STUDIES ON THE SiH/NH DEHYDROCOUPLING REACTIONS OF SECONDARY/PRIMARY ORGANOSILANES AND CARBOSILANES WITH BIGUANIDE LIGANDS - SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOR OF SILYLBIGUANIDES

by

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DOCTOR OF PHILOSOPHY

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con compounds
gands
ilanes

Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled, "Studies on the SiH/NH dehydrocoupling reactions of secondary/primary organosilanes and carbosilanes with biguanide ligands - Synthesis, characterization and thermal behavior of silylbiguanides", being submitted by Ms. Pooja Kumar to the Indian Institute of Technology, Delhi for the award of Degree of Doctor of Philosophy is a bonafide research work carried out by her. Ms. Pooja Kumar has worked under my supervision and guidance and has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results embodied in this thesis have not been submitted, in part or in full to any other University or Institute for the award of any degree or diploma.

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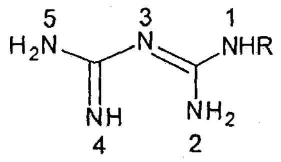
ABSTRACT

The work embodied in the present thesis relates to a detailed study on the SiH/NH dehydrocoupling reactions of secondary/primary organosilanes and carbosilanes with 1-propylbiguanide/1-phenylbiguanide. The choice of these ligands (chart 1) stems from their interesting structural and electronic features which are well documented in literature. Biguanide(s) are known to act as strong σ- and π-donors and these properties are reflected in a large number of coordination complexes with transition metals. However, with the exception of a few reports on boron complexes of biguanide, its potential in the main group has not been realized so far. Thus the primary impetus of the present study is to synthesize novel SiN bonded compounds incorporating biguanide in the structural framework. A variety of organosilane/carbosilane precursors have been chosen for the study with an aim to understand the effect of the nature of the silane (SiH_2/SiH_3) precursors as well as aryl/alkyl substituents on silicon on the SiH/NH dehydrocoupling reactions with substituted biguanides. For clarity of the discussion, biguanide ligands are abbreviated as H_6bigR.



Biguanide

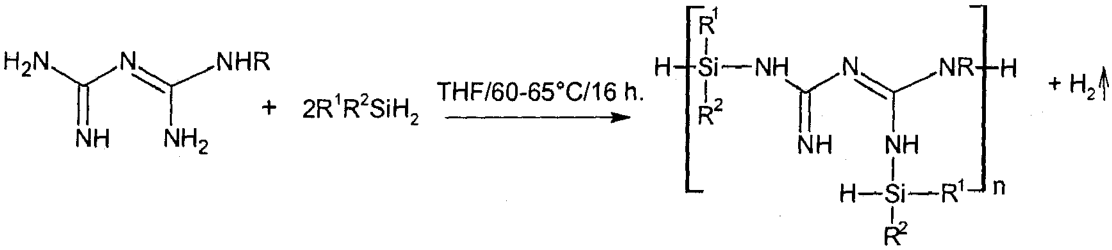
(H_6bigR) R = H, alkyl, aryl

Chart 1

Chapter III is devoted to a systematic study on the reactions of secondary organosilanes, $R^1R^2SiH_2$ (R^1, R^2 = Ph, Me) and carbosilanes $R^1R^2_2SiCH_2CH_2SiMeH_2$

(R^1, R^2 = Me, Et, Ph) with 1-propylbiguanide/1-phenylbiguanide. Although these reactions are found to proceed via thermally induced SiH/NH dehydrocoupling pathway, a significant difference in the reaction rates is discernable depending upon the nature of the silane precursors. The products derived from organosilanes are well-defined linear oligomers while the carbosilanes yield low melting molecular compounds bearing biguanide in the structural framework.

The reactions of methylphenylsilane or diphenylsilane with 1-propylbiguanide/1-phenylbiguanide proceed at elevated temperatures (60-65°C/16h) and afford the corresponding 1,4-bis(silyl)-5-propyl/phenylbiguanides (**1-4**) as shown in scheme 1. These compounds are white, moisture sensitive solids and are soluble in polar organic solvents such as $CHCl_3$, CH_2Cl_2, THF and DMSO.



R^1 = Ph, R^2 = Me, R = ^{n}Pr (**1**), Ph (**2**)

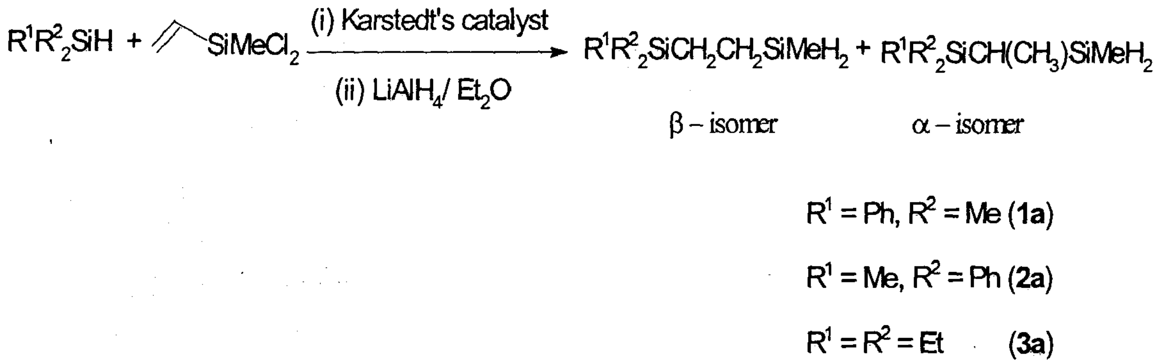
R^1 = R^2 = Ph; R = ^{n}Pr (**3**), Ph (**4**)

