

ANIONIC REARRANGEMENTS OF ORGANOSILICON COMPOUNDS

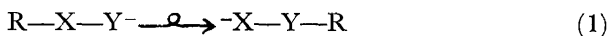
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In comparison to the rearrangements of carbonium ions so long known and well studied in organic chemistry, anionic rearrangements have been much less thoroughly explored¹. Recently, we have found that certain anionic rearrangements proceed with unprecedented speed when the migrating group is an organosilicon moiety. The realization of the very high mobility of silyl substituents in anionic rearrangements opens a new area of organo-metallic chemistry, and at the same time offers a highly useful technique for the study of anionic rearrangements generally.

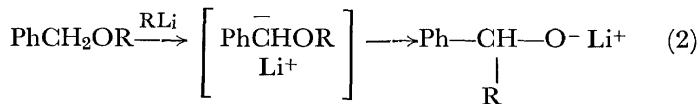
Types of anionic rearrangements

We shall be concerned initially and principally with 1,2-anionic rearrangements, in which the migrating group moves from one atom to an adjacent bonded atom bearing a negative charge:

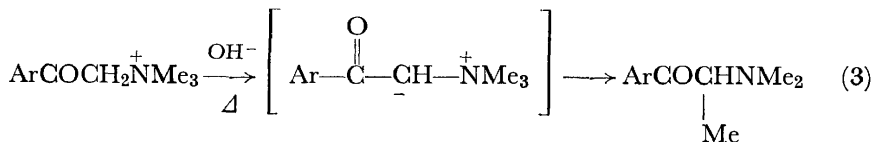


Most of the best-known anionic rearrangements are of this 1,2 type. Rearrangements involving migration to more remote anionic sites, sometimes classed together as "Smiles Rearrangements",² will be dealt with briefly later.

The classical examples of 1,2 anionic rearrangement are the Wittig rearrangement^{3,4} involving migration from oxygen to carbon:



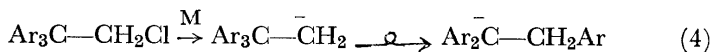
And the Stevens rearrangement,⁵ in which the substituent migrates from nitrogen to carbon:



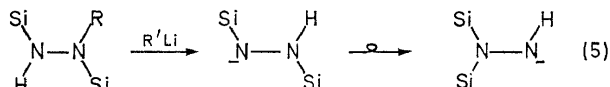
† Work described here was supported by the Air Force Office of Scientific Research (SRC) O.A.R., U.S.A.F., Grant No. AF-AFOSR 1061-66.

These and similar rearrangements in which the atoms X and Y in Eq. 1 are of different kind will be called *heteroatomic*.

Recently, 1,2 anionic rearrangements have been observed in which the atoms X and Y are of the same kind (though they may be differently substituted). These we will term *homoatomic* 1,2 anionic rearrangements. At present just two examples are known: the ethane rearrangement, discovered independently by Grovenstein^{6,7} and by Zimmerman and his co-workers^{8,9} in 1957:



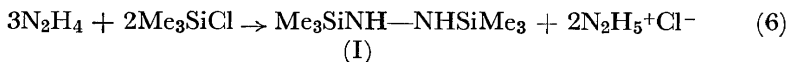
And the hydrazine rearrangement, observed by Bailey and West in 1964:¹⁰



(Si = triorganosilyl group)

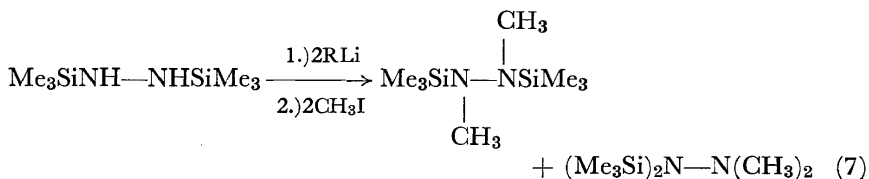
The silylhydrazine rearrangement: origins

The history of the anionic rearrangement of silylhydrazines provides an excellent example of the role of chance, coincidence, and even unrecognized error in scientific discovery. In 1964, Robert Bailey of our laboratories set out to prepare N,N'-bis(trimethylsilyl)hydrazine (I), as a starting material for oxidation to the disilyldiazene, $\text{Me}_3\text{Si}-\text{N}=\text{N}-\text{SiMe}_3$. (Compounds of the latter type were then unknown but have recently been synthesized by a quite different route^{10a}.) The synthesis of compound I from trimethylchlorosilane and hydrazine was reported in 1957¹¹, a part of the now classic work of Wannagat and his students in the area of silicon-nitrogen chemistry¹²:

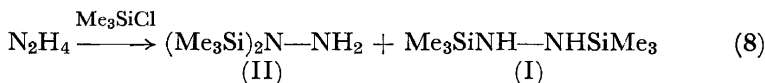


The disilylhydrazine was reported to have the N,N' structure (I) as shown. We found that the product, *after careful distillation through a platinum spinning band distilling column*, showed only one N—H resonance and one Si—CH₃ resonance in the n.m.r. spectrum, indicating that it was a single isomer.

