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The Brook Rearrangement and Beyond– Then and Now

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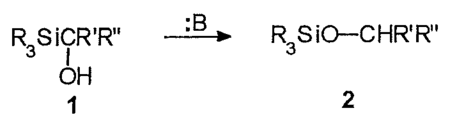
Introduction

What is the Brook Rearrangement? Originally the name was given to a base-catalyzed intramolecular rearrangement of silylcarbinols **1** (α-hydroxysilanes) to their isomeric silyl ethers **2** (siloxyalkanes), a reaction which involved a 1,2-shift of a silyl group from carbon to oxygen, as illustrated in Eq.1.[1,2]



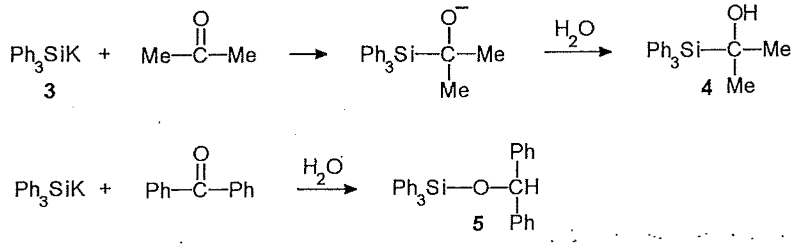
$$R_3Si\underset{OH}{C}R'R'' \xrightarrow{:B} R_3SiO{-}CHR'R'' \qquad (1)$$

1 **2**

With the passage of time, and further investigations of the behavior of functionally substituted organosilicon compounds, examples of other rearrangements involving the migration of a silyl group from carbon to oxygen under basic conditions were discovered. Thus 1,3-silyl shifts (sometimes called homo-Brook rearrangements) 1,4-, 1,5- and even 1,6-silyl shifts have been observed, and in many cases they were called Brook rearrangements. Nor was this appellation restricted to base-catalyzed systems. 1,2-, 1,3-, and related 1,n-silyl shifts from carbon to oxygen involving radical intermediates have become known as radical Brook rearrangements. Rearrangements involving the shift of a silyl group from carbon to nitrogen have also been observed and have been labeled Aza-Brook rearrangements. To complete this picture, the reverse of a Brook Rearrangement, namely the 1,2-shift of a silyl group from oxygen to carbon, an analog of the Wittig Rearrangement, which required a full equivalent of a strong base to effect, has been studied and on occasion was called a Reverse-Brook or a Retro-Brook rearrangement. Thus, at the beginning of the 21st century the term "Brook rearrangement" is being used to describe all manner of 1,n-silyl shifts from carbon to a more electronegative atom within the molecule, at least by some investigators. In a brief review of the present kind it is impossible to review exhaustively all these types of "Brook" rearrangement, and the main focus will be on 1,n-C to O silyl rearrangements, dealing both with the historical developments in our laboratories, and with some modern examples of their applications to synthesis. Other reviews, both past and present, have covered the full scope of rearrangements of organosilicon compounds, including the Brook rearrangement.[3, 4, 5, 6, 7]

Discovery of the 1,2-Silyl C to O Rearrangement.

The discovery and elaboration of the Brook rearrangement, namely the base-catalyzed rearrangement of silylcarbinols to their isomeric silyl ethers, arose as a result of the finding in the laboratories of Professor Henry Gilman of Iowa State College that whereas silylmetallic reagents such as triphenylsilylpotassium, **3**, the first known silylmetallic reagent, appeared to add normally to the carbonyl group of simple ketones such as acetone to give the expected silylcarbinol **4** after aqueous workup, the product obtained on workup of the reaction with aromatic ketones such as benzophenone was the isomeric ether 5 (Eq. 2).[8,9]

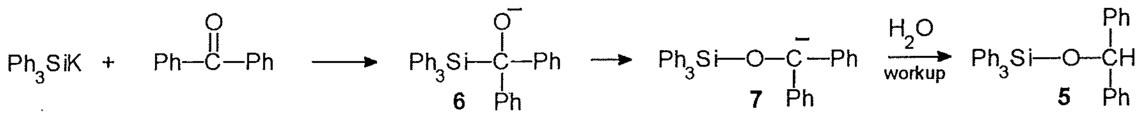


$$\underset{\mathbf{3}}{Ph_3SiK} + Me{-}\overset{O}{\overset{\|}{C}}{-}Me \longrightarrow Ph_3Si{-}\overset{O^-}{\underset{Me}{C}}{-}Me \xrightarrow{H_2O} Ph_3Si{-}\overset{OH}{\underset{\mathbf{4}\ Me}{C}}{-}Me \qquad (2)$$

$$Ph_3SiK + Ph{-}\overset{O}{\overset{\|}{C}}{-}Ph \xrightarrow{H_2O} Ph_3Si{-}O{-}\overset{Ph}{\underset{Ph}{C}}H \quad \mathbf{5}$$

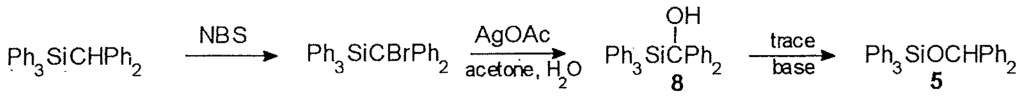
We suggested[1] that a reasonable interpretation of this behavior was that normal addition of the silylmetallic to the carbonyl group of the ketone occurred, but that for some reason, the alkoxy ion adduct **6** derived from the aromatic ketone subsequently rearranged to the carbanion **7** prior to hydrolysis (Eq. 3).

(3)



To test this theory the expected silylcarbinol **8** was synthesized as shown in Eq. 4.

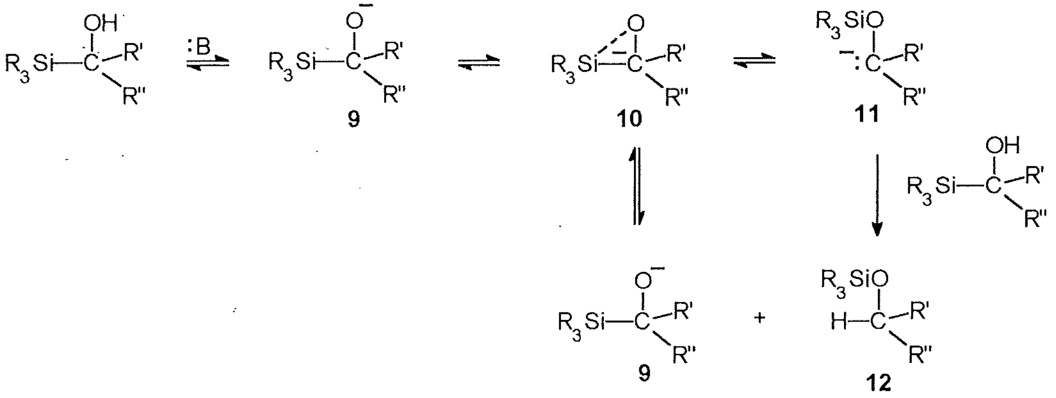
(4)



$$Ph_3SiCHPh_2 \xrightarrow{NBS} Ph_3SiCBrPh_2 \xrightarrow[\text{acetone, }H_2O]{AgOAc} Ph_3Si\overset{OH}{C}Ph_2 \ (\mathbf{8}) \xrightarrow[\text{base}]{\text{trace}} Ph_3SiOCHPh_2 \ (\mathbf{5})$$

This stable compound, **8**, on treatment with a trace of any of a wide variety of bases in non-protic solvents, rapidly gave rise to the isomeric silyl ether **5** without intervention of any added proton source. Detailed mechanistic studies[10] of the reactions of a series of silylcarbinols $R_3SiC(OH)CR'R''$ with bases led us to propose the mechanism shown in Eq. 5, involving formation of alkoxide ion **9** on treatment of the carbinol by base, followed by intramolecular carbon-to-oxygen silyl migration via the intermediate or transition state **10**, to yield the carbanion **11**. This was then rapidly and irreversibly protonated by unrearranged silylcarbinol, giving rise to the silyl ether product **12** and more alkoxide **9**, which continued the chain reaction.

(5)

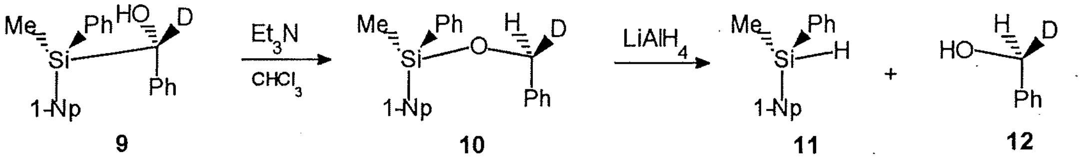


An obvious driving force for this isomerization was the very strong silicon-oxygen bond being formed at the expense of the much weaker silicon-carbon bond being broken.

The rates of rearrangement of different silylcarbinols varied greatly, and depended strongly on whether the R' and R" groups attached to carbon were electron withdrawing or electron donating, as well as on the solvent. Since protonation of the carbanion **11** was irreversible under the experimental conditions, to the extent that the R' and R" groups stabilized the carbanion, the rearrangement was facilitated. It was shown in other studies that if sufficient time was allowed before workup of the original reaction between silylcarbinol and a trace of base, that most silylcarbinols, regardless of the substituents attached, were converted into the isomeric silyl ether in high yields.[11, 12]

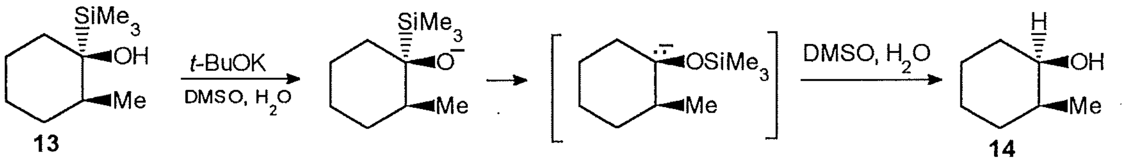
When these observations are applied to the previously mentioned reaction of triphenylsilylpotassium with benzophenone (Eq.3) it follows that at the time of workup (hydrolysis) of the reaction mixture, the stabilized carbanion **7** was the major component of the reaction mixture, by virtue of the stabilizing influence of the attached phenyl groups, so that protonation gave predominantly the silyl ether **5**. In the case of the reaction with acetone the electron-releasing methyl groups destabilized the potential carbanion and the alkoxide ion predominated at the time of workup, resulting in the silylcarbinol being the major product formed on hydrolysis.

The stereochemistry of the silylcarbinol to alkoxysilane rearrangement reaction was studied in ether using Na/K alloy to create the alkoxide ion, and it was shown that there was complete retention of stereochemistry at a chiral silicon centre.[13] Also, if the carbinol contained a chiral carbon centre bearing an aryl group, inversion of configuration occurred under the conditions we employed (Eq. 6),[14, 15] results also observed by others.[16] In the example shown in Eq. 6, the configurations of **9**, **11,** and **12** were known from previous studies, and the *S*- configuration of **12** clearly showed that inversion of configuration had occurred at chiral carbon during the rearrangement.



