Cope Rearrangement. Dewar and coworkers have calculated the structure of the symmetric intermediates in the biallyl Cope rearrangement[26] and also in some semibulvalene Cope rearrangements,[27] the calculated energies of the latter agreeing remarkably well with experimental activation energies. In the biallyl rearrangement, it was found that the "chair" form of the intermediate was more stable than the "boat" form, in agreement with the classic Doering and Roth experiment.[28] Additional MINDO/2 calculations of the biallyl rearrangement reveal that both the chair and boat symmetric structures actually are shallow minima and the two transition states are nonsymmetrical structures lying between the intermediates and biallyl.[29] All of these results are in complete accord with the symmetry arguments of the preceding section since we would expect a small interaction force constant between the two partially broken bonds in these systems.

Conclusions

On the basis of these calculations (and the preceding symmetry arguments), it would appear that Nature is not being cooperative in giving us nicely symmetrical transition states. Perhaps we should not be too surprised, though, since there is no *a priori* reason why they should be symmetric. We impose symmetry on a transition state for reasons of simplicity. Thus, the symmetric intermediate structure in a Woodward–Hoffmann correlation diagram need not be the actual transition state, just as the "reactant" and "product" symmetric structures need not be the actual equilibrium geometries of these species. In the Woodward–Hoffmann "allowed" Diels–Alder reaction, for example (Figure 1), the correlation diagram requires that a plane of symmetry be maintained throughout the reaction. Yet, this is an example in which neither the reactant nor the product possesses this symmetry plane,[30] so why should the transition state? If it should turn out that the correct transition states are nearly symmetrical, then of course there would be little effect on predicted rates or stereochemistry. This can be settled however, only by more extensive calculations, calculations that are currently under way in several research groups.

(26) A. Brown, M. J. S. Dewar, and W. Schoeller, *J. Amer. Chem. Soc.,* **92,** 5516 (1970).

(27) M. J. S. Dewar and W. Schoeller, *J. Amer. Chem. Soc.,* **93,** 1481 (1971).

(28) W. V. Doering and W. R. Roth, *Tetrahedron,* **18,** 67 (1962). See also M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.,* **94,** 7147 (1972).

(29) A. Komornicki and J. W. McIver, Jr., to be published.

(30) *cis*-Butadiene appears to be skewed (B..Dumbacher, *Theor. Chim. Acta,* **23,** 346 (1972)), and boat cyclohexene is a barrier to the half-chair inversion (F. Anet and M. Hag, *J. Amer. Chem. Soc.,* **87,** 3647 (1965); N. L. Allinger and J. T. Sprange, *J. Amer. Chem. Soc.,* **94,** 5734 (1972)).

Some Molecular Rearrangements of Organosilicon Compounds

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The growing interest in recent years in organosilicon chemistry, made despite the gloomy predictions of F. S. Kipping in 1936 that "the prospects of any immediate and important advance in this section of organic chemistry do not seem to be very hopeful,"[1] has been catalyzed both by the commercial development of the silicones and, more recently, by the interest of chemists in introducing new and exotic hetero atoms into molecules for a wide variety of reasons.

The interests in our laboratory have focused on organosilicon compounds which have functional groups (OH, C=O, S→O, C=N etc.) attached to carbon adjacent to silicon, where the interactions of these groups with the silicon atom may lead to, or facilitate, a variety of molecular rearrangements. Most of the rearrangements described below are restricted to cases studied in the author's laboratory which involve interactions between silicon and oxygen: these constitute only a small part of a growing literature on molecular rearrangements of organosilicon compounds.

In the 1950's Gilman and coworkers[2-4] found that

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(1) F. S. Kipping, *Proc. Roy. Soc. Ser. A,* **159,** 139 (1937).

(2) H. Gilman and T. C. Wu, *J. Amer. Chem. Soc.,* **75,** 2935 (1953).
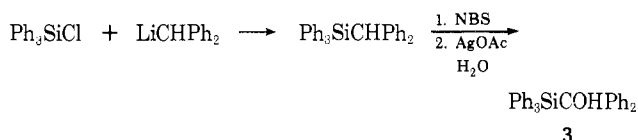
(3) H. Gilman and T. C. Wu, *J. Amer. Chem. Soc.,* **76,** 2502 (1954).