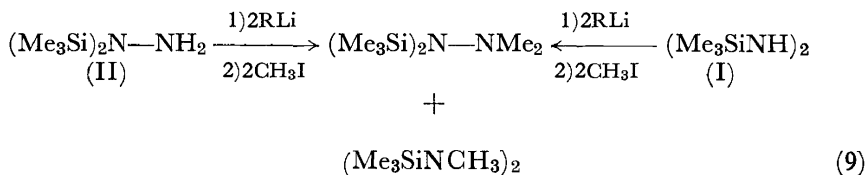
In the course of characterizing the disilylhydrazine, it was treated with two equivalents of *n*-butyllithium and then with two equivalents of methyl iodide, in order to convert it to the symmetrical dimethyl derivative. The product distilled over a relatively narrow boiling range, but gas chromatographic analysis showed it to be a nearly 1:1 mixture of *two* compounds, identified as the N,N and N,N'-isomers¹⁰:



It seemed, then, that a new rearrangement had been observed¹⁹. However, we learned at this point by private correspondence with Professor Wannagat that he now believed the disilylhydrazine product of equation (6), originally thought to be pure I, was actually a mixture of the N,N' and N,N isomers, I and II. Although our analytical sample after purification had been isomerically pure, we nevertheless repeated the preparation according to reaction (6), this time distilling the product *rapidly in glass apparatus*. Under these conditions the bis(trimethylsilyl)hydrazine is indeed a mixture of nearly equal amounts of the two possible isomers!

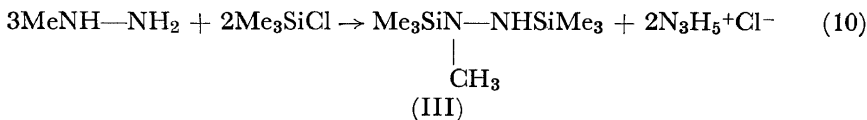


We were able to separate I and II by preparative gas chromatography, and to show that the separated compounds both gave the same 1:1 mixture of dimethylated isomers upon treatment with *n*-butyllithium and methyl iodide:



Rearrangement does, therefore, take place with either I or II. But why had our original, carefully purified sample consisted only of one isomer? By coincidence, we had chosen the very purification conditions which led to the selective decomposition of the N,N' isomer—namely, heating with platinum in the spinning band distillation column¹³. Thus our original sample was actually pure II, rather than I as we had assumed from the literature reports¹¹⁻¹⁶.†

In order to avoid the troublesome separation of isomers I and II, for further study of the anionic rearrangement reaction N,N'-bis(trimethylsilyl)methylhydrazine, III, was employed. This compound can also be made following directions given by Wannagat and Liehr¹⁸ from methylhydrazine and trimethylchlorosilane:



† Earlier workers¹⁴⁻¹⁶ had assigned the N,N' structure I to the bis-silylhydrazine product, based on chemical reactions with reagents such as phenyl isocyanate, assumed to take place at the N—H bond. These fail to distinguish between the isomers, because in fact the Si—N bond in the disilylhydrazines is about equally as reactive as the N—H bond. All chemical methods of structure proof for silylhydrazine are ambiguous for this reason. The correct assignment of isomeric structure was only successful when physical methods (n.m.r. and i.r. spectroscopy) were used.^{13,17}

The proton n.m.r. spectrum of the product of equation 10, shown in *Figure 1*, indicates that it is the isometrically pure N,N' isomer, III. Note that two equal $\text{Si}-\text{CH}_3$ resonances are observed, corresponding to the two different kinds of silylmethyl protons. In the N,N isomer IV, all silylmethyl groups are equivalent and only one $\text{Si}-\text{CH}_3$ resonance is found (*Figure 1*).

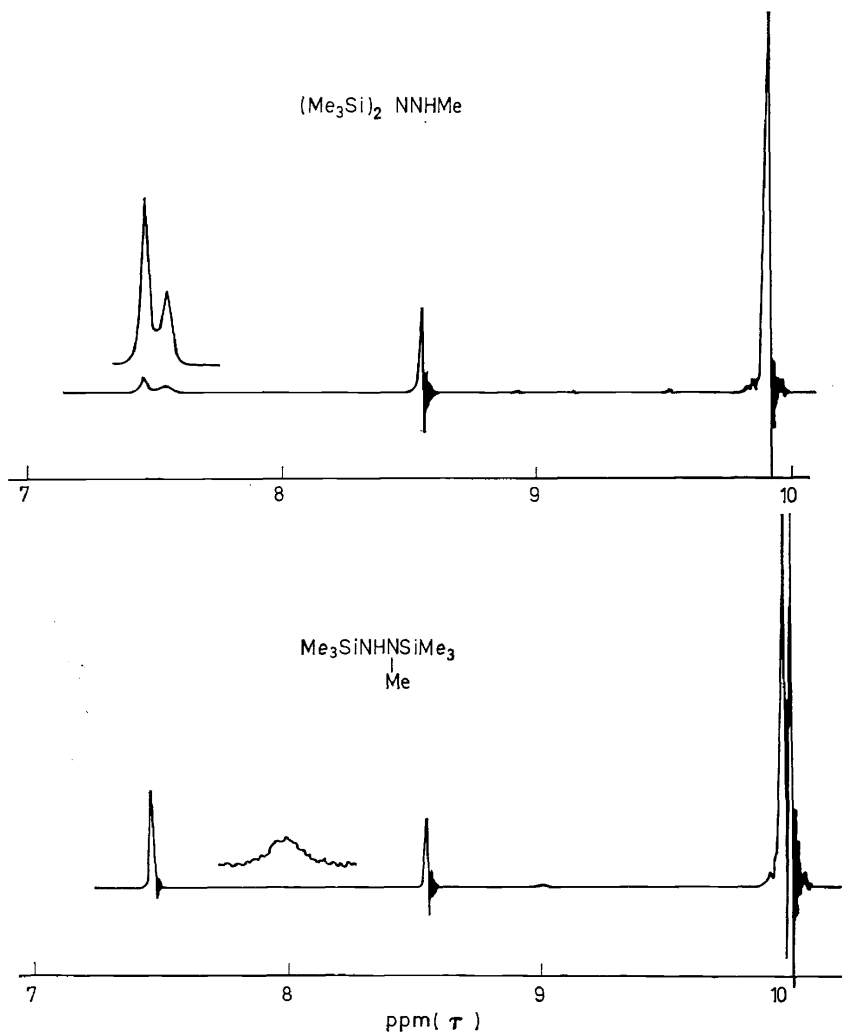
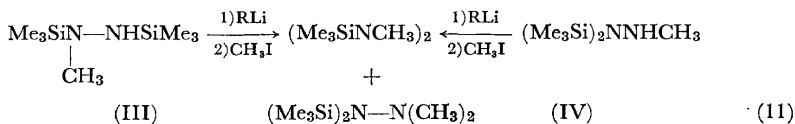
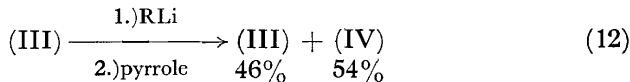


