

Synthesis of Some New Derivatives of 1,3-Dichloro-1,1,3,3-tetraphenyldisilazane

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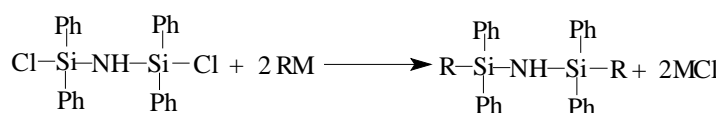
Abstract: The reactive properties of 1,3-dichloro-1,1,3,3-tetraphenyldisilazane (DCTPS) with water, methanol, phenylamine and lithium salt of hexamethylcyclotrisilazane (D_3^{NLi}) were investigated, and four new derivatives were obtained.

Keywords: 1,3-Dichloro- 1,1,3,3-tetraphenyldisilazane; derivatives; reactive properties.

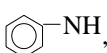
Recently, the silicon-nitrogen compounds have received more consideration for their attractive application prospects. Both low molecular weight silazane and polysilazane with high molecular weight are widely used in many aspects. For example, in the processing industry of silicone rubber, silazanes not only can be used as “structure-control additives”¹, but also can be used to improve the rubber’s heat-resistance and mechanical properties; silicon-nitride ceramics can be prepared by pyrolysis of silazanes or polysilazanes²⁻⁴; and Si-N compounds are very useful reagents in organic synthesis. Thus, the research on Si-N compounds has been developed rapidly, both in theory and application.

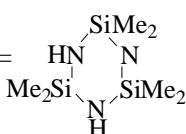
In 1971, Wannagat⁵ reported the preparation of 1,3-dichloro-1,1,3,3-tetraphenyl-disilazane (DCTPS). However, during the past 30 years, there have been few reports related to the reactive properties of the compound. We have reported the synthesis of new polysilazane containing linear-cyclic structure⁶ and that of a new polysiloxane containing octaphenylcyclodisilazane in the main chain^{7,8}, in these synthesis DCTPS was the important starting material. Considering the large potential interest of DCTPS in the field of organosilicon chemistry, we re-investigated the compound. Two facile routes to synthesize DCTPS in higher yields were given⁹⁻¹¹. In addition, the reactive properties of DCTPS with water, methanol, phenylamine and lithium salt of hexamethyl-cyclotrisilazane (D_3^{NLi}) were studied, and its four new derivatives were synthesized (**Scheme 1**). The resistance to hydrolysis of these new derivatives were also studied¹². This paper will report synthesis of these derivatives.

Scheme 1



1: R=HO, M=H 2: R=CH₃O, M=H

3: R= , M=H

4: R= , M=Li

Experimental

¹H NMR and ²⁹Si NMR spectra were recorded with a Unity 200 spectrometer, CDCl₃ as solvents, hexamethyldisiloxane (MM, δ 6.9) as an external standard in ²⁹Si NMR determination. IR spectra were measured on FT-IR spectrophotometer, PE-80. Elemental analysis was determined with a Carlo Erba 1106 analyser. Melting point was obtained with a WRS-1A melting point apparatus.

General procedure for the reactions

- (A) At the temperature of -15°C, to a stirred mixture of H₂O (0.29 g), NH₄OH (20 mL), and Et₂O (35 mL) was added a mixture of DCTPS (3.65 g) and Et₂O (20 mL). The reaction mixture was then stirred for 20 minutes below -5°C. The organic phase was separated and dried with Na₂SO₄. Then the filtrate was rotor-evaporated to remove solvents. The residue was purified by re-crystallization from Et₂O/n-hexane to give a white solid **1**, (yield 75.7%). m.p. 92.2~93.1°C, ²⁹Si NMR: δ -23.6. Anal. Calcd for C₂₄H₂₃NO₂Si₂: C, 69.73; H, 5.57; N, 3.39. Found C, 70.58; H, 5.27; N, 3.35.
- (B) To a stirred mixture of CH₃OH (0.64 g), Et₃N (28 mL), and THF (40 mL) was added a solution of DCTPS (4.50 g) in THF (10 mL). The reaction mixture was then stirred for 2 hours at room temperature. The white precipitate was removed and the filtrate was rotor-evaporated to remove solvents. The residue was purified by re-crystallization from Et₂O/n-hexane to give a white solid **2**, (yield 86.2%). m.p. 68.3~68.6°C, ²⁹Si NMR: δ -22.9. Anal. Calcd for C₂₆H₂₇NO₂Si₂: C, 70.75; H, 6.12; N, 3.17. Found C, 70.38; H, 6.38; N, 3.17.
- (C) To a stirred mixture of PhNH₂ (0.90 g), Et₃N (20 mL), and THF (35 mL) was added

a solution of DCTPS (2.17 g) in THF (10 mL). The reaction mixture was then stirred for 3 hours at room temperature. The white precipitate was removed and the filtrate was rotor-evaporated to remove solvents. All the operation was carried out under the protection of nitrogen. The residue was purified by re-crystallization with Et₂O/n-hexane to give a white solid **3**, (yield 34.5%). m.p. 150.9~151.2°C, ²⁹Si NMR: δ -25.9. Anal. Calcd for C₃₆H₃₃N₃Si₂: C, 76.74; H, 5.86; N, 7.46. Found C, 76.58; H, 5.74; N, 7.24.

- (D) To a stirred mixture of D₃^{NLi} (6.96 g), THF (20 mL) and n-hexane (20 mL) was added a solution of DCTPS (6.90 g) in THF (10 mL). The reaction mixture was then stirred for 6 hours at room temperature. The white precipitate was removed and the filtrate was rotor-evaporated to remove solvents. All the operation was carried out under the protection of nitrogen. The residue was purified by re-crystallization from n-hexane to give a white solid **4**, (yield 60.2%). m.p. 149.9~150.1°C, ²⁹Si NMR: δ -3.8, SiMe₂, -4.2, SiMe₂, -22.9, SiPh₂. Anal. Calcd for C₃₆H₆₁N₇Si₈: C, 53.01; H, 7.48; N, 12.02. Found C, 53.18; H, 7.46; N, 12.46.

Acknowledgment

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- The D₃^{NLi} was prepared by using the method of Fink¹⁴⁻¹⁶ with some modifications. The example was given as follows: To a stirred mixture of 36.88 mmol n-butyllithium and 30 mL n-hexane was added a solution of 38.00 mmol hexamethylcyclotrisilazane (D₃^N) in 20 mL n-hexane. The reaction mixture was then stirred for 3 hours at room temperature. Then the solvent was removed by filtration under nitrogen. The white precipitate was with n-hexane and dried under vacuum to give 8.11 g D₃^{NLi} (98%). D₃^{NLi} is very sensitive to air and moisture, so all the manipulation was carried out under the protection of an inert atmosphere. It is necessary to indicate that the proper handle, adding D₃^N /n-hexane into a solution of n-butyllithium/n-hexane, should be used. If an inverse addition sequence was adopted, the product would be a mixture of three kinds of lithium salts, (Me₂SiNH)₂ (Me₂SiNLi)₃ and (Me₂SiNH)(Me₂SiNLi)₂. In addition, in order to avoid the n- butyllithium react with DCTPS, it is necessary to wash D₃^{NLi} with n-hexane.

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