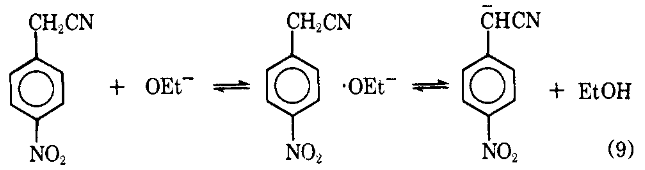

(9)

centration are curved. The results are interpreted in terms of the *simultaneous* formation of a complex, probably the σ complex II,[12] the reaction having a low equilibrium constant (6 M^{-1}) at 25°; the possibility that this complex is an intermediate in the formation of the TNT⁻ ion is not, however, excluded by the kinetic results.

The reactions of ethoxide ion with TNT and TNT-d_3 proceed at almost twice the rate in EtOD as the respective reactions in ethanol. The kinetic solvent isotope effects of 1.81 and 1.97 at 25° may be compared with the following values: 1.96 for σ-complex formation between methoxide ion and 2,4-dinitroanisole in methanol,[16] 1.67 for σ-complex formation between methoxide ion and 2-cyano-4,6-dinitroanisole in methanol,[17] 1.84 for σ-complex formation between ethoxide ion and 2,4-dinitrochlorobenzene in ethanol,[18] and 1.92 for the reaction between ethoxide ion and 1,3,5-trinitrobenzene in ethanol.[19] Bunton and Shiner[20] have suggested that such solvent isotope effects arise principally from differences in zero-point energy changes during formation of the activated complex in the two solvents (see also ref 21). Desolvation occurs during the formation of the activated complex of ethoxide ion and TNT, and this results in a change in the stretching frequencies of the OH bonds concerned. On a simple electrostatic model the expected value of $k_f(\mathrm{EtOD})/k_f(\mathrm{EtOH})$ is 1.28 at 25°, and on a covalent model the expected value is 2.09. The estimates are very approximate because the stretching frequencies are not accurately known, and no attempt has been made to take into account possible changes in solvation of nitro groups of the TNT. The estimates do, however, bracket the experimental value of $k_f(\mathrm{EtOD})/k_f(\mathrm{EtOH})$, and the desolvation model provides a reasonable explanation of the kinetic solvent isotope effect. A similar explanation has been put forward[18] for the kinetic solvent isotope effect observed in the reaction of ethoxide ion with 2,4-dinitrochlorobenzene.

Acknowledgment. The authors are grateful to the National Research Council of Canada for financial support of this work, and to Dr. P. Sheridan for discussion. We thank Dr. C. F. Bernasconi for sending us a copy of his manuscript in advance of publication.

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(19) L. H. Gan and A. R. Norris, *Can. J. Chem.*, **49**, 2490 (1971).

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New Anionic Rearrangements. XIV.[1] Temperature-Dependent Proton Nuclear Magnetic Resonance of Organosilylhydrazine Anions[2,3]

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Abstract: The rearrangement of organosilylhydrazine anions has been studied by variable-temperature proton nmr spectroscopy, and approximate rates have been determined from coalescence temperatures for nonequivalent organosilyl groups. Spectra are included for lithium tris(trimethylsilyl)hydrazide (**1a**) and the N,N and N,N′ isomers of various lithium bis(organosilyl)methylhydrazides. Evidence is presented for a dimer–monomer equilibrium of **1a** in diethyl ether in which intramolecular organosilyl migration takes place in the dimer and monomer forms at different rates. Low-temperature proton nmr also provides evidence for formation of mixed aggregates of alkyllithium and lithium bis(trimethylsilyl)methylhydrazide.

The 1,2 anionic rearrangement of bis(organosilyl)hydrazines in which organosilyl groups move from one nitrogen to another has been described in a recent series of papers.[4–8] The rearrangement is rapid, intramolecular, base catalyzed, and proceeds to equilibrium.[6] The kinetics of the catalyzed rearrangement and a tentative description of the mechanism of reaction have also been presented.[7] Protonation and deprotonation are the rate-determining steps in the catalytic rearrangement. Since the process is catalyzed

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[1] Previous paper in the series: R. West and G. A. Gornowicz, *J. Organometal. Chem.*, **28**, 25 (1971).

[2] For a review of silyl anionic rearrangements, see R. West, *Pure Appl. Chem.*, **19**, 291 (1969).

[3] Research sponsored by Air Force Office of Scientific Research (NC) O.A.R., USAF, Grant No. AF-AFOSR, 70-1904.

[4] R. E. Bailey and R. West, *J. Amer. Chem. Soc.*, **86**, 5369 (1964).

(5) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966).

(6) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4068 (1967).

