] and Conr ny and Urry[11] to prepare organosilylazides. Briefly the procedure (A) consists of reacting the appropriate organohalosilane with lithium or sodium azide in anhydrous aprotic solvents such as bis(dimethoxyethyl) ethane[10] or THF [10,11,12,13], in the presence of anhydrous aluminum chloride [10,11,12,13].

$$R_3SiCl + M\text{-}N_3 \xrightarrow[AlCl_3]{THF} R_3SiN_3 + M\text{-}X \qquad (A)$$

(R=alkyl, aryl; M=Li, Na)

Mixed chloroaluminum azides, having appreciable solubility in the solvents employed, are believed the active azidizing agents in these reactions [6,12]. A report that chlorosilanes are quantitatively formed on interaction of azidosilanes with aluminum chloride would suggest further work however [24].

Halosilane, ionic azide, organic solvent

Perhaps the most common and widely used procedure involves modification[14] of Luijten's original method by omitting the $AlCl_3$ and employing THF or more polar solvents containing trivalent nitrogen atoms. Preparation involves slurrying of lithium or sodium azide in a suitable anhydrous solvent such as THF [15,24,25,27], pyridine,[12,16,26] lutidine or quinoline[16] with the appropriate chlorosilane.(B) (Toluene has also been used)[44]. The mixture is generally stirred 24 to 48 hours either at reflux or room temperature, filtered, the solvent removed and product distilled or crystallized. Individual compounds prepared by this and other techniques can be found listed in Table 1.

$$R_3SiCl + MN_3 \xrightarrow[Solvent]{} R_3SiN_3 + MCl \qquad (B)$$

(R= alkyl, aryl, Cl, N_3; M= Li, Na)

Good to excellent yields for most common organosilyl azides in reaction times of 1-2 hours were recently reported through use of DMF or hexamethyl phosphorous triamide (HMPT) as solvent [17]. Regardless of the solvent employed, this method has broad application and permits azido derivatives of silanes containing MeO- and Me_2N- functionalities bound to silicon. Synthesis of azidosilanes containing Si-H bonds cannot be prepared by this route however. Reichle reported the reaction of trichlorosilane with lithium azide in pyridine afforded SiH_4, spontaneously flammable in air [16]. (1) Similar results have also been recently reported [17].

$$HSiCl_3 + LiN_3 \xrightarrow[0\,^\circ C]{C_5H_5N} SiH_4 \quad (87\%) \qquad (1)$$

Halosilane, ionic azide, fused salt solvent

Molten salts have also been used as solvents in the preparation of organosilicon azides by application of a previously described preparative method for organometallic pseudohalides [18]. Sundermeyer[19,21] passed vapors of organochlorosilanes over a fused salt bath (KCl, 46 mole %, $ZnCl_2$, 54 mole %) containing NaN_3 at 230-250°(C). Products were obtained by fractional distillation of the condensed vapors. This

$$R_xSiCl_{4-x} + NaN_3 \xrightarrow[230\text{-}250^\circ]{ZnCl_2/KCl} R_xSi(N_3)_{4-x} + NaCl \qquad (C)$$

($R=CH_3, C_6H_5$; x=3,2,1)

method is particularly suited to the preparation of the mixed chloroazidosilanes, (Table 1), but does not appear applicable to derivatives containing -H, -OR or $-NR_2$ bonded to silicon.

Halosilane, azidosilane, $AlCl_3$

Aluminum trichloride in the absence of solvents is an effective azide transfer agent when added to a mixture of organochloro- and organoazidosilanes [19,22] The azido exchange reactions usually employ trimethylazidosilane (TMAS) and a higher boiling mono-, di-, or trichloroorganosilane in the presence of a catalytic amount of $AlCl_3$ (D). The

reaction mixture is heated and the lower boiling Me_3SiCl distilled off, affording the product in nearly quantitative yields.

$$4\text{-}X\ R_3SiN_3 + R'SiCl_{4-x} \xrightarrow{-R_3SiCl} R'Si(N_3)_{4-x} \qquad (D)$$

(R=Me, R'=Me, Ph, x=3,2,1.)

The reaction proceeds without aluminum chloride and as mentioned previously, $AlCl_3$ may even be deleterious as cleavage of Si-N_3 by $AlCl_3$ is known to occur [23,24] (2).

$$(CH_3)SiN_3 + AlCl_3 \longrightarrow (CH_3)_3SiCl + Cl_2AlN_3 \qquad (2)$$

Similar results were achieved by Ettenhuber and Ruhlmann[15] without the use of $AlCl_3$. Equimolar quantities of TMAS and an organochlorosilane heated 5 hours at reflux afforded the azidosilane product after removal of Me_3SiCl through a heated column. This particular modification appears particularly suited to synthesis of azidosilanes containing the Si-H functionality, as it permitted isolation of Ph_2SiHN_3 and $PhMeSiHN_3$ in yields of 88% and 83% respectively.

Aminosilane, Acid Azide, $AlCl_3$

Interaction of an acid azide such as benzazide or hippuric acid azide with N-silylalkylamines or N-silylaminoacid esters in the presence of anhydrous $AlCl_3$ has been demonstrated by Ruhlmann *et al.*[15,28] to give good yields of azidosilanes and the correponding acid amides (E). The reaction of acid azides with diaminosilanes afforded diazido or aminoazidosilanes depending on the molar ratio of reactants [28].

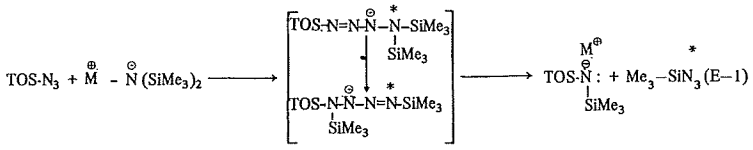
$$R_2R''SiNHR' + R'''N_3 \xrightarrow{AlCl_3} R_2R''SiN_3 + R'''NHR' \qquad (E)$$

(R=alkyl, aryl; R' =alkyl; R''=alkyl, aryl, alkylamino, amino acid ester residue, hydride, alkoxy; R''' =benzoyl, N-benzoylglycyl-)

Synthesis of azidosilanes by this method involves mixing the aminosilane, acid azide and $AlCl_3$ at room temperature for 1 hour. Without

the addition of $AlCl_3$ the reaction starts at temperatures near the decomposition point of the azide which loses N_2 forming the isocyanate and reacting with aminosilane to give silylated ureas. Good yields and syntheses of azidosilanes containing -OR, -H, and -NHR moieties bonded to silicon are favored by this procedure.

A modification of this method which utilizes the reaction of tosylazide with metal derivatives of hexamethyldisilazane (HMDS) was introduced by Wiberg *et al.*[38]. Reaction of the starting materials in ether at low temperatures affords a diazo intermediate which undergoes rearrangement and cleavage affording tosylamide salt and TMAS. (E-1)



Yields of TMAS increased as the metal (M) became more electropositive: Na(40%), Li(50%), BrMg(100%). This reaction should permit synthesis of TMAS containing the azide group specifically labelled in the α position.

Azidosilane, alkylaminosilane scrambling

A modification of the foregoing method (E) allows synthesis of aminoazidosilane by mixing equimolar quantities of di(alkylamino) silanes with diazidosilanes. (F) The reaction proceeds exothermally and quantitatively to completion. The product is obtained by distillation after two hours at room temperature. No Lewis acid is required [28].

$$R_2Si(NHR') + R_2Si(N_3)_2 \longrightarrow 2\ R_2Si(N_3)NHR' \qquad (F)$$

Similar scrambling of substituent groups bonded to organosilanes have been observed and extensively studied[29,30,31]. Muller and Van Wazer[32] recently reported fluoro, methoxyl, methylthio and dimethylamino derivatives of the dimethylazidosilane moiety *via* scrambling reactions

similar to (F). No attempt at separation or isolation of the derivatives was reported.

Silazane, hydrazoic acid

The sensitivity of the Si-N bond of silazanes and silylamines toward acids and protic reagents has long been recognized and is a very general reaction.[33] One of the earliest reports of the synthesis of an azidosilane derivative employed this method of preparation [34,35,36].

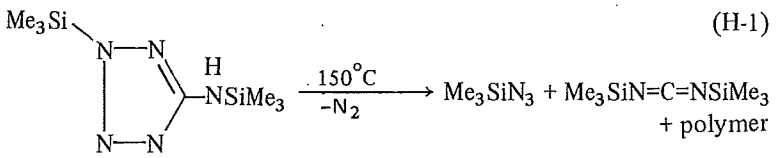
$$(R_3Si)_2NR' + 2\,HN_3 \xrightarrow{\text{solvent}} 2\,R_3SiN_3 + H_2NR' \qquad (G)$$

(R=Me, H, R′=H, H_3Si–)

While it has since received very little attention from a synthetic standpoint it has been employed to prepare azidosilane derivatives such as H_3SiN_3.[37] This method should be applicable to a large majority of the silazanes and silylamines currently known.

Miscellaneous Methods

One of the earlier reports of the preparation of an azidosilane was by a novel method which unlike all other methods, does not employ the azido moiety as a starting material. Birkofer, Ritter and Richter obtained TMAS from thermolysis of 1-(N-trimethylsilylamino)-3-trimethylsilyltetrazole(H-1)[34,35,36].