Scheme 1

GPC analyses of **1-4** reveal M_w ranging between 1689-1462 with polydispersity 1.14-1.08. Evidence in favor of oligomeric nature of these compounds comes from the FAB mass spectra which reveal a number of fragment ions at m/z values much higher than expected for monomeric structural unit. For 1,4-bis(methylphenylsilyl)-5-propylbiguanide (**1**), the highest ion at m/z 1438 $[M-2C_3H_8]^+$ is assigned based on a tetrameric structure [M], while the assignments of fragment ions at m/z 661 [M-$2C_6H_6$-Me]$^+$ (for **2**), 955 [M-NPr]$^+$ (for **3**) and 757 [M-3Ph-NHPh]$^+$ (for **4**) are based on dimeric structures. A number of commonly observed fragment ions in the spectra of **1** and **2** as well as **3** and **4** are also evident and are primarily associated with the skeletal backbone. Pertinent IR absorptions due to νNH, νC=N and νNCN modes are observed at 3350-3280, 1625 and 1560, 1428 cm^{-1} respectively. The νSiH mode appears as two medium intensity absorptions at *ca* 2200 and 2100 cm^{-1} and suggest the presence of conformational mixtures in these compounds. Absence of absorptions due to νNH_2 (3420 cm^{-1}) and δSiH_2 (920 cm^{-1}) modes provides a qualitative evidence in favor of SiH/NH dehydrocoupling. ^{1}H NMR spectra (DMSO-d_6) of 1,4-bis(methylphenylsilyl)-5-propyl/phenylbiguanide (**1**, **2**) provide a fairly good estimate of the suggested composition as evident from the integral intensities of various groups. On close examination, it is observed that resonances due to Si*Me* group (δ 0.40-0.10) display three distinct doublets ($^3J_{HH}$ = 7.2-7.4 Hz) associated with PhMeSi(H)N along with four singlets due to Ph$MeSiN_2$ moieties. These spectral features may be attributed to arise from the presence of different conformers and are in accord with the IR spectral data. Inspite of the complex pattern of signals due to Si*Ph* groups (δ 7.66-7.18), the spectrum of 1,4-bis(diphenylsilyl)-5-propylbiguanide (**3**) reveals distinct signals for NPr groups (2.98, t, NCH_2; 1.45, m, NCH_2CH_2; 0.89, t, CH_3). The integral intensities of SiPh and NPr groups appear in 2:1 ratio and is consistent with the structural proposition. ^{1}H NMR spectrum of 1,4-bis(diphenylsilyl)-5-phenylbiguanide (**4**) is much less informative due to close chemical shift values of SiPh and NPh groups (δ7.70-6.80). It is imperative to mention that the signals due to SiH protons are generally obscured by broad NH resonances (δ 6.21-3.64) and thus gives a large uncertainty in its integrals. Various organic functionalities in each compound have been detected by their characteristic resonances in $^{13}C\{^1H\}$ NMR spectra. An important feature is the presence of two signals for each of the carbon atoms associated with Si*Ph* (δ 138.7-127.4) and Si*Me* (δ -0.6 to 0.1) groups and suggests the identity of conformational mixtures in these compounds. $^{29}Si\{^1H\}$ NMR spectra of 1,4-bis(methylphenylsilyl)-5-propyl/phenylbiguanide (**1**, **2**) are quite similar and reveal two distinct resonances each in the region δ -33.4 to -32.5 and -30.8 to -30.1. Based on the $^{29}Si\{^1H\}$ NMR spectra in DEPT-135 mode, the former values are assigned to $PhMeSiN_2$ and later to PhMeSi(H)N moieties. On the other hand, the spectra of 1,4-bis(diphenylsilyl)-5-propyl/phenylbiguanide (**3**, **4**) display only two resonances at δ -41.7, -38.5 (for **3**) and -42.8, -33.8 (for **4**) and have been assigned to Ph_2SiN_2 and $Ph_2Si(H)N$ moieties respectively. The chemical shift values obtained herein find a close analogy with those of related silylcarbodiimides reported in literature. TGA profiles of the oligomers **1-4** are quite similar and show no perceptible weight loss upto 130-140°C. Subsequent degradation was observed between 130-300°C and 350-600°C with the observed weight loss of 25-40% and 50-70% respectively. The low residual yields (5-10%) suggest extensive breakdown of these compounds under thermal conditions.

In order to understand the effect of substituents on silicon on the SiH/NH dehydrocoupling phenomena discussed above, it was desired to study analogous reactions with alkyl substituted secondary silanes. Preliminary studies with butylmethylsilane have revealed extremely slow reactivity towards biguanide at room temperature. High volatility of butylmethylsilane impairs the use of elevated temperatures in these reactions.

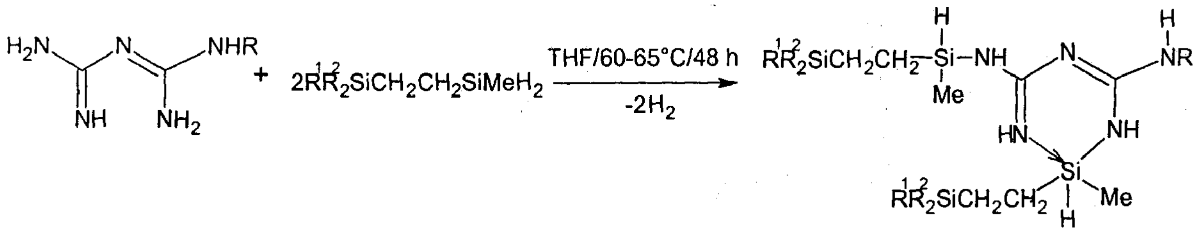
Alternatively, a few secondary carbosilanes $R^1R^2_2SiCH_2CH_2SiMeH_2$ (R^1 = Ph, R^2 = Me (**1a**), R^1 = Me, R^2 = Ph (**2a**), R^1 = R^2 = Et (**3a**)) have been chosen as alkyl analogs to secondary organosilanes and their reactions with biguanide ligands investigated. The carbosilanes **1a-3a** have been synthesized by the hydrosilylation reaction between dichloromethylvinylsilane and the appropriate hydrosilane in presence of Karstedt's catalyst (scheme 2).