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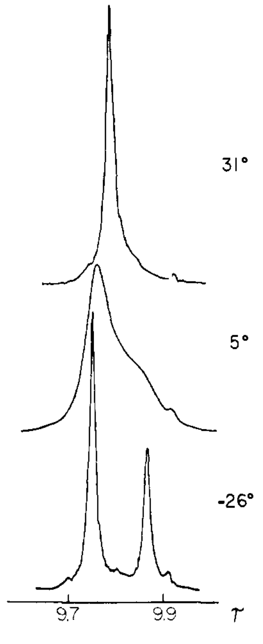
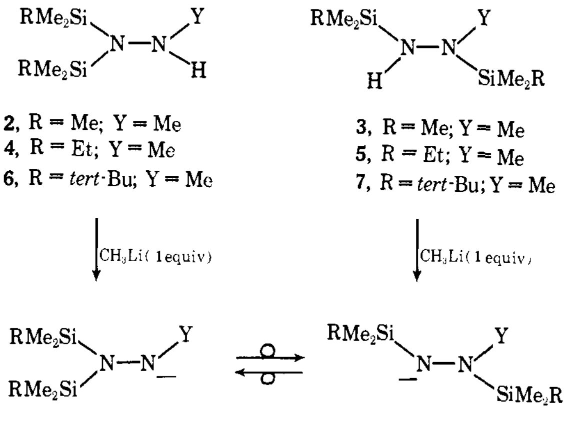


Figure 1. Variable temperature proton nmr spectra of lithium tris(trimethylsilyl)hydrazide (**1a**) in hexane reveals the temperature dependent intramolecular trimethylsilyl migration. Temperatures are recorded in °C.

only by bases capable of deprotonating the hydrazine,[6] rearrangement apparently takes place only through the anion, as in other intramolecular anionic rearrangements.[9]

This paper reports a study of several organosilylhydrazide anions, as their lithium salts, by variable-temperature nmr spectroscopy. Addition of 1 equiv of alkyllithium compound to the silylhydrazine causes rapid and complete deprotonation to the silylhydrazide anion, or lithium silylhydrazide, which can then undergo rearrangement. The possible reactions for the hydrazines investigated are outlined in eq 1.

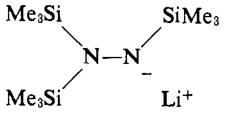


2, R = Me; Y = Me
4, R = Et; Y = Me
6, R = *tert*-Bu; Y = Me

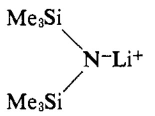
3, R = Me; Y = Me
5, R = Et; Y = Me
7, R = *tert*-Bu; Y = Me

1, R = Me; Y = $SiMe_3$ (1)

Tris(trimethylsilyl)hydrazine (1).[10] Because the anion of **1** is identical before and after rearrangement, this compound gives proton nmr spectra which are relatively easy to interpret. In benzene or toluene solution **1** has resonances in the Si–C–H region at τ 9.86 and 9.87 with intensity 2:1, respectively, as well as an N–H resonance at τ 8.01. When **1** is converted to its anion by addition of 1 equiv of alkyllithium, only a single resonance at τ 9.79 is observed, indicating that rapid exchange of the trimethylsilyl groups between the two nitrogen atoms is taking place. As the temperature of the sample is lowered, this peak broadens and splits into two peaks with a 2:1 intensity ratio at τ 9.75 and 9.87. Similar results are found in hexane[11,12] solutions (Figure 1). This suggests that the organosilyl migration is temperature dependent and that in the limit of slow exchange at low temperature the anion, as lithium tris(trimethylsilyl)hydrazide (**1a**), is observed as having two different types of trimethylsilyl groups.



1a



8

In a system involving lithium cations, dimerization or higher association of the lithium organosilylhydrazide must be considered. Incidental to a study of the preparation of tris(trimethylsilyl)hydrazide derivatives of zinc, cadmium, and mercury, the molecular weight of **1a** was determined cryoscopically in benzene as 481[13] which indicates that this species is dimeric in this solvent.

The lithium organosilylhydrazides are soluble in hydrocarbons to the extent of 0.2 *M* even at -70°, suggesting that the lithium–nitrogen linkage may have significant covalent character. The related compound lithium bis(trimethylsilyl)amide (**8**) is dimeric in benzene[14] and trimeric in the solid state[15] with lithium atoms bridging the nitrogen atoms. In a recent study involving ^{7}Li and ^{1}H nmr, Kimura and Brown[16] have shown that **8** exhibits temperature, solvent, and concentration dependence which can be attributed to monomer–dimer equilibrium in THF and dimer–tetramer equilibrium in hydrocarbons. (Solubility limitations prevented a complete study of **8** in diethyl ether.)

The proton nmr of **1a** was also studied at variable temperatures in diethyl ether with results more complicated than in hydrocarbon solvents. Figure 2 shows that the behavior in ether is similar to that in hexane in that the room-temperature singlet splits into two peaks with relative areas of 2:1 at -20°. However, upon further cooling, a third peak is observed at τ 9.98, which increases at the expense of the first two peaks. At still lower temperatures this peak also broadens and separates into two peaks having a 2:1 ratio. We interpret all of this in terms of the equilibria in eq 2.

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[9] (a) H. E. Zimmerman, "Molecular Rearrangements," Vol. 1, Interscience, New York, N. Y., 1963, p 345; for recent developments in carbanion chemistry, see (b) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

[10] U. Wannagat and H. Niederprüm, *Z. Anorg. Allg. Chem.*, **310**, 32 (1961).

[11] Compound **1** in CCl_4, hexane, or ether exhibits only one peak in the Si–C–H region at all temperatures indicating that accidental degeneracy of the two types of trimethylsilyl groups occurs in these solvents.