(6)

However, studies of the Brook rearrangement by Hudrlik *et al.* on the very different cyclic α-hydroxysilane **13** (which lacked aromatic groups on the carbanionic carbon and which used a full equivalent of *t*-BuOK in DMSO), indicated that retention of configuration occurred at the chiral carbon centre of the product **14** (Eq. 7),[17] reflecting again the importance of the substituents on the carbinol carbon in determining some features of the reaction. In this study, the silyl ether initially formed was subsequently cleaved to the alcohol by the base and solvent.



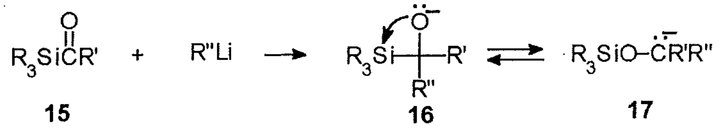
(7)

Retention of configuration was also observed by Wilson *et al.* using a different aliphatic silylcarbinol.[18]

Other Anionic Rearrangement Systems.

The oxyanions involved in simple Brook rearrangements can arise from numerous reactions. The addition of silylmetallic reagents to aldehydes and ketones, mentioned above, was the original source investigated, where an oxyanion-carbanion mixture was formed, whose proportions were determined by several variables, of which the electron withdrawing or donating properties of the substituents on carbon were of paramount importance. Similar circumstances will prevail in any situation in which equimolar proportions of reagents are involved, as for example the addition of an organometallic reagent to an acylsilane **15** (Eq. 8). Here again, an initially formed oxyanion **16** may isomerize to carbanion **17**, but no product will be formed until the system is hydrolytically worked up, or unless some additional intra- or intermolecular process takes place.

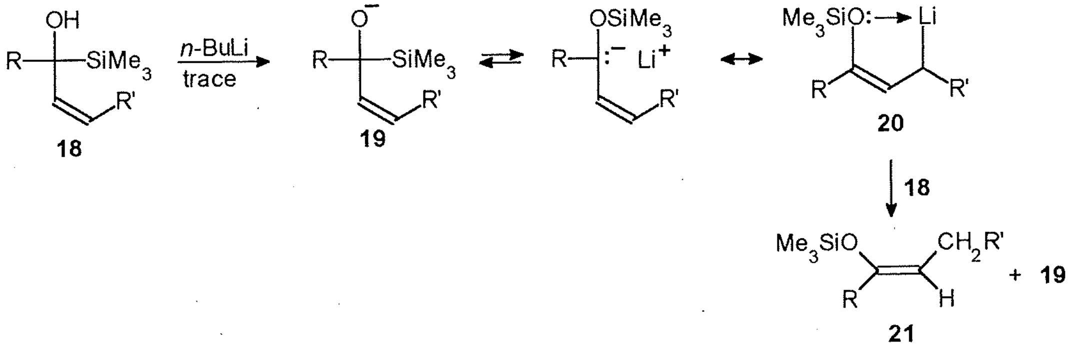
(8)



In both the cases of a silyl metallic reagent R_3SiM reacting with an aldehyde or ketone, or of an organometallic reagent RM reacting with an acylsilane R_3SiCOR', what happens depends on several factors. If the metal strongly coordinates to oxygen, as would occur if RM was a Grignard reagent RMgX, the oxyanion component will be stabilized and rearrangement to carbanion inhibited, so that on hydrolysis the silylcarbinol will be found to be the main product formed.[19] Further, if the R groups attached to the potential carbanionic centre are electron-releasing (e.g. alkyl groups), this will further relatively stabilize the oxyanion favoring formation of the silylcarbinol on workup. Conversely, if the potential carbanionic centre is stabilized by electron-withdrawing groups, its formation will be favoured, especially if the metal involved coordinates only weakly to oxygen (Na, K). In these cases, formation of the silyl ether was found to be the major product, as in the reactions of R_3SiK with Ph_2CO and related reactions.[20, 21, 22] Lithium ions will coordinate moderately strongly to the oxyanions, but the coordination is greatly weakened in the presence of solvents such as HMPA which strongly coordinate with the cation, thus greatly facilitating C to O rearrangement.

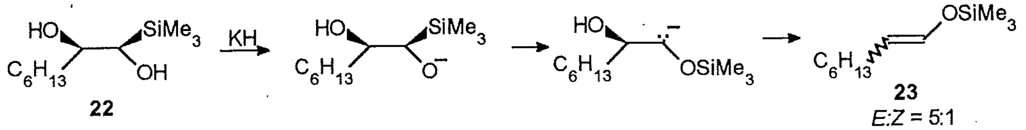
Reactions of silylcarbinols which lead on hydrolysis to silyl ethers are generally not of great synthetic interest, since there are usually much easier routes to the ethers. However, important synthetic applications arise if the one of the groups on the carbinol carbon is α,β–unsaturated. Thus, Kuwajima *et al.* treated the silylcarbinols **18** with traces of *n*-BuLi and the initially formed oxyanions **19** rearranged to the stabilized allylic carbanions **20**, which then were protonated by unrearranged carbinol in the γ position to give silyl enol ethers **21** with considerable stereoselectively, as illustrated in Eq. 9.[23]

(9)



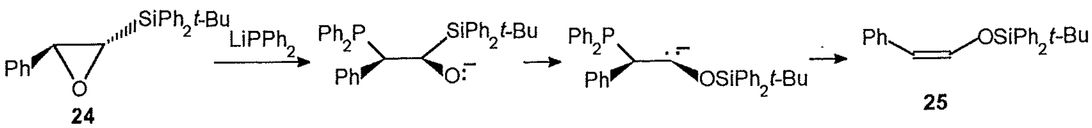
Also, Hudrlik *et al.*[24, 25] treated the α,β–dihydroxysilane **22** with KH and explained the stereoselective formation of the *E*-siloxyalkene **23** as the result of a Brook rearrangement, as shown in Eq. 10.

(10)



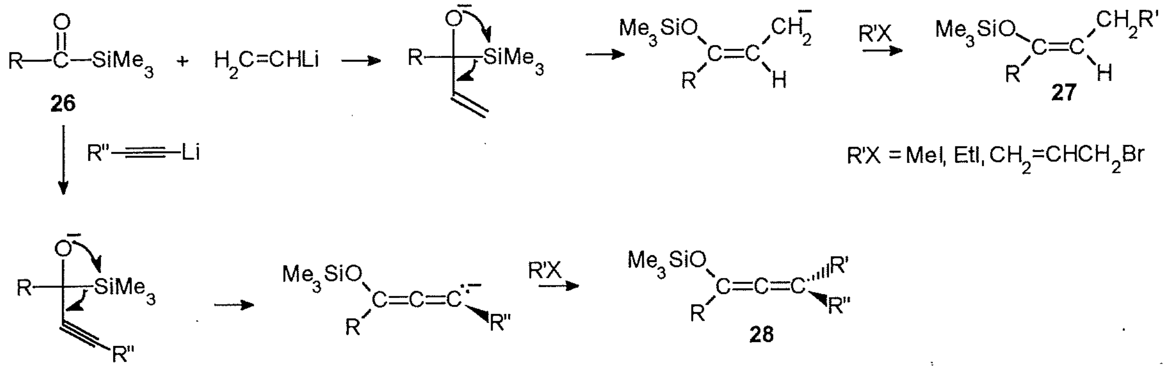
When the epoxysilane **24** was treated with lithium diphenylphosphide followed by methyl iodide, ring opening followed by Brook rearrangement followed by a clean *anti*-elimination resulted in *Z*-siloxyalkene **25** as shown in Eq. 11.[26]

(11)



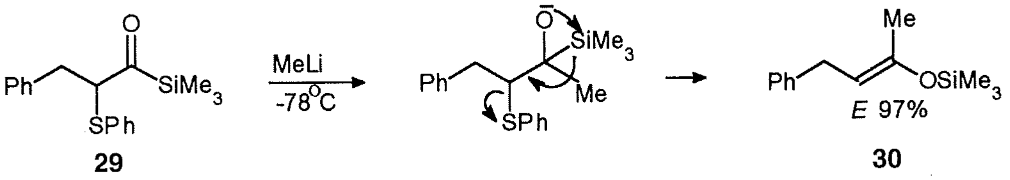
A variation of the above process, which involved solvent-controlled Brook rearrangements, has been described by Smith and Boldi[27] in which multicomponent linchpin couplings of silyldithianes with epoxides led to complex products readily convertible to polyols of potential importance in natural product synthesis.

A very important synthetic route to a variety of types of compound, involves the addition of organolithium reagents to acylsilanes. This leads directly to the formation of the oxyanion species of a potential Brook rearrangement. Reich *et al.*[28] added simple acylsilanes **26** to a full equivalent of vinyllithium at -78°C, and then worked the reaction up by adding simple alkyl iodides or disulfides to the reaction mixture. This resulted in complex silyl enol ethers **27** formed in good yield. The reaction is shown in Scheme 1. Using an alkynyllithium in place of vinyllithium gave rise to allenyl silyl ethers **28** in good yield.



Scheme 1

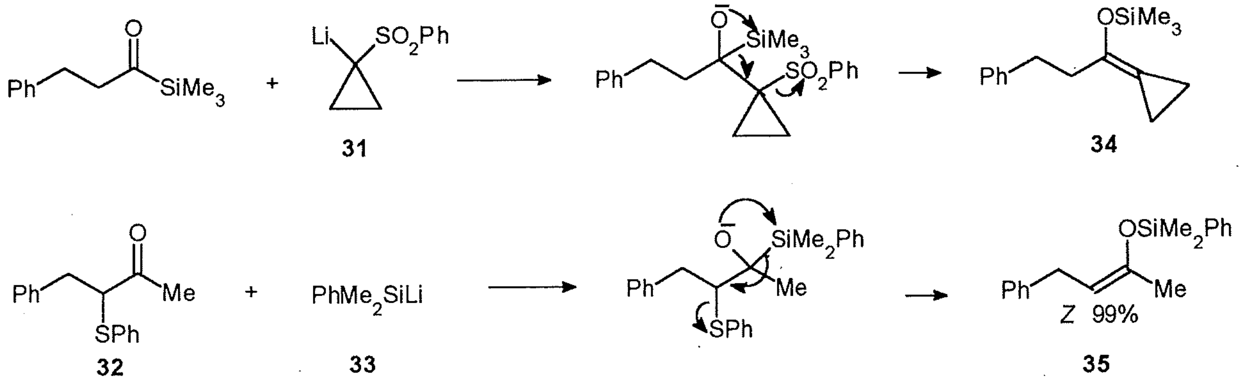
Alternatively, the reaction of simple organolithium reagents with acylsilanes **29** substituted in the α-position by one of several groups (-SPh, -SC_6H_4-*m*-CF_3, -SePh) gave rise, following rearrangement of the initial oxyanion to the isomeric carbanion, to spontaneous elimination of the substituent and the formation of primarily *E*-silyl enol ethers **30** with high stereoselectively.[29] An example is shown in Eq. 12.



