CHROM. 4676

REDISTRIBUTION REACTIONS OF TRIS(N-ALKYL)HEXAMETHYL-CYCLOTRISILAZANES

A. D. M. HAILEY AND G. NICKLESS

Department of Inorganic Chemistry, School of Chemistry, The University, Bristol 8 (Great Britain)
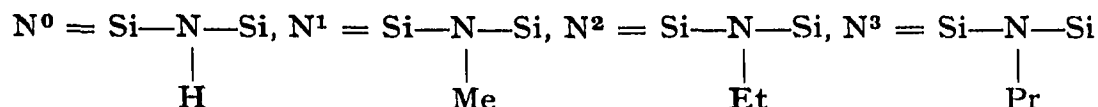
SUMMARY

Some preliminary investigations into the interchanges involving different cyclotrisilazanes have been carried out. This reaction was found to proceed very easily at moderate temperatures, especially in a polar solvent. Dimethyldichlorosilane was used as the starting material in the preparation of all the heterocycles, synthesis in all cases being relatively straightforward.

INTRODUCTION

MOEDRITZER AND VAN WAZER[1,2] reported the reaction between hexamethylcyclotrisilthian and nonamethylcyclotrisilazane to form two new cyclosilthiazanes. In view of the growing interest in the chemistry of silicon heterocycles containing sulphur and nitrogen atoms in the ring, it was decided to investigate a range of compounds of this type, to see if similar redistributions occurred in other mixed heterocycle systems. It was found that interchange of N-alkyl groups occurred very readily at moderate temperatures, no catalyst being required for the reaction. For each pair of cyclotrisilazanes that were heated together, two new mixed N-alkylcyclotrisilazanes were formed. The reaction appears to be essentially of the same class as that reported for borazoles by McCLOSKEY et al.[3].

NOMENCLATURE

In the present work, several cyclotrisilazanes were used, and the shorthand notation employed is as follows:

$$N^0 = \underset{\underset{H}{|}}{Si-N-Si}, \quad N^1 = \underset{\underset{Me}{|}}{Si-N-Si}, \quad N^2 = \underset{\underset{Et}{|}}{Si-N-Si}, \quad N^3 = \underset{\underset{Pr}{|}}{Si-N-Si}$$

Each cyclotrisilazane can then be written as $N^x N^y N^z$. Thus $N^1 N^1 N^1$ is nonamethylcyclotrisilazane.

EXPERIMENTAL

Preparation of cyclotrisilazanes

Tris(N-methyl)- and tris(N-ethyl)hexamethylcyclotrisilazanes were prepared as described by ABEL AND BUSH[4]. Hexamethylcyclotrisilazane and octamethyl-cyclotetrasilazane were prepared by the method of OSTHOFF AND KANTOR[5].

Preparation of cyclotrisilazanes containing large N-alkyl groups is known to be difficult or in some cases almost impossible by synthetic routes known to date. For example, BREED AND ELLIOTT[6] were unable to prepare the compound $(Me_2SiNBu)_3$, and could recover only 27% of the original bis(N-butyl)dimethylsilane. However, these authors made no reference to any attempt to prepare the tris(N-propyl) compound. In the present work, this compound was synthesized, but could not be isolated in a pure condition.

179 g n-propylamine were dissolved in 250 ml dry hexane and cooled in ice. To the well stirred solution was added a solution of 84 g dimethyldichlorosilane in 200 ml n-hexane, over a period of 40 min. The reaction mixture was allowed to come to room temperature, and stirred for a further 4 h. The n-propylamine hydrochloride was filtered off from the reaction product, n-hexane removed by distillation and the residue fractionated to give 81 g bis(n-propylamino)dimethylsilane, b.p. 53–54° (12 mm). Microanalysis gave %C = 55.31, %H = 12.83, %N = 15.94 ($C_8H_{22}N_2Si$ requires %C = 55.2, %H = 12.65, %N = 16.1).

77 g of this product was refluxed with 0.1 g ammonium sulphate for 22 h. After this time gas chromatographic analysis indicated the formation of a high-boiling product, but most of the silylamine still remained. An additional small quantity of ammonium sulphate was added, and refluxing continued for a further 16 h.