[12] K. Witke, P. Reich, and H. Kriegsmann, *J. Organometal. Chem.*, **15**, 37 (1968).

[13] K. Seppelt and W. Sundermeyer, *Chem. Ber.*, **103**, 3939 (1970).

[14] U. Wannagat, *Pure Appl. Chem.*, **19**, 329 (1969).

[15] D. Mootz, A. Zinnius, and B. Böttcher, *Angew. Chem. Int. Ed. Engl.*, **8**, 378 (1969).

[16] B. Y. Kimura and T. L. Brown, *J. Organometal. Chem.*, **26**, 57 (1971).

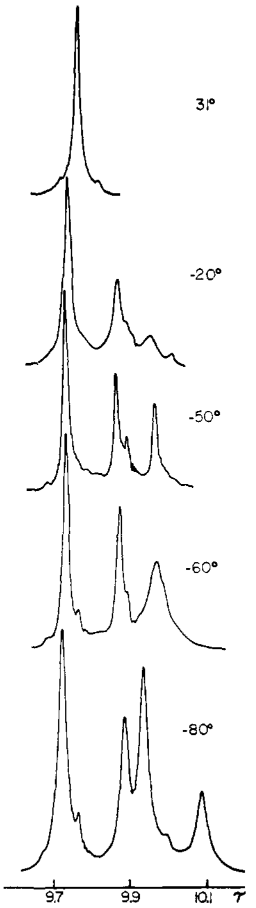

Figure 2. Proton nmr spectra of **1a** in diethyl ether is indicative of the existence of a dimer ⇄ monomer equilibrium as well as independent temperature dependence of trimethylsilyl migration in both dimer and monomer forms.

At room temperature the species exists mainly as a dimer, and migration of the trimethylsilyl groups is rapid on the nmr time scale. As the sample is cooled to −20°, trimethylsilyl migration becomes slow so that two peaks are observed for the dimer. Below −20°,

$$\begin{tikzcd}
{[(Me_3Si)_2\text{-}N,N'\text{-}(Li)SiMe_3]_2} \arrow[r, shift left, "\circ"] \arrow[d, shift left] & {[Me_3Si(Li)\text{-}N,N'\text{-}(SiMe_3)_2]_2} \arrow[l, shift left, "\circ"] \arrow[d, shift left] \\
{(Me_3Si)_2\text{-}N,N'\text{-}(Li)SiMe_3} \arrow[u, shift left] \arrow[r, shift left, "\circ"] & {Me_3Si(Li)\text{-}N,N'\text{-}(SiMe_3)_2} \arrow[u, shift left] \arrow[l, shift left, "\circ"]
\end{tikzcd} \tag{2}$$

monomer is observable in equilibrium with dimer. Between −20 and −60° silyl migration is rapid in the monomer but slow in the dimer (compared to the proton spin relaxation time). Finally at −80° anionic rearrangement in the monomer also becomes slow, so that two pairs of peaks are observed. Since **1a** is dimeric in benzene, it is not unreasonable that there should be dimer–monomer equilibrium in diethyl ether in agreement with the reported equilibrium of **8** in THF.[16] The thermodynamic characteristics of the dimer–monomer equilibrium obtained by a plot of log K_{eq} *vs.* $1/T$ (10^3 °K^{-1}) (Figure 3) are $\Delta H° = -4.4$ kcal mol^{-1} and $\Delta S° = -25$ cal deg^{-1} mol^{-1}. These values match well with those found by Kimura and Brown for the dimer–monomer equilibrium of **8** in THF: $\Delta H° = -4.0$ kcal mol^{-1} and $\Delta S° = -17$ cal deg^{-1} mol^{-1}. Both dimer and monomer are undoubtedly solvated, but to an unknown extent. The dissociation of the dimer of **1a** in diethyl ether is exothermic; the negative values of $\Delta H°$ and $\Delta S°$ indicate that diethyl ether solvates lithium in the monomer to a greater extent than in the dimer.[17] That the spectra are concentration dependent was demonstrated by varying the concentration of **1a** in ether from 0.04 to 0.46 *M* (see Table I); at a given low temperature the relative ratio of monomer to dimer increases as the overall concentration is decreased.

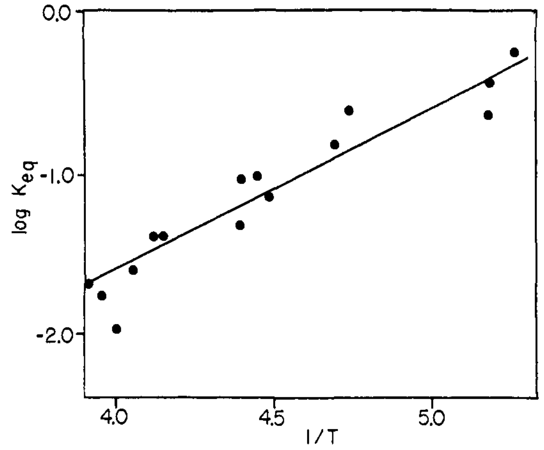

Figure 3. Plot of log K_{eq} *vs.* $1/T$ (10^3 °K^{-1}) for temperatures between −16 and −83° determines the thermodynamic factors involved in the dimer ⇄ monomer equilibrium of **1a** in diethyl ether.