Figure 1. Proton n.m.r. spectra of compounds III and IV, 20% v/v in carbon tetrachloride, with cyclohexane ($\tau = 8.56$) as internal standard.

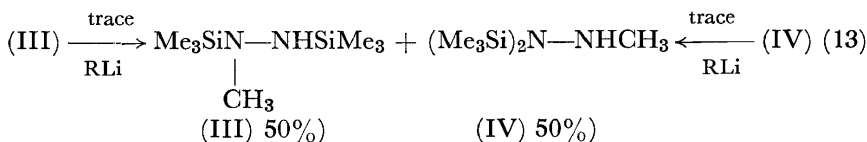
When either III, or IV, are treated with one equivalent of *n*-butyllithium and then one equivalent of methyl iodide, the same mixture of dimethyl bis(trimethylsilyl) isomers is produced¹⁹:



These products are the same as those formed in reaction (9), and once again about equal amounts are formed. If either III or IV are lithiated and then treated with pyrrole rather than methyl iodide, reprotonation takes place and a nearly equimolar mixture of III and IV is obtained. This reaction provides a means for synthesis of IV, which can be separated from the mixture by gas chromatography¹⁹:



At this point, it was found that complete lithiation and reprotonation are unnecessary. If III or IV is simply treated with a *trace* of *n*-BuLi, it is rapidly converted to a similar mixture of III and IV:



This finding is of great significance, for most previously known anionic rearrangements require one full equivalent of base, and are usually even then quite slow. In the silylhydrazine rearrangement, then, we have an example of a *catalytic anionic rearrangement*¹⁹.

The catalytic silylhydrazine rearrangement

The scope of the catalyzed rearrangement has been systematically studied¹⁹⁻²¹. The rearrangement was followed by n.m.r. spectroscopy of the equilibrating silylhydrazine solution, and by gas chromatography of the mixture after equilibration. *n*-butyllithium (0.03 to 0.3 equivalent per equivalent of silylhydrazine) was ordinarily used as a catalyst, but any base strong enough to deprotonate the silylhydrazine will cause rearrangement.

Silylhydrazines which have been studied are listed in *Table 1*. The known examples where rearrangement occurs all involve hydrazines with two triorganosilyl groups, but there is no reason to believe that the rearrangement is not a completely general reaction for all silylhydrazines which can form anions. From the data in *Table 1*, both steric and electronic effects can be seen to shift the position of equilibrium. For example, *N,N*-bis(*t*-butyldimethylsilyl)hydrazine undergoes 86 per cent rearrangement to the *N,N'* isomer, because of strong steric interference between *t*-butylsilyl groups when they are on the same nitrogen atom²¹. Phenyl groups strongly stabilize the isomers bearing a hydrogen on the same nitrogen as the aromatic ring,

so that, for example, *N,N'*-bis(trimethylsilyl)phenylhydrazine undergoes 96 per cent rearrangement at equilibrium; and *N*-trialkylsilyl-*N'*-phenylhydrazines do not rearrange at all¹⁹. We believe that the effect of phenyl is largely electronic, due either to (i) reduced opportunity for *N*→*Si* pi-bonding in the *Ph*—*N*—*Si* compounds, or (ii) specific stabilization because of the presence of the *Ph*—*N*—*H* system, or both.

Table 1. Equilibration of organosilylhydrazines with *t*-butyllithium in benzene

	% Rearranged at equilibration	<i>t</i> _½ , (min) ^a
(Me ₃ Si) ₂ NNH ₂	51	< 1
(EtMe ₂ Si) ₂ NNH ₂	53	< 1
Me ₃ Si(EtMe ₂ Si)NNH ₂	52	< 1
<i>t</i> -BuMe ₂ SiN(SiMe ₃)NH ₂	73	~ 2
(<i>t</i> -BuMe ₂ Si) ₂ NNH ₂	86	4
Me ₃ SiNHN(CH ₃)SiMe ₃	50	3·5
EtMe ₂ SiNHN(CH ₃)SiEtMe ₂	47	4·5
<i>t</i> -BuMe ₂ SiN(SiMe ₃)NHMe	68 ^b	80
Me ₃ SiNHNHPh	0	—
EtMe ₂ SiNHNHPh	0	—
<i>t</i> -BuMe ₂ SiNHNHPh	0	—
Me ₃ SiNHN(Ph)SiMe ₃	96	600
EtMe ₂ SiNHN(Ph)SiEtMe ₂	91	900
<i>t</i> -BuMe ₂ SiNHN(Ph)SiMe ₃	80 ^b	2800 ^c
<i>t</i> -BuMe ₂ SiNHNHMe	0	—

^a 0·4 M Hydrazine, 0·04 M *n*-BuLi.

^b Two different products formed.²¹

^c At 65°

In the absence of strong steric or electronic constraints, the bis(organosilyl)hydrazines and bis(organosilyl)methylhydrazines give *essentially equal amounts* of the *N,N* and *N,N'* isomers at equilibrium¹⁹. For these simple cases, the reaction is therefore *thermoneutral*, with no enthalpic driving force. This observation differentiates the silylhydrazine rearrangement from all other anionic rearrangements, which are thermodynamically driven reactions proceeding essentially to completion.