From the fractionation of the reaction product were obtained 35 g unchanged bis(n-propylamino)dimethylsilane, and 9 g of a brown oil, b.p. 56° (20 mm). Gas chromatographic analysis* of the oil showed the presence of a high boiling compound thought to be the desired tris[N-(n-propyl)]hexamethylcyclotrisilazane. The oil also contained appreciable quantities of components of low retention volume, and was therefore stripped of these by vacuum sublimation. Microanalysis of the stripped product gave %C = 44.1, %H = 9.48, %N = 10.29 ($C_{15}H_{39}N_3Si_3$ requires %C = 52.1, %H = 11.3, %N = 12.2). Subsequent gas chromatographic analysis indicated that more of the low-boiling impurities had formed. It is possible that some sort of ring-chain equilibrium was occurring, although in such equilibria the chain compound is normally present in very small quantities. The redistribution reactions and gas chromatographic retention data described in this paper leave little doubt that the major component in the oil was, in fact, tris[(N-(n-propyl)]hexamethylcyclotrisilazane. The compound also gave an expected distribution of products when heated with hexamethylcyclotrisilthian. Nevertheless, isolation of this compound would obviously be highly desirable.

Redistribution reactions

A series of reactions was run in which $N^1N^1N^1$ and $N^2N^2N^2$ were heated together

---

* A Pye F104 gas chromatograph, equipped with dual flame ionisation detectors, columns of 6 ft. × $^1/_4$ in. O.D., containing a stationary phase of 12% w/w Silicone Gum SE-30 on Chromosorb W, at a flow rate of 60 ml/min, at 180°.
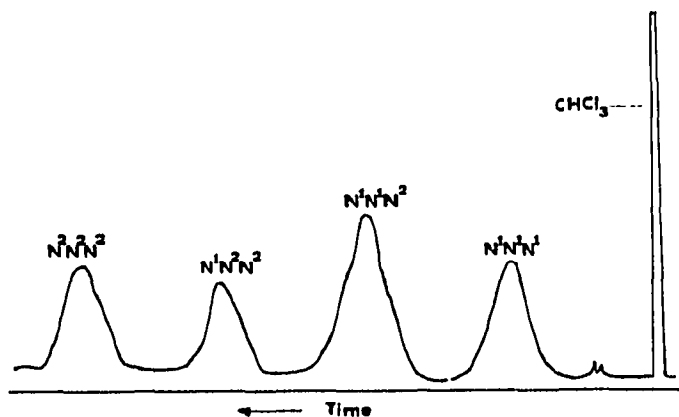
Fig. 1. Chromatogram of the equilibrated mixture from the $N^1N^1N^1$–$N^2N^2N^2$ system in chloroform.

with several solvents at 150° in sealed glass tubes. It was found that two new compounds were formed, with retention volumes intermediate between those of the starting materials (Fig. 1). Neither of these new compounds was formed when the cyclotrisilazanes were heated individually, and their identities were tentatively assigned as $N^1N^1N^2$ [N-ethyl-bis(N-methyl)hexamethylcyclotrisilazane], and $N^1N^2N^2$ [bis(N-ethyl)-N-methylhexamethylcyclotrisilazane], *i.e.*
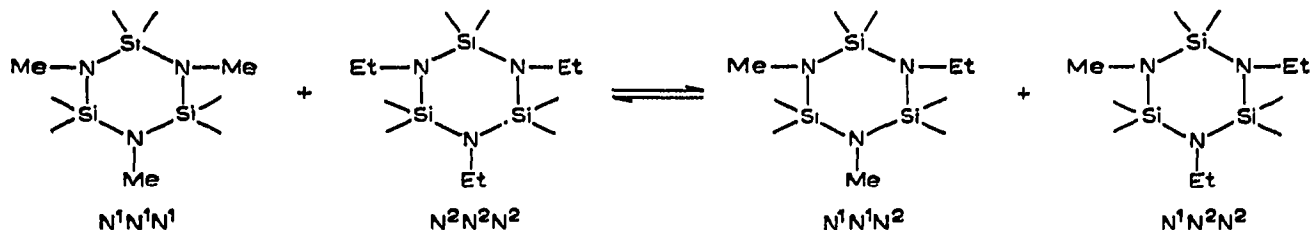
It was found that formation of the new compounds was enhanced when chloroform was used as solvent, whereas benzene and hexane tended to inhibit the reaction (Fig. 2). The reaction also occurred when no solvent was used, and in less than 4 h in chloroform. The reaction also proceeded at room temperature (24°) in chloroform, equilibrium being reached in about three weeks. Analysis of the reaction mixture
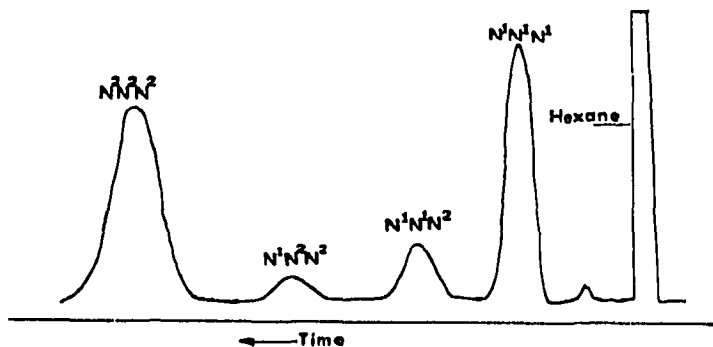