Table I. Data for the Dimer ⇄ Monomer Equilibrium of **1a** in Diethyl Ether

T, °C	Concn, *M* (total as monomer)	Concn, *M* Dimer	Concn, *M* Monomer	$K_{eq} = m^2/d$
−20	0.46	0.20	0.059	0.01_7
−23	0.37	0.17	0.041	0.01_1
−30	0.46	0.19	0.086	0.03_9
−32	0.36	0.14	0.076	0.04_0
−45	0.37	0.14	0.085	0.05_1
−46	0.46	0.17	0.124	0.08_7
−49	0.35	0.12	0.11	0.10
−50	0.46	0.17	0.111	0.07_0
−60	0.46	0.15	0.151	0.15
−62	0.37	0.11	0.153	0.21
−80	0.044	0.005	0.034	0.23
−80	0.46	0.12	0.212	0.36

The unsymmetrical nature of the trimethylsilyl nmr peaks at low temperature and the concentration dependence of the dimer–monomer equilibrium of **1a** negate the possibility that hindered rotation or nitrogen inversion is the cause of this temperature dependence. Neither the parent organosilylhydrazines nor their anions in solution exhibit behavior of this kind to −80°.[18] It is, of course, possible that even lower temperatures will cause further temperature dependence due to hindered rotation as is observed for other substituted acyclic hydrazines.[19]

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[17] In this dimer–monomer equilibrium $\Delta S°$ for **1a** is even more negative than $\Delta S°$ for **8**. This could indicate that there is greater solvation of the monomer of **1a** by diethyl ether than of **8** by THF, and less solvation of the dimer of **1a** by ether than the dimer of **8** by THF.

[18] For a recent report of the first observation of restricted rotation in N-silylated hydrazines, see O. J. Scherer and U. Bültjer, *Angew. Chem. Int. Ed. Engl.*, 10, 343 (1971).

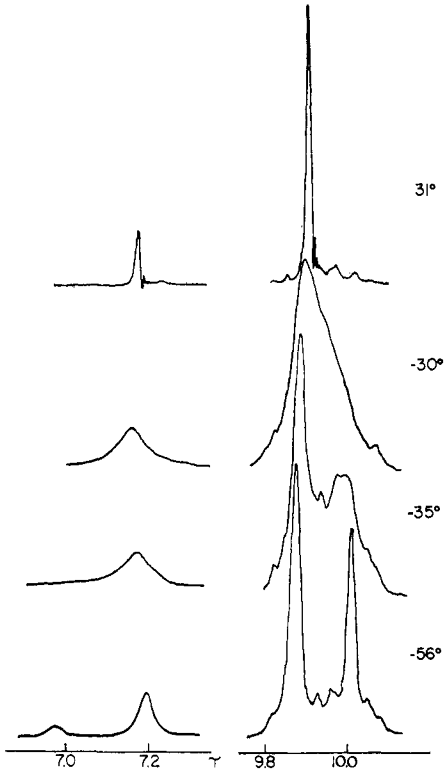
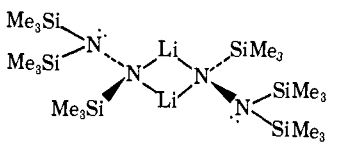


Figure 4. Nmr spectra of the *N*-methyl and trimethylsilyl regions of **2a** and **3a** at low temperatures reveal the presence of 80% **3a** and 20% **2a** in diethyl ether.

The relative rates of intramolecular trimethylsilyl migration are reflected in the coalescence temperatures for 1,2 anionic rearrangements. The dimer and monomer of **1a** have coalescence temperatures of +5 and −62°, respectively. This is further evidence that the lithium in the monomer form is preferentially solvated thereby lowering the activation energy necessary to reach the transition state, which is thought to be a pentacoordinate bridged silicon species similar to that postulated for the anions of bis(organosilyl)hydrazines.[7]

By analogy with the structure suggested for **8**,[14] the dimer of **1a** in solution is probably a four-membered ring with two bridging lithium atoms (**1b**).[20]



1b

A possible transition state for the rearrangement in the dimer might involve two nitrogen atoms of one hydrazide unit in a five-membered ring with one trimethylsilyl group equally bonded to each nitrogen (**1c**).

It is conceivable, but less likely, that trimethylsilyl migration could take place in both hydrazide units at the same time, leading to a six-membered ring transition state. Another less likely interpretation is that trimethylsilyl migration occurs only in the monomer through a dissociation–recombination process involving the dimer.