(H-1)

Heavy metalazides have not found wide application in preparative methods due to their extreme shock sensitivity. However silver azide has been reported to react with trimethylchlorosilane affording TMAS [13].

$$Me_3SiCl + AgN_3 \xrightarrow{Et_2O} Me_3SiN_3 + AgCl \qquad (H\text{-}2)$$

Table 1

Organoazidosilanes: Physical Properties and Preperative Methods

Organoazidosilane	bp(°C/torr)	mp (°C)	n_D(C°)	Prep.Method	% Yield (Ref.)
H_3SiN_3	25.8/760	-81.8	-	G	25 (*37*)
D_3SiN_3	-	-	-	G	- (*37*)
Me_3SiN_3	87/760	−95.1	-	A	- (*11*)
Me_3SiN_3	95-96/760	-	1.4155(20)	B	87 (*35*) - (*24*)
Me_3SiN_3	95-96/760	-	-	B	67 (*16*) 84 (*17*)
Me_3SiN_3	96-96.5/760	-	1.4161 (20)	E	36 - 95 (*28*) 93 (*15*)
Me_3SiN_3	92-93/760	-	-	G/H	62 (*36*)/35 (*35*)
Me_3SiN_3	-	-	-	E-1	40 - 100 (*38*)
Et_3SiN_3	104/95	-	1.4155 (20)	B	- (*24*)
$(n\text{-}Pr)_3SiN_3$	96-97/13	-	1.4468 (23)	A	40 (*39*)
$(n\text{-}Bu)_3SiN_3$	88/0.001	-	1.4522 (22)	B	- (*24*)
$Me_3SiSiMe_2N_3$	47-49/10	-	1.4572 (20)	E	93 (*15*)
$Me_2Si(Cl)N_3$	120/760	-	-	D	- (*19*)
$Me_2Si(NMe_2)N_3$	34-35/20	-	-	B	68 (*96*)

Table 1 (Continued)

Organoazidosilane	bp(°C/torr)	mp(°C)	n_D(C°)	Prep. Method	% Yield (Ref.)
$Me_2Si(NHBu)N_3$	75/17	–	1.4405 (20)	E/F	79/83 (*15*)
$Me_2Si(NHBu)N_3$	75/20	–	1.4409 (20)	E/F	82/100 (*28*)
$Me_2Si(OEt)N_3$	36/18	–	1.4046 (20)	E	79 (*15*)
$Me_2Si(Ph)N_3$	70/0.15	–	–	A	- (*10*)
$Me_2Si(Ph)N_3$	89-90/11	–	1.5191 (20) 1.5189 (20)	E	90 (*15*), 91 (*28*)
	152/6.5	–	1.5745 (25)	B	37 (*44*)
$MePh_2SiN_3$	112/0.4 114/1	–	1.5799 (20)	E/B	90 (*28*)/85 (*15*)
$MePh_2SiN_3$	136-137/1	–	1.5760 (18)	A	36 (*39*)
$MePhSi(C_5H_{11})N_3$	111-113/1.0	–	1.4978 (17)	A	47 (*39*)
$MePhSi(Bu)N_3$	98-99/1.5	–	1.5009 (27)	A	48 (*39*)
$MePhSi(H)N_3$	95/15	–	1.5182 (20)	D	83 (*15*)
$Ph_2Si(H)N_3$	139/2	–	1.5885 (20)	D	88 (*15*)
$Ph_2Si(Cl)N_3$	134-135/0.05	–	1.5838 (20)	H	72 (*15*)
$Ph_2Si(NMe_2)N_3$	144-145/0.05	–	–	B	75 (*96*)
Ph_3SiN_3		81	–	A	90 (*10*), 79 (*12*)

Table 1 (Continued)

Organoazidosilane	bp(°C/torr)	mp(°C)	n_D(C°)	Prep. Method	% Yield (Ref.)
Ph_3SiN_3	-	84 83.5-84.5	-	B	87 (*15*), 58 (*16*)
Ph_3SiN_3	100-105/0.001	83	-	B	- (*24*)
Ph_3SiN_3	-	80	-	D	100 (*19*)
	-	189	-	-	- (*24*)
	-	65-68	-	B	70 (*24*)
$(Me_2N)_3SiN_3$	76/11	-	1.4494 (20)	B	70 (*24*)
$(MeO)_3SiN_3$*	18/4	-	1.3969 (20)	B	70 (*24*)
$MeSi(Cl_2)N_3$	100.5/760	-	-	C	- (*22*)
Diazidosilanes					
$Me_2Si(N_3)_2$	144-145/60	-	-	B	87 (*17*)
$Me_2Si(N_3)_2$	144.3/760	-	-	D/C	100 (*21*), 60 (*20*) (*19*)
$Me_2Si(N_3)_2$	40/40 32/32	-	1.4582	E	85 (*15*), 80 (*28*)
$(MeC)_2Si(N_3)_2$*	18/0.001	-	-	*	- (*24*)

*$2(MeO)_3SiN_3 \longrightarrow (MeO)_4Si + (MeO)_2Si(N_3)_2$

Table 1 (Continued)

Organoazidosilane	bp(°C/torr)	mp(°C)	n_D(C°)	Prep. Method	%Yield (Ref.)
$Me(CH{=}CH_2)Si(N_3)_2$	49-52/19**	–	–	B	53 (*17*)
$MePhSi(N_3)_2$	120-122/22	–	1.5368 (19)	A	56 (*39*)
$MePhSi(N_3)_2$	76/0.15 84/0.20	–	–	B	85 A 85 (*17*)
$Ph_2Si(N_3)_2$	85-90/0.001	–	1.5887 (20)	B	70 (*24*) (*26*)
$Ph_2Si(N_3)_2$	108-110/0.03	–	–	B	63 (*16*), 71 (*17*)
$Ph_2Si(N_3)_2$	126/0.01	–	–	D	
Triazidosilanes					
$MeSi(N_3)_3$	75-78/22	–	–	B	90 (*19*)
$MeSi(N_3)_3$	70/20-exploded	–	–	C	25 (*16*)
$PhSi(N_3)_3$	67-71/0.03	–	–	B	Mixture (*22*)
$PhSi(N_3)_3$	62.5-63.5/0.01	–	–	D	- (*16*)
Miscellaneous Azidosilanes					100 (*22*) (*19*)
$(Me_3Si)_2N\text{-}N_3$	40-42/11	–	–	B	100 (*66*)

The following azidosilanes have been reported spectroscopically (Table 7), but isolation or physical constants were not reported.[32]
$Me_2Si(F)N_3$; $Me_2Si(SMe)N_3$; $Me_2Si(OMe)N_3$; $Me_2Si(NMe_2)N_3$.

** Exploded on heating @ 90°

Reaction of the chlorine in CCl_4 at low temperatures with organoazidosilanes containing the Si-H functionality permits isolation of mixed organochloroazidosilanes [15].

$$R_2SiHN_3 + Cl_2 \xrightarrow[-15^{\circ}]{CCl_4} R_2Si(Cl)N_3 + HCl \qquad \text{(H-3)}$$

PHYSICAL PROPERTIES

Organoazidosilanes are transparent colorless liquids or white crystalline, low-melting solids possessing boiling/melting points higher than the corresponding chlorides and bromides. They are insoluble in water but miscible with all organic solvents [13]. All are sensitive to hydrolysis or solvolysis with protic reagents. The more volatile, lower molecular weight derivatives hydrolize most rapidly, many on contact with atmospheric moisture. Qualitative hydrolysis studies of azidosilanes (aqueous acetone) have indicated that rates are increased in acidic solution as compared to neutral or basic media. Similarly, chlorosilanes were found much less hydrolytically stable than their corresponding azide derivatives [10]. Increased sensitivity toward hydrolysis was also noted if a methyl was substituted for a phenyl in a given compound and when the number of azide groups bound to silicon increases; $3>2>1$ [10,19] Hydrolysis with water produces hydrazoic acid and di- or polysiloxanes depending on the number of hydrolyzeable groups in the starting material.

Organoazidosilanes are the most thermally stable class of covalent azide derivatives presently known. Comparison of the decomposition temperatures of triphenylmethylazide (190°C) and triphenylsilylazide (380°C) indicates the greatest stability achieved through replacement of carbon by silicon in similar molecules. Vapor phase pyrolysis requires temperatures greater than 590°C to cause measureable decomposition of the triphenylazidosilane. Phenyltriazidosilane ($C_6H_5N_9Si$), the molecular formula of which contains 54% nitrogen, refluxes vigorously without nitrogen evolution when heated at 325°C and methyltriazidosilane (containing 74% nitrogen) is stable to 180°C [16]. (Table 2) Greater thermal stability is achieved with phenyl groups bound to silicon.

