1012. 1,3,5-*Triazines. Part VI.*[1] *The Reaction of Hexamethyldisilazyl-lithium with Cyanuric Chloride*

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Hexamethyldisilazyl-lithium reacts with cyanuric chloride to give bis(trimethylsilyl)carbodi-imide, 2,4,6-tris(hexamethyldisilazyl)-1,3,5-triazine, and tris(trimethylsilyl)amine. Interconversions of some of these products are reported, and possible reaction schemes are discussed.

Melamine is known to undergo acylation more readily by acid anhydrides than by acid halides.[2] There is no reaction between melamine and trimethylchlorosilane in boiling pyridine, and attempts to prepare silazyl derivatives of 1,3,5-triazine by this method were unsuccessful. Hexamethyldisilazyl-lithium is a versatile reagent, which reacts with a variety of inorganic acid halides to give hexamethyldisilazyl derivatives and lithium halides.[3] Cyanuric chloride behaves as an acid halide,[4] and reactions between these two compounds are reported here. Preliminary experiments established that tetrahydrofuran is a more satisfactory reaction medium than ether.

Reaction of hexamethyldisilazyl-lithium (3 moles) with cyanuric chloride in boiling tetrahydrofuran gives low yields of the expected 2,4,6-tris(hexamethyldisilazyl)-1,3,5-triazine, together with a monomeric species identified as bis(trimethylsilyl)carbodi-imide.[5] Tris(trimethylsilyl)amine [3] and traces of hexamethyldisilazane are also formed. The yellow insoluble residue, m. p. >300°, is believed to contain *N*-lithio-*N'*-trimethylsilylcarbodi-imide and lithium chloride.

The overall reaction is visualised as follows. Nucleophilic attack by hexamethyldisilazyl-lithium on cyanuric chloride gives 2,4,6-tris(hexamethyldisilazyl)-1,3,5-triazine.

$$3(Me_3Si)_2NLi + N_3C_3Cl_3 \longrightarrow N_3C_3[N(SiMe_3)_2]_3 + 3LiCl$$

This compound is comparatively volatile. Its proton magnetic resonance (p.m.r.) spectrum ($\tau = 9{\cdot}76$) shows, by the position of its Si-methyl protons in the series $(Me_3Si)_2NR$, that these are more deshielded than those in $N(SiMe_3)_3$, where $R = SiMe_3$,[3] in line with the electron-withdrawing properties of the 1,3,5-triazine ring. Thermal dissociation gives bis(trimethylsilyl)cyanamide which isomerises rapidly to form the carbodi-imide. Dissociation occurs under the conditions of the reaction, but the reverse reaction, polymerisation of the monomer, has not been observed at temperatures up to 250°.

$$N_3C_3[N(SiMe_3)_2]_3 \longrightarrow [3(Me_3Si)_2NCN] \longrightarrow 3Me_3Si{\cdot}N{:}C{:}N{\cdot}SiMe_3$$

The monomeric product is identical with that obtained by reaction of trimethylchlorosilane with silver cyanamide, which has been identified as bis(trimethylsilyl)carbodiimide by a number of authors,[5] having identical infrared (i.r.) and p.m.r. ($\tau = 9{\cdot}45$) spectra and the same gas–liquid chromatography retention time. The isomeric cyanamide is unknown. Hexamethyldisilazyl-lithium reacts with 2,4,6-tris(hexamethyldisilazyl)-1,3,5-triazine and with the carbodi-imide to give tris(trimethylsilyl)amine, and a yellow

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[1] Part V, R. A. Shaw and P. Ward, preceding Paper.

[2] E. M. Smolin and L. Rapoport, "*s*-Triazines and Derivatives," Interscience, New York and London, 1959, p. 337.

[3] See, *e.g.*, E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, *J.*, 1965, 2997, and refs. cited therein.

[4] W. Hewertson, R. A. Shaw, and B. C. Smith, *J.*, 1962, 3267.

[5] J. Pump and U. Wannagat, *Angew. Chem., Internat. Edn.*, 1962, **1**, 112; *Annalen*, 1962, **652**, 21. L. Birkofer, A. Ritter, and P. Richter, *Tetrahedron Letters*, 1962, 195. J. Pump, E. G. Rochow, and U. Wannagat, *Monatsh.*, 1963, **94**, 588. U. Wannagat, J. Pump, and H. Bürger, *ibid.*, p. 1013.

solid residue whose i.r. spectrum is similar to that of the yellow solid described above, showing peaks characteristic of carbodi-imide absorption.

$$Me_3Si{\cdot}N{:}C{:}N{\cdot}SiMe_3 + (Me_3Si)_2NLi \longrightarrow (Me_3Si)_3N + Me_3Si{\cdot}N{:}C{:}NLi$$