(4) H. Gilman and G. D. Lichtenwalter, *J. Amer. Chem. Soc.,* **80,** 2680 (1958).

silylmetallic compounds such as triphenylsilylpotassium add normally to aliphatic aldehydes or ketones (*e.g.*, formaldehyde) to give the expected carbinols **1**, but with aromatic aldehydes or ketones (*e.g.*, benzophenone) the isomeric alkoxysilanes **2** are formed instead. It was not established whether this abnormal product arose from abnormal addition of the silylmetallic to the carbonyl group or whether it was the result of normal addition, followed by some kind of rearrangement.

$$Ph_3SiK + CH_2=O \longrightarrow Ph_3SiCH_2OH$$
$$\mathbf{1}$$

$$Ph_3SiK + Ph_2CO \longrightarrow Ph_3SiOCHPh_2$$
$$\mathbf{2}$$
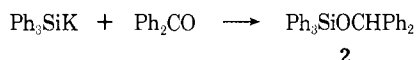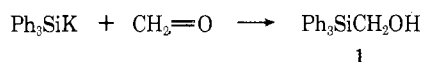
Accordingly, the expected carbinol **3** was synthesized by coupling of benzhydryllithium with triphenylchlorosilane followed by bromination and mild hydrolysis.[5] When the carbinol was treated with a trace

$$Ph_3SiCl + LiCHPh_2 \longrightarrow Ph_3SiCHPh_2 \xrightarrow[\substack{2.\ AgOAc \\ H_2O}]{1.\ NBS}$$

$$Ph_3SiCOHPh_2$$
$$\mathbf{3}$$

of sodium–potassium alloy, a not unexpected impurity in triphenylsilylpotassium (disilane + Na–K → ≡SiK), the carbinol was found to rearrange rapidly and essentially quantitatively to the alkoxysilane.

$$Ph_3SiCOHPh_2 \xrightarrow{Na-K} Ph_3SiOCHPh_2$$
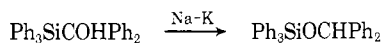
Subsequent investigations revealed that all types of silylcarbinols rearrange, often fairly readily, when treated with small amounts of active metals, organometallic reagents, or bases such as pyridine, diethylamine, or triethylamine.[6-9]

$$R_3Si-\underset{\underset{OH}{|}}{C}R_2' \longrightarrow R_3Si-O-CHR_2'$$
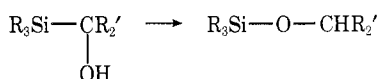
R = aryl, alkyl
R' = aryl, alkyl, hydrogen
isomerizing agents: Na–K, Na, NaH, RLi, Et₂NH, R₃N

It was of interest to investigate the mechanism of this hitherto unobserved type of rearrangement. The reaction was first order in silylcarbinol but, since the rates doubled when the trace amounts of isomerizing agent (which was not consumed) were doubled, it was clear that the reaction was obeying pseudo-first-order kinetics overall.[10] Typical rate constants, involving some extrapolations or interpolations because of differences in temperature, solvent, or isomerizing agent, are given in Table I.

The rates are very sensitive to the nature of the group on the carbinol carbon. Carbinols bearing phenyl groups rearrange 10^3 times faster than when

(5) A. G. Brook, *J. Amer. Chem. Soc.*, **80**, 1886 (1958).
(6) A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Amer. Chem. Soc.*, **81**, 981 (1959).
(7) A. G. Brook and N. V. Schwartz, *J. Amer. Chem. Soc.*, **82**, 2435 (1960).
(8) N. V. Schwartz and A. G. Brook, *J. Amer. Chem. Soc.*, **82**, 2439 (1960).
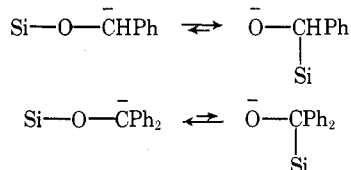(9) A. G. Brook and B. Iachia, *J. Amer. Chem. Soc.*, **83**, 827 (1961).
(10) A. G. Brook, G. E. LeGrow, and D. M. MacRae, *Can. J. Chem.*, **45**, 239 (1967).