Table 2

Thermal Stabilities of Azidosilanes and Related Compounds

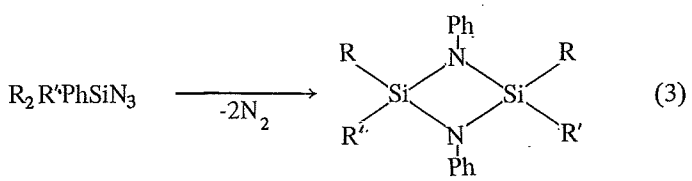
Compound	Temperature (°C)	Ref.
HN_3	290	*73*
H_3SiN_3	25	*37*
$HSi(N_3)_3$	0	*6, 16*
Ph_3SiN_3	380; 400	*16, 25*
Me_3SiN_3	500	*11, 16**.
$Ph_2Si(N_3)_2$	320	*16*
$PhSi(N_3)_3$	325-400	*6, 16*
$MeSi(N_3)_3$	180	*16***
Ph_3CN_3 (1)	180-190	*16*
Ph_3GeN_3 (1)	375	*16*
Ph_3SnN_3 (1)	300	*16*
Ph_3PbN_3 (1)	190-200	*16*

*Vapor phase

**In solvent (quinoline)

(1) Included for purpose of comparison

Reichle[16] has reported that pyrolysis of triphenylazidosilane affords dimeric 1, 1, 2, 3, 3, 4-hexaphenylcyclodisilazane and low molecular weight poly- 1, 1, 2-triphenylsilazane. Dimer formation with phenyl migration from silicon to nitrogen was found on thermolysis of diorganophenylazidosilanes[15,40] (3).



(3)

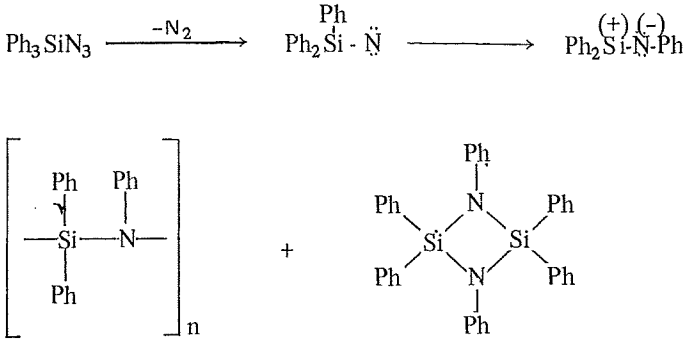
(R=R'=Ph; R=Me, R'=Ph; R=R'Me)

The high thermal stability of organoazidosilanes has been explained on the basis of $(p\rightarrow d)\pi$ interactions in which empty π 3d-orbitals of silicon are able to overlap the filled p-orbitals of the α-nitrogen, forming a dative π-bond between the azide group and silicon [10,16]. Such $(p\rightarrow d)\pi$ interactions have been used previously to explain Si-N bond characteristics and effects on structure in silylamines, silazanes etc.[33,41,42]. The differences and variations in reported stabilities indicate that factors other than $(p\rightarrow d)\pi$ bonding are also important. The difference in electronegativities[43] between the silicon and nitrogen may be contributory to stability but no studies with azidosilanes have yet been conducted.

Generalizations for predicting thermal stability of organometallic azides as given by Thayer may be adapted to organoazidosilanes.[6] They state:(1) the thermal stability will decrease as the number of azides bonded to silicon increases, (2) thermal stability depends on nature of organic group (s) attached, aromatic groups being more stablizing than aliphatic groups, and (3) presence of an electronegative inorganic substituent other than azide will increase thermal stability.

CHEMICAL PROPERTIES AND REACTIONS

Organoazidosilanes possess chemical properties and undergo reactions more analagous to those of organic azides than to most organometallic azide derivatives. Both the organic and silylazides lose a molecule of nitrogen on pyrolysis forming an electron deficient nitrene intermediate. The nitrenes so generated have a lifetime of several microseconds[45] and stabilize by a number of routes. These include dimerization, heterocycleformation (hydrogen abstraction followed by ring closure) and bimolecular insertion into C-H bonds, and heterocycle formation through addition to unsaturated substrates such as olefins[4]. Carbon nitrenes also isomerize to imines whereas corresponding iminosilanes are unstable and have only been detected spectroscopically after photolysis of azidosilanes in argon matrices near $4^{\circ}K$ [46]. As described previously, the thermolysis of triphenylazidosilane (TPAS) proceeds *via* a nitrene intermediate and phenyl migration (4) exactly analogous to thermolysis of triphenylazidomethane.

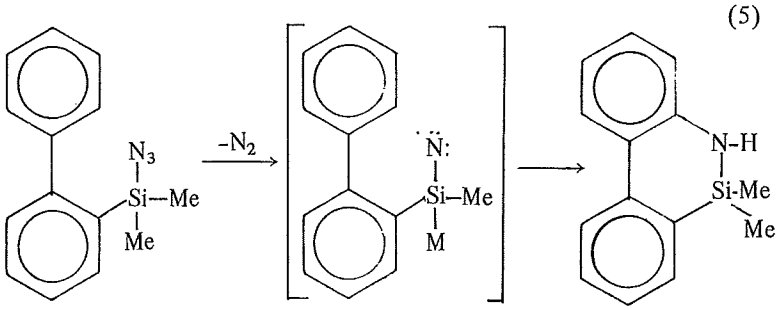


(I) (II)

(where n= 2,3)

Vapor phase pyrolysis of TPAS through a quartz tube heated to ~680°C afforded 47% of crude dimeric product [16].

Heterocycle formation *via* hydrogen abstraction followed by ring closure afforded 10, 10-dimethyl -10,9-silaza-phenanthrene on photolysis of dimethyl(2-biphenyl)azidosilane [44].



(III)

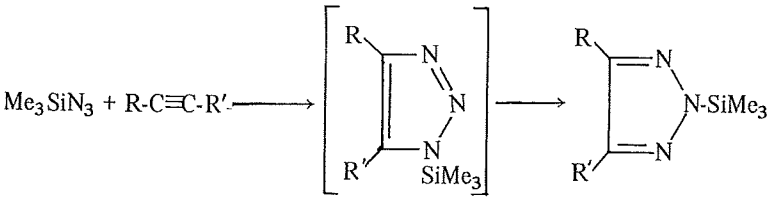
Pyrolysis or similar decomposition of TMAS in a mercury arc produces a volatile mixture of hydrogen, nitrogen, methane, ethane, ethylene, acetylene, hydrogen cyanide, hydrozoic acid, ammonium azide and a non-volatile polymer [11].

Photolysis of organoazidosilanes has been investigated in only a cursory manner and no detailed studies have yet been conducted. Early reports indicate that prolonged ultraviolet irradiation at 30° causes complete decomposition of TPAS[10,12] and irradiation (2537 Å) in cyclo-

hexane for 19 hours produced partial decomposition but no pure products could be isolated. Photolysis of TMAS produced nitrogen, a trace of hydrogen and uncharacterized non-volatile oil [16].

Heterocycle formation through 1,3-cycloaddition of azidosilanes to unsaturated substrates gives promise of further synthetic utility. Birkofer and Wegner first demonstrated azidosilane cycloaddition reactions by reacting TMAS with substituted acetylenes in an autoclave at 120-150°C for 10 - 20 hours (6). Distillation afforded products in generally good yields[47,48] (Table 3).

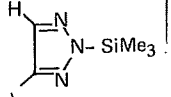
(6)



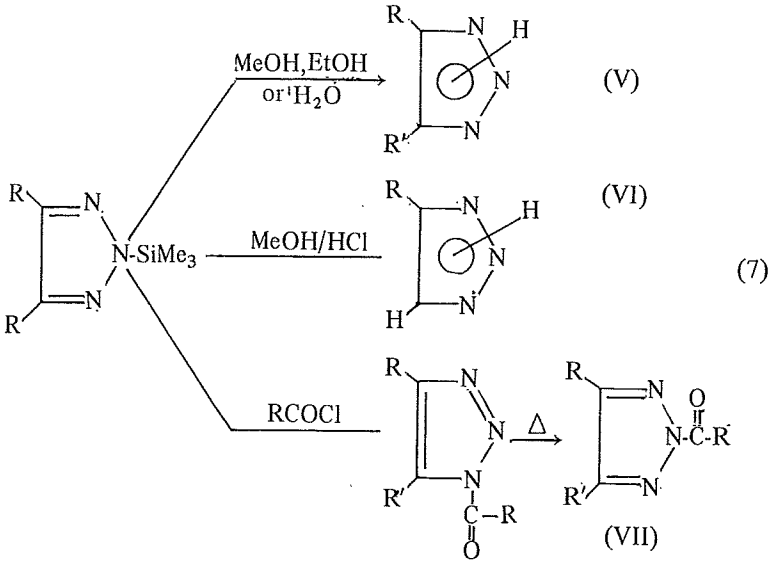
(IV)

Table 3

Compounds Prepared Through Reaction (6)

