541. *Compounds of Silicon. Part IV.*[1] *Reactions of Hexamethyldisilazyl-lithium with Chlorosilanes*

By E. H. AMONOO-NEIZER, R. A. SHAW, D. O. SKOVLIN, and B. C. SMITH

THE ammonolysis of halogenosilanes, R_3SiX (R = Alk or Ar) gives aminosilanes, R_3SiNH_2, or disilazanes, $(R_3Si)_2NH$.[2] Reaction of an excess of trimethylchlorosilane with ammonia gives hexamethyldisilazane,[3] and the remaining hydrogen atom is not replaced by a trimethylsilyl group, even when the disilazane is heated with trimethylchlorsilane and pyridine in a sealed tube at elevated temperatures.[4] Until recently, the only representatives of a class of compounds in which nitrogen is bonded to three silicon atoms, were trisilylamine, $N(SiH_3)_3$, and trismethylsilylamine, $N(SiH_2Me)_3$.[2] Steric hindrance was originally advanced as a possible reason for this, but the use of metal derivatives of hexamethyldisilazane has led to the preparation of a range of substituted trisilylamines.[4,5] Reactions of hexamethyldisilazyl-lithium with chlorosilanes have been described by Wannagat and Niederprüm.[5] One or more chlorine atoms are replaced by hexamethyldisilazyl groups, and lithium chloride is formed, *e.g.*,

$$R_{4-n}SiCl_n + (Me_3Si)_2NLi \longrightarrow (Me_3Si)_2NSiCl_{n-1}R_{4-n} + LiCl$$

Similar work carried out concurrently in this laboratory is reported here.

Hexamethyldisilazyl-lithium reacts readily with trimethylchlorosilane in boiling ether or tetrahydrofuran to give tris(trimethylsilyl)amine. This compound has been prepared also by reaction of trimethylchlorosilane with hexamethyldisilazyl-lithium in a sealed tube at 120°,[5] hexamethyldisilazylsodium or hexamethyldisilazylpotassium-bisdioxan in boiling benzene,[5] and hexamethyldisilazane, sodium, and styrene, in dioxan at 30—40°.[4]

Only one chlorine atom in dimethyldichlorosilane, diethyldichlorosilane, or diphenyldichlorosilane is replaced by reaction with hexamethyldisilazyl-lithium in boiling tetrahydrofuran. The compounds $(Me_3Si)_2NSiClMe_2$ and $(Me_3Si)_2NSiClPh_2$ have been prepared previously, and the remaining chlorine atom of the former is replaced by reaction with hexamethyldisilazyl-lithium in a sealed tube at 100°.[5] It was reported that hexamethyldisilazyl-lithium does not react with triphenylchlorosilane at 200—250°,[5] but reaction occurs in boiling tetrahydrofuran to give bis(trimethylsilyl)triphenylsilylamine. This compound is prepared also by reaction between triphenylsilylamine, n-butyl-lithium (2 mole), and trimethylchlorosilane.

The greater reactivity of hexamethyldisilazyl-lithium in tetrahydrofuran than in benzene or in the absence of solvent is probably due to co-ordination of the solvent to the metal. Many similar derivatives of alkali metals show increased reactivity with increasing donor power of the solvent, because of increased dissociation of aggregates and ion-pairs.[6] Hexamethyldisilazyl-lithium is dimeric in hydrocarbon solvents, but monomeric addition compounds are formed with ethers and pyridine.[5]

The proton magnetic resonance spectra of the compounds $(Me_3Si)_3N$ and $(Me_3Si)_2NSiPh_3$ in carbon tetrachloride and $(Me_3Si)_2NH$ and $(Me_3Si)_2NMe$ in the absence of solvent contain singlets attributed to *Si*-methyl groups at $\tau = 9{\cdot}82$ (lit.,[7] 9·82), 9·97, 9·95 (lit.,[7] 9·97) and 9·92, respectively. That of $(Me_3Si)_2NMe$ also contains a singlet ($\tau = 7{\cdot}55$) attributed to *N*-methyl groups.