Fig. 2. Chromatogram of the equilibrated mixture from the $N^1N^1N^1$–$N^2N^2N^2$s ystem after two days at 140° in *n*-hexane.

by a gas chromatograph coupled to a selective nitrogen detector (flowing conductivity cell) of the type described by COULSON[7] indicated that each component contained approximately equal quantities of nitrogen.

The proton resonance spectrum of the initial $N^1N^1N^1$–$N^2N^2N^2$ mixture contained five resonances with the following assignments[4] (Table I).

TABLE I

ASSIGNMENT OF PROTON RESONANCE IN A MIXTURE OF $(Me_2SiNMe)_3$ AND $(Me_2SiNEt)_3$

τ-value	Multiplicity	Proton environment	Molecule of origin
9.96	Singlet	Me / Si \\ Me	$N^1N^1N^1$
9.89	Singlet	Me / Si \\ Me	$N^2N^2N^2$
9.00	Triplet	C–Me	$N^2N^2N^2$
7.57	Singlet	N–Me	$N^1N^1N^1$
7.18	Quartet	$N–CH_2–C$	$N^2N^2N^2$

The compounds $N^1N^1N^2$ and $N^1N^2N^2$ can each be expected to give rise to six resonances, five of which are also given by the $N^1N^1N^1$–$N^2N^2N^2$ mixture. The only new resonance is that due to silyl methyl groups in the environment $Me_2Si(NMe)NEt$, and is common to both molecules. This resonance can be expected to have a value intermediate between those for $Me_2Si(NMe)_2$ and $Me_2Si(NEt)_2$. The proton resonance spectrum of the equilibrated mixture (Fig. 3) showed a new resonance at 9.92τ, intermediate between the original silylmethyl signals. No other new resonances were produced. The 9.92τ signal from a $N^1N^1N^1$–$N^2N^2N^2$ mixture, which had been equi-
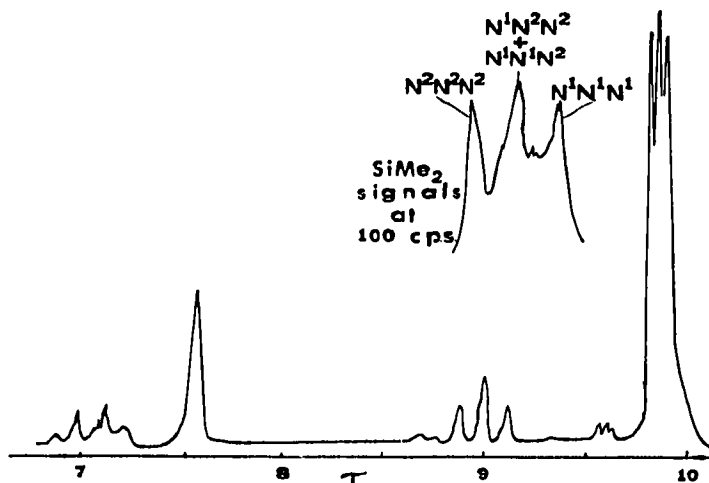

Fig. 3 Proton magnetic resonance spectrum of the equilibrated mixture from the $N^1N^1N^1$–$N^2N^2N^2$ system.

librated in chloroform at room temperature for several weeks, increased in intensity when the mixture was heated at 150° for 6 h. The change in intensity corresponded to the formation of greater quantities of the components assigned as $N^1N^1N^2$ and $N^1N^2N^2$. The compounds $N^1N^1N^2$ and $N^1N^2N^2$ should have two silylmethyl proton nuclear magnetic resonances in the ratio of 2:1, because of the environment Me_2Si-(NMe)NEt.