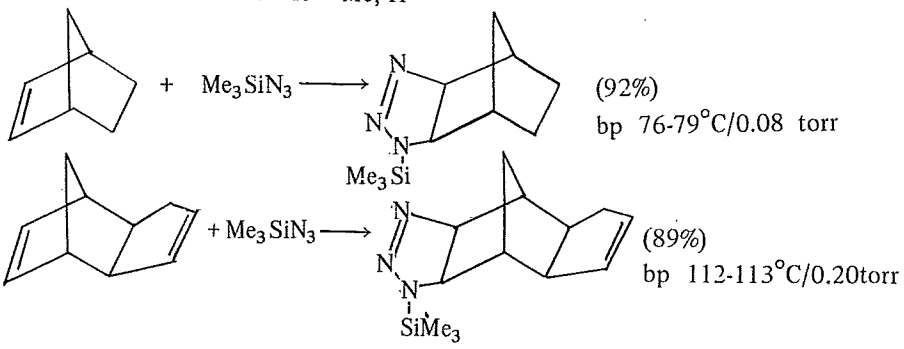
R	R'	bp(°C/torr)	Yield	n_D^{25}
Me_3Si	Me_3Si	123/21	66	-
Ph	Me_3Si	85/0.05	87	-
Me	Me	65-66/13	78-87	1.4537
n=Pr	H	77-78/13	86	1.4515
n-Bu	H	92-94/13	86	1.4527
Ph	Ph	-	85-90	-
$-(CH_2)_2-C\equiv CH$	H	102/14	40-50	1.4742
				
$-(CH_2)_2$	H	111/0.04	77	1.4852
CO_2CH_3	$-CO_2CH_3$	141/0.01[39-41]	85	-

N-alkyl and N-aryl triazoles have been obtained from similar additions of organic azides to acetylene derivatives [3,4,8,49,51,54,55]. In contrast to these however, 1,2,3-triazole derivatives containing both C- and N- trimethylsilyl substituents can be selectively desilylated.[27] (Treatment of the silylated derivative with water or methanol cleaves Si-N bonds and methanolic HCl cleaves both Si-N and Si-C bonds [48,53]. The H- substituted materials are isolated as products in both cases.) N-acyl-1,2,3-triazoles are obtained through Si-N cleavage with acyl chlorides. (7) Spontaneous migration of the trimethylsilyl moiety observed in 1,2,3-triazoles could be thermally induced in acyl derivatives [47].

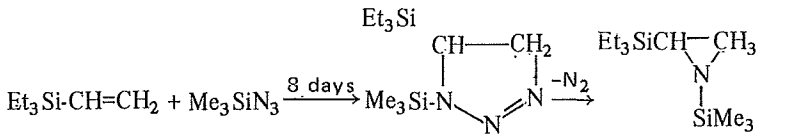


(7)

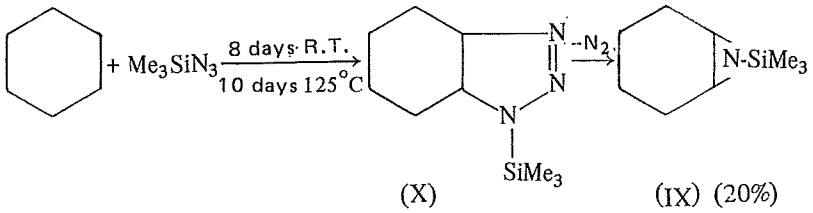
Where V: R and R′ = all compounds listed in Table 3
VI: R = Me_3Si; R′ = C_6H_5
VII: R = R′ = Me, H



Cycloaddition of TMAS with various norbornene compounds produced the corresponding N-trimethylsilyl-Δ^2-triazole derivatives. No migration of the trimethylsilyl group was expected or observed. In contrast to the thermal instability of corresponding norbornene-organic azide adducts which decompose with loss of nitrogen on heating in benzene or toluene [51,54], the norbornene-TMAS adducts were recovered unchanged after 10-12 hours in refluxing decalin [50]. Similar stability was not found for N-trimethylsilyl-Δ^2-triazoles formed from TMAS and other alkenes. Heating under conditions similar to those employed for organic azides resulted in loss of nitrogen and aziridine formation [15].



(VIII) (IX) (13%)
bp 58-60°C/15 torr



(X) (IX) (20%)
bp 84-85°C/15torr

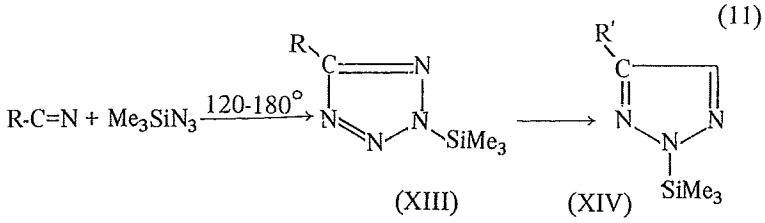
The reaction of olefins and azidosilanes in the presence of lead tetracetate did not afford cycloaddition products, but instead produced 1.2-diazido- and 1-azido-2-acetoxy compounds. A lead azidoacetate intermediate is postulated as interacting through oxidative transfer with the olefin substrate.[60]

$$Pb(OAc)_4 + Me_3SiN_3 \longrightarrow \underset{(XII)}{\left[Pb(OAc)_{4-n}(N_3)_n\right]} \qquad (10)$$

$$(XII) + PhCH{=}CHPh \longrightarrow \underset{(42\%)}{PhCHCHPh} + \underset{(42\%)}{PhCHCHPh} + PhCN + PhCHO + (PhC)_2O$$

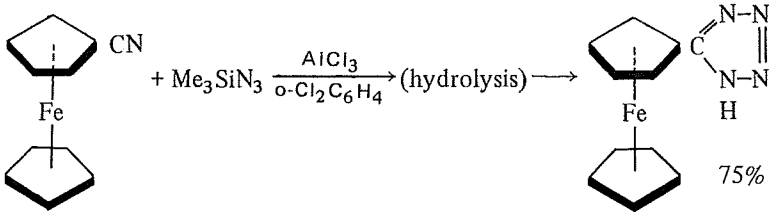
Cycloaddition reactions of azidosilanes with nitriles have also been investigated. Heating TMAS with an appropriate alkyl or aryl nitrile affords the corresponding 5-alkyl/aryl-2-trimethylsilyltetrazole in poor to good yields depending on substituent [15] (11). Triphenylazidosilane underwent no reaction with benzonitrile thermally (200°C, 20 hours) or photolytically (2537Å, cyclohexane) [16]. Similarly, 5-ferrocenyltetrazole was prepared by refluxing cyanoferrocene in o-dichlorobenzene with TMAS and anhydrous aluminum chloride (12). Despite the absence of reaction without $AlCl_3$, aluminum azide derivatives are not believed to be the azidizing intermediates [52].

(11)



(XIII) (XIV)

R	bp (°C/torr)	Yield (%)	n_D^{20}
XIVa $PhCH_2$-	122-125/1.0	40	1.5251
XIVb Ph-	120-122/1.0	80	1.5306
XIVc Et-	185-188/760	26	1.4475



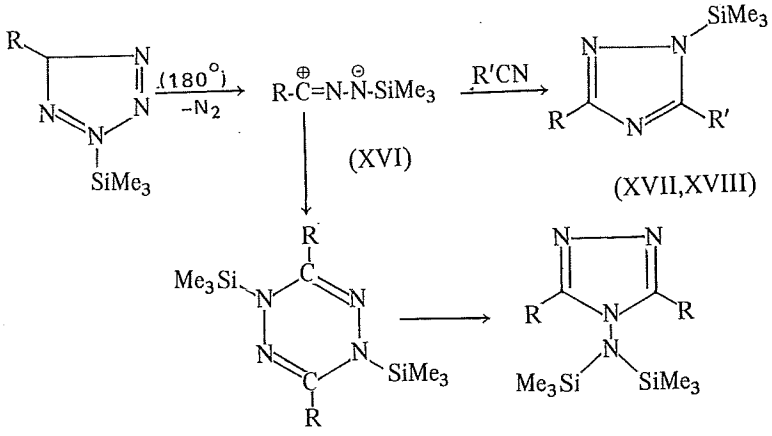
(12)

(XV) mp 264-265°C.

Reactions of 4-organopyridine or benzonitrile with TMAS and dimethyl- and diphenyldiazidosilanes afforded mixtures of tetrazoles, 3,5-diaryl- 1,2,4-triazoles and 3,6-diaryl-1,2,4,5-tetrazines which resulted from decomposition of the thermally unstable silylated tetrazole [52].

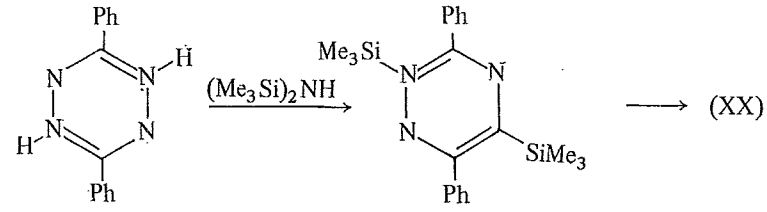
In the case of benzonitrile, the spectrum of products obtained was identical to those isolated after photolysis of 5-phenyltetrazole[56]. Isolation of a 1,2-dihydro-sym-tetrazine derivative reinforced the nitrilimine intermediate proposed for thermalysis of 5-substituted tetrazoles and 5-substituted silylated tetrazoles by Huisgen[57,58] and Birkofer[35,36], respectively. The latter has observed that silylated tetrazoles decompose as readily as correspondingly substituted phenyltetrazoles, indicating that electron withdrawal by the trimethylsilyl group favors decomposition in the same manner as does the phenyl group[27]. Ettenhuber and Ruhlmann[15] thermolyzed the cycloaddition products from (11) and obtained results similar to those of Birkofer, Ritter and Richter[35].

