

# REACTIONS AND REARRANGEMENTS OF CARBON-FUNCTIONAL ORGANOSILICON COMPOUNDS

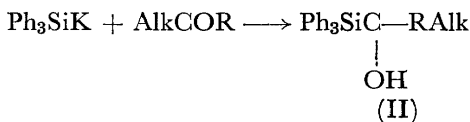
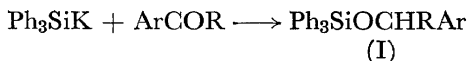
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In recent years considerable interest has developed in the synthesis of carbon-functional organosilicon compounds, and the study of their reactions. The following material outlines some of the experimental findings and interpretations related to two reactions, each of which involves interesting molecular rearrangements—the rearrangement of  $\alpha$ -silylcarbinols to their isomeric silylethers, and the rearrangement of  $\alpha$ -silylketones when treated with alkoxides.

## REARRANGEMENTS OF $\alpha$ -SILYLCARBINOLS TO SILYLEETHERS

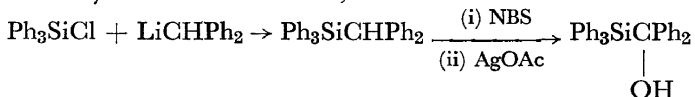
Historically, the  $\alpha$ -silylcarbinol rearrangement goes back to the year 1953 when Gilman and Wu<sup>1</sup> reported that triphenylsilylpotassium, a newly discovered reagent, reacted with aromatic aldehydes or ketones to give not the expected  $\alpha$ -silylcarbinol, but instead the isomeric silylether (I).



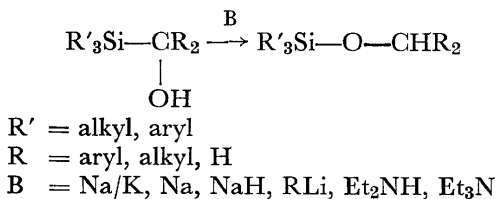
R=H, alkyl.

On the other hand, with aliphatic ketones, the expected silylcarbinol (II) was obtained. The former anomalous reaction caught our attention and led to a further investigation of the system.

Synthesis of triphenylsilyldiphenylcarbinol, a typical  $\alpha$ -silylcarbinol, was accomplished by an alternative route,

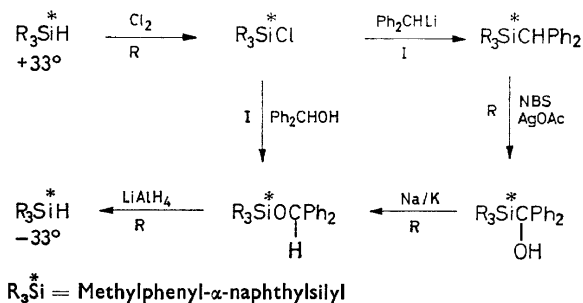


*i.e.* by coupling of benzhydryllithium with triphenylchlorosilane followed by bromination and then mild hydrolysis with silver acetate<sup>2</sup>. When treated with a catalytic quantity of any one of a wide variety of reagents, generally basic in character, the carbinol, and indeed most  $\alpha$ -silylcarbinols, were readily converted to their isomeric silylethers<sup>3</sup>.



The reactions in most cases were rapid and quantitative, and recently both stereochemical and kinetic studies of the rearrangements have been carried out.

In order to study the stereochemistry of silicon during rearrangement, advantage was taken of the elegant work of Sommer and co-workers<sup>4</sup>, who had synthesized and resolved methylphenyl- $\alpha$ -naphthylsilane, and had established the stereochemistry of a number of its transformations. The Walden cycle illustrated in *Figure 1* was carried out, and it was shown that



*Figure 1.* Walden cycle illustrating the inversion of configuration at silicon when optically active methylphenyl- $\alpha$ -naphthylchlorosilane is coupled stereoselectively with benzhydryllithium

optically active methylphenyl- $\alpha$ -naphthylchlorosilane coupled stereoselectively with benzhydryllithium, with inversion of configuration at silicon. This optically active compound could be converted, as before, to an asymmetric silylcarbinol without affecting the configuration of the asymmetric silicon centre. Rearrangement of the carbinol gave an optically active silylether, which on reduction by a reaction shown by Sommer to involve retention of configuration, gave as product optically active silane with the opposite sign of rotation and configuration to the starting material. Thus in this Walden cycle, overall inversion of configuration occurred, and since the inversion was known to occur during the coupling reaction, it was evident that the rearrangement from silylcarbinol to silylether occurred with complete retention of configuration at silicon<sup>5</sup>.