(12)

It was shown that at -78°C two diastereomeric lithiated oxyanions were formed in a 97:3 ratio. At about -20°C only the major diastereomer rearranged, followed by elimination to give the *E*-silyl enol ether, while at 0°C both isomers rearranged with elimination to give the two isomeric silyl enol ethers in an *E*:*Z* ratio of 97:3

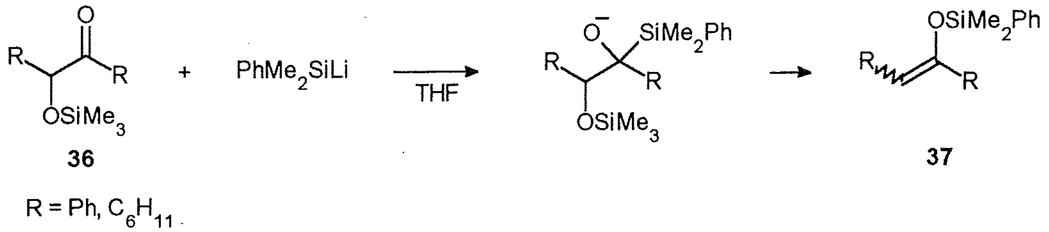
Similar results were obtained by using α-X-lithium reagents **31** (X = -SPh, -SO_2Ph) with simple acylsilanes, or from treating α-substituted ketones **32** with silyllithium reagents **33**. Both reactions gave rise to silyl enol ethers, **34** and **35** respectively, with a high *Z*:*E* ratio in the case of **35**, as illustrated in Scheme 2.



Scheme 2

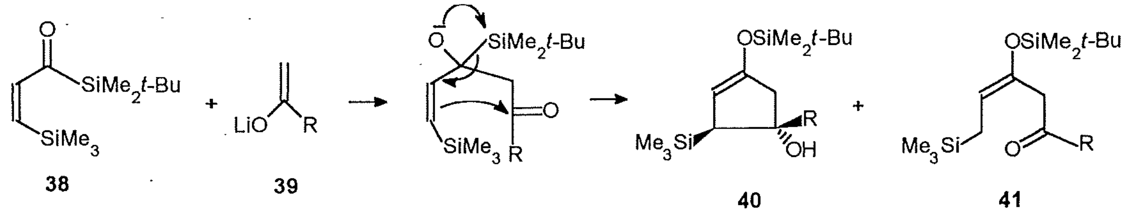
Alternatively, ketones bearing α-trimethylsilyloxy groups **36**, when treated with a silyllithium reagent in THF, were shown by Fleming[30] to lead via 1,2-Brook rearrangement to silyl enol ethers **37** as shown in Eq. 13.

(13)



A further synthetic elaboration was effected by Takeda *et al.*[31, 32] who treated α,β–unsaturated acylsilanes **38** with ketone enolates **39**. Under the low temperature conditions employed, a Brook rearrangement was followed spontaneously by a [3 + 2] cyclization to create substituted cyclopentendiols **40** together with some acyclic ketone **41**, as shown in Eq. 14.

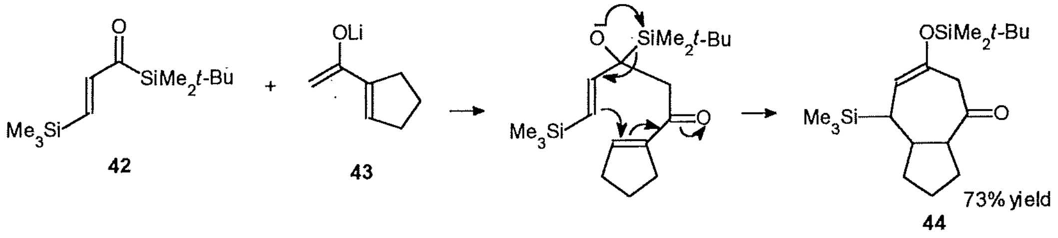
(14)



Further developments of this procedure have recently been reported.[33]

Further elaborations utilizing the reactions of α,β–unsaturated acylsilanes **42** with the lithium enolates of α,β–unsaturated ketones **43** resulted, after Brook rearrangement of the initially formed oxyanion, in a novel stereospecific [3 + 4] annulation reaction leading to the formation of bicyclic 3-siloxycyclohepten-3-ones **44**[34, 35, 36] as shown in Eq. 15, and other more complex polycyclic compounds.[37] Studies relating the carbanion stability to the yields of products in these reactions were also reported.[38]

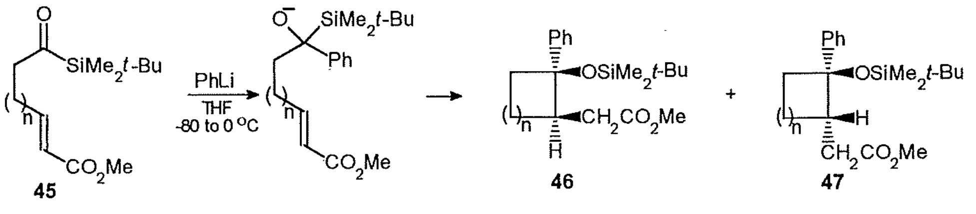
(15)



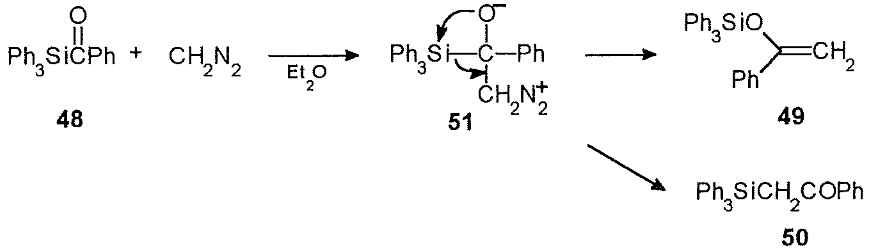
If the enolate of cycloheptenone was employed in reacting with **42** and related compounds, a route to highly functionalized eight-membered carbocycles was developed involving [3 + 4] annulation.[39]

Related tandem Brook rearrangement-intramolecular Michael reaction sequences employing phenyllithium with acylsilanes having remote unsaturation, **45**, were shown to lead to highly functionalized cyclic diastereomers **46** and **47** in moderate yields, as shown in Eq.16.[40]

(16)

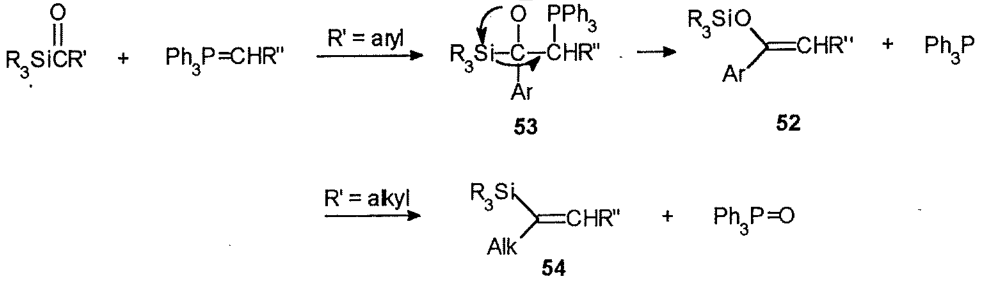


Novel 1,2-silyl C to O rearrangements have also been observed in reactions of acylsilanes with several non-metallic reagents, namely diazomethane and Wittig reagents. While not of great synthetic importance, these reactions indicate the breath and versatility of the Brook rearrangement. Thus, the reaction of the acylsilane **48** with diazomethane yielded two products, the siloxyalkene **49**, and the β-ketosilane **50**. The formation of these products can be interpreted as arising from the adduct **51**, which may either undergo a Brook rearrangement leading to the siloxyalkene **49** as shown, or a conventional 1,2-carbon-to-carbon silyl migration to the CH_2 group with expulsion of nitrogen leading to the β-ketosilane **50** (Eq.17).[41]



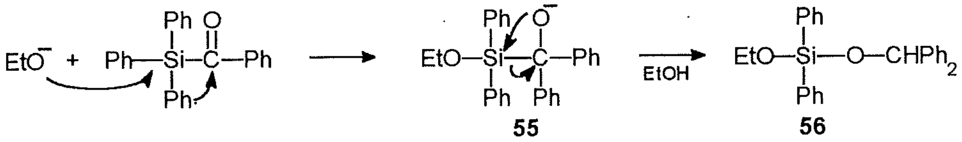
(17)

Related behavior was observed in the reactions of acylsilanes with Wittig reagents. In cases where the group R' attached to the carbonyl carbon atom was an aryl group, Brook rearrangement was favoured by electron delocalization, and cleavage of the Si-C bond occurred leading to the siloxyalkene **52** and expulsion of triphenylphosphine from the intermediate **53**. When R' was an alkyl group, a normal Wittig reaction took place, leading to the expected alkene **54** and triphenylphosphine oxide (Eq. 18).[42] Related results were reported by Nakajima *et al.*[43]



(18)

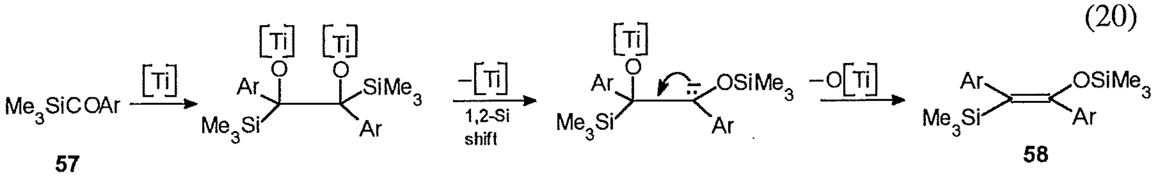
Brook rearrangements are also involved in the reactions of acylsilanes with alkoxide ions[44, 45] where a new oxyanion **55**, formed as the result of a 1,2-migration of an aryl group from silicon to carbon, undergoes a 1,2-silyl shift from carbon to oxygen, leading to the product **56** after protonation by the solvent, as shown in (Eq. 19)



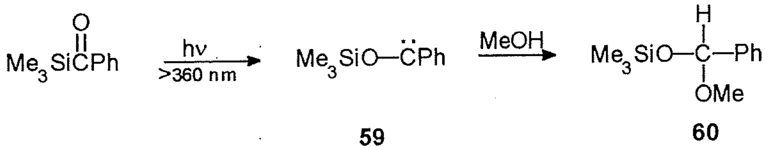
(19)

Fürstner *et al.*[46] found that when aroylsilanes **57** were coupled using McMurry conditions the resulting products on workup were the siloxyvinylsilanes **58** and not the normal McMurry symmetrical alkene products. It was suggested that loss of the Ti species resulted in a Brook rearrangement followed by loss of the OTi species as shown in Eq. 20.