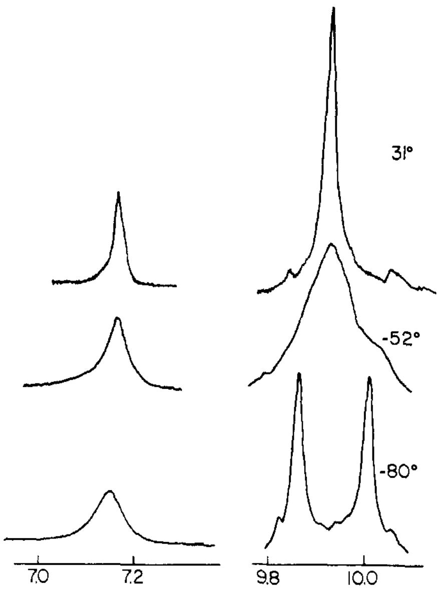
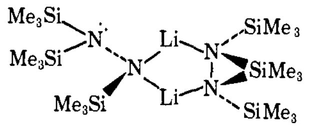


Figure 5. Temperature dependent proton nmr spectra of the *N*-methyl and dimethylsilyl regions for lithium bis(*tert*-butyldimethylsilyl)methylhydrazide indicates that only **7a** is found in solution in any detectable amount.



1c

Bis(organosilyl)methylhydrazines. Whereas the anion of **1** can exist in only one form, the anions of bis(organosilyl)methylhydrazines can form two different isomers (eq 1), and in fact these are observable by nmr at low temperatures. Solutions of either *N*,*N*-bis(trimethylsilyl)methylhydrazine (**2**) or *N*,*N*′-bis(trimethylsilyl)methylhydrazine (**3**) with 1 equiv of methyllithium in diethyl ether produce identical proton nmr spectra. The N–H absorption disappears and two single peaks in a 6:1 ratio are found at τ 9.90 and 7.18, respectively, indicative of rapid migration of the trimethylsilyl groups at room temperature. (It is known that the methyl group attached to nitrogen does not migrate under these conditions.)

Figure 4 shows that each trimethylsilyl resonance broadens reversibly and eventually separates into two peaks of unequal intensity. The *N*-methyl absorptions are in a 1:4 ratio, but the two trimethylsilyl peak areas have an 18:12 ratio. The equilibrium solution at low temperatures therefore consists of 80% of the *N*,*N*′-bis(trimethylsilyl)methylhydrazide anion (**3a**) (τ 7.20, 9.87, and 10.01 at −56°) and 20% of the *N*,*N*-bis(trimethylsilyl)methylhydrazide anion (**2a**) (τ 6.98 and 9.87 at −56°). The Si–C–H absorption for **2a** is accidentally degenerate with one of the trimethylsilyl resonances of **3a**, accounting for the unequal peak heights in the τ 10 region.

The possible effect of steric hindrance on the ratio of the N,N to N,N′ isomer anions of bis(organosilyl)-

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(19) J. E. Anderson, D. L. Griffith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 6371 (1969); M. J. S. Dewar and B. Jennings, *ibid.*, **91**, 3655 (1969); J. R. Fletcher and I. O. Sutherland, *Chem. Commun.*, 706 (1969).

(20) Although a six-membered ring could also be postulated for the dimer of **1a**, this possibility is less likely since the lithium atoms would be at a considerable distance from each other contrary to what is known about other lithium aggregates. In addition, it would seem that if six-membered rings could form, other polymer aggregates could also form and this is not observed.

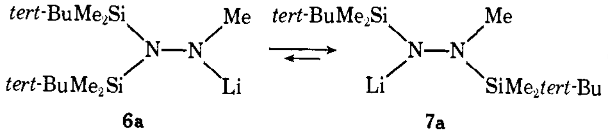
Table II. Data for Various Lithium Organosilylhydrazides in Solution

Compd	Solvent	% anionic concn below T_c	$\Delta\nu$, Si-C-H below T_c, cps	τ_c, sec (T_c, °C)[a]	$G^{\ddagger}_c$, kcal/mol
1a dimer	Hexane		7	0.032 (+5)	14.7
1a dimer	Ether		8	0.028 (+2)	14.4
1a monomer	Ether		9	0.025 (−62)	10.9
2a	Ether	20			
3a	Ether	80	8	0.028 (−33)	12.5
3a	Toluene		2	(+5)	
3a	Hexane		6	0.038 (>+31)	>16.2
4a	Ether	20			
5a	Ether	80	8	0.028 (−33)	12.5
6a	Ether	<1			
7a	Ether	100	9	0.025 (−51)	11.5

[a] τ_c is the half-life of the anion at the coalescence temperature.

methylhydrazines and the coalescence temperature was investigated. The data in the table indicate that the ratio of anions of *N*,*N*- and *N*,*N*′-bis(ethyldimethylsilyl)methylhydrazine[6] (**4a** and **5a**, respectively) at low temperature and the coalescence temperature are unchanged by the replacement of a methyl with an ethyl group.

However, quite different results were obtained when *N*,*N*′-bis(*tert*-butyldimethylsilyl)methylhydrazine (**7**)[8] was allowed to react with 1 equiv of base and studied at low temperature. As expected, the room-temperature spectrum of the anion solution exhibits one methyl, one *tert*-butyl, and one dimethylsilyl resonance. Figure 5 shows that below the coalescence point there is only one N-CH_3 peak, and the *tert*-butylsilyl and methylsilyl resonances are each split into two peaks of equal intensity, indicating that the equilibrium in eq 3 so favors **7a** at low temperatures that none of **6a** can be observed.



(3)

6a **7a**

The bulky *tert*-butyldimethylsilyl group dramatically alters the equilibrium anion ratio in solution. It has been shown[8] that the catalytic rearrangement of **7** yields only 1% of *N*,*N*-bis(*tert*-butyldimethylsilyl)methylhydrazine (**6**).