It also seemed of importance, from mechanistic considerations, to attempt to study the possible stereochemistry at an asymmetric carbinol-carbon centre, and to this end a new Walden cycle was studied as shown in *Figure 2*. Coupling of (–)-chlorosilane with benzyllithium occurred with inversion of configuration, but low temperature and other special conditions were required to achieve a high degree of stereoselectivity. Bromination with

## REARRANGEMENTS OF ORGANOSILICON COMPOUNDS

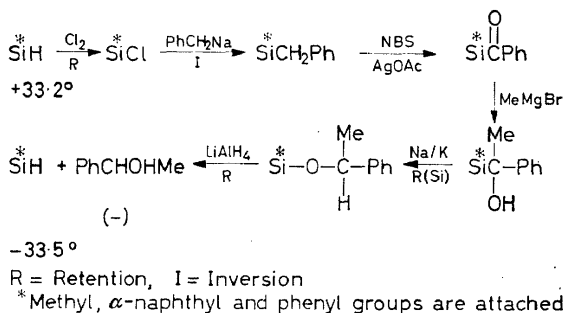


Figure 2. Walden cycle showing the coupling of (–)-chlorosilane with benzylnsodium with inversion of configuration, and subsequent reactions

two moles of N-bromsuccinimide followed by mild hydrolysis gave optically active benzoylmethylphenyl- $\alpha$ -naphthylsilane. Treatment of the ketone with methyl Grignard reagent gave a diastereomeric mixture of silylmethylphenylcarbinols. These could not be separated but were rearranged to a diastereomeric mixture of silylethers, which on reduction with lithium aluminum hydride gave (–)-silane, opposite in configuration to the starting material, and 1-phenylethanol which was optically active, possessing an excess of the (–)-enantiomer.

At the time this work was carried out, the absolute configuration of methylphenyl- $\alpha$ -naphthylsilane was unknown and we were able to propose an absolute configuration from these results<sup>6</sup>. This configuration was subsequently confirmed as correct by the X-ray studies of Ashida *et al.*<sup>7</sup>. Using this now-established configuration, the stereochemistry of these reactions is shown in Figure 3. The (+)-methylphenyl- $\alpha$ -naphthylsilane shown in Figure 3 in Fischer projection would give rise to benzoylsilane of the configuration shown, taking into account the inversion involved in coupling. When such an asymmetric ketone is treated with methyl Grignard reagent Cram's rule<sup>8</sup> of asymmetric induction may be expected to apply, *i.e.* with the ketone in the conformation shown, the Grignard reagent may be expected to add mainly from the less hindered back side of the carbonyl group, giving the diastereomer shown as the major product. If retention of configuration occurred during rearrangement, the major diastereomeric ether would be that shown, which on reduction with lithium aluminum hydride, would give (–)-silane and as well 1-phenylethanol of the designated absolute configuration. This is in fact the known absolute configuration of (–)-1-phenylethanol which experimentally was always obtained in excess, and in one experiment, in the ratio 80 parts of the (–)-enantiomer to 20 parts of the (+)-enantiomer. Since the stereochemistry of all steps in the cycle except the rearrangement is known, these results indicate that retention of configuration occurred at the carbon centre.

It is important to ascertain the stereoselectivity of each of the various steps in the reaction sequence which eventually lead to the observed 80 : 20 mixture of enantiomeric 1-phenylethanols. That is, in what proportions are the diastereomeric carbinols formed during the Grignard

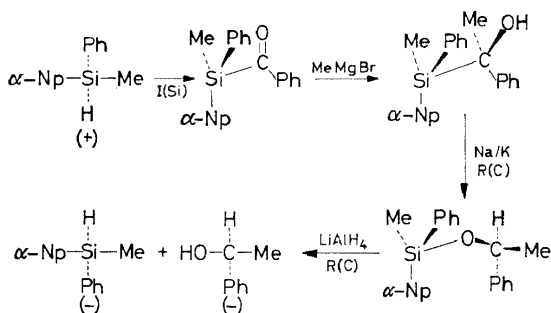


Figure 3. Absolute configurations of compounds in silylcarbinol rearrangement

addition and to what extent, if any, does racemization occur during rearrangement?

The proportions of carbinols and ethers can be established by n.m.r. techniques. The signal for the methyl group attached to silicon for each of the two diastereomers will occur at slightly different fields because of the different asymmetric environments. Using the peak heights or peak areas, it was found that the diastereomeric carbinols were formed, under one set of experimental conditions, in the ratio of 81 : 19, and the corresponding diastereomeric silyl ether ratio was 78 : 22, a slightly less accurate measurement because of the smaller separation of the two signals. Reduction of this mixture of ethers led to (–) and (+)1-phenylethanols in the ratio of 80 : 20. Since the proportions of ethers and enantiomeric 1-phenylethanols are found to be the same as the proportions of diastereomeric carbinols formed from the methyl Grignard addition, it is clear that no racemization is involved in the silylcarbinol to silyl ether rearrangement, and that the reaction is a completely stereospecific one.

