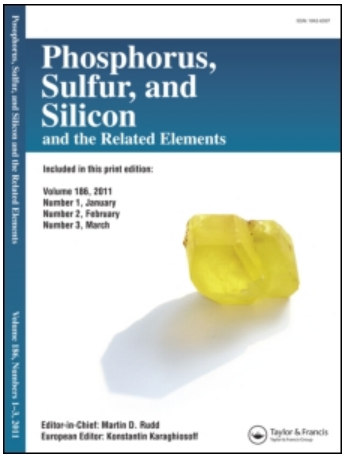

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SYNTHESIS OF 1,3-DICHLORO 1,2,3,3-TETRAMETHYL, 1-VINYL DISILAZANE AND ITS REACTIONS WITH PRIMARY AMINES

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Silazadiamines H(Me)N[(Me)$_2$Si]N(Me)[Si(Me)(CH$_2$=CH)]N(Me)H (***II***) H(n-Pr)N[(Me)$_2$Si]N-(Me)[Si(Me)(CH$_2$=CH)]N(n-Pr)H (***III***) and H(Bu^t)N[(Me)$_2$Si] N(Me) [Si(Me)(CH$_2$=CH)]N(Bu^t)H (***IV***) having one vinyl group attached to one of the silicon atoms were prepared by the reaction of 1,3-dichloro 1,2,3,3-tetramethyl 1-vinyl disilazane (***I***) with methylamine, n-propylamine and t-butylamine respectively. The latter was prepared by the ring opening reaction of nonamethylcyclotrisilazane with dichloromethyl vinyl silane. The compounds were purified by vacuum distillation and characterized by IR, ^{1}H NMR and mass spectral analysis.

Keywords: silazadiamine; synthesis; 1,3-dichloro 1,2,3,3-tetramethyl, 1-vinyldisilazane; methylamine; n-propylamine; t-butylamine

INTRODUCTION

Inorganic heterocycles with substituents such as vinyl and allyl moieties attached to the ring frame work have attained a lot of interest recently as they can be used as precursors for pendant chain polymers with the inorganic heterocycles as pendants. Allen and coworkers have prepared monovinyloxy substituted chlorophosphazenes by the reaction of lithium enolate of acetaldehyde with halocyclophosphazene[1] (A) while B-vinyl borazine (B) having one vinyl group attached to the ring have been prepared by the reaction of $B_3N_3H_6$ with acetylene using a $RhH(CO)(PPh_3)_3$ as catalyst.[2] It has also been shown that such heterocycles can easily be polymerized at the vinyl groups using initiators such as

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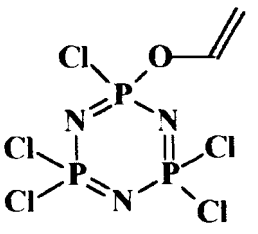
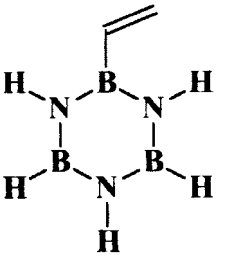


A



B

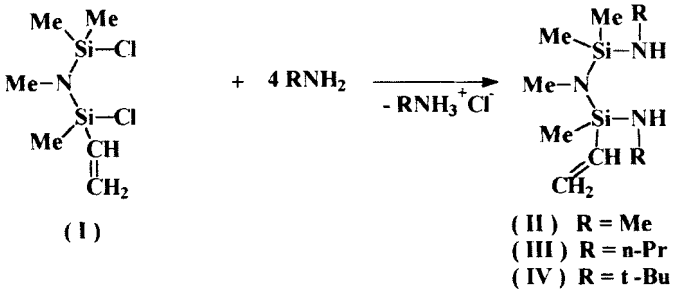
AIBN resulting in novel organic polymers with the inorganic heterocycles as pendant groups.[3]

Although cyclosiloxanes and cyclosilazanes are legion, only a few compounds have been prepared of these heterocycles having vinyl or allyl groups on the silicon atom.[4,5] Except a few, in all such examples of cyclosilazanes,[4] all the ring silicon atoms possess the unsaturated substituent. In reactions where alkenyl amines have been used for the synthesis of cyclosilazanes, heterocycles with more than one alkenyl group on the ring framework are found to form.[5] The absence of a suitable synthon has so far eluded the development of chemistry of 1,3-diaminodisilazanes with only one vinyl group on the molecule which are potential starting materials for monovinyl substitited silaza, metallosilaza and heterosilaza heterocyles.[4b,6,7] Herein we report the synthesis of 1,3-dichloro 1,2,3,3-tetramethyl 1-vinyl disilazane and its reactions with primary amines to make a variety of 1,3-diaminodisilazanes.