Discussion

The 1,2 anionic rearrangement of organosilylhydrazines is far faster than the other anionic rearrangements presently known. This rearrangement is remarkably clean; no secondary reactions occur if the proper precautions are taken against moisture, oxygen, and other contaminants. These nmr results rule out a stable intermediate involving pentacoordinate silicon[21] and clearly show the existence of individual anionic isomers. The fact that silicon can easily become pentacoordinate must considerably lower the transition state energy and account for the remarkable migratory ability of silicon.

Data for the lithium organosilylhydrazides are listed in Table II. The relative rates of rearrangement can be determined from the temperature dependence of the nmr line shapes. Rates of intramolecular exchange at the coalescence temperature, T_c, were obtained from the equation $k_c = (\pi/\sqrt{2})\Delta\nu$.[22,23] The free energies of activation, $\Delta G_c^{\ddagger}$, were then calculated from the Eyring rate equation using the rate constant at T_c.[24]

It has been shown that bis(organosilyl)-*o*-phenylenediamines[25] undergo 1,4 intramolecular anionic rearrangement with rates of organosilyl migration similar to those of the silylhydrazides. The organosilylethylenediamine[26] and organosilylpropylenediamine[27] anions also rearrange but with a half-life of minutes at 30°, much slower than the rate for the silylhydrazine anions. In contrast, arylhydrazine monoanions[28] are not observed to undergo rearrangement in several days at 120°; the half-time for rearrangement is surely greater than 10^5 sec. Allowing for the temperature difference, the migration rate of trimethylsilyl must be $>10^{10}$ faster than for phenyl in hydrazine monoanions.

As expected the solvent plays an important role in affecting the rate of anionic rearrangement of organosilylhydrazines. The basic solvents diethyl ether or tetrahydrofuran best facilitate the organosilyl migration. The rearrangement is slower in toluene and still slower in hexane. For example, the coalescence temperatures for the equilibrium of **2a** and **3a** in diethyl ether, toluene, and hexane are −33, +5, and >31°, respectively, in agreement with the relative polarity characteristics of these solvents. This may imply that the transition state is more polar than the individual anions. The nature of the solvent does not seem to significantly affect the ratio of the anion isomers at low temperatures.

It is not yet known why the bis(organosilyl)methylhydrazine anions do not exhibit a dimer–monomer equilibrium like that found for **1a** in diethyl ether. This equilibrium may occur at even lower temperatures which have not been investigated. Another possibility is that the lithium bis(organosilyl)methylhydrazides are monomers in ether over this temperature range, al-

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(21) For evidence of a stable triorganosilicon species involving nitrogen atoms, see J. Y. Corey and R. West, *J. Amer. Chem. Soc.*, **85**, 4034 (1963).

(22) The validity of this approximate rate equation has recently been examined and was found to yield reliable estimates of free energies of activation with specified limits.[23]

(23) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

(24) (a) H. Kessler, *Angew. Chem. Int. Ed. Engl.*, **9**, 219 (1970); (b) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

(25) H. F. Stewart, D. G. Koepsell, and R. West, *J. Amer. Chem. Soc.*, **92**, 846 (1970).

(26) R. West, M. Ishikawa, and S. Murai, *ibid.*, **90**, 727 (1968).

(27) R. West and S. Murai, unpublished studies.

(28) R. West and H. F. Stewart, *J. Amer. Chem. Soc.*, **92**, 853 (1970).

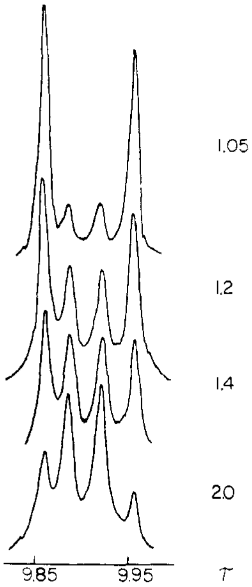

Figure 6. The dependence of the proton nmr spectra of the trimethylsilyl region of **2** or **3** at −56° on the number of equivalents of *n*-butyllithium in hexane provides evidence for the formation of mixed aggregates of alkyllithium and lithium bis(trimethylsilyl)methylhydrazide.

though the remarkable similarity in the spectra obtained with hexane, toluene, and ether would seem to make this less than likely.

It is curious that the coalescence temperature of −51° for the rearrangement of anions **6a** and **7a** in diethyl ether is lower than that of **2a** and **3a** or of **4a** and **5a**. At first glance it would seem that the migration of the very bulky *tert*-butyldimethylsilyl group should be slower than that of the trimethylsilyl group, whereas in fact it is faster. The coalescence temperature for the rearrangement of **6a** and **7a** is slightly higher than that for the **1a** monomer rearrangement, suggesting that **7a** may be monomeric in ether solution as a result of the increased bulk of the *tert*-butyl group. However, further discussion of this point must await conclusive molecular weight determinations of **7a** and the other *N*-methylhydrazines.