So far nothing has been specified about the mechanism of this rearrangement. From data that will be discussed shortly it seemed probable, as shown in Figure 4, that the rearrangement involved an intramolecular attack by

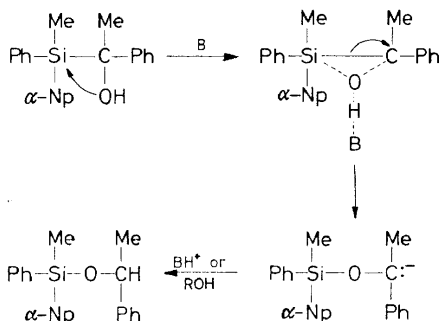


Figure 4. Rearrangement of a silylcarbinol to silyl ether

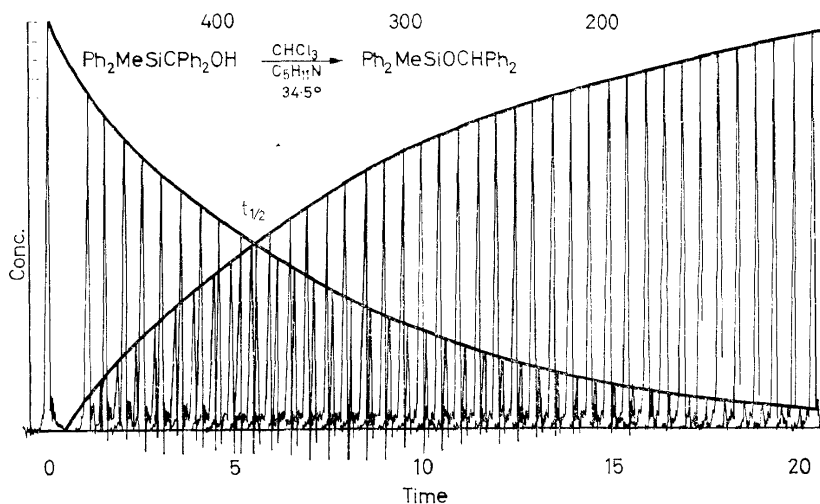
## REARRANGEMENTS OF ORGANOSILICON COMPOUNDS

carbinol-oxygen on silicon, leading to cleavage of the silicon-carbon bond with the formation of a carbanion or carbanion-like species which subsequently became protonated. Protonation, occurring with complete retention of configuration would be quite consistent with the generally known behaviour of carbanions in a low-dielectric solvent such as ether. However, if this simple carbanion picture is correct, Cram's work with carbanions would predict that in aprotic high dielectric solvents such as dimethyl sulphoxide, some racemization should occur and in protic high-dielectric solvents, inversion of configuration should be observed<sup>9</sup>. In fact, whether the rearrangement was run in ether, in dimethyl sulphoxide, or in methyl cellosolve, complete retention of configuration was observed. Hence, if a carbanion is involved, its stereochemical independence of the solvent medium can best be explained if the carbanion is considered to be part of an intimate ion pair with protonated base, such that, as carbanion character develops during the rearrangement, a rapid stereospecific protonation can occur. This problem will be referred to again later.

Kinetic investigations of the silylcarbinol to silylether rearrangement became possible when it was found that the rearrangement could be carried out under homogeneous conditions using diethyl- or triethylamine as catalysts.

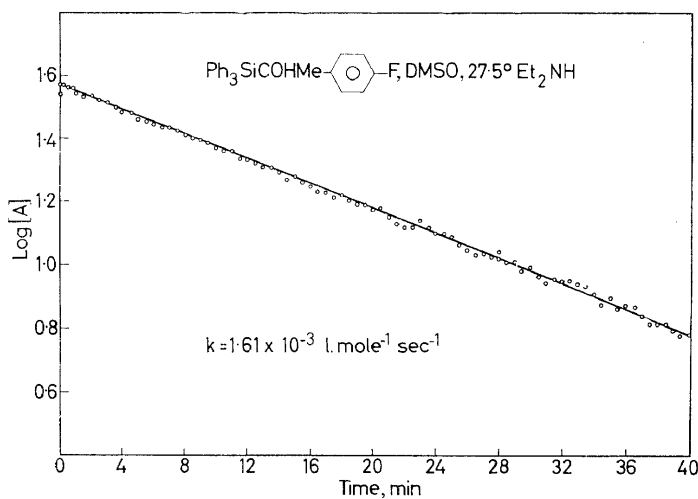
It was found that with a wide variety of  $\alpha$ -silylcarbinols, the rearrangement was first order in  $\alpha$ -silylcarbinol and first order in amine catalyst. Further, since the amine is not consumed during the rearrangement, its concentration remains constant and the kinetics appear as pseudo-first order.

Most of the kinetic data was obtained using n.m.r. techniques by following the intensity of suitable signals, for example, methyl attached to silicon or carbon, with respect to time. Generally, the signal for the group in the  $\alpha$ -silylcarbinol fell at slightly different field strength than the signal for the same group in the silylether, so that, as shown in *Figure 5*, it was possible



*Figure 5.* NMR signals in the 0.6–0.7 p.p.m. region of the spectrum corresponding to methyl attached to silicon

to follow not only the decrease in  $\alpha$ -silylcarbinol concentration but also the increase in silylether concentration. *Figure 5* shows a series of signals in the 0.6–0.7 p.p.m. region of the spectrum, corresponding to methyl attached to silicon, which have been horizontally displaced every 30 seconds. Such data is easily converted to the more normal log concentration versus time plot, an example of which is shown in *Figure 6*. This technique is obviously a very



*Figure 6.* Log concentration vs. time plot

good way to get kinetic data, and we have been able to measure reactions with half-lives down to 2–3 minutes.