(20)



Another set of circumstances giving rise to 1,2-silyl shifts from carbon to oxygen occurs during the photolysis of simple acylsilanes in protic solvents. It was found that photolysis in protic solvents (alcohols, carboxylic acids) or protic reagents (HX, HCN) involves a Brook type 1,2-silyl shift of the silyl group from carbon to the carbonyl oxygen, resulting in a transient siloxycarbene **59** which then is trapped by the solvent or reagent to give the mixed acetal **60**,[47] as illustrated by the example in Eq. 21 employing methanol.



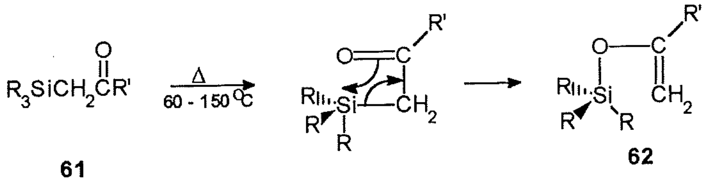
$$Me_3SiC(=O)Ph \xrightarrow[>360\ nm]{h\nu} Me_3SiO{-}\ddot{C}Ph \xrightarrow{MeOH} Me_3SiO{-}CH(OMe){-}Ph$$

59 **60**

(21)

1,3-Silyl C to O Rearrangements (Homo-Brook Rearrangements).

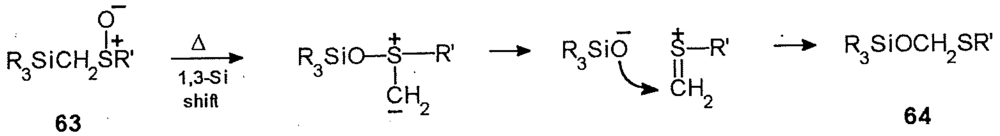
Our investigations first encountered 1,3-C to O silyl shifts when studying the chemistry of β-ketosilanes (R_3SiCH_2COR') **61**. These were shown to undergo facile thermal rearrangements to the isomeric siloxyalkene (silyl enol ether) **62** as shown in Eq. 22. When the silicon was chiral, complete retention of configuration at the silicon centre was observed.[48, 49]



61 **62**

(22)

Similar behavior was observed with α-silylsulfoxides **63**. These rather unstable species readily underwent a thermal rearrangement, a sila-Pummerer rearrangement, leading to the isomeric siloxymethylsulfide **64**, as shown in Eq. 23.[50]



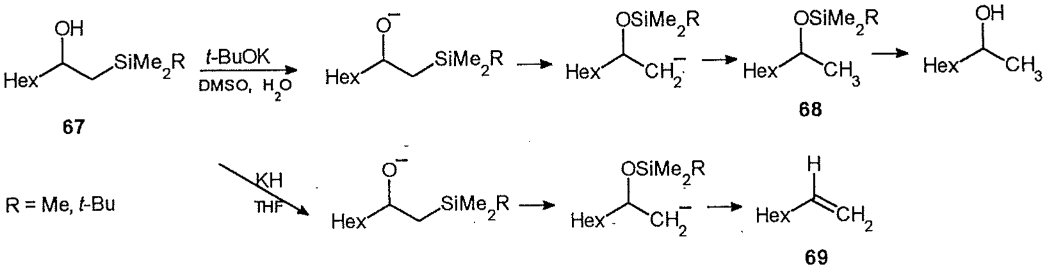
63 **64**

(23)

Anionic versions of the 1,3-silyl rearrangements are known. Brook *et al.* showed that silylacetic acids **65** were converted to the isomeric silylacetate esters **66** with a catalytic amount of triethylamine at room temperature, as shown in Eq. 24.[51]

$$\underset{\mathbf{65}}{Ph_3SiCRR'COOH} \xrightarrow{Et_3N} Ph_3SiCRR'CO\bar{O} \longrightarrow RR'\bar{C}COOSiPh_3 \xrightarrow{\mathbf{65}} \underset{\mathbf{66}}{RR'CHCOOSiPh_3} \quad (24)$$

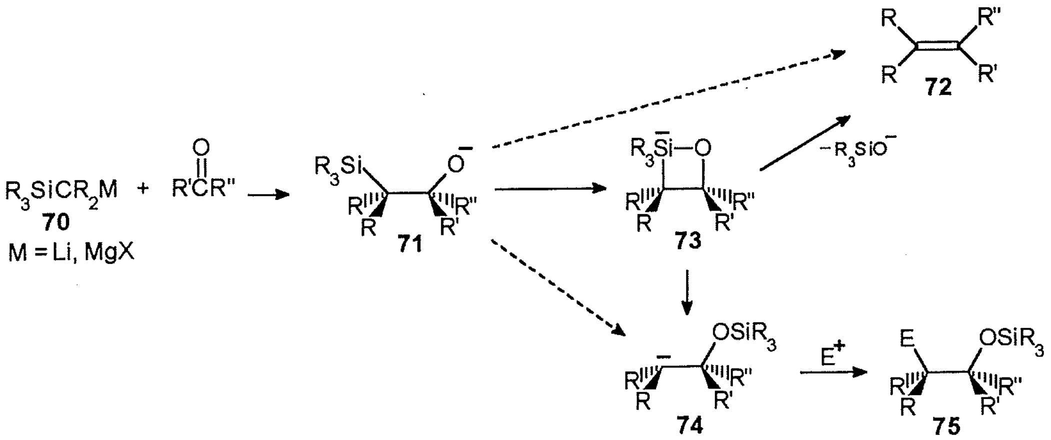
Hudrlik *et al.*[17] showed that simple β-hydroxysilanes **67,** when treated with potassium *t*-butoxide in DMSO/H_2O, rearranged to the silyl ethers **68** (although the silyl group was subsequently hydrolyzed by the reagent) as shown in Eq. 25. If KH in THF was used as the base, β-elimination (Peterson reaction) to the alkene **69** occurred.



67 **68** **69**

(25)

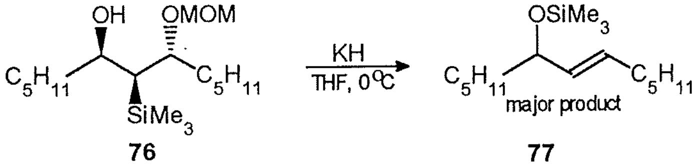
It is well-known that reactions of silylmethyl metallic reagents **70** with carbonyl compounds form β-silyl oxyanions, **71**, logical precursors to a 1,3-silyl shift, but these often readily eliminate, undergoing an overall loss of silanolate ions, leading to alkenes **72**. This behavior, shown in Scheme 3, has been named the Peterson reaction, has been well studied[52] and is often a useful alternative to the Wittig reaction.



Scheme 3

It should be noted that recent evidence by Kawashima *et al.*[53, 54] suggests that both the Peterson reaction, and the homo-Brook silyl-shift may occur through the same cyclic 1,2-oxasiletanide **73** intermediate (a review of these postulated intermediates is available[55]). The tendency for a 1,3-silyl shift to occur leading to the carbanion **74** is enhanced if the potential carbanion can be rapidly trapped, or stabilized in some manner. Thus if an electrophile is present the carbanion may be trapped to give the product **75**.

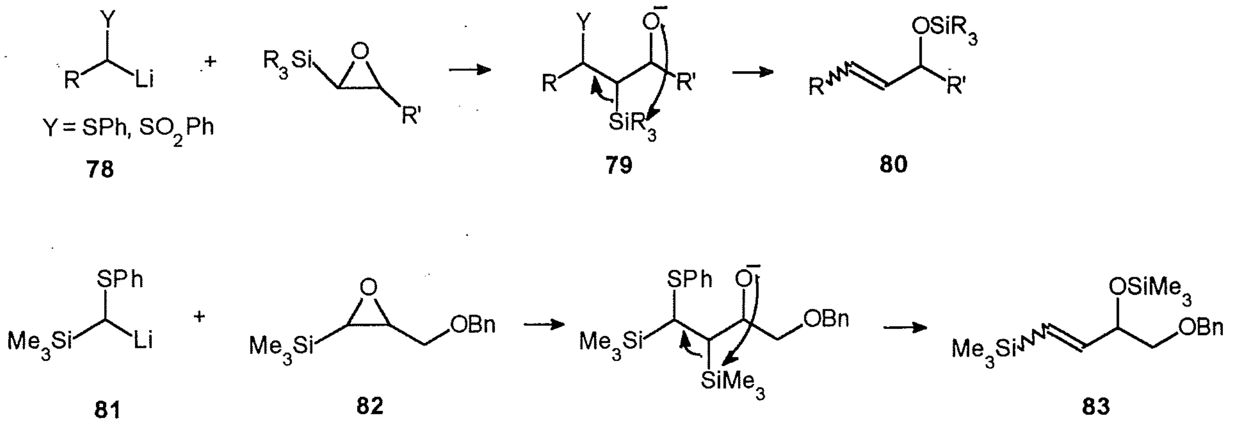
Yamamoto *et al.*[56, 57, 58] showed that if one starts with β-silylcarbinols possessing a good leaving group α to the silyl group such as **76** (MOM- was better than MeO-), then a tandem silyl migration-elimination occurred leading to the siloxyalkenes **77**, which were formed in some cases with considerable stereoselectively, as shown in Eq. 26.



(26)

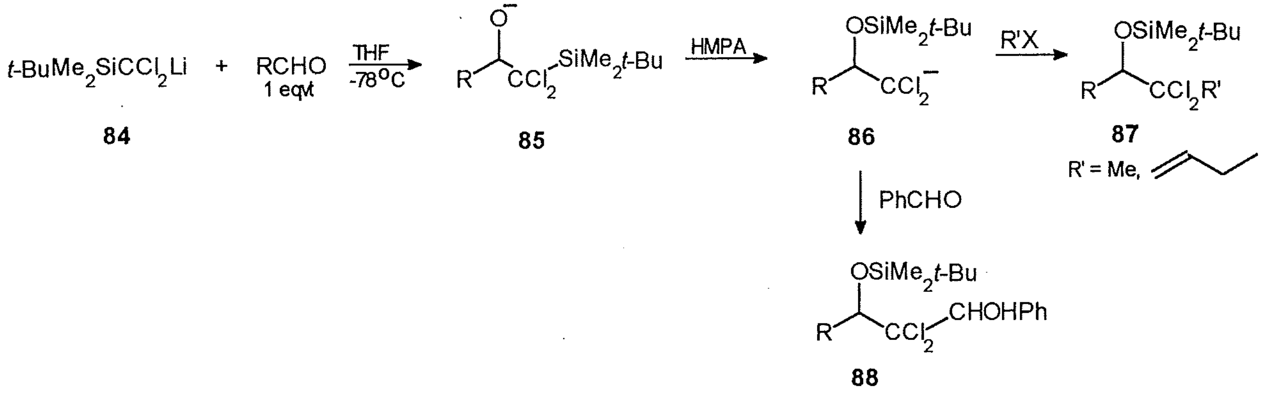
The application of the 1,3-silyl shift for synthetic purposes is most successful either when there is a good leaving group in the γ position facilitating elimination, or there are strong electron-withdrawing groups that will stabilize the carbanion formed on rearrangement prior to its trapping in some manner. Jankowski, Raubo and Wicha have summarized a variety of applications involving reactions of various organometallic reagents with silyloxiranes[59]

Masnyk and Wicha,[60] successfully used 1,3-rearrangments in syntheses by reacting sulfur-substituted organolithium reagents **78** with silyl epoxides **79** as shown in Scheme 4, leading to siloxyalkenes **80**: these often reacted in a regioselective manner. Alternatively, they used substituted silylmethyllithium reagents **81** reacting with silyl epoxides **82** to form highly functionalized vinylsilanes **83**.



