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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 methylvinyldichlorosilane. 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 Verbeek[1], 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 years [2]. The structures and the chemical composition of the precursors strongly effect the properties of the final ceramic materials. According to literature [3], 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−dichlorosilazane[4]. 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 DCTPS[5] from the reaction of octamethylcyclotetrasilazane (D_4^N) and $(C_6H_5)_2SiCl_2$, however, the reaction needs long heating time (50 hours) and a large excess of $(C_6H_5)_2SiCl_2$. In this paper, we provided a simpler procedure with high yields for synthesis of DCTPS, which needs much shorter reaction time (17 hours), and $(C_6H_5)_2SiCl_2$ need not excess.

Experimental

^{1}H NMR and ^{29}Si NMR spectra were recorded with a Unity 200 spectrometer, $CDCl_3$ as solvents, tetramethylsilane (TMS) as an external standard in ^{29}Si NMR. IR spectra were measured on FT-IR spectrophotometer, PE-80. Elemental analysis was determined with a Carlo Erba1106 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

$$Me_3SiNHSiMe_3 + 2RR'SiCl_2 \longrightarrow ClRR'SiNHSiRR'Cl + 2Me_3SiC$$

DMDV: R=Me, R'=Vi
DCTPS: $R=R'=C_6H_5$

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