The data in *Table 1* summarizes the effect of changing substituents on

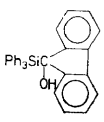
*Table 1.* Rates of rearrangement of diphenylcarbinols in chloroform by diethylamine at 25°C.

$\text{Ph}_3\text{SiCOHPh}_2$	$60.0 \times 10^{-4}$	$\text{l. mole}^{-1}\text{sec}^{-1}$
$\text{Ph}_2\text{MeSiCOHPh}_2$	$9.8 \times 10^{-4}$	$\text{l. mole}^{-1}\text{sec}^{-1}$
$\text{PhMe}_2\text{SiCOHPh}_2$	$1.5 \times 10^{-4}$	$\text{l. mole}^{-1}\text{sec}^{-1}$
$\text{Me}_3\text{SiCOHPh}_2$	$0.25 \times 10^{-4}$	$\text{l. mole}^{-1}\text{sec}^{-1}$

silicon from phenyl to methyl for a series of diphenylcarbinols. It will be noted that there is a decrease in rate by a factor of about 6 for each replacement of phenyl by methyl. Much more profound changes in rate occur as the groups attached to the carbinol-carbon are changed, as shown in *Table 2*. 9-Hydroxy-9-triphenylsilylfluorene rearranges very much faster than the related diphenylcarbinol, and replacement of a phenyl group by methyl, hydrogen or benzyl results in changes of rate by factors of 1000 or more. Dialkylcarbinols under these conditions cannot be observed to rearrange, and this

## REARRANGEMENTS OF ORGANOSILICON COMPOUNDS

 Table 2. Rates of rearrangement of silylcarbinols by Et<sub>2</sub>NH

	<i>in</i> CHCl <sub>3</sub> , 26°C.	<i>in</i> DMSO, 36°C.
	1.18 l.mole <sup>-1</sup> sec <sup>-1</sup>	
$\begin{array}{c} \text{Ph} \\   \\ \text{Ph}_3\text{SiCPh} \\   \\ \text{OH} \end{array}$	$6.1 \times 10^{-3}$	$7.6 \times 10^{-3}$ l. mole <sup>-1</sup> sec <sup>-1</sup>
$\begin{array}{c} \text{Me} \\   \\ \text{Ph}_3\text{SiCPh} \\   \\ \text{OH} \end{array}$	$4.3 \times 10^{-6}$ *	$6.7 \times 10^{-3}$
$\begin{array}{c} \text{H} \\   \\ \text{Ph}_3\text{SiCPh} \\   \\ \text{OH} \end{array}$		$5.7 \times 10^{-3}$
$\begin{array}{c} \text{CH}_2\text{Ph} \\   \\ \text{Ph}_3\text{SiCPh} \\   \\ \text{OH} \end{array}$		$1.1 \times 10^{-1}$
$\begin{array}{c} \text{Me} \\   \\ \text{Ph}_2\text{SiCMe} \\   \\ \text{OH} \end{array}$		too slow to measure

\* Rates not directly measured but calculated from other data.

great spread in rate of rearrangement makes it quite clear why, in the reactions of silylmetallics with aliphatic ketones the carbinols can be isolated, whereas with aromatic ketones, the ethers are obtained.

It is also evident that the rearrangement occurs much more readily in polar solvents, rearrangements in dimethylsulphoxide occurring about 1000 times more rapidly than in the much less polar solvent chloroform.

Using a variable temperature probe on the n.m.r. instrument it was possible to obtain reasonably linear Arrhenius type plots. The activation parameters obtained for two isomeric carbinols in two different solvents are shown in Table 3. In each case, relatively small activation energies are

Table 3. Activation energies and entropies of rearrangement

		E <sub>act.</sub>	ΔS <sup>‡</sup>
Ph <sub>3</sub> SiCOHMePh	DMSO	11.2 kcal/mole	-34.3 e.u.
Ph <sub>2</sub> MeSiCOHPh <sub>2</sub>	CHCl <sub>3</sub>	8.65	-45.6

found but at the same time the activation entropies involved are exceedingly large. Activation entropies of this magnitude are of course consistent with a highly oriented cyclic transition state.

In order to learn more about the transition state involved in the rearrangement, the effect of *para*-substituents on the rates of rearrangement of certain series of phenylcarbinols has been investigated. A typical Hammett  $\log k$  versus  $\sigma$  plot for a series of triphenylsilylphenylmethylcarbinols is shown in Figure 7. Here the points for the *p*-chloro, *p*-bromo, hydrogen and *p*-*t*-butyl

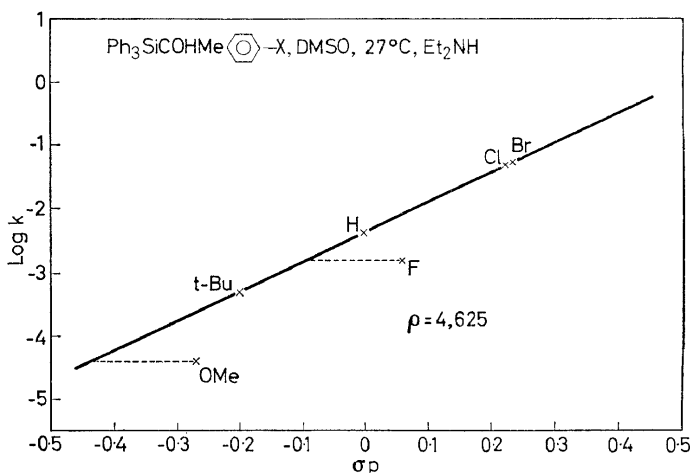


Figure 7. Hammett  $\log k$  vs.  $\sigma$  plot for a series of triphenylsilylphenylmethylcarbinols