Scheme 2

These have been characterized by EI mass, IR and multinuclear (^1H, ^{13}C, ^{29}Si) NMR spectroscopy. Mass spectrum of each compound reveals $[M-H]^+$ ion at m/z 208 (for **1a**), 269 (for **2a**) and 187 (for **3a**). IR spectra reveal characteristic absorptions due to νSiH and δSiH_2 modes at 2123-2126 and 945-946 cm^{-1} respectively while medium intensity bands at 1110-1114 and 1249-1250 cm^{-1} (wherever applicable) are assigned to νSiPh and νSiMe modes respectively. Predominant formation of the carbosilanes as β-isomers is evident from ^1H and $^{13}C\{^1H\}$ NMR (DEPT-135) spectra. For carbosilanes **1a** and **2a**, presence of minor amounts of α-isomer (4-5%) have also been detected. These results have been supplemented by HPLC data. $^{29}Si\{^1H\}$ NMR spectrum of **1a** reveals prominent signals at δ -1.0 and -28.5 due to $PhMe_2$*Si* and *Si*MeH_2 groups respectively while the corresponding resonances for the α-isomer are observed as weak intensity signals at δ 0.1 and -29.4. The assignments for compound **2a** have been made accordingly (δ -4.9/-4.0, Ph_2Me*Si* and -28.8/-29.5, *Si*MeH_2). Exclusive formation of β-isomer in **3a** is evident from a singlet at δ 8.3 (Et_3*Si*) and triplet at -26.2, -29.3, -32.5 (*Si*MeH_2, $^1J_{SiH}$ = 189 Hz) in the ^{29}Si NMR (^{1}H coupled) spectrum.

The reactions between secondary carbosilanes **1a-3a** and 1-propylbiguanide/1-phenylbiguanide afford monomeric 1,4-bis(silyl)-5-propyl/phenylbiguanides (**5-8**) as products of SiH/NH dehydrocoupling (scheme 3). Formation of monomeric compounds **5-8** may be attributed to the slow reactivity of the carbosilanes in relation to SiH/NH dehydrocoupling than analogous reactions of arylsilanes discussed above. These compounds are low melting, hygroscopic solids and are soluble in polar organic solvents such as $CHCl_3$, CH_2Cl_2, THF, DMSO etc.



R^1 = Ph, R^2 = Me , R = ^{n}Pr (**5**)
R^1 = Ph, R^2 = Me , R = Ph (**6**)
R^1 = Me, R^2 = Ph , R = ^{n}Pr (**7**)
R^1 = R^2 = Et , R = Ph (**8**)

Scheme 3

The identity of these compounds is firmly established from the observed $[M]^+$ ion in the FAB mass spectrum of each compound (m/z 555 (for **5**); 589 (for **6**); 627 (for **7**) and

549 (for **8**)). A critical appraisal of group frequencies in the IR spectra (KBr pellet) and their comparison with the precursors reveal the following salient features. The absorption due to νNH (imine) in the compounds **5-8** (3160-3120 cm^{-1}) undergoes a shift to lower frequency as compared to those observed in the parent ligand (3265-3260 cm^{-1}) and suggests coordinative association of the imine NH to the silicon atom. However, no perceptible change is observed in the νC=N and νNCN modes which are observed at 1623-1614 and 1560, 1428 cm^{-1} respectively. The νSiH mode appears as two medium intensity absorptions at *ca* 2100 and 2200 cm^{-1} which persist in solution state (CH_2Cl_2) as well. By analogy with similar spectral features in the compounds **1-4**, the presence of conformational mixtures can be suggested in the present compounds too. The absorptions due to νNH_2 (3420) and δSiH_2 (945 cm^{-1}) modes are absent implying the occurrence of SiH/NH dehydrocoupling in the SiN bond forming process. ^1H NMR spectra of compounds **5-8** reveal resonances due to $PhMe_2SiCH_2CH_2$, $Ph_2MeSiCH_2CH_2$, $Et_3SiCH_2CH_2$, SiMe and NPr/NPh groups (wherever applicable) at their characteristic chemical shift values. Although the spectral features associated with the carbosilyl groups are usually broad and devoid of J-coupling information, the integral intensities of various groups conform to the general composition as shown in scheme 3. The signals due to SiH protons are obscured by the broad NH signals and thus lack quantification. A common feature in the spectra of all the compounds is a downfield signal at δ 6.96-6.88 (br) which can be attributed to C=NH protons and suggest coordinative association of the imine nitrogen to silicon. Presence of different organic functionalities associated with the carbosilyl and NPr/NPh groups are evident in $^{13}C\{^1H\}$ NMR spectrum of each compound. Appearance of two distinct resonances for each carbon associated with $SiCH_2$