The finding that I and II, or III and IV, have identical thermodynamic stability is quite surprising, for the silyl and methyl substituents might be expected to stabilize one isomer over the other. The simplest rationalization of the results is that the organosilyl and methyl substituents have little influence on the stability of the hydrazines. However, examination of models shows that there is moderate steric interference between trimethyl- or ethyldimethylsilyl groups attached to the same nitrogen atom in the 1,1 isomers, which is relieved in the 1,2 compounds. This steric hindrance might be compensated by increased *N*→*Si* pi-bonding in the 1,1 isomers, which would stabilize the 1,1 bis-silyl compounds electronically relative to the 1,2. This explanation requires that special stabilization is conferred by the silazane bond (*Si*—*N*—*Si*) over and above that of two separate *N*—*Si* linkages, or else that there is a "beta pi-interaction" between the lone pair of the remote nitrogen atom and the silicon in the (R₃Si)₂NNH₂ isomers.

Neither the nature of the solvent nor the base concentration had any

marked effect on the amounts of isomers present at equilibrium. These variables did affect the rate of equilibration, which will be discussed in the next Section

Mechanism and rate

The rate of catalyzed equilibration of silylhydrazines was followed by n.m.r. spectroscopy²⁰. The reaction solution was made up in an n.m.r. sample tube, placed in the spectrometer, and the methylsilyl resonance region was traced repeatedly until no further change could be observed. Some typical results for the rearrangement of III are shown in *Figure 2*. In experiments with bis(trialkylsilyl)methylhydrazines, half-times for equilibration were typically a few minutes.

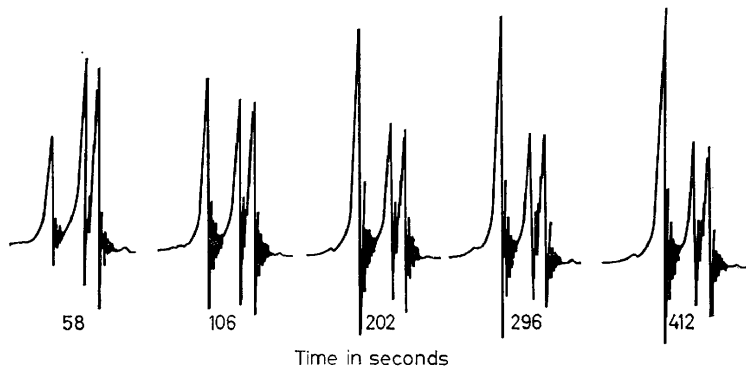
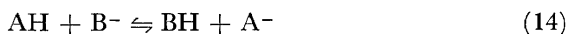


Figure 2. Proton n.m.r. spectra in methylsilyl region showing catalyzed rearrangement of III to IV. Sample is 0.4 M III in cyclohexane with 0.8 M *n*-BuLi. No further change is observable after 412 seconds.

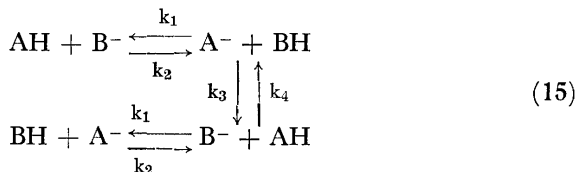
In determining the mechanism it was important to find out if the reaction was inter- or intramolecular in nature. The compound analogous to III, but with EtMe_2Si in place of Me_3Si groups is bis(ethyl-dimethylsilyl)methylhydrazine, V. III and V were shown to undergo base-catalyzed equilibration at similar rates. A mixture of III and V was then made up and treated with *n*-butyllithium. The reaction mixture contained III, IV, V, and the N,N-isomer of V, $(\text{EtMe}_2\text{Si})_2\text{N}-\text{NHCH}_3$, but *no* crossover products containing both Me_3Si - and EtMe_2Si - groups in the same molecule were observed. The rearrangement therefore appears to be intramolecular¹⁹.

Experiments showed that the alkyl lithium added as "catalyst" is completely consumed within the time of mixing, so that the actual base catalyst during most of the rearrangement reaction is hydrazide anion. Consider now the situation after the initial alkyl lithium has reacted. Let one hydrazine isomer be symbolized AH, with anion A^- , and the other be BH, with anion B^- . A molecule of AH can be deprotonated by reaction with A^- , but this reaction can be ignored since it leads to no net change in the system. Only deprotonation of AH by B^- is kinetically significant (Eq. 14). Rearrangement of A^- to B^- can then take place. Finally, B^- must be reprotonated to give the rearranged isomer BH; but in the reprotonation only reaction of

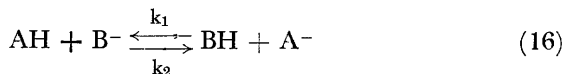


B^- with AH is kinetically significant, so the equation for the reaction is identical with (Eq. 14).

