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NOTE

THE THERMAL EQUILIBRATION OF TRIMETHYLSILYL DERIVATIVES OF ETHYLENEDIAMINE

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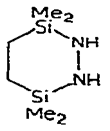
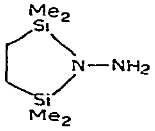
In a series of comprehensive publications[1], West and his co-workers have described both the kinetic and thermodynamic aspects of the intramolecular anionic rearrangement of bis(trialkylsilyl)derivatives of hydrazines. Recently West, Ishikawa and Murai[2] have extended these studies to bis(trialkylsilyl) derivatives of ethylenediamines, and have shown that these compounds will likewise undergo intramolecular anionic rearrangment. Pitt and Skillern[3] have previously observed that in at least two cases, specifically *N,N*- and *N,N'*-bis(trimethylsilyl)hydrazine and 3,3,6,6-tetramethyl-1,2-diaza-3,6-disilacyclohexane (I) and 1-amino-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (II), the hydrazine rearrangement will proceed thermally in the absence of any added catalyst; and at least in the system (I) $\rightleftarrows$ (II), an intramolecular mechanism must be operative. We have now investigated the rearrangement of *N,N*- and *N,N'*-bis(trimethylsilyl)ethylenediamine in the absence of added catalysts, and find that equilibration will occur at 140°. However, under these conditions, the rearrangement occurs by an intermolecular process.



(I)



(II)

EXPERIMENTAL PROCEDURE

Because of the complexity of the thermal rearrangement, GLC (2% SE 52 on siliconized Chromosorb G) was found to be the superior method of analysis. The ratios of the GLC peak areas of equilibria mixtures were calibrated by using standard mixtures of the pure components. *N,N'*-Bis(trimethylsilyl)ethylenediamine and *N,N,N'*-tris(trimethylsilyl)ethylenediamine were prepared by literature procedures[4,5]. *N,N*-Bis(trimethylsilyl)ethylenediamine was prepared by methanolysis of *N,N,N'*-tris(trimethylsilyl)ethylenediamine. This method of preparation of the *N,N*-isomer, which has been developed independently by West[2], promises to be a useful synthetic technique*. The rearrangement of *N,N*- and *N,N'*-bis(trimethylsilyl)ethylenediamine was carried out in sealed tubes at 140° in the absence of solvent. The equilibrium position was approached from both the *N,N*- and *N,N'*-isomers, and the small discrepancy in the material balance at equilibrium is attributed to the difficulty in determining the GLC peak areas, particularly for *N*-(trimethylsilyl)ethylenediamine, because of tailing, small amounts of hydrolysis during the analysis, and minor side reactions. *N*-(Trimethylsilyl)ethylenediamine was too unstable to be isolated pure**, readily disproportionating to ethylenediamine and *N,N'*-bis(trimethylsilyl)ethylenediamine, and its structure is inferred from the GLC retention time and its formation when a large excess of ethylenediamine is treated with trimethylchlorosilane. No *N,N,N',N'*-tetrakis(trimethylsilyl)ethylenediamine[5] was detected during rearrangement, or after equilibrium was established.

RESULTS

The composition of typical equilibrating mixtures *vs.* time are shown in Table 1. Inspection of the composition during the early stages of the rearrangement reveals large concentrations of *N,N,N'*-tris(trimethylsilyl)ethylenediamine and *N*-(trimethylsilyl)ethylenediamine. Clearly in contrast to the base catalyzed rearrangement, an intermolecular process is at least partially responsible for the isomerization. Ammonium chloride had no effect on the rate. However, it is pertinent to note that for the analogous hydrazine rearrangement, when a sample of *N,N*-bis(trimethylsilyl)-

TABLE 1

EQUILIBRATION OF *N,N*- AND *N,N'*-BIS(TRIMETHYLSILYL)ETHYLENEDIAMINE AT 140°
Figures refer to mole %.