(13)

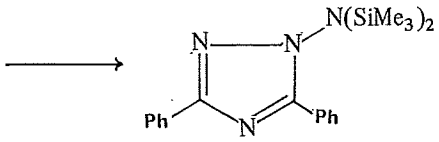


XVII R = R′ = Ph; bp 205-207°C/0.5torr (56%)
XVIII R = C_6H_5-CH_2, R′ = Ph; bp 209-212°C/1.0torr (51%)
XIX R = Ph (isolated as hydrolyzed prod.)
XX R = Ph; bp 200-205°C1.0torr; mp 98° C (81%)
XXI R = $C_6H_5CH_2$; bp 200-204°C/1.0torr(–)

Birkofer prepared intermediate (XIX) and demonstrated conversion to(XX)and further rearrangement to 1-(bistrimethylsilylamino)-3,5-diphenyl-1,2,4-tetrazole[35] (XXII).



(XIX)

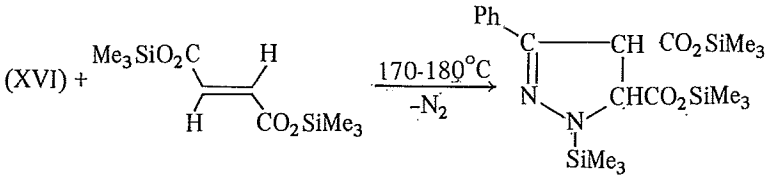


(XXII)

bp 180-185°C/0.1torr(60%)
mp 96°C (also 98°C)

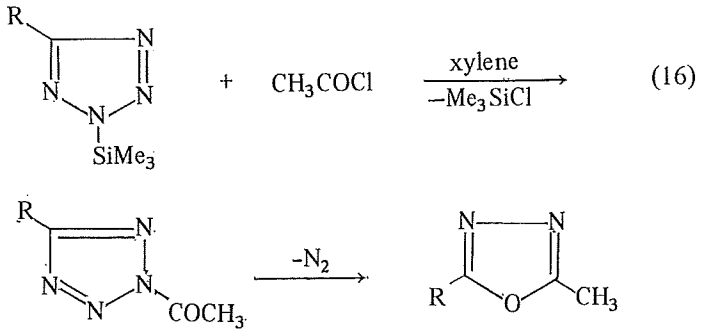
Nitrilimine intermediates(XVI)may be trapped by inclusion of 1,3-dipolarophiles such as bis(trimethylsilyl) fumarate into reaction mixtures [27,35].

(15)



(XXIII)bp 145-150°C/0.2torr (66%)

Silylated tetrazoles prepared *via* silylazides and organonitriles can be reacted readily with acylchlorides in a fashion analogous to triazoles (7). The resulting 1-acyltetrazoles rearrange with loss of nitrogen to 1,3,4-oxadiazoles [15].



(16)

(XXIV) R=C_6H_5; mp 65-66°C (87%)
(XXV) R=$PhCH_2$; bp 163-165°C/12torr (84%)

Azidosilanes undergo 1,3-cycloaddition reactions with isocyanates to produce moisture sensitive 3-silyl-4-organo-5-tetrazolinones (17). Preliminary evidence indicates the reactions are reversible at high temperatures [59].

A similar reaction has recently been reported in which carbonyl azides react with alkylisocyanates affording heterocycles [72].

(17)

(XXVI) R=C_6H_5; bp 114-116°C/0.1torr (17%)
(XXVII) R=Bu; bp 78-79°C/0.025torr (9%)
(XXVIII) OCN-  -Me undistillable oil (90%)

N-silylated benzanilides have been prepared by heating azidosilanes and benzophenone at 250-270°C [15]. A N-diazonium intermediate initially formed decomposes with loss of nitrogen and phenyl migration.

Reaction between TMAS and aldehydes or epoxides in the presence of a Lewis type acid have produced α-trimethylsiloxy alkylazides and β-trimethylsiloxy alkylazides, respectively. Azidozinc intermediates are not believed involved (18).

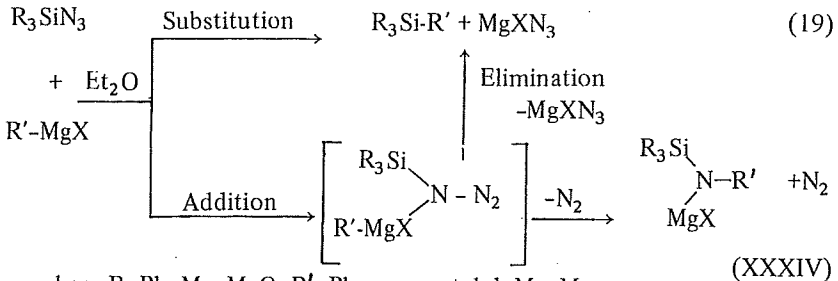
$$RCHO + Me_3SiN_3 \xrightarrow{ZnCl_2} RCH(OSiMe_3)(N_3) \quad (18)$$

(XXIX-XXXIII)

Compound	R	bp(°C/torr)	%
(XXIX)	n-C_3H_7	65	73
(XXX)	n-C_4H_9	84	71
(XXXI)	n-C_5H_{11}	97	73
(XXXII)	Me_2CH	59.5	77
(XXXIII)	t-C_4H_9	66.5	78

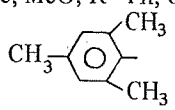
Thermolysis of the products afforded N-trimethylsilylamides or N-trimethylsilyl-N-alkyl formamide derivatives in quantitative yields [61].

In contrast to organic azides, triorganoazidosilanes have been reacted with aryl Grignard reagents. The products, are isolated from hydrolyzed reaction mixtures after loss of N_2 *via* thermolysis. This reaction shows promise as a synthetic procedure for conversion of arylhalides to arylamines [62,68]. Studies based upon product yield (dependent upon reactant concentration, reaction medium and type of reactant) indicate that azidosilanes react with both the monomeric and dimeric species of Grignard that are present in equilibrium with each other. The monomeric form of the organomagnesium halide behaves as a Lewis-base, which reacts in a nucleophilic substitution of the azide by the organyl group (19).The dimeric form however, acts as a Lewis-acid, forming a complex with azidosilane. After elimination of R'MgX, the resultant thermally instable adduct decomposes into R_3SiR' and $MgXN_3$ and into $R_3SiN(R')MgX$ and N_2 [63].

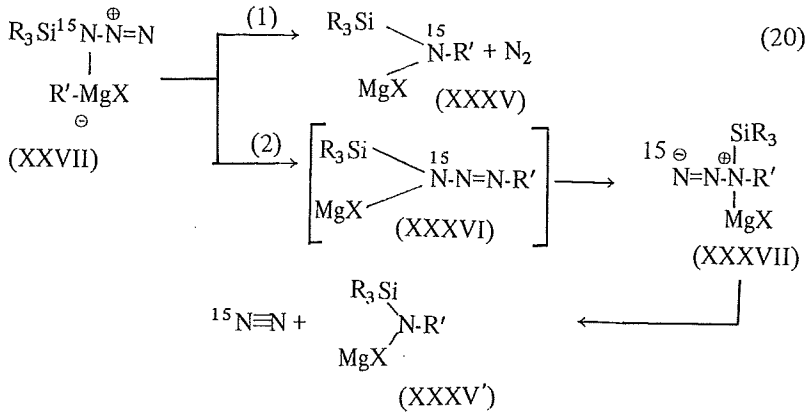


(19)

(XXXIV)

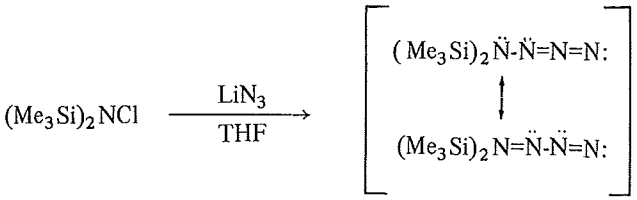
where R=Ph, Me, MeO; R'=Ph, o, m, p-tolyl, Me, Mes, x=Br, I. (Mes = ).

The adducts (XXXIV) were shown to decompose *via* two pathways by employing ^{15}N: (1) migration of R′ to the α-nitrogen of the azide group with synchronous elimination of N_2; (2) migration of R′ to the γ-nitrogen of the azide group with formation of non-isolable triazenes (XXXVI) which decompose to products (XXXV)[64].



(20)

Triazenes (XXXVI) have been involved as intermediates previously, especially in reactions with phosphines[65]. Recently a stable silylated tetrazdiene has been synthesized and isolated. The product may also be considered an N-azidohexamethyldisilazane derivative [66].