The catalytic rearrangement of **2** or **3** (eq 1) has been shown to yield approximately equivalent amounts of **2** and **3** as products.[6] Attempts were made to correlate the ratio of 80% **3a** to 20% **2a** at low temperature in ether as determined by nmr with actual derivatized products of the anions. Additionally, the derivatizations of the anions **2a** and **3a** with diphenylamine or methyl iodide under a variety of temperatures and concentrations yield not the expected 80% but only 45% of **3** or 1,2-bis(trimethylsilyl)dimethylhydrazine, respectively. It appears that the rate of derivatization of the anion must be greater at that less sterically hindered nitrogen atom bearing the lone methyl group and a more localized partial negative charge. Since it is likely that the rate of rearrangement is faster than the rate of derivatization, the relative amounts of product, **2** and **3**, are not necessarily determined by the relative populations of anion isomers **2a** and **3a**.[29,30] This derivatization then is a kinetically controlled process.

The nmr spectra of the lithium bis(organosilyl)methylhydrazides change below the coalescence temperature with the addition of more than 1 equiv of base. This effect is displayed in Figure 6 for a mixture of anions **2a** and **3a** in hexane at −56°. Two new peaks are found in the $Si-CH_3$ region which increase in direct proportion to the amount of excess *n*-butyllithium. These data provide evidence for the formation of mixed aggregates in solution. The phenomenon can also be observed with methyllithium in diethyl ether. At low temperatures exchange between mixed aggregates is slowed sufficiently to reveal at least two peaks in the methyllithium absorption region at τ 11.3. One appears to be due to the methyllithium tetramer in ether and the other somewhat broad peak is attributed to mixed aggregates of methyllithium and lithium bis(trimethylsilyl)methylhydrazide.

The exact role of the lithium atoms in these anionic rearrangements is not completely known. A low-temperature ^7Li nmr study of these compounds has not been made, but it is expected that they are contact- rather than solvent-separated ion pairs in agreement with the conclusions reached for **8**[16] in solution. However, there may be more than one mechanism for the migration of the lithium atoms between nitrogens. Both intramolecular and intermolecular lithium exchange may occur in solution.

Numerous attempts were made to solve the nmr spectra of the monoanions of bis(trimethylsilyl)hydrazine and bis(*tert*-butyldimethylsilyl)hydrazine in ether, toluene, and hexane solutions.[31] The N–H absorption of the anion cannot be found in the nmr spectra at any temperature studied. In addition there are several temperature-dependent peaks which so complicate the methylsilyl region that the spectra seem to be uninterpretable. One can imagine that, in addition to organosilyl exchange in the anion, rapid intermolecular and intramolecular exchange of the N–H proton and aggregation equilibria could be involved in the complex spectra.

The compound 1-trimethylsilyl-1,2-dimethylhydrazine (**9**)[32] was prepared in an effort to observe by nmr the silyl migration in a monosilylhydrazide anion. This compound is thermally unstable in the gas chromatograph and partially disproportionates to 1,2-bis(trimethylsilyl)-1,2-dimethylhydrazine and other products. In addition, **9** will partially disproportionate at room temperature over a period of 1 day. Previously, decomposition products had been observed during the preparation of several monosilyl-substituted hydrazines.[32] However, the anion of **9** could be prepared in the usual manner. Unfortunately the solubility of the anion in ether or hexane is very low. That, and the fact that the anion itself may disproportionate in solution, made reliable spectral interpretation impossible.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen. *n*-Butyllithium in hexane and methyllithium in diethyl

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[29] This is an application of the Curtin–Hammett principle[30] which relates product distribution to the difference in free energy of the transition states rather than to the ratio of starting isomers.

[30] (a) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, pp 119–120; (b) D. Y. Curtin, *Rec. Chem. Progr.*, **15**, 111 (1954).

[31] Temperature dependent nmr spectra of the anion of bis(ethyldimethylsilyl)hydrazine in toluene have been published previously.[7]

[32] U. Wannagat and F. Höfler, *Monatsh. Chem.*, **97**, 976 (1966).

ether were obtained from Foote Mineral Co.; concentration was determined by proton nmr. Other materials were all reagent grade. Diethyl ether, cyclohexane, benzene, and Skelly B, used as solvents, were purified by lengthy reflux over $LiAlH_4$. Toluene was purified by refluxing over sodium. All were distilled immediately prior to use.

The bis(organosilyl)hydrazines and bis(organosilyl)methylhydrazines were prepared as described in earlier papers.[5,6,8] Tris(trimethylsilyl)hydrazine[10] and 1-trimethylsilyl-1,2-dimethylhydrazine[32] were made according to published procedure. Properties of these compounds agreed with those reported in the literature.

The various silylhydrazines were purified by preparative gas-liquid chromatography on an Aerograph Model A700 gas chromatograph equipped with a thermal conductivity detector. Isomers were separated using a $^3/_8$ in. × 15 ft aluminum column packed with 20% SE-30 on 40–60 mesh Chromosorb W, and a helium flow rate of 200 cc/min.

Formation of Anions. Gas chromatograph collection tubes and Varian nmr sample tubes were carefully cleaned with various solvents and dried in a 160° oven for at least 1 hr. They were then flushed with dry nitrogen and capped with a rubber septum. Samples were prepared immediately after collection from the gas chromatograph. Care must be taken to prevent traces of oxygen or water from entering the system.