The sequence of events is diagrammed in Eq. (15). Only the concentrations of AH and BH are known, but fortunately k_3 and k_4 are rapid compared to



k_1 and k_2 , so they can be replaced in the kinetic analysis by an equilibrium constant, $K = A^-/B^-$. The deprotonation step is therefore rate-limiting, and the kinetic equation reduces to (16):



The rate equation is:

$$\frac{d(\text{BH})}{dt} = k_1(\text{AH})(\text{B}^-) - k_2(\text{BH})(\text{A}^-) \quad (17)$$

From which the following first-order rate law can be derived:

$$-\ln \{[(\text{BH})_e - (\text{BH})]/(\text{BH})_e\} = [k_1(\text{B}^-) - k_2(\text{A}^-)]t \quad (18)$$

In agreement with this analysis, the equilibration reaction follows first order kinetics²⁰. The kinetic analysis also demands that the rate of equilibration starting either from AH or BH should be the same, that is, that the rate of forward and reverse reactions must be equal. This is true at low silylhydrazine concentrations, but deviations from equal rate are found at higher concentration, probably due to specific solvation of the lithium-hydrazide ion pair by excess silylhydrazine²⁰. Specific solvent effects are also noted in the strong influence of very small amounts of complexing ethers on the reaction rate. For example, the rate of catalyzed rearrangement of N,N'-bis(ethyltrimethylsilyl)methylhydrazine is increased about fifty-fold when dimethoxyethane is a solvent instead of cyclohexane. But a tenfold increase in rate is observed when only 5×10^{-5} molar dimethoxyethane is added to the cyclohexane solution.

The fact that the actual migration of silicon from one nitrogen to the other is very rapid follows from the kinetic results, but is shown even more convincingly from the n.m.r. of the silylhydrazide anions. Figure 3 shows the n.m.r. of N,N'-bis(trimethylsilyl)methylhydrazine after treatment with 1 equivalent of *n*-BuLi. The mixture of anions should have at least two different environments for silylmethyl groups, but at room temperature the n.m.r. in the methylsilyl region consists of a single sharp line. At -60° or -80° , a single line is again observed, but greatly broadened (the broadening is much larger than viscosity broadening for other protons in the solution). These results indicate that rapid equilibration is averaging the silylmethyl

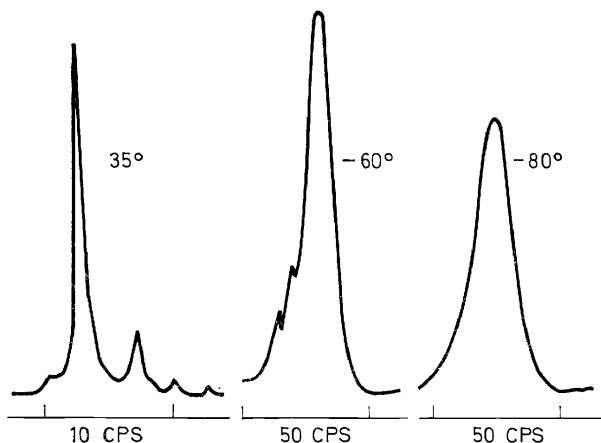
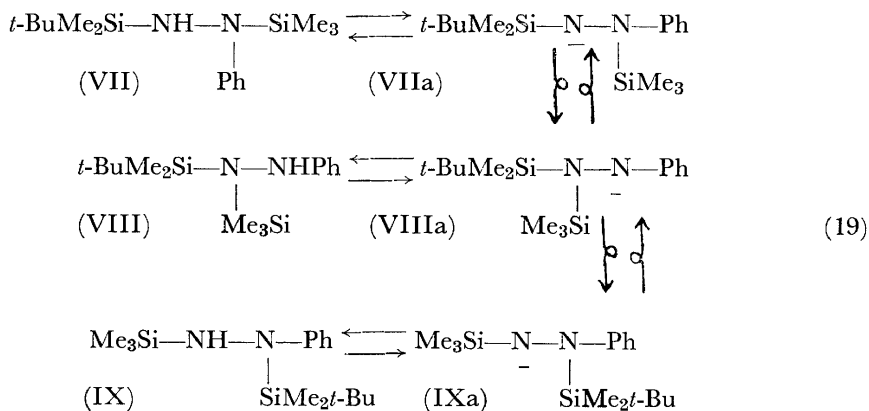


Figure 3. Silylmethyl region of proton n.m.r. spectrum of anion of *N,N'*-bis(ethyldimethylsilyl)hydrazine in toluene at various temperatures.

resonances at room temperature. At -80° the rate of equilibration is slowed so that it is comparable to the spin relaxation rate (but not significantly slower, or else several distinct lines would be resolved). The half-time for equilibration of silylhydrazide anions can therefore be estimated as about 10^{-3} sec at -80° .²⁰ This rate estimated to be at least 10^6 faster than any previously known anionic rearrangement.

Corroboration of the mechanistic pathway discussed above (Eq. 15) is provided by an interesting example in which the two organosilyl groups in the rearranging hydrazine molecule are different. The compound *N*-phenyl-*N'*-trimethylsilyl-*N'*-*t*-butyldimethylsilylhydrazine, VII, can be prepared isomerically pure and undergoes catalytic rearrangement, albeit quite slowly²¹. This compound can lose a proton to form the anion VIIa, which can rearrange by migration of the Me_3Si group to form anion VIIIa. The latter anion can become protonated to give VIII, or alternatively can undergo a second rearrangement to give the anion IXa, which would give IX upon protonation:



Note that *two sequential rearrangements* are necessary to form IX.

The concentration of all three species in the reacting solution can be followed by n.m.r. spectroscopy. Results of a typical run are shown in Figure 4. Compound IX, the double-rearrangement product, is formed *more rapidly than VIII* in the early stages of the reaction. The amount of IX passes through a maximum after about 30 hours, then declines to the equilibrium value of about 5 per cent as kinetic control of the product distribution is replaced by thermodynamic control. These results show that rearrangement *cannot* be rate-limiting. Protonation must be the rate-determining step in the rearrangement, and further, protonation of IXa must be more rapid than that of VIIIa²¹.