Scheme 4

Halogen-substituted silylmethyllithium reagents **84** were found by Oshima *et al.*[61, 62] to react with aldehydes in THF at -78°C as shown in Scheme 5. The initially formed oxyanion adduct **85** rearranged to the carbanion **86** which was trapped either by alkyl or allyl halides giving **87**, or by a different aldehyde to give highly-functionalized products **88**. The rate of the silyl migration was observed to be highly solvent dependent in this, as in most reactions involving oxyanion to carbanion isomerizations, due to the solvent's effect on the strength of the O^- to Li^+ coordination.



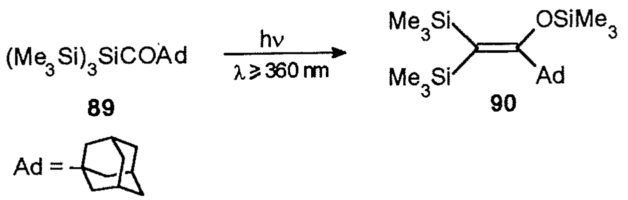
Scheme 5

Eaborn and colleagues observed a slightly different 1,3-rearrangement in that the silyl group migrated from carbon to an oxyanion derived from a silanol rather than a carbinol.[63] Several examples were reported, and a typical case is shown in Eq. 27 in which the starting silanol was converted to the silanolate by methoxide ion in methanol. The 1,3-shift of the silyl group gave the carbanion, which was protonated by the methanol present to yield the disiloxane.

$$\begin{tikzcd}
(PhMe_2Si)_3CSiMe_2OH \arrow[r, "MeO^-", "MeOH"'] & (PhMe_2Si)_3CSiMe_2O^- \arrow[r] & (PhMe_2Si)_2\bar{C}SiMe_2OSiMe_2Ph \arrow[d, "MeOH"] \\
 & & (PhMe_2Si)_2CHSiMe_2OSiMe_2Ph
\end{tikzcd} \qquad 27)$$

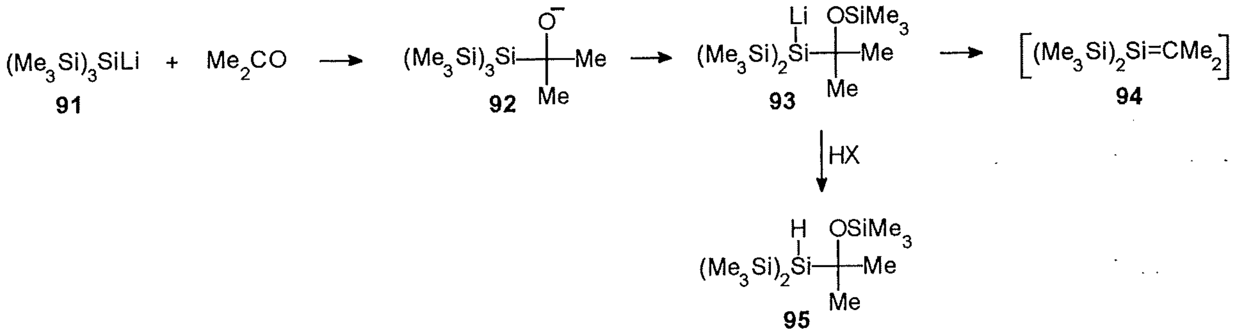
Finally, another type of 1,3-silyl shift is observed either when polysilylacylsilanes are photolyzed or thermolyzed, or when polysilyllithium reagents are added to ketones, both of which involve a 1,3-silyl shift from silicon to oxygen. While not strictly Brook rearrangements, and as yet unnamed, these could be called Sila-Brook rearrangements. The former case, the photolysis of adamantoyltris(trimethylsilyl)silane **89** shown in Eq. 28, led to the first stable and isolated silene, **90**, a class of compounds containing a silicon-carbon double bond (Si=C).[64]

(28)



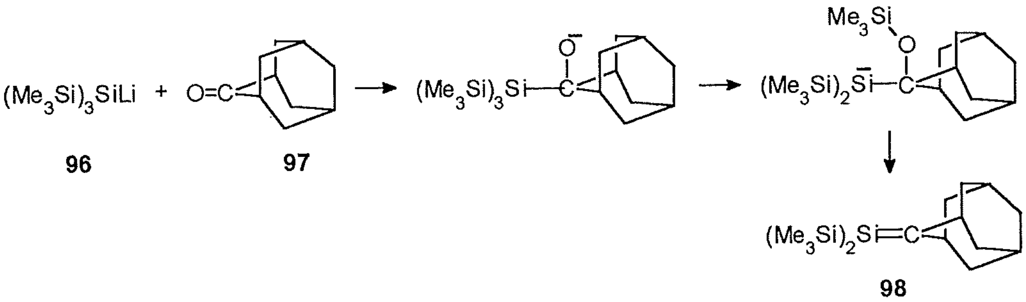
The alternative approach has also led to silenes. Oehme *et al.* showed that addition of tris(trimethylsilyl)silyllithium reagents **91** to simple ketones gave products obviously derived from an oxyanion **92** to silylanion **93** rearrangement, followed by loss of silanolate ion yielding the unstable silene **94**.[65] In this study they clearly established the intermediary formation of a lithium silanide species **93** by trapping it as the silane **95**. (Eq. 29).

(29)



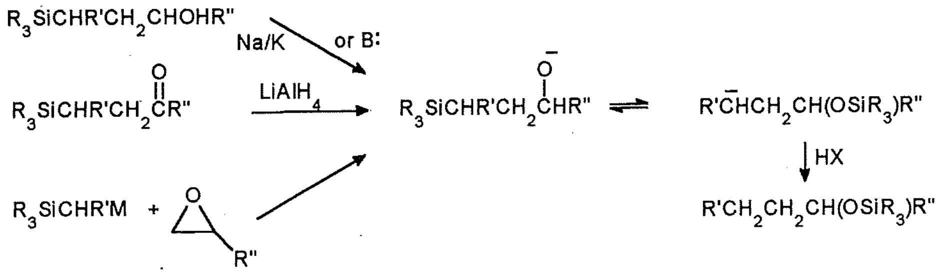
Apeloig and colleagues also used the reactions of various tris(silyl)silyllithium reagents with 2-adamantanone to yield several stable silenes: an example using tris(trimethylsilyl)silyllithium **96** reacting with adamantanone **97** to yield the silene **98** is shown in Eq. 30. Some of the silenes formed were fully characterized.[66, 67]

(30)



1,n-Silyl Migrations from C to O (n ≥4).

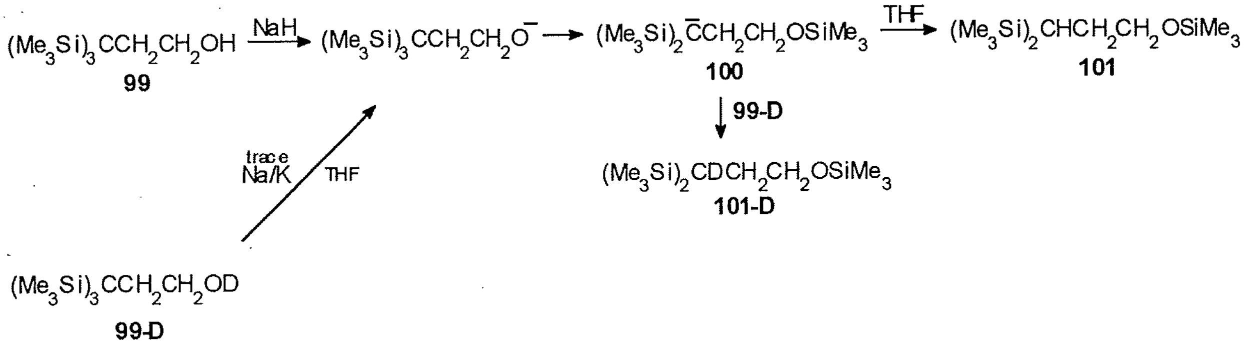
1,4-Silyl rearrangements can arise from numerous sources, e.g., treatment of γ-hydroxysilanes with Na/K alloy or base, hydride reduction of γ-ketosilanes, and reaction of silylmethylmetallic reagents with epoxides. These reactions are shown in Scheme 6. To facilitate the O⁻ to C⁻ rearrangement the group R' needs to be electron withdrawing.



Scheme 6

Of these routes, the most common involves the reactions of silylmethyllithium reagents with epoxides, a convenient method of creating the oxyanion γ to the silyl group from readily available starting materials.

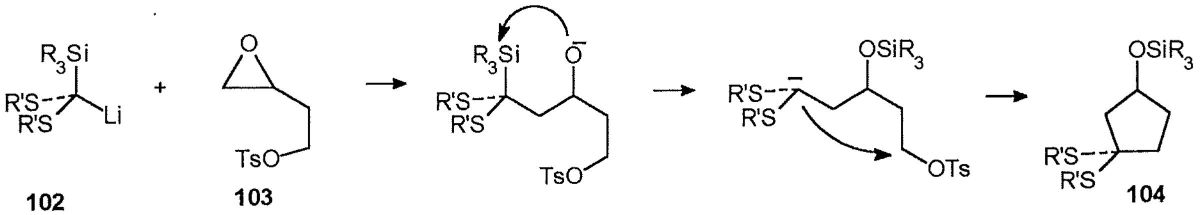
Fleming *et al.*[68] observed that 3,3,3-tris(trimethylsilyl)propanol **99** (obtained from the reaction of $(Me_3Si)_3CLi$ with ethylene oxide) on treatment with NaH in THF gave rise, via the carbanion **100**, to the isomeric silyl ether **101**, as shown in Scheme 7. They proposed that the source of the proton required to convert the carbanion **100** to the final product was derived from the solvent. Later studies by Brook and Chrusciel[69] established that, like the original 1,2-Brook rearrangement, the proton (deuteron) almost certainly arose from reaction of the carbanion with unrearranged alcohol **99-D**.