---

[1] Part III, R. A. Shaw, *J.*, 1958, 521.

[2] C. Eaborn, " Organosilicon Compounds," Butterworths, London, 1960, ch. 11.

[3] R. O. Sauer, *J. Amer. Chem. Soc.*, 1944, **66**, 1707; R. O. Sauer and R. H. Hasek, *ibid.*, 1946, **68**, 241.

[4] J. Goubeau and J. Jiménez-Barberá, *Z. anorg. Chem.*, 1960, **303**, 217.

[5] U. Wannagat and H. Niederprüm, *Angew. Chem.*, 1959, **71**, 574; *Z. anorg. Chem.*, 1961, **308**, 337; *Chem. Ber.*, 1961, **94**, 1540.

[6] G. Wittig and E. Stahnecker, *Annalen*, 1957, **605**, 69; H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Amer. Chem. Soc.*, 1960, **82**, 2895; H. E. Zaugg, *ibid.*, p. 2903, *ibid.*, 1961, **83**, 837; H. D. Zook and T. J. Russo, *ibid.*, 1960, **82**, 1258; H. D. Zook and W. L. Gumby, *ibid.*, p. 1386.

[7] H. Schmidbaur and M. Schmidt, *J. Amer. Chem. Soc.*, 1962, **84**, 1069; *Angew. Chem. Internat. Edn.*, 1962, **1**, 327; H. Schmidbaur, *J. Amer. Chem. Soc.*, 1963, **85**, 2336.

Thus the protons in the series $(Me_3Si)_2NR$ are deshielded progressively in the order $R = SiPh_3 \leqslant H \leqslant Me < SiMe_3$. It would be tempting to explain the chemical shifts in terms of $p\pi - d\pi$ bonding between nitrogen and silicon; this has been attempted for some compounds in which silicon is attached to atoms with lone pairs of electrons.[7,8] Recent work by Ebsworth and Frankiss shows that similar effects occur in carbon compounds,[9] so there is no justification at present for explaining these results in terms of multiple bonds involving silicon.

Experimental.—Tetrahydrofuran was boiled under reflux with sodium (24 hr.) before distillation. Reactions were carried out in an atmosphere of dry nitrogen.

n-Butyl-lithium (0·3 mole) in pentane (150 ml.) was added slowly to a stirred solution of hexamethyldisilazane (66·0 ml., 0·32 mole) in ether (100 ml.). The mixture was boiled under reflux ($\frac{1}{2}$ hr.). Evaporation of the solvents and distillation *in vacuo* gave colourless crystalline hexamethyldisilazyl-lithium (44·2 g., 88%), m. p. 71—72° (lit.,[5] 70—72°), b. p. 80—84°/0·01 mm. (lit.,[5] 115°/1 mm.) (Found: C, 44·6; H, 10·6; Li, 3·9; N, 8·4. Calc. for $C_6H_{18}LiNSi_2$: C, 43·1; H, 10·8; Li, 4·2; N, 7·8%). The compound is unstable in air and catches fire when compressed.

Reactions of hexamethyldisilazyl-lithium with chlorosilanes (1 mol.) were carried out in boiling tetrahydrofuran (or ether in the case of trimethylchlorosilane). The solutions were filtered and evaporated, and the products were redissolved in light petroleum (b. p. 60—80°) and filtered to remove the last traces of lithium chloride. Evaporation of the solvent and distillation or sublimation *in vacuo* gave colourless *products*. Preparative and analytical data are recorded in Tables 1 and 2.