Table I
Approximate Rates of Rearrangement of
Silylcarbinols in Me₂SO by Et₂NH at 36°

Carbinol	Rate, l. mol⁻¹ sec⁻¹
Ph_3SiCPh_2OH	7.6
$Ph_3SiCMePhOH$	6.7×10^{-3}
$Ph_3SiCHPhOH$	5.7×10^{-3}
$Ph_3SiC(CH_2Ph)PhOH$	1.1×10^{-1}
Ph_3SiCMe_2OH	Too slow to measure
$MePh_2SiCPh_2OH$	1.2
$Me_2PhSiCPh_2OH$	2×10^{-1}
Me_3SiCPh_2OH	3.3×10^{-2}

alkyl groups or hydrogen are substituted for phenyl. However, replacement of phenyl on silicon by methyl reduces the rates only by a factor of about 6.

A study of the effect of temperature on the rates of rearrangement of two isomeric carbinols, (triphenylsilyl)methylphenylcarbinol and (diphenylmethylsilyl)diphenylcarbinol, showed that for both compounds the energies of activation were rather low, of the order of 8–11 kcal/mol, but that ΔS^* was very large and negative, -35 to -45 eu (Ph_3SiCOH-MePh, $E_{act} = 11.1$ kcal/mol, $\Delta S^* = -34.2$ (Me_2SO); $Ph_2MeSiCOHPh_2$, $E_{act} = 8.7$ kcal/mol, $\Delta S^* = -45.6$ ($CHCl_3$). A study of the Hammett ρ–σ relationship for several series of (triphenylsilyl)-mono-(para-substituted phenyl)carbinols gave values of ρ of from 3.4 to 4.6, indicating a very great sensitivity of the rearrangement to the substituents and specifically that considerable negative charge develops on the benzylic carbon during formation of the transition state, which was stabilized by electron-withdrawing and destabilized by electron-releasing substituents.[10]

The kinetic data are satisfactorily explained by the mechanism shown in Scheme I.

Scheme I
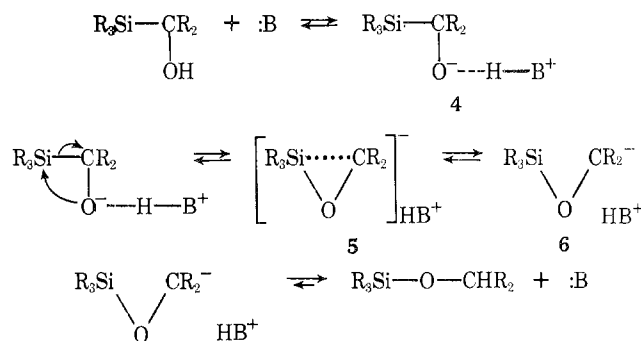
The function of the basic catalyst is to remove the acidic carbinol proton, forming an α-oxyanion, **4**. This ion subsequently attacks intramolecularly at silicon, passing through a transition state, **5** (or intermediate, by utilizing d orbitals; it has not been possible to differentiate between these possibilities), in which significant silicon–oxygen bond formation and silicon–carbon bond breaking have occurred, placing negative charge on carbon. This charge can be delocalized by electron-withdrawing substituents, consistent with the large positive Hammett ρ value observed. The cyclic species **5**, possibly with the protonated base closely associated (*vide infra*), accounts for the large negative entropy of activation. As the reaction proceeds, a carbanion-like species, **6**, is

formed which is rapidly protonated to give the alkoxysilane.

The reactions have been written as reversible, not because any evidence of such reversibility is observed when catalytic amounts of base are employed under our conditions, but because West, *et al.*,[11] and ourselves[12] have observed that, on treatment with excess strong base (typically 1 mol equiv or more of *tert*-butyllithium) in the cold, benzyloxysilanes (but not benzhydryloxysilanes) convert to the isomeric carbinols (or other O-substituted derivatives). With excess strong base, it is evidently the relative stabilities of the anions which are important, the oxyanion being more stable in the benzyl case but the carbanion being more stable in the benzhydryl case.

$$\text{Si—O—}\overset{-}{\text{C}}\text{HPh} \rightleftharpoons \overset{-}{\text{O}}\text{—CHPh} \atop | \atop \text{Si}$$

$$\text{Si—O—}\overset{-}{\text{C}}\text{Ph}_2 \rightleftharpoons \overset{-}{\text{O}}\text{—CPh}_2 \atop | \atop \text{Si}$$

Under the conditions in which the silylcarbinol to alkoxysilane rearrangement is run, generally with only traces of weak base, it is evidently the relative stabilities of the neutral compounds which are of importance, with the alkoxysilane being favored by virtue of the greater strength of the silicon–oxygen bond (120–130 kcal/mol) relative to the silicon–carbon bond (75–85 kcal/mol).