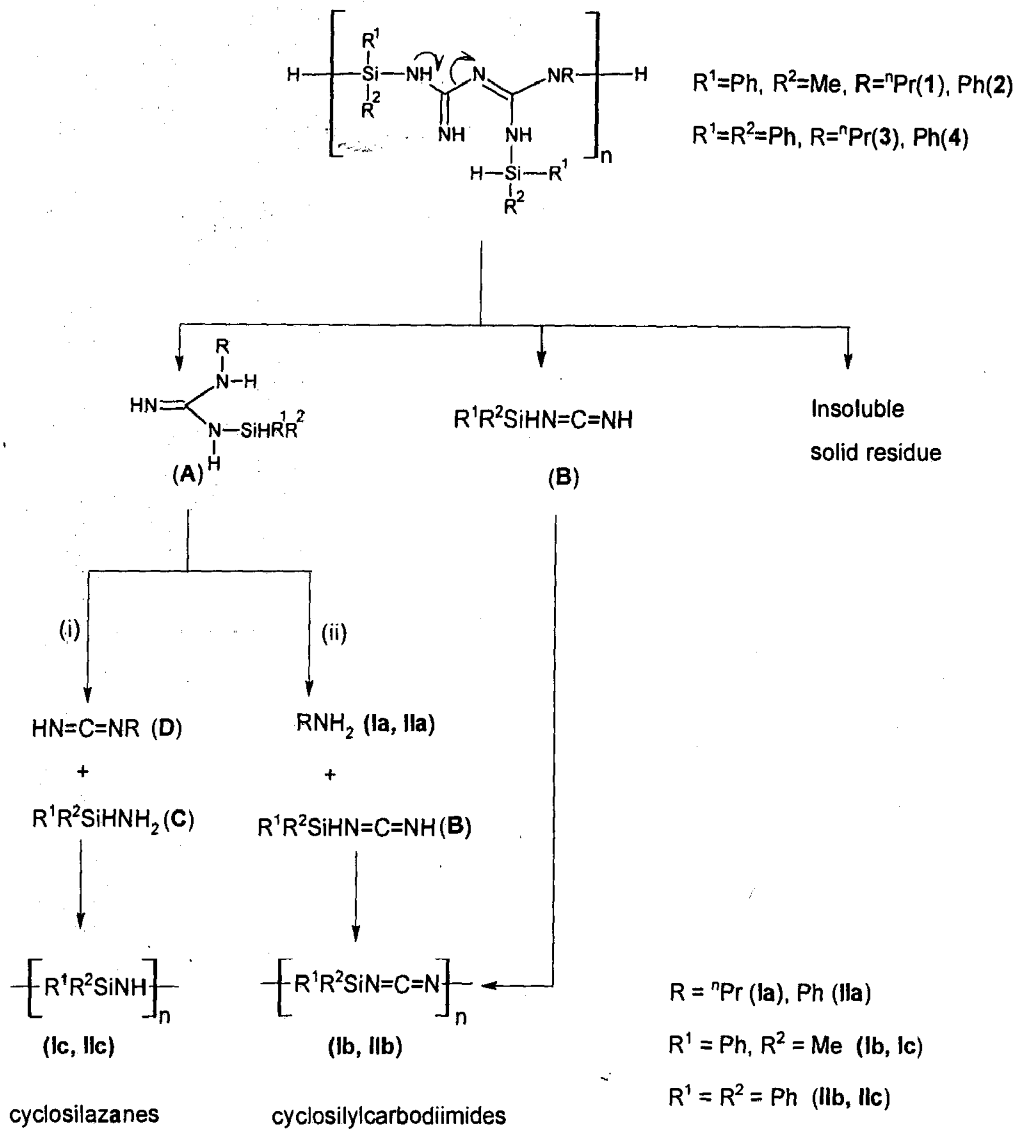
and SiMe groups linked to biguanide units may be interpreted in the light of presence of conformers, by analogy with similar results obtained in related compounds **1-4**. $^{29}Si\{^1H\}$ NMR spectra of **5-8** are quite similar and exhibit three distinct resonances at δ -4.8 to 8.3, -7.8 to -7.5, and -86.5 to - 85.4. The presence of $R^1R^2_2Si$ group is identified by the characteristic resonance at δ -1.3 (for **5**, **6**), -4.8 (for **7**) and 8.3 (for **8**). The signals at δ -7.8 to -7.5 and -86.5 to -85.4 persist in the DEPT-135 mode. Accordingly, the former value is assigned to tetracoordinate $C_2Si(H)N$ moieties. The later values are quite upfield than normally expected for tetracoordinate silicon and are assigned to pentacoordinate $C_2Si(H)N_2$ moieties.

Based on the above studies, a few significant observations which deserve special comments are as follows. Although the formation of SiN bonds under thermally induced SiH/NH dehydrocoupling has been previously reported in the reactions of primary silanes with N-ligands such as hydrazine, majority of the diorganosilanes require transition metal catalysts for SiH bond activation. The formation of silylbiguanides **1-8** discussed in this chapter proceeds smoothly under uncatalyzed conditions at elevated temperatures. It is believed that strong basic character of biguanide ligands (pk_a = 11.3 to 10.6) and their ability to coordinate with the metal center provide the driving force for SiN bond forming process in the absence of a catalyst. An interesting feature in the monomeric compounds **5-8** is the presence of pentacoordinate silicon atom by coordinative association of C=NH groups, a feature not observed in oligomeric silylbiguanides **1-4**. It appears that in compounds **5-8**, silicon atom in the vicinity of the imine group lies in the plane of biguanide ligand thereby favoring pentacoordination while any deviation from such planarity disfavors the N→Si interaction as observed in the compounds **1-4**.

