

A Facile Synthesis Route to 1,3-dichlorodisilazanes

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Abstract: A new 1,3-dichlorodisilazane, 1,3-dichloro-1,3-dimethyl-1,3-divinyldisilazane (DMDV), was prepared from the reaction of hexamethyldisilazane (MM^{N}) and methylvinylchlorosilane. And use the same method, 1,3-dichloro-1,1,3,3-tetraphenyldisilazane (DCTPS) was also obtained in a high yield.

Keywords: Silazanes, synthesis, dichlorodisilazanes.

Since the pioneering work of Verbeek¹, considerable attention has focussed on research devoted to the preparation of silicon nitride- and silicon carbide- based ceramic materials. Owing to their promising potential for the formation of high-purity non-oxide silicon-based ceramics, organosilicon compounds (precursors) have attracted considerable interest in recent years². The structures and the chemical composition of the precursors strongly effect the properties of the final ceramic materials. According to literature³, the ideal precursor should (a) contain cages or rings, to decrease the polymer skeleton degradation; (b) have latent chemical reactivity to obtain thermosetting or curing properties. Thus, we prepared a novel class polysilazane precursors containing chain-cyclic structure as well as reactive groups *via* the reaction of lithium salt of hexamethylcyclotrisilazane (D_3^{Nli}) and α , ω -dichlorosilazane⁴. In this paper, we report the facile synthesis of two starting materials, 1,3-dichloro-1,3-dimethyl-1,3-divinyldisilazane (DMDV), 1,3-dichloro-1,1,3,3-tetraphenyldisilazane (DCTPS), and to the best of our knowledge, the former has never been reported.

We have reported the preparation of DCTPS⁵ from the reaction of octamethylcyclotetrasilazane (D_4^{N}) and $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$, however, the reaction needs long heating time (50 hours) and a large excess of $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$. In this paper, we provided a simpler procedure with high yields for synthesis of DCTPS, which needs much shorter reaction time (17 hours), and $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$ need not excess.

Experimental

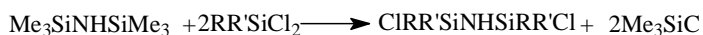
¹H NMR and ²⁹Si NMR spectra were recorded with a Unity 200 spectrometer, CDCl_3 as solvents, tetramethylsilane (TMS) as an external standard in ²⁹Si NMR. IR spectra were

measured on FT-IR spectrophotometer, PE-80. Elemental analysis was determined with a Carlo Erba 1106 analyser.

General procedure for the reaction

The reaction was performed in a three-necked flask equipped with a thermometer, an inlet for the gas purge and a reflux condenser. MM^N (0.1mol) and $RR'SiCl_2$ (0.2mol) was rapidly added under N_2 . The mixture was heated under reflux, and at the same time, the produced Me_3SiCl was removed by distillation. When the reaction was completed, for $R=Me$, $R'=Vi$, the condenser was then replaced by a short Vigreux column connected to vacuum line *via* a receiver and a liquid nitrogen trap, as the mixture was heated, DMDV were got in the receiver (68%), which was determined by ^{29}Si NMR (δ 1.20). For $R=R'=C_6H_5$, the precipitated crystals were filtered off and washed with hexane, pure DCTPS were obtained (76%), ^{29}Si NMR: δ 7.53.

Scheme 1



DMDV: $R=Me$, $R'=Vi$

DCTPS: $R=R'=C_6H_5$

References

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