Time (h)	*N*[a]	*N,N*[b]	*N,N'*[c]	*N,N,N'*[d]	Siloxane, etc.[e]
0	0	100	0	0	0
1	20	38	6	36	3
1.5	17	30	9	44	2
2.5	12	16	26	46	1
69	2	0	84	14	1
162	2	0	83	15	2
0	0	0	100	0	0
69	10	0	81	9	2.5
162	10	0	80	10	5

[a] *N*-(Trimethylsilyl)ethylenediamine. [b] *N,N*-Bis(trimethylsilyl)ethylenediamine. [c] *N,N'*-Bis(trimethylsilyl)-ethylenediamine. [d] *N,N,N'*-Tris(trimethylsilyl)ethylenediamine. [e] Includes silanol, siloxane, ethylenediamine and other volatile unidentified products; numbers refer to % of total mixture and are not included in material balance.

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* For example, *N,N*-bis(trimethylsilyl)hydrazine can be separated from a mixture with the *N,N'*-isomer by selective destruction of the latter with isopropanol, thus avoiding either a tedious fractional distillation or preparative GLC.

** For this reason, the GLC peak area of this isomer could not be calibrated, and the percentages shown in Table 1 must represent minimum numbers.

hydrazine was prepared via distillation from a catalytic amount of potassium methoxide, the rearrangement of this sample proceeded at a reasonable rate at 100° only when hydrazine hydrochloride was added. Thus, it is possible that all cases of thermal isomerization in these systems[3] may involve catalysis by a small concentration of ammonium salts. The results of this study are essentially in agreement with those reported for the anionic rearrangement, where the *N,N'*-isomer predominates (>97%) at equilibrium. As West *et al.*[2] have pointed out, the relative thermodynamic stabilities of the *N,N*- and *N,N'*-bis(silyl) derivatives in both the ethylenediamine and hydrazine series will be influenced by numerous factors. Steric effects alone cannot explain the complete absence of *N,N*-bis(trimethylsilyl)ethylenediamine in the thermal rearrangement, for *N,N,N'*-tris(trimethylsilyl)ethylenediamine must be more sterically hindered and yet persists at equilibrium.

In order to determine whether the relative thermodynamic stabilities of the bis(silyl) derivatives of hydrazine and ethylenediamine might be reflected in their relative basicities, we have compared the ability of these bases to shift the C–D stretching frequency of $CDCl_3$. This method has been used by Abel[6] to compare the base strengths of a variety of Group IV amines. Although our data (Table 2) are limited, it is interesting to note that the least basic isomer predominates in both equilibria, suggesting that the energy of the nitrogen lone pair electrons may play a role in determining the equilibria compositions. In agreement with previous studies[6] and the postulate of p_π–d_π bonding, trimethylsilylation reduces the basicity of hydrazines and ethylenediamine. The generally greater values of $\Delta\nu$(C–D) and the lower percentage of unshifted C–D absorption observed for the unsymmetrically substituted trimethylsilyl derivatives of the hydrazines and ethylenediamine, relative to the corresponding trimethylsilyl derivatives of ammonia and alkylamines[6], suggest that $\Delta\nu$(C–D) is determined primarily by the more basic (non-silylated)

TABLE 2

BASICITY OF SUBSTITUTED HYDRAZINES AND ETHYLENEDIAMINES

Compound	$\Delta\nu$(C–D)[a]	Compound	$\Delta\nu$(C–D)[a]
Disubstituted hydrazines		*Tetrasubstituted hydrazines*	
$Me_2N–NH_2$[b]	58	$(Me_3Si)_2N–NMe_2$[10]	41[d]
MeNH–HNMe[8]	70	$Me_3SiNMe–MeNSiMe_3$[10]	40[e]
$(Me_3Si)_2N–NH_2$[1,3,9]	31	$Me_2N–NMe_2$[11]	74
$Me_3SiNH–HNSiMe_3$[1,3,9]	35[c]		
Trisubstituted hydrazines		*Ethylenediamines*	
$(Me_3Si)NH–NMe_2$[10]	51	$(Me_3Si)_2NCH_2CH_2NH_2$	60
$MeNH–NMe_2$[11]	66	$Me_3SiNHCH_2CH_2NHSiMe_3$[4]	50