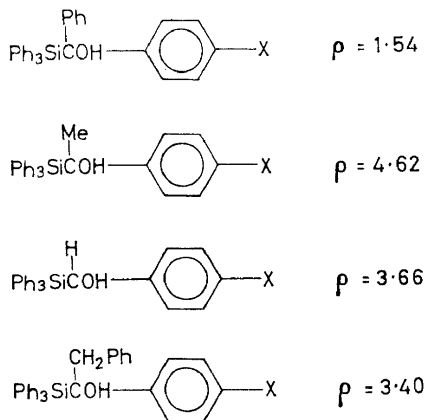
compounds fall on a straight line with a correlation coefficient of 0.999, and a slope corresponding to a Hammett  $\rho$  or reaction parameter of 4.62. This very large and positive value indicates great sensitivity of the reaction to substituent effects, and more particularly, indicates the development of considerable negative charge on the phenyl group or on the carbinol-carbon next to the phenyl group, in the transition state. The *p*-fluoro and *p*-methoxy points fall considerably off the line, the *p*-fluoro compound in fact reacting more slowly than the hydrogen compound despite the fact that its Hammett substituent constant, either sigma or sigma minus, is positive. These deviations have been found throughout this work and in fact have been noted before in systems where large positive values of  $\rho$  are found, and seem to involve substituents that may inductively withdraw electrons but which may release electrons through resonance interactions.

Table 4 gives the results of other series of compounds which we have investigated. With the diphenylcarbinols a considerably smaller  $\rho$  is found and intermediate values of  $\rho$  are found for the hydrogen and benzyl series. Since there appears to be every evidence for the existence of a species with considerable carbanion character in the transition state the smaller value of  $\rho$  in the diphenylcarbinols must reflect the delocalization of negative charge into the second, unsubstituted ring.

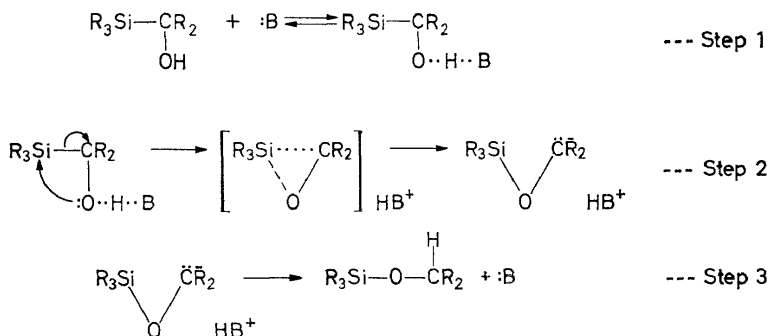


## REARRANGEMENTS OF ORGANOSILICON COMPOUNDS

Table 4. Hammett reaction constants for silylcarbinols



Any general mechanism proposed for this silylcarbinol to silylether rearrangement, must be consistent with the stereochemical and kinetic data just described. In particular, it must account for the stereochemistry observed at both asymmetric silicon and carbon centres, and for the kinetics which involve processes with very high entropies of activation and very large positive Hammett reaction parameters. A possible mechanism is shown in *Figure 8*. The first step, which involves removal of the carbinol



*Figure 8.* A mechanism for the rearrangement of silylcarbinol to silylether

proton is certainly rapid and reversible—on addition of a few mole per cent of amine to a solution of the carbinol in DMSO, the sharp O–H peak completely disappears, although no rearrangement has occurred. The second step undoubtedly involves intramolecular attack by the carbinol oxygen on the silicon atom, presumably facilitated by the available *d*-orbitals on silicon. This is either concerted with, or precedes the cleavage of the carbon–silicon bond. The species written in brackets is best regarded as a description of the transition state in which the silicon–oxygen bond formation is virtually complete, and the silicon–carbon bond cleavage is substantially complete so that the transition state has a high degree of carbanion character on the

carbon atom, consistent with the high  $\rho$  values. The cyclic character of the species, together with its necessary strict orientation, considering the bulky groups attached, and with the associated protonated base, accounts for the very high entropies of activation observed. However, it is not entirely clear what happens next. It is possible that the transition state proceeds to carbanion as written, which in a third step is rapidly, irreversibly and stereospecifically protonated to give the silylether of required stereochemistry. The only objection to this is in the sense that the "carbanion" is not a "normal" carbanion, because of its very unusual stereochemical behaviour but must be regarded as an intimate ion-pair. In addition, carbanions of silylethers have been prepared as the potassium salts by other routes, but attempts to prepare them from silylcarbinols have always failed.