The fractions collected by trapping the effluent from the analytical gas chromatographic column suspected of being $N^1N^1N^2$ and $N^1N^2N^2$ showed in their resultant PMR spectra that these peaks were in the ratio of 2:1. Attempts were made to prepare further samples by large column preparative gas chromatography, however, the efficiency of the separation was too low to allow isolation of pure components.

Using the mixture containing $N^3N^3N^3$ two more systems, *viz.* $N^1N^1N^1$–$N^3N^3N^3$ and $N^2N^2N^2$–$N^3N^3N^3$, were studied. In each case two new compounds were formed with retention volumes intermediate between those for the starting materials. None of the new compounds was formed when the $N^3N^3N^3$-containing mixture was heated on its own. The suggested equilibria in the two systems are:
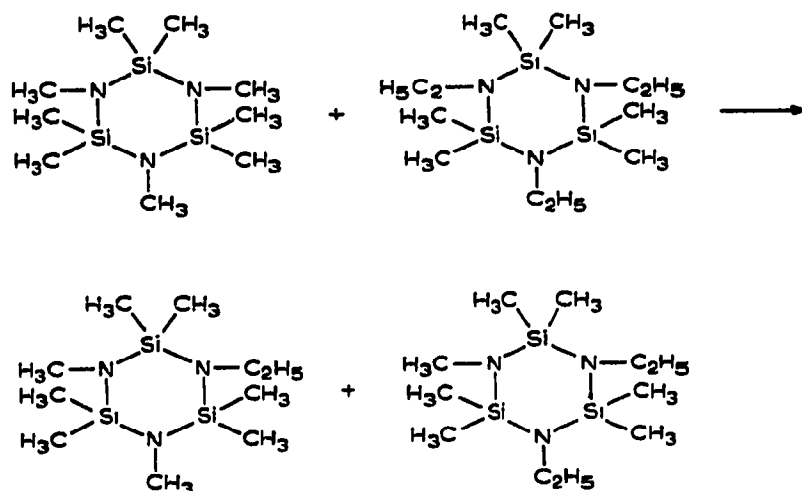
These systems also contained numerous components of low retention volume, which originated from the original $N^3N^3N^3$ mixture. In both systems the new components were formed more readily when chloroform was present than when hexane was used as a solvent.

The compounds $N^1N^1N^1$ and $N^1N^1N^2$ form a homologous series, the unit of difference being a methylene group. A plot of log corrected retention volume (or retention time) *versus* carbon number for these compounds should therefore be a straight line, if there are no complicating factors in their chromatography. A plot of log corrected retention time *versus* N-alkyl carbon number was made for the three systems studied, assuming the identities given above for the newly formed compounds. This resulted in a straight line (Fig. 4) which tended to confirm these identities. It is of interest to note that the most asymmetric cyclotrisilazanes, $N^1N^1N^3$ and $N^1N^3N^3$, both had slightly higher retention times than the more symmetrical compounds with the same carbon number. This chromatographic behaviour parallels that observed in these laboratories for asymmetric tetraalkylsilanes[8,9].
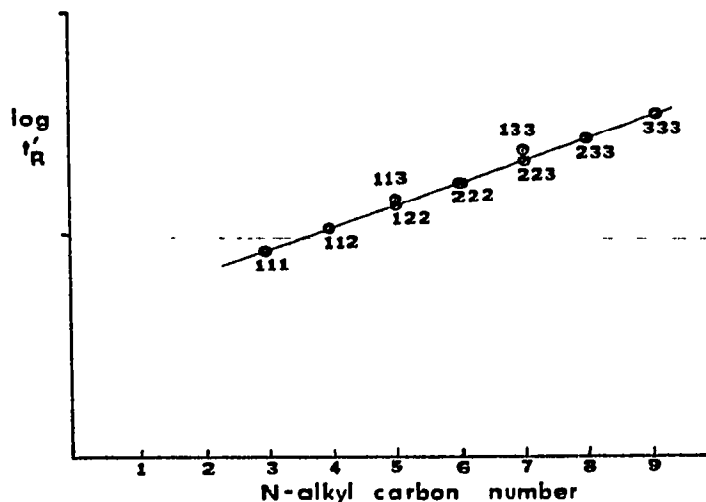
Fig. 4. Plot of log t_R' versus N-alkyl carbon number for cyclotrisilazanes.