Scheme 7

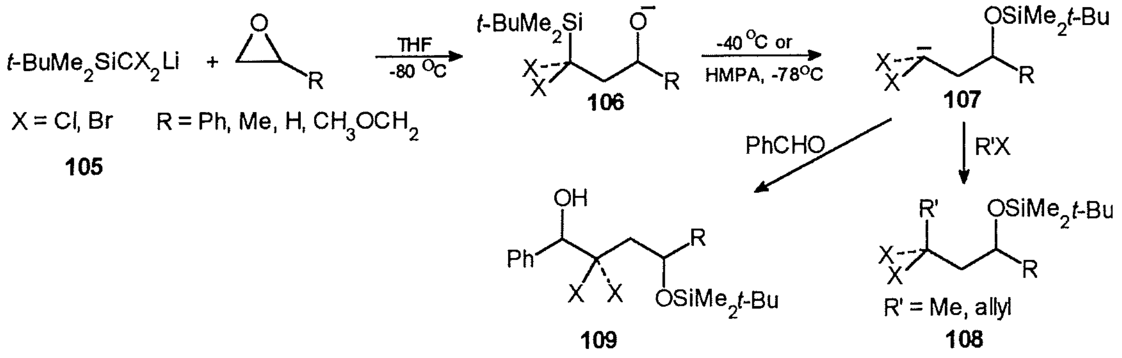
Treatment of substituted silylmethyllithium reagents **102** with a substituted epoxide **103** was found by Schauman *et al.*[70, 71] to yield substituted siloxycyclopentanes **104**, as a result of 1,4-silyl migration and then ring closure, as shown in Eq. 31.

(31)



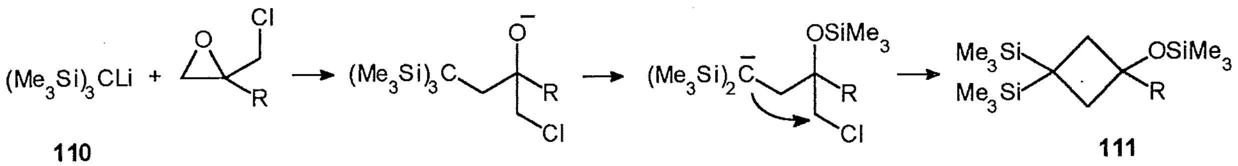
It is also possible to have alkylation as the terminal step of 1,4-silyl rearrangements. Addition of the silyllithium reagent **105** to epoxides in THF at -78°C gave rise to the intermediate oxyanion **106**. No rearrangement occurred until either the temperature was raised to -40°C, or HMPA was added at -78°C, giving rise to the carbanion **107** which was alkylated with methyl iodide or allyl bromide to give the products **108**, or reacted with an aldehyde to give the 1,4-diol derivative **109** as shown in Eq. 32.[61, 62]

(32)



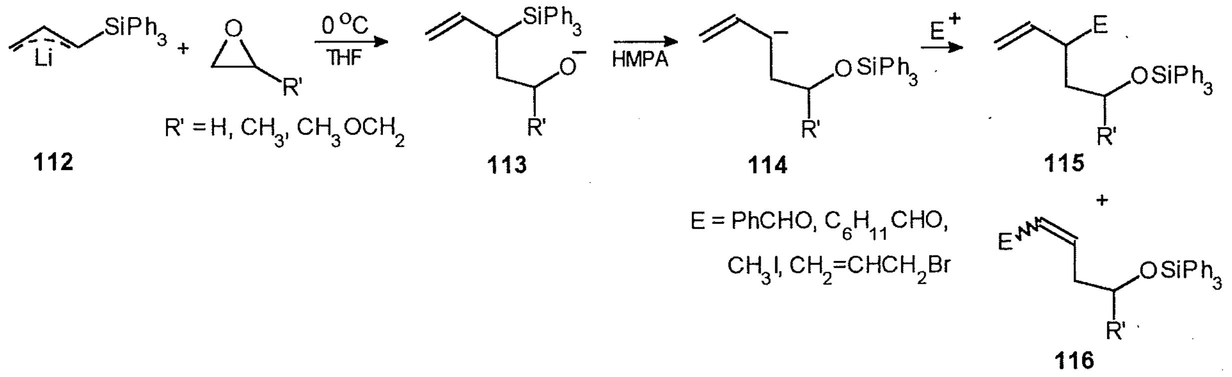
Takeda *et al.*[72] used the reaction of tris(trimethylsilyl)methyllithium ((Me$_3$Si)$_3$CLi) **110** with substituted epoxides to yield cyclobutanes **111** after 1,4-silyl rearrangement and ring closure, as shown in Eq. 33.

(33)



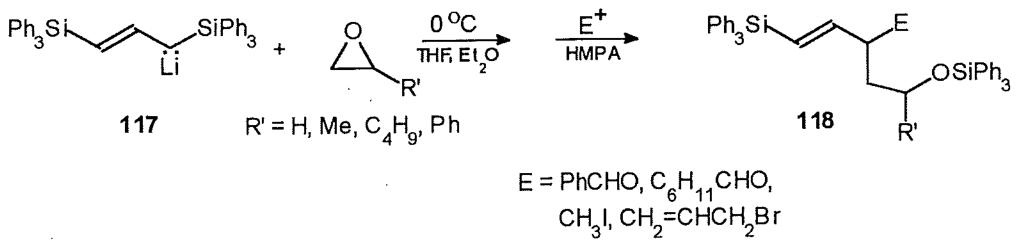
Another study of interest described by Oshima and co-workers[73] involved the reaction of triphenylsilylpropenyllithium reagents **112** with epoxides. The unsubstituted reagents reacted in THF at 0°C to give the oxyanion **113**. When cooled to -78°C and HMPA was added, and then the mixture was warmed to room temperature, rearrangement to the carbanion **114** occurred. Trapping with a variety of electrophiles led to a mixture of products **115** and **116** generally with low regioselectivity.(Eq. 34).

(34)



However, if 1,3-bis(triphenylsilyl)-1-propenyllithium **117** was employed as starting material, (from treatment of the parent hydrocarbon with *n*-butyllithium in ether-THF (2:1) at 0°C) and the epoxide was added, followed by the electrophile in HMPA, reaction occurred to give the product **118** with almost total regioselectivity (trapping with alkyl halides was less selective than with other electrophiles). The R' groups on the epoxide could be alkyl or aryl, and as electrophiles, aldehydes, or methyl- or allyl halides could be employed. These reactions are summarized in Eq. 35.

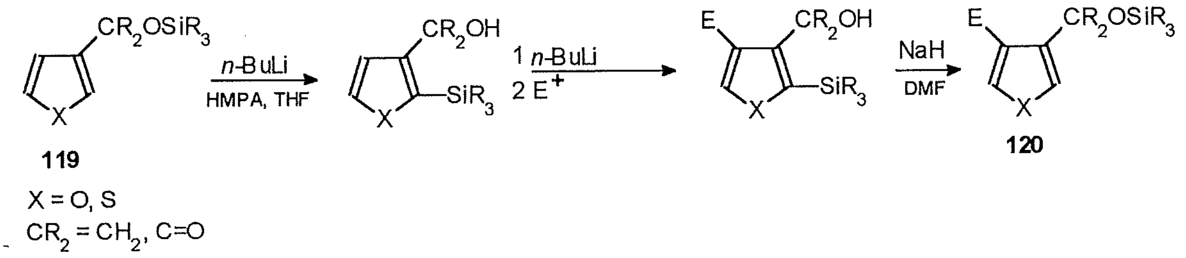
(35)



Lautens *et al.* observed a 1,4-silyl shift from carbon to oxygen when a 1,1-bis-silylsubstituted-3-hydroxy-1-butene was treated with excess NaH in DMF, atypical since the silyl group which shifted was attached to sp^2-hybridized carbon.[74]

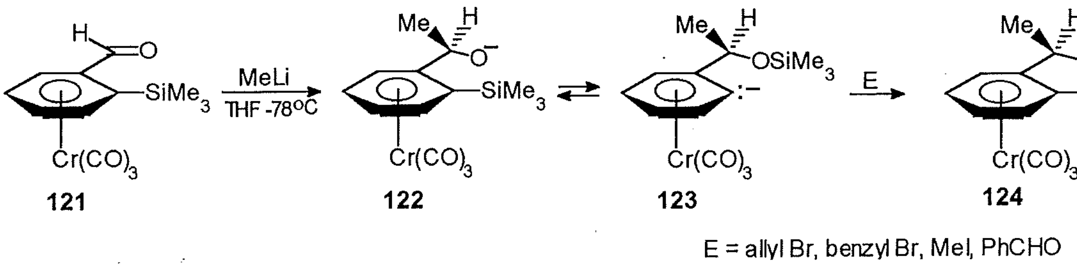
An unusual but useful route to convert substituted furans and thiophenes **119** into 3,4-disubstituted furans and thiophenes **120** involved the sequence of reactions shown in Eq. 36, in which both 1,4-silyl C to O and the reverse O to C rearrangements were involved. A review of this methodology is available.[75]

(36)



Moser *et al.*[76] have recently described an unusual example of a 1,4-silyl rearrangement, as shown in Eq. 37. Here, the silyl group migrated from an aromatic ring, which was coordinated to chromium tricarbonyl, to an oxyanion derived from an attached aldehyde group. The addition of methyllithium to the coordinated aldehyde **121** yielding the oxyanion **122** occurred with good facial selectivity (88:12), and the subsequent trapping of the rearranged anion **123** by various electrophiles gave products **124** with good diastereoselectivity.

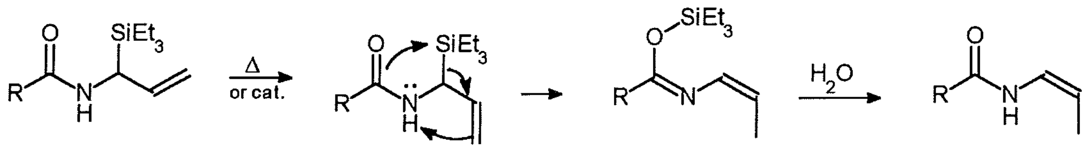
(37)



More recently, compound **121** was treated with a variety of lithium ester enolates, which led ultimately to substituted indanones, some of which contained spiro systems. One of these, formed in high yield and diasteroselectivity, contained rings B,C,D and E of the compound Fredericamycin A, a species which possesses potent antitumor activity.[77]

Danishefsky *et al.* recently utilized a thermal 1,4-silyl shift within a silyl-substituted allylamide to create a *cis*-enamide group essential to the synthesis of the cyclic polypeptide proteasome inhibitors TMC-95A and TMC-95B.[78] The basic reaction is illustrated in Eq. 38.

(38)



Few 1,5- silyl rearrangements have been reported, and those observed have either been thermal or photochemical rearrangements[79, 80] which will not be discussed.

A 1,6-anionic rearrangement of a silyl group from C to O has been reported by Eaborn *et al.*[81] and involved treatment of 5,5,5-tris(trimethylsilyl)pentanol **125** with sodium methoxide in methanol yielding the product **126** as shown in Eq. 39.