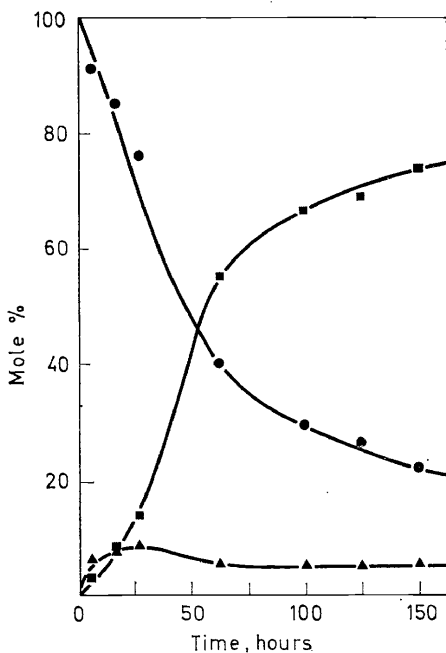


Figure 4. Catalytic rearrangement of VII as a function of time²¹. ●, VII; ▲, VIII; ■ IX

Unique mobility of silicon in anionic rearrangement

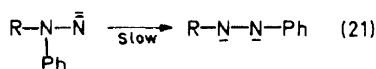
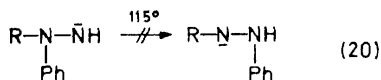
We have seen that organosilyl groups migrate rapidly from one nitrogen to the other in hydrazide anions. Let us now compare the migration rate with those for more conventional methyl and phenyl substituents.

All experiments designed to include methyl migration in 1,1 or 1,2-dimethylhydrazines have failed. Even in the presence of excess base and at temperatures up to 150°, no rearrangement of either of these methylhydrazines is observed. Still higher temperatures lead to complete decomposition²².

With phenylhydrazines, we were also quite unable to induce phenyl migration of the monoanions. When 1 equivalent of RLi is added to 1,1-diphenylhydrazine or 1-phenyl-1-methylhydrazine, no rearrangement is observed, even after many days at 115° in bis(2-methoxyethyl) ether

(Eq. 20). The rearranged anions should be more stable, because the negative charge could be delocalized onto the aromatic ring, but the energy of activation for phenyl migration must be so great that it does not take place²².

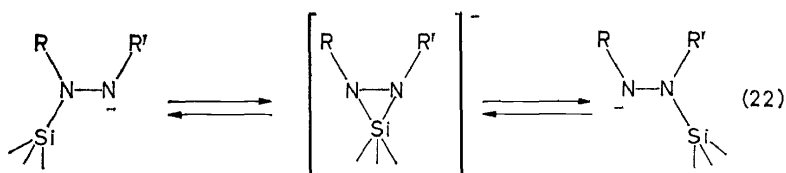
Rearrangement of phenylhydrazines can be brought about, however, if more than one equivalent of base is used, so that the hydrazide dianion is generated. The driving force for rearrangement is very much greater for the dianion than for the monoanion. Even so, the rearrangement is slow, requiring many hours at 30°. ²²



R = phenyl or methyl

It is possible now to make a crude comparison of the migration rates of trimethylsilyl and phenyl groups in the hydrazine rearrangement. Because no rearrangement of the monoanion of N,N-diphenylhydrazine was observed at 120°, the half-time for migration of phenyl under these conditions must be at least 10⁶ sec. The half-time for migration of Me₃Si in silylhydrazide anions was estimated from the n.m.r. results as about 10⁻³ sec at -80°. The difference of 200° in temperature can be conservatively estimated to alter the rate by a factor of at least 10⁵. Multiplying these factors, we can conclude that in the anionic rearrangement of hydrazines, the migration rate of Me₃Si is at least 10¹⁴ faster than for phenyl.

The reason for this enormous difference in mobility must reflect differences in the transition state for rearrangement. At some point in the rearrangement the migrating group will be equidistant between the nitrogen atoms, and equally bonded to each:

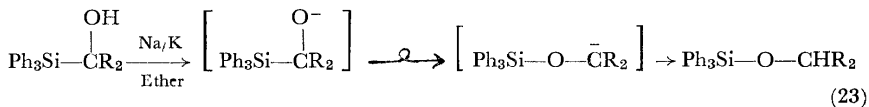


X

The equally-bonded form X may be the transition state for rearrangement, or (particularly for silicon) it might be a true reaction intermediate. In any case, because silicon can make use of unfilled low-energy orbitals to become pentacoordinate, the bridged structure X must be very much more favourable for silicon than for phenyl. The energy of activation for the reaction is therefore much less for silicon, accounting for the > 10¹⁴-fold difference in rate.

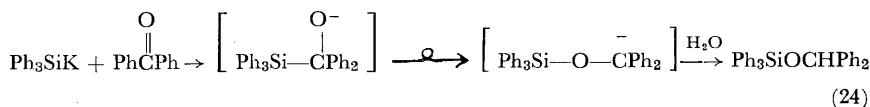
The Anti-Wittig rearrangement of silicon

There is one other anionic rearrangement reaction where silicon groups are known to be exceptionally mobile, although a direct comparison with organic migrating groups is not possible. A. G. Brook and his coworkers²³⁻²⁵ have shown that when α -silylcarbinols are treated with catalytic amounts of strong base (Na-K alloy) in ether, rearrangement to the alkoxy silane takes place:

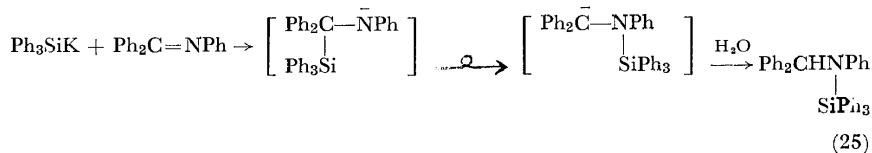


The reaction involves migration of silicon from carbon to oxygen, and so is exactly opposite from the Wittig rearrangement; we can call it an "anti-Wittig" rearrangement. The reaction takes place at 25° with only small amounts of base, and so is very much more rapid than the conventional Wittig reaction. Again, the relative stability of a bridged pentacoordinate intermediate or transition state with silicon can account for the high rate of the anti-Wittig rearrangement.