In a typical preparation 50 μl (0.240 mmol) of 1,2-bis(trimethylsilyl)methylhydrazine was syringed into a capped nmr tube containing 0.3 ml of diethyl ether. The solution was cooled to −78° and 0.143 ml (0.240 mmol) of 1.68 *M* methyllithium in ether was slowly added. The solution was carefully mixed while warming to room temperature. Methane is allowed to escape through a hypodermic needle connected to the dry nitrogen system. Best results were obtained with fresh methyllithium solution and when the hydrazide anion solution remained colorless or very slightly yellow. Concentrations of the anions were usually 10–15% (v/v) since too large a concentration causes lithium hydrazide salt precipitation. The nmr tubes, if carefully sealed, gave reproducible nmr spectra for several weeks.

The silylhydrazine anions can also be prepared on a larger scale using standard glassware and nitrogen atmosphere before transferring the solution by syringe to the capped nmr tube.

Proton Nmr Spectra. The proton nmr spectra were obtained with a Varian A60-A spectrometer using cyclohexane (τ 8.56) as internal standard. The appropriate regions for each sample were scanned at 50 or 100 cycle sweep width. The sweep time was 250 sec in all cases. Variable-temperature spectra were obtained with a Varian V-6040 variable-temperature controller and probe. Temperatures were checked before and after each spectrum was taken by measuring the chemical shift difference in the absorption peaks of methanol at low temperature and ethylene glycol at high temperature. Temperatures are estimated to be accurate to ±1°. Temperature-dependent spectra are reproducibly reversible in all cases.

The peak areas were measured by planimeter or the method of triangulation. The measurement precision is estimated as ±2%.

Rearrangement and Insertion Reactions of 2-Methylbenzylidenes

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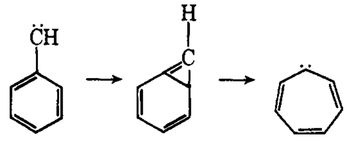
Abstract: (2-Methylphenyl)diazomethane (**4**), generated by thermolysis of the sodium salt of 2-methylbenzaldehyde tosylhydrazone, decomposes at 150° to styrene (**6**), benzocyclobutene (**7**), and *o*-xylene along with *cis*- and *trans*-2,2′-dimethylstilbenes, 2,2′-dimethylbibenzyl, 2,2′-dimethylbenzaldazine, 2-methylbenzonitrile, and 2-methylbenzaldehyde. At higher temperatures conversion of **4** to **6** and **7** is increased; **6** is not formed, however, by isomerization of **7**. Pyrolysis of (2,5-dimethylphenyl)diazomethane (**8**) and (2,6-dimethylphenyl)diazomethane (**13**) was investigated to determine which methylstyrenes are produced. At 179–181° **8** decomposes to 4-methylstyrene (**10**), *cis*- and *trans*-2,2′,5,5′-tetramethylstilbenes, 2,2′,5,5′-tetramethylbenzaldazine, and 2,5-dimethylbenzonitrile; 3-methylstyrene is not formed. Neat **13** thermolyzes (176–194°) to 3-methylstyrene (**12**), 3-methylbenzocyclobutene (**15**), 2,6-dimethylbenzonitrile, and bimolecular products; 2-methylstyrene is not obtained. Conversion of α-deuterio(2-methylphenyl)diazomethane (**33**) at 350° to 2-deuteriostyrene (**35**) and 1-deuteriobenzocyclobutene (**36**) provides additional mechanistic information concerning isomerization of 2-methylbenzylidenes. In conversion of **4**, **8**, **13**, and **33** to **6**, **10**, **12**, and **35**, respectively, the intermediate 2-methylbenzylidenes (**17**) may isomerize to fused cyclopropenes **25** and their corresponding 2-methylcycloheptatrienylidenes (**26**) which (1) undergo carbon–hydrogen insertion to yield fused alkylidenecyclopropanes (**27**) and then styrenes and/or (2) rearrange to fused cyclopropenes **29** which isomerize to 1-phenyl-1-ethylidenes and their subsequent styrenes. An alternate possibility involves direct conversion of cyclopropenes **25** to cyclopropenes **29** and then to styrenes. The consequences of other possible isomerization processes in these systems are discussed.

Recently benzylidene (**1**) and 4-methylbenzylidene, as generated by pyrolysis (250°) of the sodium salts of the tosylhydrazones of benzaldehyde and 4-methylbenzaldehyde, respectively, were found to give heptafulvalene and dimethylheptafulvalene, apparently by dimerization of cycloheptatrienylidene (**3**) and methylcycloheptatrienylidene derived by isomerization (eq 1) of their parent carbenes.[1] Shortly thereafter, it was communicated that 4-, 3-, and 2-methylbenzylidenes, upon generation from the corresponding diazo compounds at 450°, each yield styrene (**6**) and benzocyclobutene (**7**) by multiple processes possibly involving intraconversion of the carbenes *via* intermediate cycloheptatrienylidenes.[2] We should like to report in detail


1 **2** **3** (1)

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[1] (a) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); (b) P. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *ibid.*, **92**, 2147 (1970); (c) C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

[2] W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *J. Amer. Chem. Soc.*, **92**, 4739 (1970).[3]