(21)

(XXXVIII)
bp= 41-43°C/11 torr

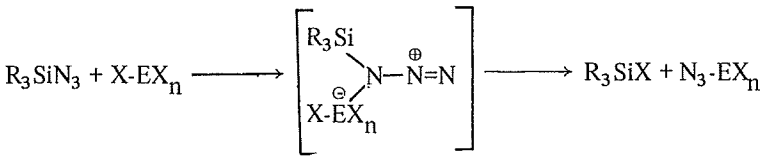
A similar reaction with the corresponding germanium hydride affords the mixed derivative $Ph_3Si\text{-}NHGePh_3$, but with triphenylstannane fails to give products containing the Sn-N bond due to secondary reactions [67]. Mixtures of triphenylsilane and TPAS react when heated to produce hexaphenyldisilazane.

$$Ph_3SiN_3 + Ph_3MH \xrightarrow{100\text{-}240^\circ C} Ph_3SiNH\text{-}R + N_2$$

M=Si, R=Ph_3Si; mp 174°C (59%)	(XXXIX)	(22)
M=Ge, R=Ph_3Ge; mp 163°C (80%)	(XL)	
M=Sn, R=H mp 59°C(31%)	(XLI)	

Lewis acids react with azidosilanes at the α-nitrogen to produce N-diazonium, 1:1 adducts. Dependent on the nature of the Lewis acid, the adducts may be stable and isolatable or decompose rapidly to silyl-halide and azide salts[68].

(23)



R=alkyl, aryl. E=Element

Isolatable adducts are white, crystalline compounds soluble in organic solvents but decomposed by acetone, water and alcohols. Some exhibit remarkable thermal stability[69]. More recent studies indicate the reactions to be more complex than originally believed.

More common is reaction of azidosilanes with Lewis acids which results in cleavage of the silicon-nitrogen bond and formation of a new azide-Lewis acid bond[83]. By this method Paetzold and Hansen[84] prepared dimethylborazide[24] and Wiberg *et al.*[85] successfully azidized methylaluminum iodides (25-27).

$$(n\text{-}C_4H_9)_3SiN_3 + Me_2BBr \longrightarrow Me_2BN_3(60\%) + (n\text{-}C_4H_9)SiBr \quad (24)$$

$$Me_3SiN_3 + Me_2AlI \xrightarrow[6\ hrs.]{20^\circ} MeAlIN_3 + Me_4Si \quad (25)$$

$$Me_3SiN_3 + MeAlIN_3 \xrightarrow[20^\circ C/12\ hrs.]{} MeAl(N_3)_2 + Me_3SiI \quad (26)$$

$$Ph_3SiN_3 + Me_2AlI \xrightarrow[0^\circ C/2\ hrs.]{} Me_2AlN_3 + Ph_3SiI \quad (27)$$

A comprehensive series of papers by Wiberg and Schmid on reactions of TPAS and TMAS with tin tetrachloride and antimony penta-

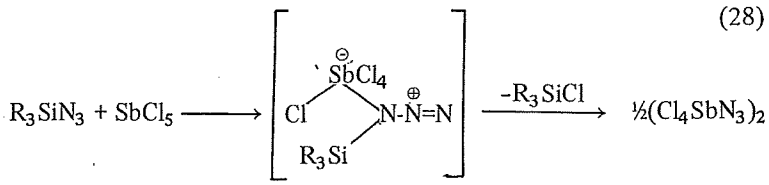
chloride[71, 75](28) have shown that decomposition of the initial N-diazonium adducts produces dimeric products (Table 4).

Table 4

Azidosilane - Lewis Acid Adducts

Azidosilane	Lewis Acid	Products (Yield)	Ref.
H_3SiN_3	BF_3	SiH_4, H_3SiF	*35*
Me_3SiN_3	BCl_3	Me_3SiCl, $(Cl_2BN_3)_3$	*68, 76*
Me_3SiN_3	BBr	$Me_3SiN_3 \cdot BBr_3$	*69*
Me_3SiN_3	BBr_3	Me_3SiBr, $(Br_2BN_3)_3$	*76*
Me_3SiN_3	$SbCl_5$	$Me_3SiN_3 \cdot SbCl_5$(65%)	*69*
Me_3SiN_3	SbF_5	Me_3SiF, $(F_4SbN_3)_2$	*68, 77*
Me_3SiN_3	$SbCl_5$	R_3SiCl, $(Cl_4SbN_3)_2$ (99%)	*71, 75*
Me_3SiN_3	$TiCl_4$	Me_3SiCl, $Cl_2Ti(N_3)_2$	*74*
Me_3SiN_3	$TiBr_4$	Me_3SiBr, $Br_2Ti(N_3)_2$	*74*
Me_3SiN_3	$SnCl_4$	$Me_3SiN_3 \cdot SnCl_4$ (38%)	*69*
Me_3SiN_3	$SnCl_4$	Me_3SiCl, $Cl_2Sn(N_3)_2$	*74*
Me_3SiN_3	Et_3Al	$Me_3SiN_3 \cdot AlEt_3$	*78*
$MePh_2SiN_3$	BBr_3	$MePh_2SiN_3 \cdot BBr_3$	*69*
Ph_3SiN_3	BBr_3	$Ph_3SiN_3 \cdot BBr_3$	*69*
Ph_3SiN_3	$SnCl_4$	$Ph_3SiN_3 \cdot SnCl_4$(a)	*69*
Ph_3SiN_3	$SbCl_5$	Ph_3SiCl, $(Cl_4SbN_3)_2$ (60%)	*71, 75*
Ph_3SiN_3	Et_3OBF_4	Ph_3SiF, EtN_3, $Et_2O \cdot BF_3$	*70*
Ph_3SiN_3	$ClAlMe_2$	Ph_3SiCl, $(Me_2AlN_3)_3$	*78*

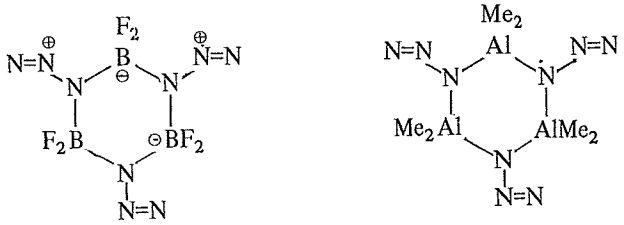
(a) not isolated



(28)

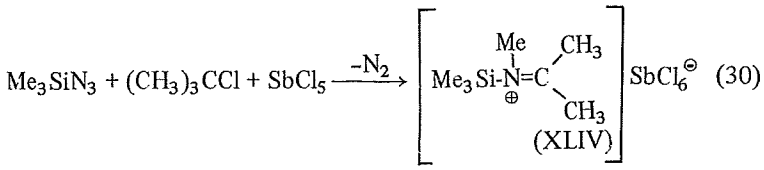
(XLII) (XLIII)

Trimeric species (29) have been isolated in reactions of triorganoazidosilanes with boron trifluoride and dimethylaluminum [78].



(29)

Ettenhuber and Ruhlmann formed an adduct at -75°C in methylene chloride by reaction of TMAS, tert.-butylchloride and antimony pentachloride. Warming above -60°C caused loss of nitrogen and formation of the interesting 2-(trimethylsilylmethylimonio) propane hexachloroantimoniate [15] (XLIV).



(30)

Adducts of Me_3Ga and Me_3Al with N-silylphosphineimines resulting from reaction of azidosilanes with trialkylphosphine have also been reported [79] (See Table 5).

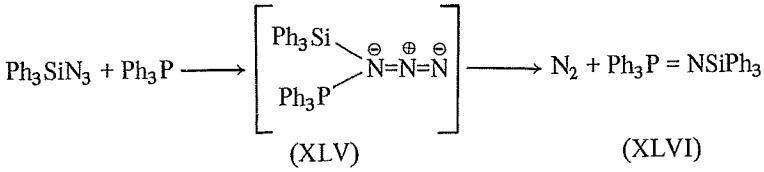
As with most organic azides, azidosilanes react with tertiaryphosphines to give nitrogen and phosphineimines.

$$R_nSi(N_3)_{4-n} + (4\text{-}n)\ R_3P \xrightarrow{50\text{-}150^\circ C} R_nSi(N{=}PR_3)_{4-n} + (4\text{-}n)N_2 \quad (31)$$

where R= alkyl, aryl

Triphenylphosphine reacts with TPAS forming a stable complex structurally not unlike Lewis acid adducts, which decomposes on warming to nitrogen and N-(triphenylsilyl)triphenylphosphineimine[12,16,25,26,85] (XLVI).