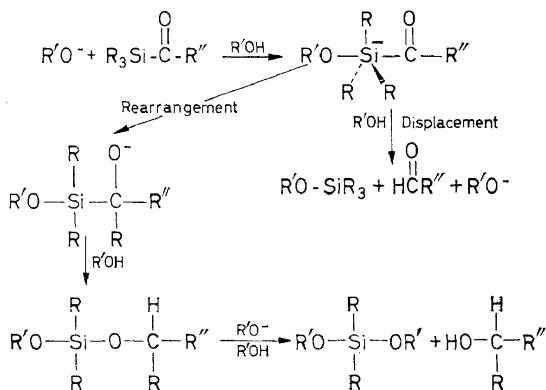
An equally acceptable and perhaps simpler description, which at present cannot be distinguished from the mechanism involving the unusual carbanion intermediate, is that the transition state, as written, may collapse directly to products by a stereospecific protonation from the gegenion associated with it.

Other variants of this mechanism can be written. Thus, additional steps could be added such that a cyclic pentacovalent silicon intermediate was formed which in subsequent steps collapsed to carbanion or directly to products. However, there is at present no evidence for the existence of a pentacovalent intermediate in this system and the simpler mechanism appears adequate until further experiments may throw more light on the situation.

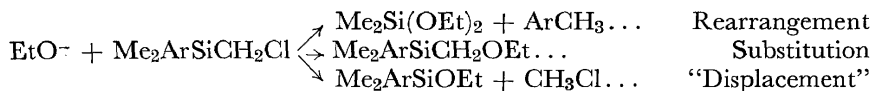
### THE REARRANGEMENT OF $\alpha$ -SILYLKETONES

Another reaction of carbon-functional organosilicon compounds which involves rearrangements is the reaction of  $\alpha$ -silylketones with alkoxide ions. When an  $\alpha$ -silylketone is treated with an alkoxide ion a variety of products are formed: a dialkoxysilane in which an R group originally attached to silicon has become attached to carbon, a simple alkoxide and an aldehyde, together with smaller amounts usually of symmetrical dialkoxysilanes and carbinols. These reactions are fairly general, in the sense that they have been shown to occur with a variety of simple alkoxides, and with a fairly wide variety of silylketones<sup>10, 11</sup>. Both alkyl and aryl migrations were observed, although alkyl migrations were observed only in the absence of a possible aryl migration. These results were interpreted as occurring through two reactions, which for simplicity can be written as occurring from a single pentacovalent silicon intermediate, although evidence for the actual formation of this species is tenuous. The reactions are outlined in *Figure 9*. On the one hand the pentacovalent silicon intermediate formed by attack of alkoxide on the silicon atom of the silylketone could be visualized as decomposing by displacement, *i.e.* loss of the acyl group, leading to alkoxy silane and the aldehyde corresponding to the acyl group of the ketone. Alternatively, rearrangement of an R group from silicon to the adjacent carbonyl-carbon atom would lead to an  $\alpha$ -silylalkoxide ion which, as has been seen from the preceding study, readily rearranges to a silylether—in this case a dialkoxysilane. Subsequent ether interchange with the alkoxide in the system accounts for the other products—the symmetrical dialkoxysilane, and the carbinol, isolated from the reaction mixture.

## REARRANGEMENTS OF ORGANOSILICON COMPOUNDS


 Figure 9. Reaction of  $\alpha$ -silylketones with alkoxide ions

About the only analogy to this reaction is some work of Eaborn and Jeffrey<sup>12</sup>, shown below



in which they treated aryldimethylchloromethylsilanes with ethoxide ion. The products isolated could be accounted for in terms of rearrangement, *i.e.* migration of an aryl group from silicon to carbon, followed by further reaction with ethoxide ion leading to a toluene and a diethoxy silane; normal substitution also occurred and finally products of displacement were also isolated. It was shown that rearrangement and displacement were facilitated by electron-withdrawing groups on the aromatic ring, an observation at least consistent with the intermediacy of a pentacovalent silicon species, which would be stabilized by electron-withdrawing groups.

It seemed possible to learn something more about the reaction of silylketones with alkoxides by attempting an investigation of its stereochemistry. The reaction of optically active methylphenyl- $\alpha$ -naphthylbenzoylsilane with, for example, potassium *t*-butoxide could be expected to lead to an immensely complicated mixture of products, as shown in *Figure 10*. Apart from the *t*-butoxysilane and benzaldehyde expected from displacement, it could be foreseen that both the phenyl and  $\alpha$ -naphthyl groups might migrate leading to a complex mixture of alkoxy silanes and alcohols as shown. The successful separation of this mixture seemed unlikely and consequently it was decided to reduce the entire reaction mixture with excess lithium aluminum hydride. This would reduce the *t*-butoxysilane to methylphenyl- $\alpha$ -naphthylsilane, and this would be the only source of this product. Hence the yield and stereochemistry of any methylphenyl- $\alpha$ -naphthylsilane isolated would be diagnostic of the ‘displacement’ reaction.