Similar carbon to oxygen anionic rearrangements have been invoked to explain unusual products obtained in certain reactions of silicon compounds, *i.e.*, the production of an alkoxy compound in the reaction of triphenylsilylpotassium with benzophenone:²⁶



Similarly, anionic migration of silicon from C to N may take place in the reaction of triphenylsilylpotassium with benzophenone anil:²⁷



Unknown 1,2 anionic rearrangements

From experience with the hydrazine rearrangement, it now seems clear that the way to find new anionic rearrangements is to introduce an organosilyl substituent as the potential migrating group. If the rearrangement is successful with the silyl compound, the much more difficult migration of organic substituents can then be sought.

Of the many possible 1,2-anionic rearrangements, only a few have been studied. Let us consider homoatomic rearrangements first. The possibilities are summarized in *Figure 5*. The known reactions are the C→C (ethane) rearrangement and the N→N hydrazine rearrangement. The other unknown reactions can be classified as "detectable" or "undetectable", the latter implying that isotopic substitution would be necessary for detection. Con-

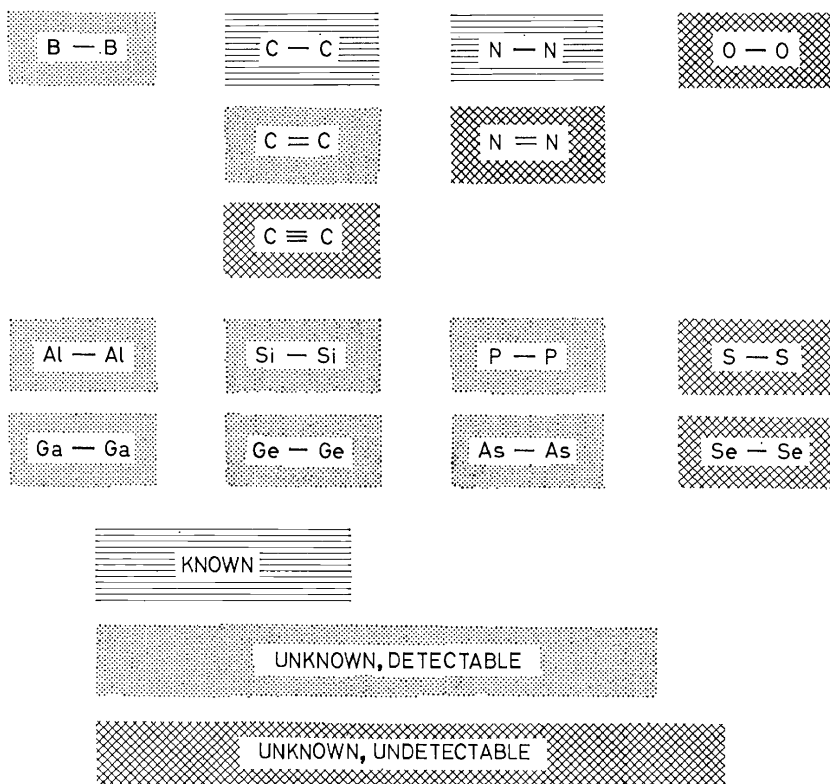
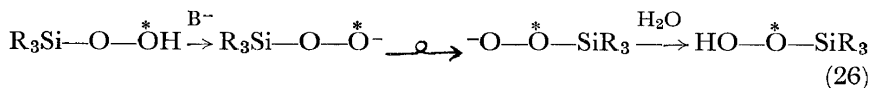


Figure 5. Possible homoatomic 1,2-anionic rearrangements. "Undetectable" implies that observation of the rearrangement would be impossible without isotopic labelling.

sider, for instance, the anionic O→O rearrangement. An organosilyl hydroperoxide anion might undergo anionic rearrangement, but the product is identical with the starting material, so the migration would be unobserved unless the hydroperoxide were selectively labelled with isotopic oxygen:



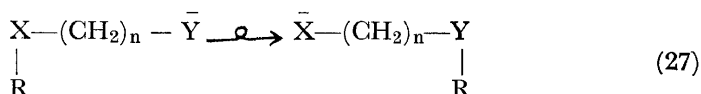
These cases will be worthwhile to study eventually, but of greater interest at the moment are the unknown, "detectable" cases (detectable here implying that the rearrangement can be observed by differentially substituting the two atoms). Of these cases, the C=C and Si—Si rearrangements seem most promising, and these are currently under investigation.

Of the heteroatomic 1,2-anionic rearrangements, only the C—O (Wittig and anti-Wittig) and C—N (Stevens) systems are known. The N→O (hydroxylamine) rearrangement is especially promising for study using organosilicon substituents as, due to the work of Wannagat²⁸ and of West and Matuszko,²⁹ several organosilyl hydroxylamines have recently been

synthesized. Anionic rearrangements involving second-row atoms are virtually completely unstudied, and, although problems of synthesis may be more severe, many new systems should eventually be investigated.