Relevant information from TGA studies of 1,4-bis(silyl)-5-propyl/phenylbiguanides (**1-4**) reveals the onset of thermal decomposition at 130-140°C. The work presented in section B is intended to study the structural changes involved during the initial stages of thermally induced degradation of these oligomers and conceive a plausible mechanism for their thermal behavior. The oligomers 1,4-bis(methylphenylsilyl)-5-propyl/phenylbiguanides (**1, 2**) were subjected to controlled thermolyis (130-140°C, 24h) in an atmosphere of dry nitrogen. During this period, the solid transformed into a viscous mass and subsequent workup have afforded products such as RNH_2 (R = ^{n}Pr (**Ia**)/Ph(**IIa**)), cyclo-methylphenylsilylcarbodiimide (**Ib**) and cyclo-methylphenylsilazane (**Ic**). Attempts to purify these compounds by vacuum distillation failed due to their susceptibility towards decomposition at higher temperature (> 160°C). However, their identity has been established by HPLC, IR and multinuclear (^{1}H, ^{13}C, ^{29}Si) NMR studies. Significant data for **Ib** and **Ic** are as follows. [For **Ib**, IR: 2210 (ν_{as}NCN), 795 (δNCN), 578 (νSi-NCN); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 136.8 (CN); ^{29}Si NMR ($CDCl_3$): δ -33.5, -32.7. For **Ic,** IR: 3383 (νNH), 1260 (νSiMe), 1123 (νSiPh); ^{29}Si NMR ($CDCl_3$): δ -21.5, -20.5]. The data given above suggest the existence of two cyclomers of varying ring size in each compound and the results are supplemented by HPLC data which reveals two closely spaced peaks in each case. Similar studies on the oligomers 1,4-bis(diphenylsilyl)-5-propyl/phenylbiguanides (**3, 4**) provide analogous results as discussed above. Although the resulting products i.e. cyclo-diphenylsilylcarbodiimide (**IIb**) and cyclo-diphenylsilazane (**IIc**) could not be separated by solvent extraction or distillation under reduced pressure, their identity in the mixture is confirmed by MS-MS studies which show molecular ions at m/z 667 $[M+H]^+$ and 592 $[M'+H]^+$ corresponding to $-[Ph_2SiNCN]_3-$

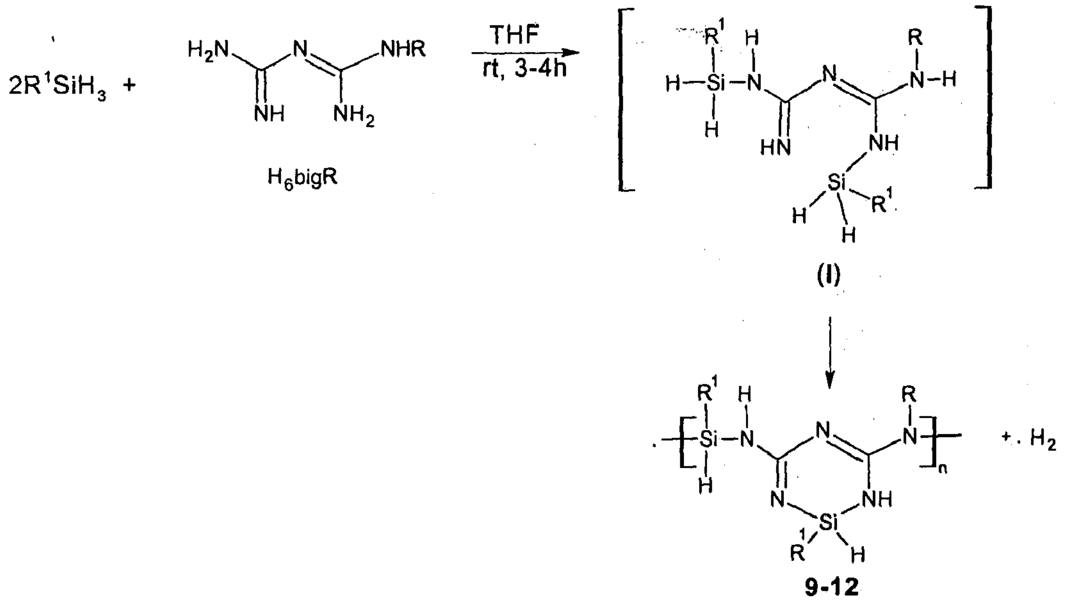
(**IIb**) and -[Ph_2SiNH]$_3$- (**IIc**) respectively. IR, ^1H and $^{13}C\{^1H\}$ NMR spectra provide fairly good evidence in favor of the formation of these compounds. ^{29}Si NMR spectrum in ^1H coupled mode reveals two signals at δ -33.7 and -21.6 which are attributed to **IIb** and **IIc** respectively. Based on the identification of the above products, a plausible mechanism (scheme 4) of thermal decomposition has been put forth which accounts for the formation of these intermediates. It is interesting to note that evidence in favor of these species also comes from the FAB mass spectra of the precursor silylbiguanides **1-4**. There has been no evidence of cross-linking in the initial stages of thermolyis which explains the low residual yields in the TGA profiles of **1-4**. Nevertheless, thermal behavior of these silylbiguanides suggest their potential in MOCVD applications.

As a logical extension of the above work, SiH/NH dehydrocoupling reactions of primary silanes, R^1SiH_3 (R^1 = *p*-Tol/Ph) with biguanide ligands have been studied. The results obtained are discussed in section A of chapter IV. Analogous reactions with a few carbosilanes bearing terminal SiH_3 groups, $R^1R^2_2SiCH_2CH_2SiH_3$ ($R^1 = R^2$ = Et; R^1 = Ph, R^2 = Me; R^1 = H, R^2 = Ph) are described in section B. Reaction rates involving SiH/NH dehydrocoupling in primary silanes/carbosilanes are found to be much faster than observed in analogous reactions of secondary silanes/carbosilanes (chapter III). Addition of two equivalents of phenylsilane or *p*-tolylsilane to a clear solution of 1-propylbiguanide/1-phenylbiguanide in dry THF (rt, 3-4h) results in the isolation of novel SiN bonded cyclic oligomers **9-12** with the general formula -[$(R^1SiH)_2.H_2bigR$]$_n$- (R^1 = Ph, R = ^nPr (**9**), Ph (**10**); R^1 = *p*-Tol, R = ^nPr (**11**), Ph (**12**)).