RESULTS AND DISCUSSION

On reacting nonamethylcyclotrisilazane with methylvinyldichlorosilane in 1:3 molar ratio, 1,3-dichloro 1,2,3,3-tetramethyl,1-vinyldisilazane (*I*) was found to form preferentially as the major product. This compound which was highly sensitive to moisture was purifed by repeated vacuum distillation under nitrogen. On reacting this compound with methyl amine, n- propylamine and t- butylamine in 1:6 molar ratio the corresponding 1,3-diamino disilazanes were obtained in moderate to good yields as per the equation (1)

Compounds H(Me)N[$(Me)_2$Si]N(Me)[Si(Me)(CH_2=CH)]N(Me)H (*II*), H(n-Pr)N[$(Me)_2$Si]N(Me)[Si(Me)(CH_2=CH)]N(n-Pr)H (*III*) and H(Bu^t)N[$(Me)_2$Si] N(Me) [Si(Me)(CH_2=CH)]N(Bu^t)H (*IV*) were distillable liquids sensitive to moisture and showed interesting similarity with respect to the spectral features.



(I)

(II) R = Me
(III) R = n-Pr
(IV) R = t-Bu

The infrared spectra of these compounds showed the vinyl streching frequencies in the range of 1582 to 1590 cm^{-1} and the N-H streching frequencies at 3390–3430 cm^{-1}. The vinyl streching frequency was observed at 1585 cm^{-1} for (*I*). ^1H NMR also showed the vinyl group uniformly at 5.90 ppm for the silazadiamines while for the dichloride it was observed at 6.13 ppm. The N-Me groups were observed at 2.45–2.50 ppm for compounds (*II*), (*III*) and (*IV*) while it was observed at 2.67 ppm for (*I*). The electron impact mass spectra of the compounds (*II–IV*) were found to give the peak corresponding to the loss of one RNH group as the highest peak. Additional fragments corresponding to disilazanes with one vinyl group were observed at m/e 157 in all the cases.

Wannagat and coworkers have shown that one of the simplest and elegant preparation of 1,3-dichlorotetramethyl disilazane is by the ring opening and equilibration of nonamethylcyclotrisilazane with dimethyldichlorosilane.[8] A variety of reactions have been carried out on this molecule to synthesize new examples of cyclic and acyclic silazanes and heterosilazanes.[4b] 1,3-diamino disilazanes[9] prepared using this dihalodisilazane has been used extensively to make other silaza heterocycles and metallacycles.[10] However the potential of this unusual equilibration reaction to realize other examples of 1,3-dihalodisilazanes, especially mixed substituted disilazanes have not been fully utilized. Reaction of diphenyl dichlorosilane with triethylhexamethylcyclotrisilazane has been reported to yield 1,3-dichloro-1,1-dimethyl, 2-ethyl-3,3-diphenyl-disilazane. However (*I*) is the first example of a vinyl substituted dihalogenated disilazane. Further reactions are currently under way to explore the reactivity of these silazadiamines.

EXPERIMENTAL

All reactions were carried out under a dry oxygen free nitrogen atmosphere using shlenk glassware. $(Me_2SiNMe)_3$ was prepared by literature method.[11] Methylvinyldichlorosilane (Fluka) was used as such. t-Butyl amine and n-pro-

pylamine were dried and distilled prior to use. Methyl amine was generated from a 40% solution in water by KOH absorption method.

Synthesis of 1,3-dichloro 1,2,3,3-tetramethyl, 1-vinyl disilazane (I)

Nonamethyl cyclotrisilazane (5.20g, 7.56 mmol) was taken in a 50 ml R.B. flask and fitted with a condenser under nitrogen. Methylvinyldichlorosilane (12.00g, 85.12 mmol) was added to it at room temperature using a syringe. The mixture was set to slow heating on an oil bath (bath temp. 80–110°C). After about 72 hours the mixture was brought to room temperature and all volatiles removed *in vacuo*. The vacuum distillation of the residue gave as the major fraction $Cl(Me)_2SiN(Me)Si(Me)(CH=CH_2)Cl$ (***I***) which was purified by repeated fractional vacuum distillation under nitrogen (6.30g, 46%). B.P. 70°C/8mmHg; IR (neat) 2980m, 1585m, 1400m, 1270vs, 1195m, 1070s, 940s, 780s cm^{-1}; ^1H NMR, δ ($CDCl_3$) 0.54 (9H, m, CH_3Si), 2.67 (3H,s, NMe), 6.13 (3H,s, $CH=CH_2$).