(32)



(XLV) (XLVI)

Table 5

N-Silylphosphineimines: Reactions of Organoazidosilanes With Tertiary Phosphines and Phosphorus Derivatives

Azide	Phosphine	Phosphineimine	Phys. Constants	Yield	Ref.
Me_3SiN_3	Ph_3P	$Ph_3P{=}NSiMe_3$	mp 76-77°C; bp 170-171°C/0.06 torr	97%	*35*
Me_3SiN_3	Et_3P	$Et_3P{=}NSiMe_3$	bp 89.5°C/11 torr	96%	*80*
Me_3SiN_3	$(n\text{-}Pr)_3P$	$(n\text{-}Pr)_3{=}NSiMe_3$	bp 119°C/n	98%	*80*
Me_3SiN_3	$(n\text{-}Bu)_3P$	$(n\text{-}Bu)_3P{=}NSiMe_3$	bp 149°C/11, torr 94°C/0.10 torr	98%	*80*
Ph_3SiN_3	Ph_3P	$Ph_3P{=}NSiMe_3$	mp 216-17°C, 213[2]-15°C, 215[2]-16°C	50%	*16, 25, 26*
Ph_3SiN_3	Ph_3P	$Ph_3P{\cdot}Ph_3SiN_3$	dec. 30°C	39%	*12*
Ph_3SiN_3	Ph_2PH	$Ph_3SiNHPPh_2{=}NSiPh_3$	mp 161-162°C	45%	*81*
Ph_3SiN_3	Ph_2PH	$Ph_3SiNHPPh_2$	mp 148-149°C	19%	*81*
Ph_3SiN_3	Ph_2PPPh_2	$Ph_3SiN{=}P(Ph_2)P(Ph_2){=}NSiPh_3$	mp 236-238°C	93%	*81*
$Ph_2Si(N_3)_2$	Ph_3P	$Ph_2Si(N{=}PPh_3)_2$	mp 194-195, 190-191, 194-195°C	50%	*16, 26, 17*
$PhSi(N_3)_3$	Ph_3P	$PhSi(N{=}PPh_3)_3$	mp 225-226°C		*16*

Table 5 (continued)

Azide	Phosphine	Phosphineimine	Phys. Constants	Yield	Ref.
$Mes_2Si(N_3)_2$*	Ph_3P	$MesSi(N{=}PPh_3)N_3$	mp 189°C	-	*24*
$Me_2Si(N_3)$	Me_3P	$Me_2Si(N{=}PMe_3)N_3$	bp 40°C/0.3torr	94%	*79*
$Me_2Si(N_3)_2$	Ph_3P	$Me_2Si(N{=}PPh_3)_2$	mp 153-155°C	87%	*17*
$Me_2Si(N_3)_2$	Me_3P	$Me_2Si(N{=}PMe_3)_2$	mp 24-25°C; bp 77-78°C/0.3 torr	90%	*79*
Me_3SiN_3	Ph_2PCl	$(Ph_2PN)_3$	mp 226-227°C	68%	*82*
Me_3SiN_3	$Ph_2P(O)Cl$	$Ph_2P(O)N_3$	bp 137-140°C/0.05torr	100%	*89*
Ph_3SiN_3	Ph_2PCl	$(Ph_2PN)_3$	mp 226-227°C	91%	*82*
H_3SiN_3	Et_3P	$SiH_4 + Et_3P$		-	*37*
$Mes_2Si(N_3)_2$*	Ph_3P	$Mes_2Si(N{=}PPh_3)N_3$	mp 189°C	-	*24*

* Mes = mesityl

Isolation of the intermediate adduct is similar to reactions of a very few organic azides such as triphenylmethylazide that give a stable complex with triphenylphosphine and which cannot be converted to the phosphineimine.

$$Ph_3C\text{-}N_3 + Ph_3P \longrightarrow Ph_3C\text{-}N{=}N\text{-}N{=}PPh_3 \qquad (33)$$

(XLVII)

Infrared studies suggest a linear structure based on absence of the asymmetric stretching frequency of the azide [86]. The TPAS ·triphenylphosphine adduct exhibits this absorption at 2018 cm^{-1}, in good agreement with the suggested structure (XLV), and is the first example of a complex of this structure type being isolated. Stability is attributed to extensive π-electron delocalization from phosphorus through nitrogen to silicon [12].

N-silylsubstituted phosphineimines are generally prepared by heating (50-120°C) equimolar quantities of reactants near or in solutions of benzene or toluene. Loss of nitrogen during the course of the reaction has been shown not to follow first order kinetics [25]. Mono- di, and trisubstituted silanes have been prepared by reaction of mono-, di- and triazidosilanes with phosphines. Mixed derivatives are obtained through adjustment of reactant ratios (Table 5).

A novel reaction of azidosilanes involves formation of phosphineimine derivatives from tetraphenyldiphosphine and diphenylphosphine [81]. Tetraphenyldiphosphine was reacted with TPAS in the first published report on the reactivity of azides toward diphosphines, which are known to be prone to rearrangements originating in the breaking of the phosphorus-phosphorus bond [88]. The diphosphineimine was the only product isolated from the reaction mixture.

(34)

$$Ph_3PN_3 + Ph_2P\text{-}PPh_2 \xrightarrow[80\text{-}115^\circ/14\ \text{days}]{C_6H_6} Ph_3SiN{=}P(Ph)\text{-}P(Ph){=}N\text{-}SiPh_3$$

(XLVIII)93% mp 236-238°C

Diphenylphosphine reacts with TPAS slowly to give a P(III) monoadduct which then reacts rapidly with additional TPAS to the oxidized P(V) adduct (L).

(35)

$$Ph_3SiN_3 + Ph_2PH \longrightarrow Ph_3SiNHPPh_2 \longrightarrow Ph_3SiNHP(Ph)=NSiPh_3$$

(XLIX) mp 148-149°C(19%)

(L) mp 161-162°C(45%)

The reactivity of the Si-N bond in N-silylated phosphineimines have made them attractive as synthetic intermediates. Birkofer and Kim[80] have prepared triaryl and trialkyl phosphineimines from the corresponding trimethylsilyl derivative by reaction with alcohol [27,80].

$$R_3P=NSiMe_3 \xrightarrow[R'OH]{} R_3P=NH + Me_3SiOR' \qquad (36)$$

(L) R′ = CH_3, R = Et; bp 94°C/11torr (89%)
(LI) R′ = CH_3, R = n-Pr; bp 129°C/11torr (86%)
(LII) R′ = CH_3, R = nBu; bp 104°C/0.1torr(87%)
(LIII) R′ = i-Pe, R = Ph; 127.5°C

Triorganophosphineimines of the type prepared above have been lithiated by Schmidbauer and Jonas and serve as intermediates in the preparation of organometallic phosphineimines [90].

$$R_3P=NH + R'Li \xrightarrow{Et_2O} R_3P=NLi + RH \qquad (37)$$

R=Me, et, Ph R'=Me (60-70%)

Noth *et al.* have reported the replacement of the trimethylsilyl moiety of N-(trimethylsilyl)triphenylphosphineimine by reaction with diphenylchlorophosphine [87] (38).

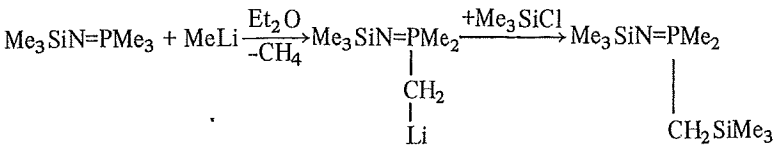
$$Ph_3P=NSiMe_3 + Ph_2PCl \longrightarrow Ph_3P=NPPh_2 + Me_3SiCl \qquad (38)$$

(LIV)

Cleavage of the N-trimethylsilyl group from trialkyl phosphineimines could not be effected with organolithium reagents. Instead, pro-

ton abstraction from phosphorus alkyl groups occurred. Treatment with trimethylchlorosilane allowed isolation of the silyl derivative [90](LV).

(39)

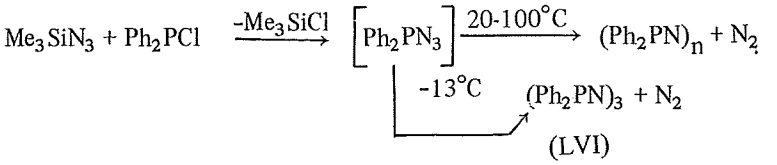


(LV) 79%; bp 93-94°C/11torr

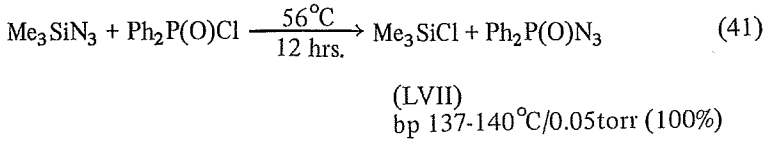
In contrast to the formation of phosphineimines in the reaction of azidosilanes with triorganophosphines, the analogous reaction with chlorophosphines produces azidophosphine intermediates which decompose to phosphoronitrilic materials and nitrogen. The rate of exchange of chlorine on phosphorus with an azido group increases with the extent of phenyl substitution on the trivalent phosphorus atom: $PCl_3 < PhPCl_2 < Ph_2PCl$.

The course of the reaction was also found to be dependent on solvent, temperature and concentration [82]. An example is the reaction of TMAS with diphenylchlorophosphine (40).

(40)



Diphenylphosphinylazide is obtained in quantitative yield from TMAS and diphenylphosphenylchloride [89].



