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Synthesis of a 2,4,6-triaza-1,3,5,7-tetrasilane with 1,3-migration of a Methyl Group

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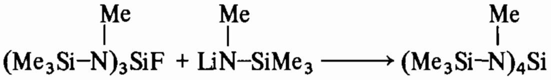
Metalated silylamines react with halogenosilanes, for example $SiCl_4$, in a molar ratio 1:1 with substitution [1]. All attempts to synthesise a tetrakis(trimethylsilylamino)silane by stepwise substitution of the Cl atoms have so far been without success [2]. When silicon chlorides are used in these reactions cyclisation [3] is observed as well as substitution. Wannagat *et al.* isolated a Si,N,C-spirane in the reaction of $SiCl_4$ with $NaN(SiMe_3)_2$ [2]. Di- and trisubstitutions of metalated silylamines with fluorosilanes are simpler [4, 5]. Bulky tris(silylamino)fluorosilanes can be prepared in the reaction of halogenosilanes with lithio-aminofluorosilanes [6].

The substitution of the fourth fluorine atom in fluoro-tris(trimethylsilyl-methylamino)silane [5] with another trimethylsilylmethylamino group was the object of this investigation.

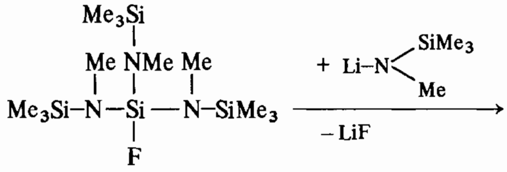
No reaction, however, took place in different solvents (PE, THF):

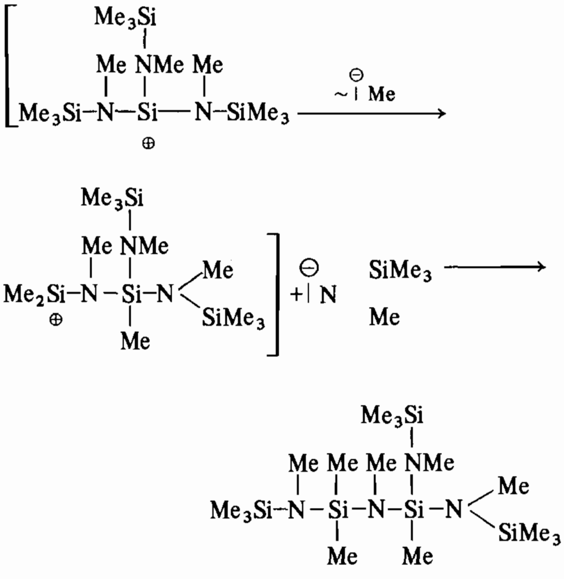


$$(Me_3Si\text{-}\overset{Me}{N})_3SiF + Li\overset{Me}{N}\text{-}SiMe_3 \longrightarrow (Me_3Si\text{-}\overset{Me}{N})_4Si$$

I

Therefore the reactants were heated, with stirring, at 150–170 °C for 10 h without solvent. Two main products were detected by gas chromatography. The mixture was distilled and the main fractions purified by gas chromatography. One of the main products was identified as unchanged fluoro-tris(trimethylsilylmethylamino)silane. Analysis and molecular mass measurements of the second compound would fit the desired compound I. However, ^1H, ^{13}C, ^{29}Si n.m.r. spectra characterised it as a 2,4,6-triaza-1,3,5,7-tetrasilane (II). The 1,3-rearrangement at silicon, which is necessary for the formation of II, is known in Si–N chemistry in ring closure reactions with migration of a methanide ion [7] and has been observed recently in Si–C chemistry [8]. For this reason, the following reaction mechanism is proposed:





II

The reaction of fluoro-tris(trimethylsilylmethylamino)silane with methyl- and n-butyllithium leads to the expected substitution. Therefore the formation of II instead of I must have steric causes.

1,2,3,4,5,6,7-Dodecamethyl-5-trimethylsilyl-methylamino-2,4,6-triaza-1,3,5,7-tetrasilane (II):
Anal. calcd. for $C_{16}H_{48}N_4Si_5$(437.02): C 43.97, H 11.07, N 12.82. Found: C 43.96, H 11.09, N 12.92; yield 45%; b.p. 105 °C/0.05 Torr; MS (70 eV): m/e = 436 (rel. int. 1%, M^+); ^1H n.m.r. (in CH_2Cl_2, TMS int. standard): 0.10 ($SiMe_3$), 0.11 (2 $SiMe_3$), 0.15 ($SiMe_2$), 0.26 (SiMe), 2.45 (NMe), 2.47 (2 NMe), 2.48 ppm (NMe); ^{13}C n.m.r. (in $CDCl_3$, TMS int. standard): 0.73 (2 SiC_3), 1.27 (SiC_2), 1.40 (SiC_3), 4.72 (SiC), 30.35 (NC), 30.49 (NC), 31.04 ppm (2 NC); ^{29}Si n.m.r. (in C_6F_6, TMS int. standard) ^1H-noise decoupled, minus ppm = upfield from TMS): –13.82 (SiMe), –2.42 ($SiMe_2$), 4.72 (2 $SiMe_3$), 5.72 ppm ($SiMe_3$).

Acknowledgement

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References

1 U. Wannagat, *Adv. Inorg. Chem. Radiochem., 6,* 225 (1964).
2 U. Wannagat, J. Herzig and H. Bürger, *J. Organometal. Chem., 23,* 373 (1970).

3 U. Klingebiel, J. Neemann and A. Meller, *Z. anorg. allg. Chem.*, *429*, 63 (1977).
4 U. Wannagat and H. Bürger, *Angew. Chem., Int. Ed. Engl. 3*, 446 (1964).
5 U. Klingebiel, D. Enterling and A. Meller, *J. Organometal. Chem.*, *101*, 45 (1975).
6 U. Klingebiel, J. Neemann and A. Meller, *Z. anorg. allg. Chem.*, in press.
7 U. Klingebiel and A. Meller, *Angew. Chem., Int. Ed. Engl.*, *15*, 312 (1976).
8 C. Eaborn, D. A. R. Happer, S. P. Hopper and K. D. Safa, *J. Organometal. Chem.*, *170*, C9 (1979).