Preparation of H(Me)N[(Me)$_2$Si]N(Me)[Si(Me)(CH$_2$=CH)]N(Me)H (II)

To a solution of excess methylamine (generated by adding a 40% solution over KOH pellets and dried by passing through KOH pellets) condensed in a flask kept at $-80°C$, (***I***) (2.30 g, 10.10 mmol) was added slowly using a syringe and the mixture stirred at $-80°C$ for 3 hours. Afterwards it was slowly brought to room temperature and then to 60°C and maintained at this temp for 4 hours. It was then filtered using a frit and the filtrate concentrated *in vacuo* and the residue distilled to yield (***II***) (1.14 g, 52%). B.P. 65°C/8 mm Hg; IR (neat) 3430m, 2940s, 2810s, 1590w, 1400m, 1365m, 1250s, 1185m, 1080 br s, 950m, 890s, 800s cm^{-1}; ^1H NMR $\delta(CDCl_3)$, 0.10 (9H,m, CH_3Si), 1.26 (2H, s, NH), 2.50 (9H,m, CH_3N), 5.90 (3H,m, ($CH_2=CH$)Si); MS(EI) m/e (%, fragment); 187 (23, M^+ - MeNH), 186 (23, MeN[(Me_2Si)Me($CH_2=CH$)Si]NMe), 157 (62, MeN(Me_2Si) [Me($CH_2=CH$)Si]).

Preparation of H(n-Pr)N[(Me)$_2$Si]N(Me)[Si(Me)(CH$_2$=CH)]N(n-Pr)H (III)

Propylamine (1.50g, 25.40 mmol) was taken in an RB flask and hexane (30 ml) was added under an atmosphere of dry nitrogen. The solution was cooled in an ice bath and (1) (1.02g, 4.50 mmol) was slowly added using a syringe. The solution was brought to room temperature and then kept at 75°C for 4 hours. Afterwards it was filtered using a frit and the filtrate concentrated and all vol-

atiles removed *in vacuo*. The residue on vacuum distillation gave (***III***) (1.07g, 87%) B.P.83°C/8 mmHg; IR (neat) 3420w, 2960s, 1585w, 1450m, 1380s, 1250s, 1140s, 1060m, 1020m, 895s, 770m cm^{-1}; ^1H NMR δ ($CDCl_3$), 0.10 (9H,m, CH_3Si), 0.70–0.80 (8H,m,CH_3,NH), 1.40(4H,m, CH_2), 2.45 (3H,s, CH_3N), 2.65(4H,t,N-CH_2), 5.90 (3H,m, ($CH_2=CH$)Si); MS (EI) m/e (%, Fragment) 215 (100, M^+ − PrNH), 185 (55, MeN[(Me_2Si)Me($CH_2=CH$)Si]NMe), 157 (31, MeN (Me_2Si) [Me($CH_2=CH$)Si]), 59 (31).

Preparation of H(Bu^t)N[$(Me)_2Si$]N(Me)[Si(Me)(CH_2=CH)]N(Bu^t)H (IV)

A reaction of t-butylamine (1.62g, 22.20 mmol) was carried out with (***I***) (1.01g, 4.42 mmol) as described in the synthesis of (***III***). On distillation of the reaction residue, a fraction was obtained which was identified as (***IV***), (1.10g, 83%); B.P. 100°C/8 mm Hg; IR (neat) 3390m, 2900s, 1582m, 1460m, 1370s, 1250s, 1050s, 1000s, 885s, 780s cm^{-1} ^1H NMR δ ($CDCl_3$) 0.10 (9H,m, MeSi), 0.90 (2H,s,NH), 1.15 (18H,s,Bu^t), 2.47 (3H,s, NMe), 5.90(3H,m,CH=CH_2); MS (EI) m/e (%, fragment) 229 (22, M^+ - t-BuNH), 185 (29, MeN[(Me_2Si)-Me($CH_2=CH$)Si]NMe), 157 (18, MeN(Me_2Si) [Me($CH_2=CH$)Si]), 58 (100)

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