[a] C–D stretching frequency shift of $CDCl_3$ (~1 mole) in amine (~10 mole) relative to corresponding mode of gaseous $CDCl_3$. [b] Commercial source, redistilled from calcium hydride; other compounds were prepared by the indicated literature methods; the purity of all samples was confirmed by GLC and refractive indices. [c] Major peak, some unshifted C–D absorption. [d] Minor peak, unshifted C–D absorption predominates. [e] Shoulder on unshifted C–D absorption.

nitrogen atom*. Thus in these unsymmetrical derivatives, silylation probably plays a secondary role, reducing the basicity by either increasing inductive electron withdrawal or decreasing non-bonded electron-electron repulsions.

Values of $\Delta\nu$(C–D) for purely methyl-substituted hydrazines** are included in Table 2 because they illustrate that the unexpectedly lower basicity of *N,N*-bis(trimethylsilyl)hydrazine, relative to the *N,N'*-isomer, can be explained by the substitution pattern rather than by any property (*e.g.*, *d*-orbitals) peculiar to the silicon atoms.

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REFERENCES

1 (a) R. West and M. Ishikawa, *J. Amer. Chem. Soc.*, 89 (1967) 4981;
(b) R. West, M. Ishikawa and R. E. Bailey, *J. Amer. Chem. Soc.*, 89 (1967) 4068, 4072, 88 (1966) 4648;
(c) R. E. Bailey and R. West, *J. Amer. Chem. Soc.*, 86 (1964) 5369.
2 (a) M. Ishikawa and R. West, *Abstr. Papers, 153rd Nat. Meeting Amer. Chem. Soc.*, Miami, Fla., April 1967, Paper L-132;
(b) R. West and M. Ishikawa, *J. Amer. Chem. Soc.*, 89 (1967) 5049;
(c) R. West, M. Ishikawa and S. Murai, *J. Amer. Chem. Soc.*, 90 (1968) 727.
3 C. G. Pitt and K. R. Skillern, *Inorg. Chem.*, 6 (1967) 865.
4 D. Kummer and E. G. Rochow, *Z. Anorg. Allg. Chem.*, 321 (1963) 21.
5 Hsiu-Chung Chou, Ch'ing-Lan Hsieh and Seng-Yu Chang, *K'o Hsueh T'ung Pao*, (1963) 63; *Chem. Abstr.*, 60 (1964) 8055.
6 (a) E. W. Abel, D. A. Armitage and G. R. Willey, *Trans. Faraday Soc.*, 60 (1964) 1257;
(b) E. W. Abel, D. A. Armitage and D. B. Brady, *Trans. Faraday Soc.*, 62 (1966) 3459;
(c) See also, E. W. Randall, C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, 6 (1967) 744.
7 R. L. Hinman, *J. Org. Chem.*, 23 (1958) 1587.
8 R. L. Hinman, *J. Amer. Chem. Soc.*, 78 (1956) 1645.
9 U. Wannagat, F. Höfler and H. Bürger, *Monatsh. Chem.*, 96 (1965) 2038.
10 U. Wannagat and F. Höfler, *Monatsh. Chem.*, 97 (1966) 976.
11 J. B. Class, J. G. Aston and T. S. Oakwood, *J. Amer. Chem. Soc.*, 75 (1953) 2937.

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* It can be assumed, for infrared frequencies, that ν(C–D) will not be the time-averaged frequency of hydrogen bonds to each nitrogen atom.

** For the pK_b's of alkyl-substituted hydrazines see ref. 7.