The formation of hexamethyldisilazane can be explained by hydrolysis caused by traces of water present despite the precautions taken.

$$(Me_3Si)_2NLi + H_2O \longrightarrow (Me_3Si)_2NH + LiOH$$

EXPERIMENTAL

Cyanuric chloride was recrystallised twice from carbon tetrachloride. Organic solvents were dried by conventional methods. Reactions and manipulations were carried out in an atmosphere of nitrogen. Standard solutions of hexamethyldisilazyl-lithium in tetrahydrofuran were prepared by methods described previously.[3]

Reaction of Hexamethyldisilazyl-lithium with Cyanuric Chloride.—A solution of hexamethyldisilazyl-lithium (19·0 g., 0·114 mole) in tetrahydrofuran (100 ml.) was added slowly (3 hr.) to a stirred solution of cyanuric chloride (7·0 g., 0·038 mole) in tetrahydrofuran (75 ml.), and the mixture was boiled under reflux (48 hr.). A yellow insoluble solid (4·6 g.), m. p. >360°, containing, C, H, N, Si, Li, and Cl, was removed by filtration. Fractional distillation of the filtrate gave: hexamethyldisilazane (0·34 g., 1·8%), b. p. 124° (Found: C, 44·6; H, 11·6; N, 8·4. Calc. for $C_6H_{19}NSi_2$: C, 44·7; H, 11·8; N, 8·6%); bis(trimethylsilyl)carbodi-imide (5·2 g., 25%), b. p. 162—164°, 71°/15 mm. (Found: C, 45·8; H, 9·7; N, 15·1; Si, 29·9%; *M*, 189. Calc. for $C_7H_{18}N_2Si_2$: C, 45·2; H, 9·7; N, 15·0; Si, 30·1%; *M*, 186); 2,4,6-*tris(hexamethyldisilazyl)*-1,3,5-*triazine* (1·6 g., 7·5%), m. p. 78—80°, b. p. 115°/0·1 mm. (Found: C, 44·7; H, 9·5; N, 15·7%; *M*, 485. $C_{21}H_{54}N_6Si_6$ requires C, 45·2; H, 9·7; N, 15·0%; *M*, 558); and tris(trimethylsilyl)amine (2·4 g., 13·5%), b. p. 42°/0·01 mm., m. p. and mixed m. p. 69°.

2,4,6-*Tris(hexamethyldisilazyl)*-1,3,5-*triazine.*—*Thermal decomposition.* The triazine (0·08 g., 0·14 mmole) was heated in a sealed tube at 100°. The liquid product was identified as bis(trimethylsilyl)carbodi-imide (0·068 g., 85%).

A solution of 2,4,6-tris(trimethylsilyl)-1,3,5-triazine (0·02 g., 0·036 mmole) in tetrahydrofuran was boiled under reflux (3 days). Distillation gave bis(trimethylsilyl)carbodi-imide (0·009 g., 45%).

Reaction with hexamethyldisilazyl-lithium. Hexamethyldisilazyl-lithium (0·05 g., 0·3 mmole) in tetrahydrofuran (20 ml.) was added to a solution of 2,4,6-tris(hexamethyldisilazyl)-1,3,5-triazine (0·05 g., 0·09 mmole) in tetrahydrofuran (10 ml.). The mixture was boiled under reflux (48 hr.), evaporated to dryness, and extracted with benzene. The solid residue (0·04 g.), m. p. >360°, containing C, H, N, Si, and Li, was insoluble in most organic solvents. Distillation of the filtrate gave bis(trimethylsilyl)carbodi-imide (0·02 g., 30%) and tris(trimethylsilyl)amine (0·03 g., 60%).

Bis(trimethylsilyl)carbodi-imide.—*Preparation.* This compound (yield 5·0 g., 90%), b. p. 163°, was prepared by adding a solution of trimethylchlorosilane (3·2 g., 0·03 mole) in benzene (10 ml.) to a suspension of silver cyanamide (7·4 g., 0·03 mole) in benzene.

Reaction with hexamethyldisilazyl-lithium. Bis(trimethylsilyl)carbodi-imide (2·8 g., 0·016 mole), was added to a solution of hexamethyldisilazyl-lithium (2·5 g., 0·016 mole), in tetrahydrofuran (50 ml.). The colourless solution became yellow on boiling (48 hr.). Distillation gave hexamethyldisilazane (0·1 g., 4%), b. p. 126°; tris(trimethylsilyl)amine (0·3 g., 9%), m. p. and mixed m. p. 69°; and an amorphous yellow solid residue (1·5 g.), m. p. >360° (Found: C, 51·8; H, 4·2; Li, 3·9; N, 29·9; Si, 10·8%).

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