Scheme 4

An interesting feature of the structural unit is the formation of N-silaheterocyclic ring (scheme 5). It is proposed that coordinative association of the imine nitrogen favors activation of SiH_2 in the intermediate (I) and result in dehydrocyclization.



9-12

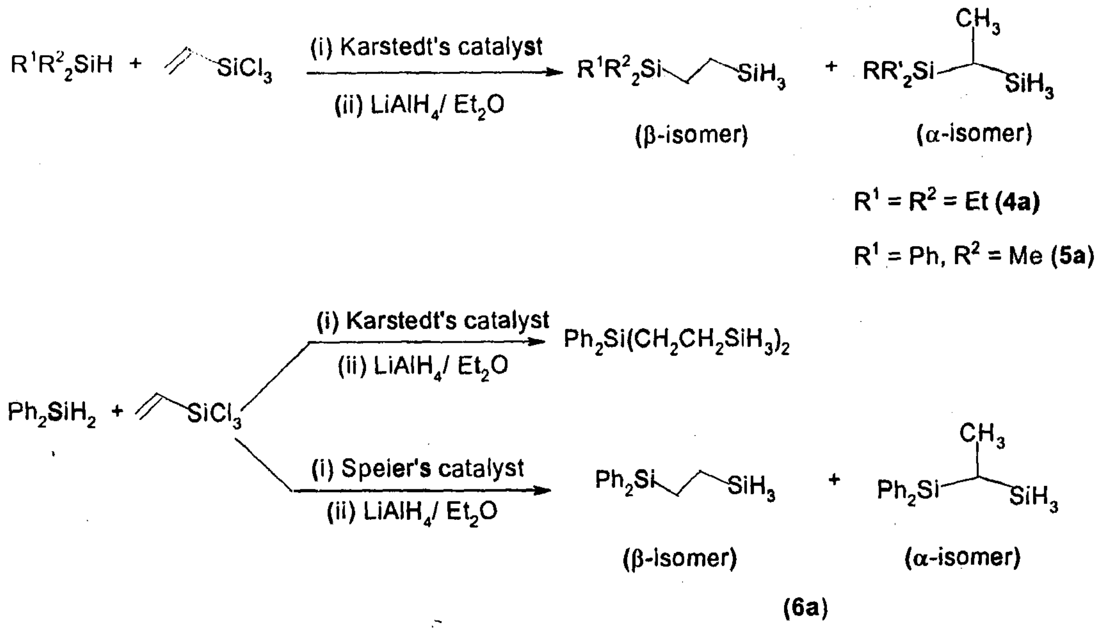
R¹=Ph, R=ⁿPr (**9**), Ph (**10**)

R¹=*p*-Tol, R=ⁿPr (**11**), Ph (**12**)