TABLE 1

$(Me_3Si)_2NLi$	Chlorosilane		Product			M. p.	B. p.
(g.)	Compound	(g.)	Compound	(g.)	(%)	(°c)	(°c/mm.)
3·5	Me_3SiCl	2·6	$(Me_3Si)_3N$	3·1	63	67—68°	79°/10[a]
10·4	Me_2SiCl_2	8·0	$(Me_3Si)_2NSiClMe_2$	3·3	21	57—58	75/1[b]
8·4	Et_2SiCl_2	7·9	$(Me_3Si)_2NSiClEt$	3·0	21	83—85	—
6·7	Ph_2SiCl_2	15·7	$(Me_3Si)_2NSiClPh_2$	3·0	20	53—55	117/0·5[c]
31·8	Ph_3SiCl	56·0	$(Me_3Si)_2NSiPh_3$	17·1	21	113—114	—

[a] Lit.,[5] m. p. 67—69°, b. p. 85°/13 mm. [b] Lit.,[5] m. p. 58—60°, b. p. 74—75°/1 mm. [c] Lit.,[5] m. p. 55—58°, b. p. 165—168°/0·5 mm.

TABLE 2

	Found (%)						Required (%)				
Compound	C	H	Cl	N	Si	Formula	C	H	Cl	N	Si
$(Me_3Si)_3N$[a]	46·3	11·9	—	6·2	36·3	$C_9H_{27}NSi_3$	46·3	11·65	—	6·0	36·1
$(Me_3Si)_2NSiClMe_2$[a]	37·8	9·5	14·0	6·5	32·4	$C_8H_{24}ClNSi_3$	37·9	9·5	14·0	5·5	33·1
$(Me_3Si)_2NSiClEt_2$	42·6	9·95	13·2	5·0	28·9	$C_{10}H_{28}ClNSi_3$	42·6	9·9	12·6	5·0	29·8
$(Me_3Si)_2NSiClPh_2$[a]	56·8	7·0	10·0	3·9	20·8	$C_{18}H_{28}ClNSi_3$	57·2	7·4	9·4	3·7	22·2
$(Me_3Si)_2NSiPh_3$	68·5	7·8	—	3·5	20·2	$C_{24}H_{33}NSi_3$	68·6	7·9	—	3·3	20·2

[a] Lit.[5]

Trimethylchlorosilane (13·6 ml, 0·11 mole) in tetrahydrofuran was added to triphenylsilylamine (13·4 g., 0·05 mole) in tetrahydrofuran (50 ml.) and n-butyl-lithium (0·10 mole) in pentane. The mixture was boiled (2 hr.), filtered, evaporated to dryness, and the residue was dissolved in benzene. Evaporation and sublimation of the product at 130—140°/0·15 mm. gave colourless crystalline *bis(trimethylsilyl)triphenylsilylamine* (8·2 g., 20%), m. p. and mixed m. p. 113—114°.

Dry methylamine was bubbled through a solution of trimethylchlorosilane (45 g., 0·4 mole) in benzene (250 ml.) (8 hr.). The mixture was boiled under reflux (5 hr.), and filtered. Fractional distillation gave *N*-methylhexamethyldisilazane (30 g., 83%), b. p. 55°/15 mm. (lit.,[10] 150°) (Found: C, 48·3; H, 11·8; N, 7·9; Si, 31·5. Calc. for $C_7H_{21}NSi_2$: C, 48·0; H, 12·0; N, 8·0; Si, 31·9%).

[8] D. E. Webster, *J.*, 1960, 5132; M. P. Brown and D. E. Webster, *J. Phys. Chem.*, 1960, **64**, 698.

[9] E. A. V. Ebsworth and S. G. Frankiss, *J. Amer. Chem. Soc.*, 1963, **85**, 3516.

[10] R. C. Osthoff and S. W. Kantor, *Inorg. Synth.*, 1957, **5**, 58.

This work was supported by the Wright Air Development Centre of the Research and Development Command, United States Air Force, through its European Office. We are indebted to Imperial Chemical Industries Limited (Nobel Division) for gifts of organosilicon compounds.

DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE, UNIVERSITY OF LONDON,
MALET STREET, LONDON W.C.1.

[*Received, August* 31*st,* 1964.]