(39)

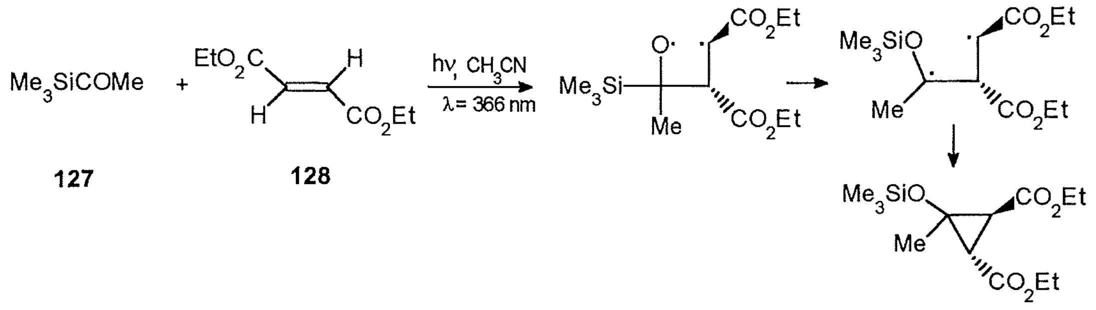
$$\underset{\mathbf{125}}{(Me_3Si)_3C(CH_2)_4OH} \xrightarrow{MeO^-,\ MeOH} \underset{\mathbf{126}}{(Me_3Si)_2CH(CH_2)_4OSiMe_3}$$

Radical Brook rearrangements.

A number of 1,n-silyl carbon to oxygen rearrangements have been observed, which unlike "normal" Brook rearrangements, clearly involve radical rather than ionic intermediates. These have been named Radical Brook rearrangements, and some of them will be briefly described below.

Radical 1,2-Brook rearrangements were first proposed by Dalton and Bourque[82] to explain the results of the photolysis of acetyltrimethylsilane **127** in acetonitrile in the presence of diethyl fumarate **128**. Evidence was presented which suggested that radical intermediates were involved in the formation of the substituted cyclopropane product **129** in which the *trans* geometry of the fumarate was preserved as depicted in Eq. 40.

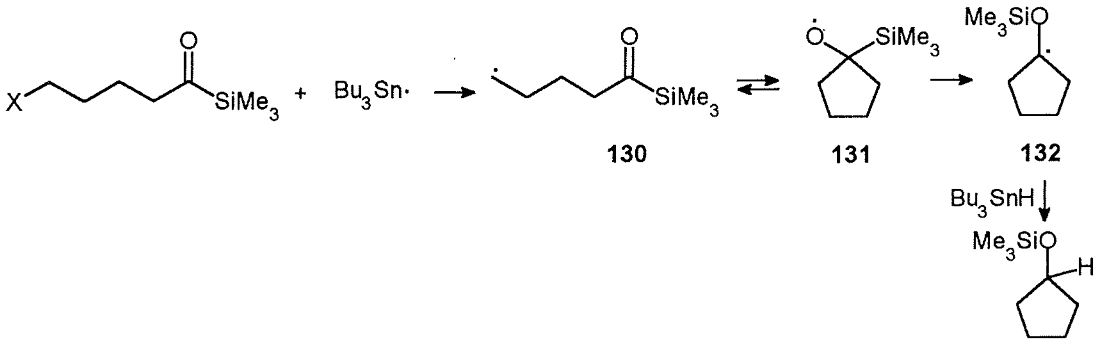
(40)



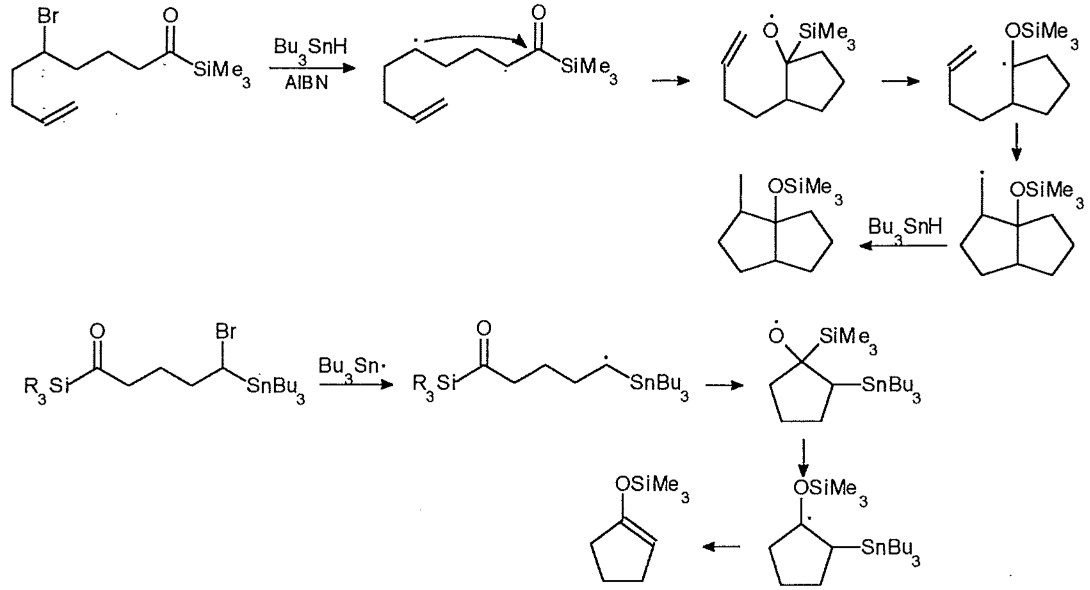
127 **128** **129**

Tsai and colleagues[83, 84, 85, 86] showed that generation, in several different ways, of a radical site δ to the carbonyl group of an acylsilane **130** resulted in cyclization into the carbonyl group leading to an oxy radical **131**. A subsequent 1,2-silyl shift stabilized the cyclopentyl radical **132** which could be trapped in various ways, as shown in Eq. 41**.** Extrapolation to the analogous cyclohexyl systems worked in some cases.

(41)



More complex examples[83, 85] of the above reaction, leading to cyclic compounds of synthetic interest, are shown in Scheme 8.

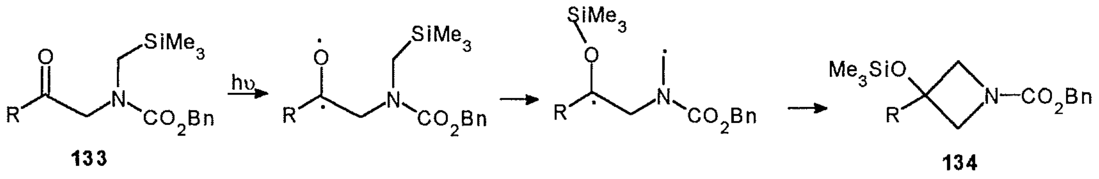


Scheme 8

Detailed mechanistic studies of the rearrangement of α-silylcarbinols and β-haloacylsilanes under radical-forming conditions have been reported by Parades and Alonso.[87]

A 1,5-silyl radical shift was observed by Kim *et al.* during the photolysis of the substituted aminomethylketone **133**, leading to substituted azetidine **134**, as shown in Eq. 42.[88]

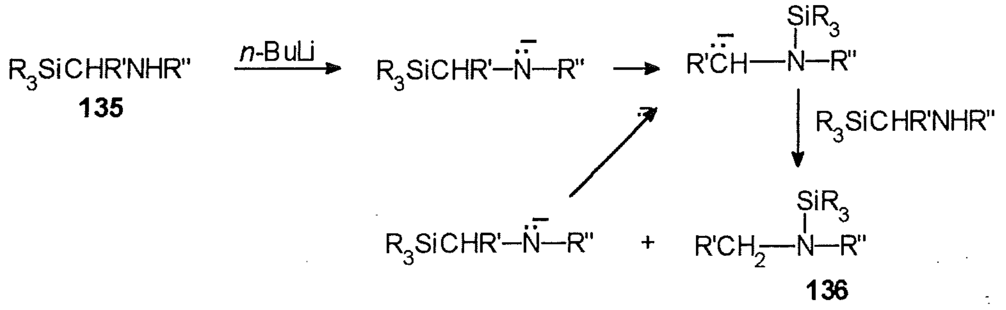
(42)



1, 2-Silyl C to N Rearrangements (Aza-Brook Rearrangements).

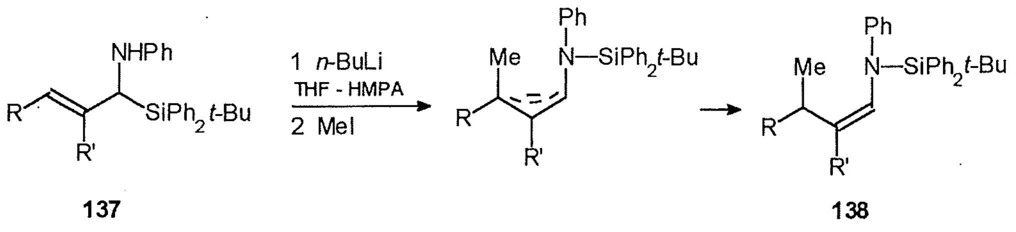
Having established the identity and basic details of the 1,2-silyl C to O rearrangement it appeared to us that an analogous 1,2-silyl C to N rearrangement should exist. A number of aminomethylsilanes $R_3SiCHR'NHR''$ **135** were treated with small amounts (0.05 to 0.2 equivalents) of *n*-butyllithium in benzene at temperatures ranging from 10 to 100°C. Catalyzed rearrangements to give N-silylamines **136** occurred for all substitution patterns except for N-phenyl compounds where no rearrangements were observed. The data obtained were consistent with a catalyzed anionic rearrangement analogous to the Brook rearrangement, as shown in Eq. 43.[89, 90]

(43)



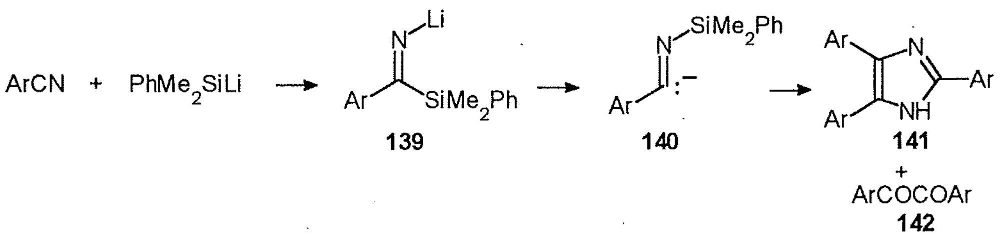
Few examples of the Aza-Brook rearrangement have been reported. Hondi and Mori[91] described the C to N rearrangement of **137** on treatment with 2 equivalents of *n*-BuLi at –78°C in THF-HMPA, followed by treatment with 2 equivalents of organic halide also at -78°C. Warming to 0°C gave rise to the enamine **138** as shown in Eq. 44, which could be hydrolyzed to the corresponding aldehyde.

(44)

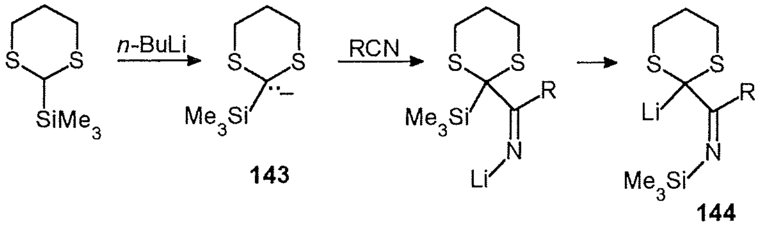


Fleming *et al.*[92] treated aryl nitriles with silyllithium reagents and observed rearrangement of the initial adduct **139** to **140** as an intermediate step in the overall remarkable synthesis (Eq. 45) of the imidazoles **141**, together with the byproduct **142**.