Scheme 5

FAB mass data of the compounds -[(PhSiH)$_2$.H$_2$bigR]$_n$- (R = ⁿPr (**9**), Ph (**10**)) propose a tetrameric structure with highest ion at m/z 1333 [M-2PhSi+H]$^+$ for **10**. The spectra also reveal a number of commonly observed fragment ions arising from the preferential cleavage of N-R bond along with additional loss of PhSiH, Ph and NH groups. An illustration to this appears in the fragment ion at m/z 1075 which is assigned to [M-4C$_3$H$_8$-C$_6$H$_6$-Ph]$^+$ for **9** and [M-5C$_6$H$_6$-Ph]$^+$ for **10**. Identity of the repeat unit (PhSiH)$_2$.H$_2$bigR is discernable in the fragment ions at m/z 817 [M-3C$_3$H$_8$-(PhSiH)$_2$.H$_2$bigPr-PhSiH]$^+$ for **9** and [M-3C$_6$H$_6$-(PhSiH)$_2$.H$_2$bigPh-PhSiH]$^+$ for **10**. A similar fragmentation pattern has been observed in the FAB mass spectra of -[(TolSiH)$_2$.H$_2$bigR]$_n$- (R = ⁿPr (**11**), Ph (**12**)) and suggest that these compounds possess similar structural motifs. The relevant assignments have been made based on tetrameric structure. A detailed analysis of the IR spectra have been carried out to identify the group frequencies present in these compounds. The spectra reveal a medium intensity absorption at 3384-3365 cm^{-1} (νNH) and differ from those of silylbiguanides **1-4** which reveal two distinct bands at 3360-3354 (νNH) and 3260-3254 cm^{-1} (imine NH). The absence of absorptions due to imine NH in compounds **9-12** suggests their involvement in dehydrocyclization process. A medium intensity band at 2170-2158 cm^{-1} is assigned to νSiH mode while the band due to δSiH_2 is completely absent. The region characteristic of νC=N and νNCN (1625-1420 cm^{-1}) shows subtle differences as compared to the free ligands. The νNCN absorptions appear at 1560 and 1470-1454 cm^{-1}, the later shows a shift to higher frequency of the order of 30-50 cm^{-1} with respect to the pure biguanide (1560, 1420-1425 cm^{-1}). Interestingly, characteristic absorptions due to νC=N at 1623-1618 cm^{-1} observed in the precursors are completely absent in the spectra of all the compounds. It thus appears that the C=N functionalities are involved in a greater degree of π-electron delocalization in the ring. Such electronic perturbations may reduce the C=N bond order and lower the absorption frequency to the νNCN domain. Similar spectral shifts are reported in a number of transition metal complexes of biguanide and provide evidence in favor of π-electron delocalization in the metal chelates. ^1H NMR spectra (DMSO-d_6/acetone-d_6) of the silylbiguanides -$[(PhSiH)_2.H_2bigPr]_n$- (**9**) and -$[(TolSiH)_2.H_2bigPr]_n$- (**11**) reveal signals characteristic of N-Pr group at their respective positions. The Si*Ph* protons for **9** appear as complex multiplets at δ 7.32-7.10 (*o*/*p*) and 7.58-7.39 (*m*) while the aromatic ring protons associated with *p*-tolyl group (for **11**) are observed at δ 7.72-7.41 (*m*) and 7.34-7.10 (*o*). On close examination, each spectral region associated with *p*-Tol groups displays two prominent doublets ($^3J_{HH}$ = 7.1-7.2 Hz) which are believed to arise from the non-equivalent character of these groups in the oligomers. This is further supported by the presence of two singlets for CH_3 (*p*-tolyl) group at δ 2.35-2.30. The relative integration of *p*-Tol/Ph : NPr is found to be 2:1 and is in conformity with the suggested composition. ^{1}H NMR spectra of the silylbiguanides -[$(PhSiH)_2.H_2bigPh]_n$- (**10**) and -[$(TolSiH)_2.H_2bigPh]_n$- (**12**) reveal a similar pattern of signals for SiPh/SiTol groups as observed for compounds **9** and **11**. The signals due to N*Ph* groups are seen as a triplet at δ 7.28-7.25 (*m*) and multiplet at 6.94-6.92 (*o*/*p*). In all the compounds, N*H* protons appear as a broad signal at δ 5.62-3.20 while a singlet at δ 4.68-4.40 is ascribed to the Si*H* protons. For compounds **9** and **11**, $^{13}C\{^1H\}$ NMR spectra reveal signals characteristic of NPr, SiPh/SiTol and C=N at their respective positions. For **10** and **12**, the spectra were recorded in quantitative mode in order to estimate the concentration of each group by relative intensities of $^{13}C\{^1H\}$ NMR signals. The integral intensities of C=N, NPh and SiPh/SiTol groups in a relative ratio of 1:3:6 are in accord with the suggested composition. Attempts to carry out ^{29}Si NMR spectral studies in non-coordinating solvents such as $CDCl_3$ have not been successful. Poor solubility of these compounds in this solvent coupled with additional effect of quadrupolar ^{14}N nuclei in the neighborhood of silicon atoms does not allow the signals to grow under the NMR experimental conditions (delay time D1 = 30s, 16h). However, $^{29}Si\{^1H\}$ NMR spectra in DMSO-d_6 show two prominent resonances in the region δ -127.2 to -131.6 in both normal as well as DEPT-135 mode and suggest the presence of two non-equivalent SiH containing species. However, the δ^{29}Si values are highly upfield and lie in the range of hypercoordinate silicon species. Although the origin of such chemical shifts have not been clearly understood, it is likely that molecular association resulting from intermolecular N→Si interaction may render each silicon in hypercoordinate state. In addition, the effect of strong donor solvent (DMSO-d_6) on the δ^{29}Si values cannot be completely ruled out. A final comment on the structure of the oligomers deserves special mention. In the absence of spectral evidence for terminal SiH_2 groups, a cyclic structure comprising of the repeat unit as shown in scheme 5 can be tentatively proposed. TGA profiles of the silylbiguanides are similar and show the thermal stability of these compounds upto a temperature of ~180°C. Subsequent degradation of these oligomers results in a weight loss of ~55-60%. These results are in close proximity with the calculated weight loss corresponding to complete elimination of RNH_2 (R = ^{n}Pr/Ph) and benzene/toluene (59-64%) from the molecule. Based on these results, it can thus be concluded that the preferential cleavage of organic substrates such as RNH_2, benzene and toluene may result in the formation of species which are rich in silicon and nitrogen along with some residual carbon. The high residual yield observed in these compounds suggest that the process of cross-linking during pyrolysis is quite significant.

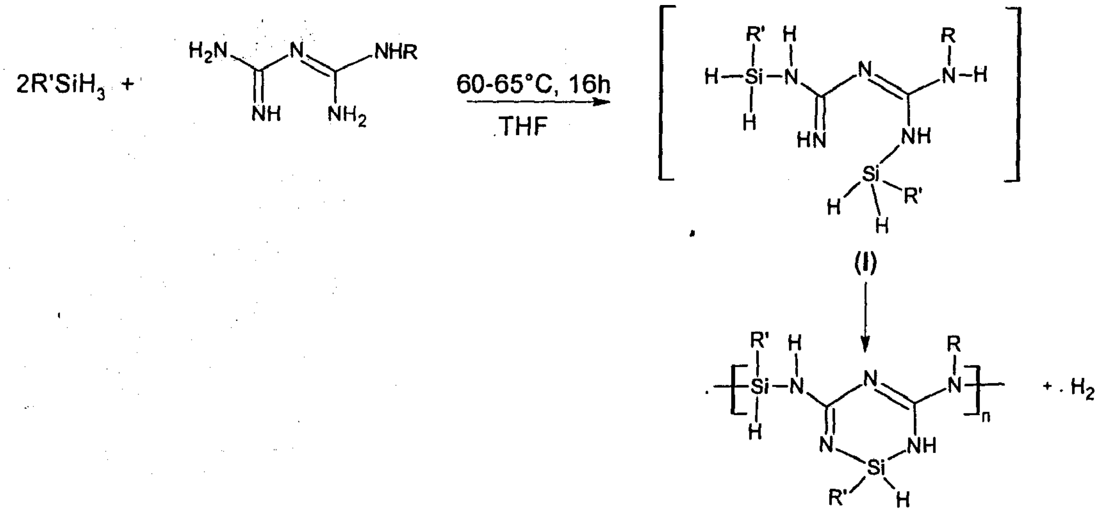
In continuation of the work discussed above, SiH/NH dehydrocoupling reactions of a few primary carbosilanes $R^1R^2_2SiCH_2CH_2SiH_3$ ($R^1 = R^2$ = Et (**4a**); R^1 = Ph, R^2 = Me (**5a**); R^1 = H, R^2 = Ph (**6a**)) with 1-propylbiguanide or 1-phenylbiguanide have been studied. The carbosilanes **4a-6a** have been prepared by the classical hydrosilylation reactions as shown in scheme 6.