Remote anionic rearrangements

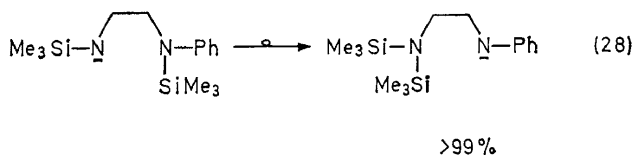
Finally, we will turn attention to the large family of anionic rearrangements in which migration takes place to a remote atom. In these "Smiles rearrangements" the anionic atoms X and Y are ordinarily separated by a carbon chain:



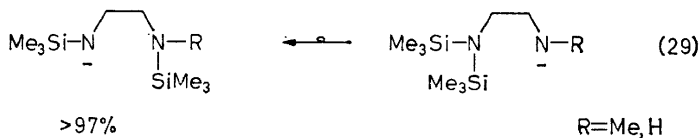
These remote rearrangements can of course be homoatomic ($X = Y$) or heteroatomic ($X \neq Y$). Recently we have studied the $N \rightarrow N$ and $O \rightarrow N$ anionic rearrangements where $n = 2, 3$ and 4 .³⁰⁻³²

Organosilyl ethylenediamines undergo 1,4 intramolecular anionic rearrangement with migration of silicon.³⁰ However, the reaction is very much slower than the rearrangement of organosilyl hydrazines, so that the actual migration in the anions can be studied by n.m.r. Typical reactions take place with a half-time of minutes at 30° , or about 10^8 slower than the silylhydrazine rearrangement.

Electronic and steric factors again influence the position of equilibrium in the ethylenediamine reaction. Phenyl substitution stabilizes a negative charge on nitrogen, so that the anion of N,N' -bis(trimethylsilyl)- N -phenylhydrazine rearranges completely to the N,N isomer:



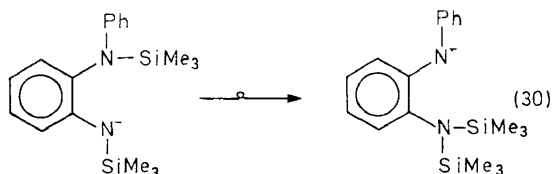
But if no aromatic group is present, rearrangement takes place in the opposite sense to put two silyl groups on the different nitrogens:



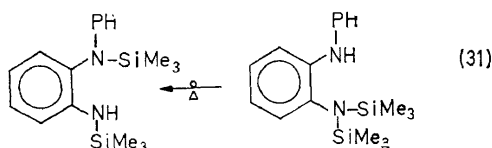
Examination of models shows that relief of steric strain in the N,N -bis(silyl) isomer may provide the driving force for the rearrangement when no phenyl group is present. The electronic stabilization gained by delocalization of the negative charge onto the aromatic ring apparently overrides this steric preference so that Eq. 28 proceeds in the direction written.

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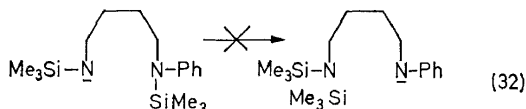
A particularly interesting case of 1,4 N \rightarrow N rearrangement is provided by the bis(organosilyl)-N-phenyl-O-phenylenediamines. Here the anion of the N,N'-bis (silyl) compound is less stable than its isomer, and undergoes complete rearrangement:³¹



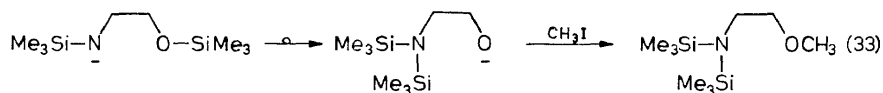
This arrangement is probably electronically driven; the negative charge in the rearranged anion can be delocalized onto both aromatic rings. But the protonated compounds can also be equilibrated thermally, and the reaction takes place in the opposite direction to give the N,N' isomer:³¹†



Entirely similar 1,5 rearrangements occur for anions of organosilyl propylenediamines, but the rates are about two orders of magnitude slower than the 1,4 N \rightarrow N rearrangements.³² When four methylene groups separate the nitrogens, in organosilyl tetramethylenediamine anions, rearrangement is not observed even for the most favourable cases under forcing conditions:



The first O \rightarrow N anionic rearrangements have recently been found for N,O-bis (organosilyl)ethanolamines, which rearrange to the N,N isomers.³² The products were identified by quenching with methyl iodide:



Here a highly energetic Si—O bond is broken and a weaker Si—N bond is formed in the rearrangement. The stability of the product alkoxide anion over the amide ion presumably provides the driving force for O \rightarrow N migration.

† Thermal rearrangements of organosilyl hydrazines and ethylenediamines have also been studied by Pitt, but in these cases the direction of rearrangement is the same as for the anionic rearrangement, and moreover the reactions are complex with side products being formed^{33,34}.

The rearrangement is accompanied by the formation of some monosilyl and trisilyl compounds, due to intermolecular exchange of trimethylsilyl groups occurring at the same time as intramolecular anionic rearrangement.

Summary

Present knowledge of organosilicon substituents in anionic rearrangements shows that they have unprecedented migratory aptitude. In the hydrazine rearrangement, the rate of migration of trimethylsilyl substituents is at least 10^{14} times that for phenyl. The silylhydrazine rearrangement is far faster than any previously known anionic rearrangement. The use of organosilyl groups as migrating substituents already has led to the discovery of several new anionic rearrangements, and this approach has great promise for the identification of anionic rearrangements as yet unknown.

There are, moreover, many important questions which remain unanswered about even the known organosilicon anionic rearrangements. The exact nature of the intermediate in the hydrazine rearrangement is uncertain, and information about the activation parameters for this very rapid reaction is lacking. The factors which govern the position of equilibrium, both among anions and neutral equilibrating species, remain speculative. And as yet there is essentially no information on the migratory aptitude of other metals than silicon. Much interesting work lies ahead.

It is a pleasure to give credit to my co-workers who have carried out the experiments described above: Drs Robert Bailey, Mitsuo Ishikawa, Shinji Murai, and Anthony Matuszko; Messrs H. Franklin Stewart and Donald Koepsell; and Miss Nancy McFadden.

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