(45)



A 1,3-Aza-Brook rearrangement was observed by Bulman Page *et al.*[93] from treatment of silyldithiane anion **143** (useful for the preparation of acylsilanes[94]) with a nitrile leading to the product **144** which could be converted to various products depending on the method of working up the reaction. (Eq. 46).



143

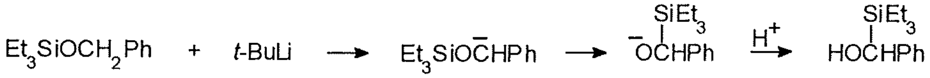
144

(46)

Takeda *et al.*[95] have reported studies in which a Thia-Brook rearrangement was observed, namely the 1,2-shift of a silyl group to a sulfur anion formed by deprotonation of a thiol with DBU. It was shown that the rate of rearrangement of the thiol was somewhat slower than the alcohol analog when rearranged under the same conditions.

Reverse (Retro) Brook Rearrangements.

1,2-Shifts of silyl groups from O to C have been observed under conditions where alkoxysilanes (particularly benzyloxysilanes) were treated with one or more equivalents of a very strong base. Equilibration between anionic species was allowed to occur, and then the reaction mixture was worked up, yielding the α-silylbenzyl alcohol.[2, 96](Eq. 47) This reaction is an analog of the classical Wittig rearrangement, and clearly indicates that under the conditions employed, the relative stabilities of the ions involved determine the direction which the reaction takes, oxyanions in general being more stable that carbanions.



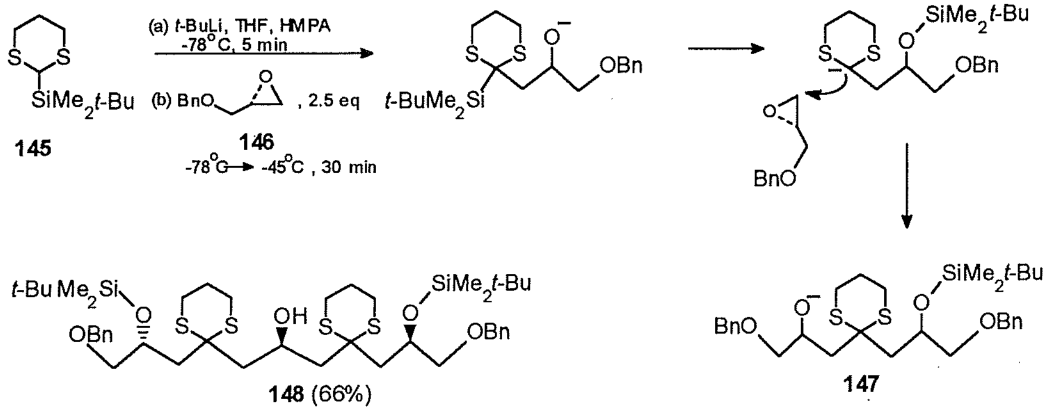
$$\mathrm{Et_3SiOCH_2Ph} \; + \; t\text{-}\mathrm{BuLi} \longrightarrow \mathrm{Et_3SiO\bar{C}HPh} \longrightarrow \mathrm{{}^{-}O\overset{\overset{SiEt_3}{|}}{C}HPh} \xrightarrow{H^+} \mathrm{HO\overset{\overset{SiEt_3}{|}}{C}HPh} \qquad (47)$$

Numerous examples of retro-Brook rearrangements applied to synthetic endeavors (which are outside the scope of this review) have been reported recently, particularly 1,4-silyl retro shifts, and references to them will be found in the excellent reviews of Kira[4] and Moser[5] and in numerous papers, e.g.[97, 98, 99, 100]

Addendum

Since this review was first completed in early 2002, additional papers of synthetic interest which involve Brook rearrangements have been noted in the literature. A few of these are briefly described below, to provide the reader with some further examples of the applications of the rearrangement to major synthetic problems.

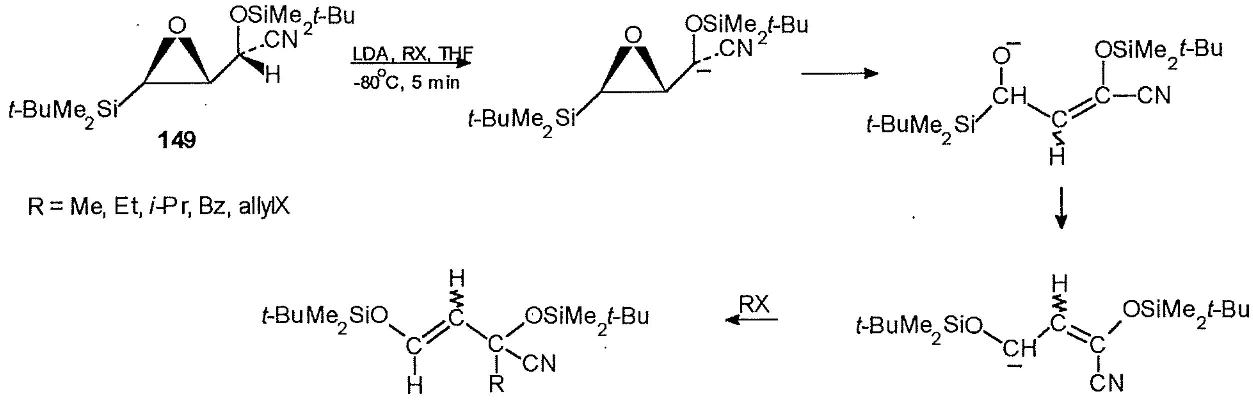
Smith and Boldi,[101] elaborating the work of Tietze and coworkers,[102] utilized the reactions of silylated dithiane anions **145** with epoxides **146**, which involved 1,4-Brook rearrangements under solvent-controlled conditions. The processes were described as multicomponent linchpin couplings and led to products **147** involving incorporation of two epoxide molecules, as shown in Scheme 9.



Scheme 9

Further elaborations, some utilizing two different epoxides, were described, which led to complex 1,3-polyol precursors of potential use in natural product syntheses, for example compound **148** .

Takeda *et al* [103] have recently reported the study of tandem base-promoted ring openings of highly-substituted β-silyl-α,β–epoxide derivatives, e.g. **149**, which involved 1,2-Brook rearrangements leading in high yields to siloxyalkenes **150**, as exemplified in Scheme 10.

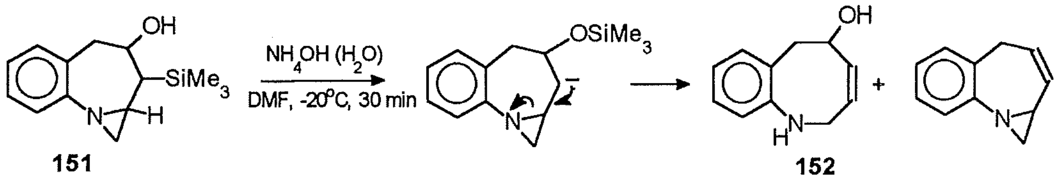


Scheme 10

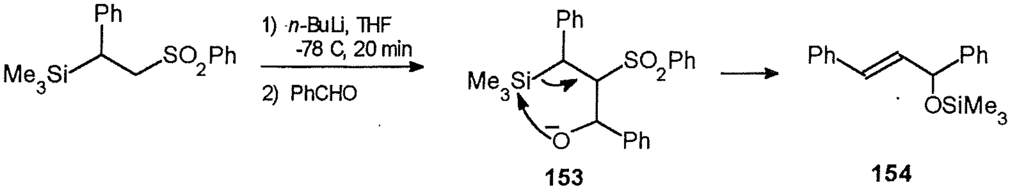
It was noted that there was considerable variation in the *E/Z* ratios of the products, which depended particularly on the base employed, sodium bases yielding the highest ratios.

A facile route to functionalized benzazoc-3-enes, **151**, potential intermediates in the synthesis of the mitomycin antitumor agents, has recently been described[104] starting with silylated *N*-aryl aziridines and utilizing a mild base-promoted 1,3-Brook rearrangement A typical example leading to the product **152** is shown in Eq. 48

(48)

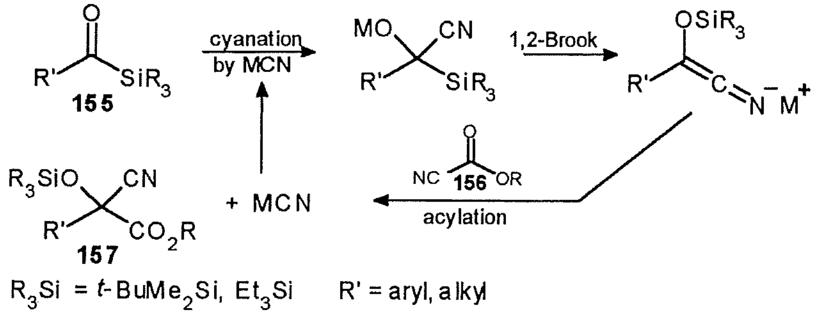


Phenyl substitution α to the carbanion centre was found to accelerate the 1,4- Brook rearrangements which occurred in the adduct **153** of the aldehyde or ketone with silyl-substituted sulphonyl anions. The products were found to be O-silylated cinnamyl alcohols **154**[105] as exemplified in Eq. 49.



(49)

Johnson *et al*[106] have recently reported conditions for an effective tandem nucleophile-catalyzed cyanation process involving the reaction of acylsilanes **155** with cyanoformates **156** using a cyanide catalyst. This reaction, following addition of the cyanide, led through 1,2-Brook rearrangement and C-acylation to functionalized unsymmetrical malonic acid derivatives **157**. The reaction appeared to involve a catalytic cycle, as illustrated in Scheme 11.



Scheme 11

Summary

The examples given above clearly show that the original studies of the base-catalyzed 1,2-silyl carbon to oxygen shifts of silyl carbinols named the Brook rearrangement have been greatly extended to a wide array of systems. It is now possible to invoke and control a wide variety of 1,n-silyl shifts under ionic, thermal, photochemical, or radical conditions. The reactions carried out under ionic conditions in particular (conditions closest to those in the original Brook rearrangement) have found numerous useful synthetic applications. This is true particularly because methods have been found to control the timing of the oxyanion to carbanion rearrangement, using both low temperature and solvent effects (particularly the use of HMPA), which allows the introduction of electrophiles at an appropriate time to capture the intermediate carbanion. As well, the use of leaving groups of appropriate functionality and location in the reagents permits the formation of stable products because of elimination reactions which can occur subsequent to the formation of the intermediary carbanions. Important applications to organic synthesis currently appear regularly in the literature and further imaginative new applications can be anticipated.

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