In a similar way the products of phenyl migration would on reduction be converted to methyl- $\alpha$ -naphthylsilane and benzhydrol and the yields of either of these products would be diagnostic of the amount of phenyl migration. Similarly, the amounts of methylphenylsilane and/or  $\alpha$ -naphthylphenyl-

A. G. BROOK

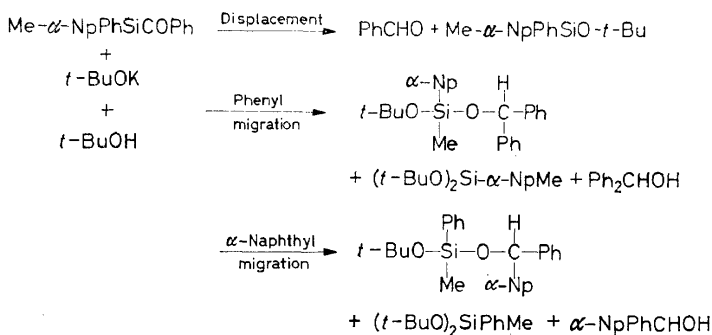


Figure 10. Reaction of optically active methylphenyl- $\alpha$ -naphthylbenzoylsilane with potassium *t*-butoxide

carbinol would be indicative of the amount of "naphthyl migration" and the further possibility existed that, were the naphthylphenylcarbinol to be optically active, some information about the stereochemistry of the migration might be acquired. Table 5 shows typical results of the reaction of (+)-

Table 5. Yields of products and rotations from (+)-Me-1-NpPhSiCOPh

	$[\alpha]_D^{25}$	Yield (%)
Crude product	-0.07° <sup>a</sup>	—
After reduction		
Me-1-NpSiH <sub>2</sub> , MePhSiH <sub>2</sub>	0.00	—
Ph <sub>2</sub> CHOH	0.00	49.7
(-)-Me-1-NpPhSiH	-29.05°	13.4
(+)-1-NpPhCHOH	+ 5.91° <sup>b</sup>	9.9

<sup>a</sup> Observed, not specific rotation.

<sup>b</sup> Rotation raised to + 11.7° by recrystallization.

methylphenyl- $\alpha$ -naphthylbenzoylsilane with *t*-butoxide ion in *t*-butyl alcohol-toluene at about 0° over two days, during which time the yellow colour of the ketone disappeared. The crude reaction product possessed only slight optical activity. After reduction and separation of products, the yields of methylphenyl- $\alpha$ -naphthylsilane and of the carbinols indicated that at least 13 per cent of the reaction took the displacement path while at least 60 per cent of the reaction involved rearrangement. The ratio of phenyl to naphthyl migration observed was about 3.6 : 1. The silane isolated, which was diagnostic of the displacement part of the reaction, had considerable optical activity—pure silane has a specific rotation of about 33° so that the observed rotation corresponds to about 95 per cent of the (-)-enantiomer and 5 per cent of the (+)-enantiomer, so that the displacement evidently occurred with considerable stereoselectivity. The stereochemistry of the displacement is shown in Figure 11. The absolute configuration of (+)-benzoylmethylphenylnaphthylsilane and of (-)-methylphenyl- $\alpha$ -naphthylsilane are as shown. Since lithium aluminum hydride reduction of alko-

## REARRANGEMENTS OF ORGANOSILICON COMPOUNDS

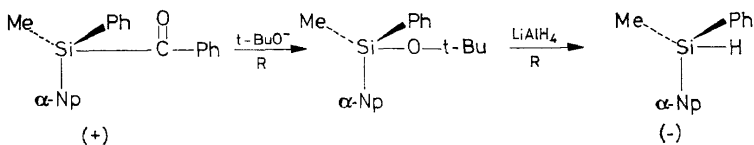
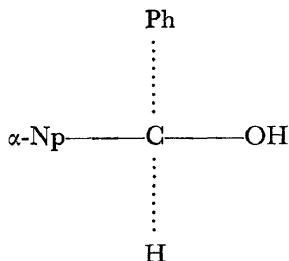


Figure 11. Stereochemistry of the displacement reaction between (+)-methylphenyl- $\alpha$ -naphthylbenzoylsilane and *t*-butoxide ion in *t*-butyl alcohol-toluene at  $\sim 0^\circ\text{C}$ .

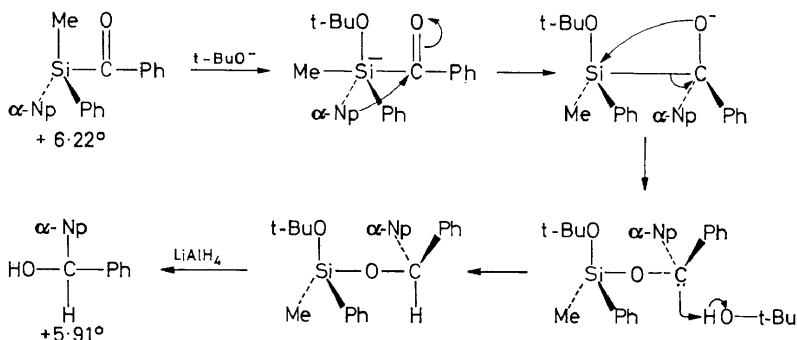
xysilanes is known to occur with retention of configuration<sup>13</sup>, it is obvious that the configuration of the *t*-butoxysilane must be as shown, and that the displacement reaction has occurred with retention of configuration at silicon. This might be expected to involve flank attack by *t*-butoxide ion on the silicon atom of the silylketone.