DISCUSSION

This type of interchange must involve fission either of nitrogen–silicon or nitrogen–carbon bonds. Fission of nitrogen–silicon linkages, involving ring opening, could be expected to give rise to higher membered rings and possible chain products. This is not in accordance with the chemistry of the cyclotrisilazanes, which are known to be thermally stable up to 300° (ref. 10), and no decomposition products of this nature could be detected. An indication that nitrogen–carbon bond fission may be involved was given by the fact that no interchange at all could be obtained in the $N^0N^0N^0$–$N^1N^1N^1$ and $N^0N^0N^0$–$N^2N^2N^2$ systems, up to a temperature of 180°. Similarly, no reaction took place when $N^0N^0N^0N^0$ and $N^1N^1N^1$ were heated together.

Using standard CALINGAERT[11] type equations for $n = 3$, the expected stoichiometries in the equilibrated redistributed product, starting from $N^1N^1N^1$ and $N^2N^2N^2$ in equimolar quantities, are

$$[N^1N^1N^1] = [N^2N^2N^2] = 0.125$$
$$[N^1N^1N^2] = [N^1N^2N^2] = 0.375$$

assuming ideality. However, there seems a bias away from $N^1N^2N^2$ in the work pre-

TABLE II

RELATIVE PROPORTIONS OF CYCLOTRISILAZANES IN THE REDISTRIBUTION OF $N^1N^1N^1$–$N^2N^2N^2$

Compound	Mole fraction at 24° after 3 weeks	Mole fraction at 150° after 4 h
$N^1N^1N^1$	0.275	0.206
$N^1N^1N^2$	0.147	0.292
$N^1N^2N^2$	0.081	0.206
$N^2N^2N^2$	0.497	0.296

sented here. The stoichiometries obtained for the $N^1N^1N^1$–$N^2N^2N^2$ reaction at room temperature and 150° are given in Table II.

As a check it would be of interest to heat a sample of $N^1N^1N^2$ which should give $[N^1N^1N^1] = 0.296$, $[N^1N^1N^2] = 0.445$, $[N^1N^2N^2] = 0.198$, and $[N^2N^2N^2] = 0.037$. It would also be of importance to check on differences from ideality by obtaining true equilibrium constants.

A similar bias appeared to occur in the two reactions involving $N^3N^3N^3$, but in these cases quantitative data were not obtained.

CONCLUSION

The evidence given above indicates that N-alkyl interchange occurs, without the aid of a catalyst, when N-alkylcyclotrisilazanes are heated together at moderate temperatures.

ACKNOWLEDGEMENT

REFERENCES

1 K. MOEDRITZER AND J. R. VAN WAZER, Inorg. Nucl. Chem. Letters, 2 (1966) 45.
2 K. MOEDRITZER AND J. R. VAN WAZER, J. Phys. Chem., 70 (1966) 2030.
3 H. C. NEWSON, W. G. WOODS AND A. C. McCLOSKEY, Inorg. Chem., 2 (1963) 36.
4 E. W. ABEL AND R. P. BUSH, J. Inorg. Nucl. Chem., 26 (1964) 1685.
5 R. C. OSTHOFF AND S. W. KANTOR, Inorg. Syn., 5 (1957) 61.
6 L. W. BREED AND R. L. ELLIOTT, Inorg. Chem., 2 (1964) 1622.
7 D. M. COULSON, Advan. Chromatog., 3 (1966) 197.
8 F. H. POLLARD, G. NICKLESS AND P. C. UDEN, J. Chromatog., 14 (1964) 1.
9 A. D. M. HAILEY, Ph. D. Thesis, University of Bristol, 1967.
10 D. V. ZHINKIN, E. A. SEMENOVA, M. V. SOBOLEVSKII AND K. ANDRIANOV, Plasticheskie Massy, 13 (1963) 16; C.A., 60 (1964) 8055.
11 G. CALINGAERT, H. SORROOS AND V. HNIZDA, J. Am. Chem. Soc., 62 (1940) 1107.