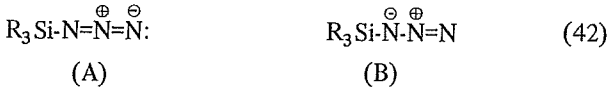
(LVII)
bp 137-140°C/0.05torr (100%)

SPECTROSCOPY

Infrared spectra

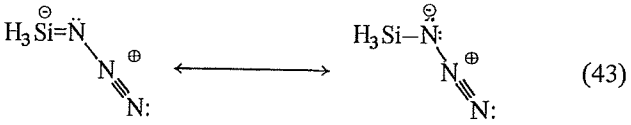
The azide group when bonded to silicon gives rise to an asymmetric stretching bond near 2100 cm^{-1}, a symmetric stretching band near 1300 cm^{-1}. Other possible bonding or stretching absorption of the azide group occur at too low a frequency, are too weak or have not been reported, and are therefore not considered here.[6] The band attributed to Si-N_3 stretching occurs near 520-570 cm^{-1} [24,37].

The asymmetric stretching vibration is usually the strongest in the spectra and occurs at higher frequency than that observed for covalent organic azides,[91] ionic azides (KN_3,2040 cm^{-1} ; NH_4N_3,2050 cm^{-1})[92] and even other organometallic azides [12,13,93]. The higher than predicted frequency is attributed to dative π-bonding between silicon and nitrogen which would be expected to increase the contribution of form (B)to the azide resonance hybrid.Increased contribution from(B)should lead to an enhancement of the asymmetric frequency [12].



(A) (B) (42)

High resolution study of the bands associated with SiH and SiD modes in the molecules H_3SiN_3 and D_3SiN_3 revealed no traces of rotational detail, indicating the molecules are bent with substantial barriers to internal rotation. A non-linear structure does not rule out (p→d)π overlap between silicon and nitrogen [37].



(43)

A linear dependence of the asymmetric azide absorption on the electronegativities of various silyl groups has been demonstrated by Ettenhuber and Ruhlmann[15] and Wiberg and Neruda [24].

Ultraviolet spectra

A limited amount of study has been directed toward the ultraviolet spectra of azidosilanes leaving a large number of compounds yet to be

Table 6

Infrared Frequencies (in cm^{-1}) for Azidosilanes

Compound	$\nu_s N_3$	$\nu_{as} N_3$	δN_3	νSi-N	Ref.
H_3SiN_3	2170	1325	681	578	*37*
D_3SiN_3	2172	1324	687	568	*37*
Me_3SiN_3	2131	1332	685	880 (?)	*13*
Me_3SiN_3	2139	1324	584	532	*24*
Me_3GeN_3*	2103	1286	675	796 (?)	*13*
Me_3SnN_3*	2045	1286	665	—	*13*
Me_3PbN_3*	2034	1279	655	—	*13*
Et_3SiN_3	2136	1320	580	528	*24*
Et_3SiN_3	2136	1324	679	—	*6*
Bu_3SiN_3	2138	1319	580	544	*24*
$(CH_3)_5Si_2N_3$	2128	1305	657	—	*6*
$(CH_3)_5Si_2N_3$	2132	—	—	—	*15*
$Me_2Si(NHC_4H_9)N_3$	2140	—	—	—	*15, 28*
Me_2PhSiN_3	2120	—	—	—	*15*
$Me_2EtO)SiN_3$	2132	—	—	—	*15*
$MePhSiHN_3$	2140	—	—	—	*15*
Ph_2SiClN_3	2150	—	—	—	*15*
Ph_2SiHN_3	2145	—	—	—	*15*
Ph_3SiN_3	2149	1308	660	—	*12*
Ph_3SiN_3	2145	1316	665	572	*24*
Ph_3CN_3*	2110	1261	666	—	*12*
Ph_3GeN_3*	2100	**	660	—	*12*
Ph_3SnN_3*	2093	**	658	—	*12*
Ph_3PbN_3*	2046	1261	655	—	*12*
$Ph_2(Me)SiN_3$	2123	—	—	—	*15*
$Mes_2(CH_3)SiN_3$	2141	1318	544	532	*24*

* Included for purpose of comparison.

** masked or missing – not reported.

Table 6 (Continued)

Compound	$\nu_s N_3$	$\nu_{as} N_3$	δN_3	νSi-N	Ref.
$Mes_2Si(NPPh_3)N_3$	2134	1322	—	—	*24*
$(Me_2N)_3SiN_3$	2137	1333	584	539	*24*
$(MeO)_3SiN_3$	2169	1344	664	570	*24*
$Me_2Si(N_3)_2$	2146	1322	—	—	*20, 21*
$Me_2Si(N_3)_2$	2150	—	—	—	*15, 28*
$MePhSi(N_3)_2$	2150	1300-1350	—	—	*39*
$MePhSi(C_4H_9)N_3$	2150	1283-1300	—	—	*39*
$MePhSi(C_5H_{11})N_3$	2155	1300-1316	—	—	*39*
$MePh_2SiN_3$	2130	1300-1350	—	—	*39*
Pr_3SiN_3	2150	1335	—	—	*39*
$Me(H_2C{=}CH)Si(N_3)_2$	2170	1316	—	—	*96*
$Me(H_2C{=}CH)Si(NMe_2)N_3$	2175	1325	700	—	*96*
Me_3SiN_3	2140	1329	690	—	*96*
$Me_2Si(N_3)_2$	2162	1319	699	—	*96*
$Ph_2Si(N_3)_2$	2150	1317	695	—	*96*
$Me_2Si(NMe_2)N_3$	2150	1310	690	—	*96*
$Ph_2Si(NMe_2)N_3$	2180	1320	700	—	*96*

explored. A study of organometallic azides showed TMAS to exhibit two bonds in the accessible portion of the ultraviolet at 396nm (ϵ 23) and 472nm (ϵ 252) in acetonitrile. Small shifts were obtained in ether and isoctane solvents [13]. These absorptions have been assigned $\pi'' \rightarrow {}''\pi^*$ and $sp_x \rightarrow \pi y^*$ transitions, respectively. Compared to organic azides which show two bands at approximately 348nm (ϵ 24) and 460 nm ($\epsilon \sim 500$),[93] the $sp_x \rightarrow \pi y^*$ transition remains largely unchanged whereas the $\pi y \rightarrow \pi x^*$ transition is shifted toward higher energies. Electron-releasing substituents such as silicon would be expected to decrease the energy of transition through inductive effects. This anamoly has been explained on the basis of dative π-bonding which is greater than the opposing inductive effects and results in increased transition energies[13]. Similar effects of d-orbitals on energy levels have been noted in α-silyl

ketones [13,94]. The ultraviolet spectrum of azidosilane (H_3SiN_3) vapor has been reported to exhibit only one peak at 211 nm (ϵ 25) [37].

It is readily apparent that a minimum amount of work has been directed toward the ultraviolet spectra of azidosilanes. With perhaps more study a better understanding of the silicon-azide band and the part played by (p→d)π bonding might be realized.

Microwave spectra

Microwave studies of TMAS[13] and azidosilane[37,37a] show the heavy atom skeletons of both molecules to be non-linear (asymmetric top molecules). The corresponding isoelectronic silyl isocyanate is believed to have a linear skeleton [37].

NMR spectroscopy

Muller and Van Wazer[32] have recently employed NMR spectroscopy in determining redistribution equilibria involving fluoro and azido groups on the dimethylsilicon moiety. Spectroscopic studies of equilibrated mixtures of pairs of dimethylsilicon derivatives revealed not only deviation from randomness in scrambling and that on grounds of quantitative thermodynamics the azide may be considered a pseudohalide, but also the existence of a number of new azidosilane derivatives. No isolation of the new materials was attempted however.

Very few reports concerning NMR spectra of azidosilanes are to be found in the literature, probably owing to the scarcity of NMR instruments at the time the majority of compounds were first synthesized. A partial listing of resonance frequencies for some selected azides is presented in the following table.

Table 7
Values (ppm) for Azidosilanes*

Azidosilane	CH_3-Si	R-Si	Ph-Si	CH_3-X	Solvent	Ref.
H_3SiN_3**	–	4.49	–	–	C_6H_{12}	*37*
Me_3SiN_3	0.18	–	–	–	CCl_4	*96*
$Me_2Si(N_3)_2$	0.38	–	–	–	Neat	*32*
$MePhSi(N_3)_2$	0.68	–	7.48m	–	CCl_4	*96*
$Me_2Si(F)N_3$	0.34	–	–	–	Neat	*32*
$Me_2Si(Cl)N_3$	0.56	–	–	–	Neat	*32*
$Me_2Si(SMe)N_3$	0.45	–	–	2.12	Neat	*32*
$Me_2Si(OMe)N_3$	0.24	–	–	3.58	Neat	*32*
$Me_2Si(NMe_2)N_3$	0.23	–	–	2.60	Neat	*32*
$Me(CH_2{=}CH)Si(N_3)_2$	0.45	6.15m	–	–	CCl_4	*96*
$Me(CH_2{=}CH)Si(NMe_2)N_3$	0.30	6.01m	–	2.60	CCl_4	*96*

* Values determined on Varian A-60 using TMS as internal standard.

** Value determined on Varian 4300B; 40MH: C_6H_{12} as internal standard.

All values are singlets unless otherwise noted.

m = multiplet.

R = H– or $H_2C{=}CH$–

X = O, N, S.

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