The naphthylphenylcarbinol isolated from the reduction of the original reaction was also found to be optically active. This implies, since this product is diagnostic of  $\alpha$ -naphthyl migration, that this occurs in some stereoselective manner, forming naphthylphenylcarbinol whose configuration presumably bears some relationship to that of the parent silylketone. Since the absolute configuration of (+)- $\alpha$ -naphthylphenylcarbinol was not known, it was necessary to establish it and this was done chemically by the application of Prelog's rule<sup>14</sup>. This involved the synthesis of the phenylglyoxalate ester of the optically active  $\alpha$ -naphthylphenylcarbinol, followed by its treatment with methyl Grignard reagent. After hydrolysis, the atrolactic acid formed was isolated and its sign of optical rotation determined, thereby defining the absolute configuration of (+)- $\alpha$ -naphthylphenylcarbinol as shown below in Fischer projection.



This configuration for the (+)-enantiomer is in accordance with that predicted by Brewster's rules<sup>15</sup>, which have been found reliable for compounds of this sort. With this absolute configuration, it is possible to speculate on the mechanism and stereochemistry of the  $\alpha$ -naphthyl migration. For simplicity it is necessary to make certain assumptions. Assume that an  $sp^3d$  pentacovalent intermediate is involved in the rearrangement, and further, that the same intermediate may lead either to phenyl or  $\alpha$ -naphthyl rearrangement or to "displacement" with the observed stereochemistry, namely retention of configuration. This seriously restricts the number of possible intermediates and in fact the only logical possibility is the one

shown in *Figure 12* in which the three bulkiest groups, *t*-butoxy, phenyl and  $\alpha$ -naphthyl, lie in a plane with methyl and benzoyl occupying the axial positions. Examination of molecular models shows in fact that this configuration is possible and is among the least sterically hindered possibilities. Back



*Figure 12.* Mechanism and stereochemistry of  $\alpha$ -naphthyl migration leading to (+)- $\alpha$ -naphthylphenylcarbinol

side migration of the  $\alpha$ -naphthyl group as shown would lead to the asymmetric alkoxide ion shown, which, being similar to the alkoxide ions intermediate in the silylcarbinol to silylether rearrangement, may be expected to rearrange similarly with retention of configuration at carbon. Lithium aluminum hydride reduction of this product would lead to  $\alpha$ -naphthylphenylcarbinol with the observed optical rotation.

Some of this latter interpretation is necessarily highly speculative. Nevertheless, the overall results provide another example of the remarkable tendency of organosilicon compounds having oxygen attached to a carbon atom adjacent to silicon, to undergo rearrangements leading to silicon-oxygen bond formation and silicon-carbon bond cleavage, which are highly stereospecific both at silicon and at carbon. It is to be hoped that through chemical studies of this type more may be learned about the chemistry of silicon and the role that its *d*-orbitals play in its chemical reactions.

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## References

- 1 H. Gilman and T. C. Wu. *J. Am. chem. Soc.* **75**, 2935 (1953).
- 2 A. G. Brook. *J. Am. chem. Soc.* **80**, 1886 (1958).
- 3 A. G. Brook, C. M. Warner, and M. E. McGriskin. *J. Am. chem. Soc.* **81**, 981 (1959).
- 4 L. M. Sommer. *Stereochemistry, Mechanism and Silicon* McGraw-Hill, New York (1965).
- 5 A. G. Brook and C. M. Warner. *Tetrahedron Lett.* **18**, 815 (1962)
- 6 A. G. Brook and W. W. Limburg. *J. Am. chem. Soc.* **85**, 832 (1963).
- 7 T. Ashida, R. Pepinski, and Y. Okaya. *Abstracts*, International Union of Crystallography Congress, Rome, Italy, September 1963.
- 8 D. J. Cram and F. A. Abd Elhafez. *J. Am. chem. Soc.* **74**, 5828 (1952).

## REARRANGEMENTS OF ORGANOSILICON COMPOUNDS

- <sup>9</sup> D. J. Cram, C. A. Kingsbury, and B. Richborn. *J. Am. chem. Soc.* **83**, 3688 (1961).  
<sup>10</sup> A. G. Brook. *J. org. Chem.* **25**, 1072 (1960).  
<sup>11</sup> A. G. Brook and N. V. Schwartz. *J. org. Chem.* **27**, 2311 (1962).  
<sup>12</sup> C. Eaborn and J. G. Jeffrey. *J. chem. Soc.* 137 (1957).  
<sup>13</sup> L. H. Sommer, C. L. Frye, *et al.* *J. Am. chem. Soc.* **83**, 2210 (1961).  
<sup>14</sup> V. Prelog. *Bull. Soc. Chim. Fr.* 987 (1956).  
<sup>15</sup> J. H. Brewster. *J. Am. chem. Soc.* **81**, 5475 (1959).