Scheme 6

The identity of each compound is evident by the observed $[M\text{-}H]^+$ ion in the mass spectrum. ^{1}H, ^{13}C and ^{29}Si{^{1}H} NMR data are consistent with predominant formation of the β-isomer although minor amounts (6-15%) of the α-isomer are also discernable for **5a** and **6a**.

The reactions of the carbosilanes **4a-6a** with biguanide ligands are shown in scheme 7. Although the rate of SiH/NH dehydrocoupling in these reactions are much slower in comparison to analogous reactions with primary silanes, the products **13-18** obtained herein possess a similar idealized structural unit as suggested for the compounds **9-12**. The identity of these compounds has been elucidated from GPC, FAB mass, IR and multinuclear (^{1}H, ^{13}C, ^{29}Si) NMR spectral data.



13-18

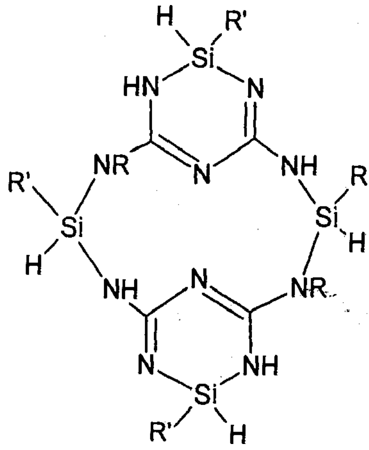
R'= $CH_2CH_2SiEt_3$, R=^nPr (**13**), Ph (**14**)

R'=$CH_2CH_2SiMe_2Ph$, R=^nPr (**15**), Ph (**16**)

R'=$CH_2CH_2SiPh_2H$, R=^nPr (**17**), Ph (**18**)

Scheme 7

Pertinent IR absorptions (cm^{-1}) of these compounds include νNH (3380-3330), νSiH (2116-2105), νC=N (1624-1619) and νNCN (1560, 1428). It is imperative to mention that group frequencies associated with νC=N and νNCN modes do not show a perceptible change with respect to pure biguanide ligands. These results are in contrast to the spectral behavior of structurally similar silylbiguanides **9-12** derived from primary arylsilanes in which a greater degree of π-delocalization has been suggested in the N-silaheterocyclic ring. It thus appears that the nature of substituents on silicon atom markedly influence the underlying electronic features in the N-silaheterocycles. In a previous report, a similar effect has been suggested in boron-biguanide chelates to explain the chemical behavior of these compounds. ^1H NMR spectral data of the compounds **13-18** invariably reveal broad resonances associated with the carbosilyl groups. On the other hand, the signals due to NPr/NPh groups show a normal splitting pattern and appear at δ 0.92-0.85 (t, CH_3), 1.51-1.42 (m, NCH_2CH_2), 3.02-2.89 (t, NCH_2) and 7.20-6.80 (N*Ph*). The relative integral ratio of the carbosilyl:NPr/NPh groups as 2:1 is in conformity with the idealized structure as shown in scheme 6. A singlet at δ 4.75-4.60 is assigned to the Si*H* protons. $^{29}Si\{^{1}H\}$ NMR spectra in DMSO-d_6 reveal two signals in each case at δ -123 to -118. By analogy with the $^{29}Si\{^{1}H\}$ NMR data of related silylbiguanide derivatives **9-12,** these highly upfield values may be rationalized by considering strong intermolecular N→Si interaction or the effect of the donor solvents which render the silicon atoms in hypercoordinate state. GPC data of these compounds reveal M_w values in the range of 1386-1245 with polydispersity 1.15-1.02 and suggest degree of oligomerization between 2-3. FAB mass spectral data reveal structurally important fragment ions which reflect the structural identity of the repeat unit in each compound. In the spectrum of -$[(Ph_2SiHCH_2CH_2SiH)_2.H_2bigPr]_n$- (**17**), the highest ion observed at m/z 902 has been tentatively assigned as $[M\text{-}2PhH\text{-}2Pr\text{-}NH_2]^+$ based on a dimeric structural entity. It is thus proposed that these compounds possess an idealized structure shown below in which the N-silaheterocyclic rings are linked by N-Si-N spacers.



In conclusion, the present study is a systematic attempt to understand the chemical behavior of secondary/primary organosilanes and carbosilanes towards biguanide ligands. Formation of well-defined oligomeric/molecular compounds by vitrue of uncatalyzed SiH/NH dehydrocoupling at room temperature or under thermally induced conditions provide the basis for further investigations. In particular, molecular structures of a few such silylbiguanide derivatives is desired to understand their structural motifs and underlying electronic behavior. In addition, detailed pyrolysis study of these oligomers is warranted to understand the nature of ceramic residues.

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