Once it was established that the reaction involved an intramolecular 1,2 rearrangement of silicon from carbon to oxygen, it was of interest to establish the stereochemistry with respect to a chiral silicon center. This was carried out through the Walden cycle described in Scheme II, which utilized the elegant work of L. H. Sommer who had synthesized, resolved, and established the relative and absolute configurations of a whole series of 1-naphthylphenylmethylsilyl (R₃Si*) systems.[13]

Using the (+) enantiomer of 1-naphthylphenylmethylsilane, we carried out the Walden cycle illustrated by chlorination, coupling, and conversion of the resulting benzhydryl compound to an optically active silylcarbinol. Treatment with either a trace of sodium–potassium alloy or amine gave optically active benzhydryloxysilane which, on reduction with lithium aluminum hydride under conditions known to involve retention of configuration at silicon, gave almost optically pure (−)R₃Si*H. Since the stereochemistry of each step of the cycle except the rearrangement was known, the observed overall inversion of configuration could only be explained on the basis that the rearrangement involved highly stereospecific retention of configuration at the chiral silicon center.[14] The retention of configuration is consistent with a "flank" attack by oxygen at silicon, as the mechanism infers, and with a pentavalent sp³d-hybridized intermediate as suggested in Scheme I.

(11) R. West, R. Lowe, H. F. Stewart, and A. Wright, *J. Amer. Chem. Soc.*, 93, 282 (1971).

(12) A. G. Brook and D. Haidukewych, unpublished results.

(13) For a summary see: L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

(14) A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, 45, 1231 (1967).
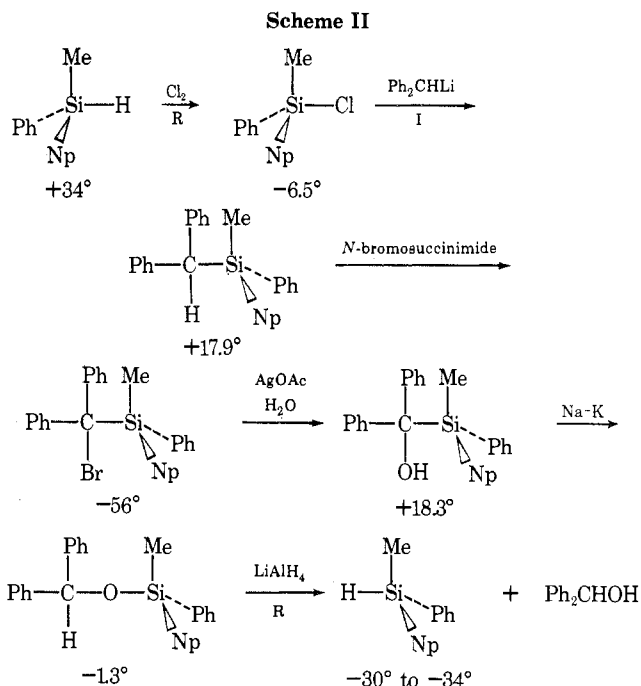
Scheme II

R = retention of configuration; I = inversion of configuration

Studies were also made of the fate of the asymmetric carbinol center during the rearrangement. The approach used is outlined in Scheme III, in which the chiral carbon center was created by addition of methyl Grignard reagent to optically active (+)-benzoyl-1-naphthylphenylmethylsilane (7) of known absolute configuration. It was shown by nmr spectroscopy that an 81:19 mixture of diastereomers was formed, with the predominant isomer formed, 8, having the configuration shown.[15] The mixture of diastereomers rearranged to a mixture of diastereomeric alkoxysilanes which on reduction gave, as ex-

Scheme III
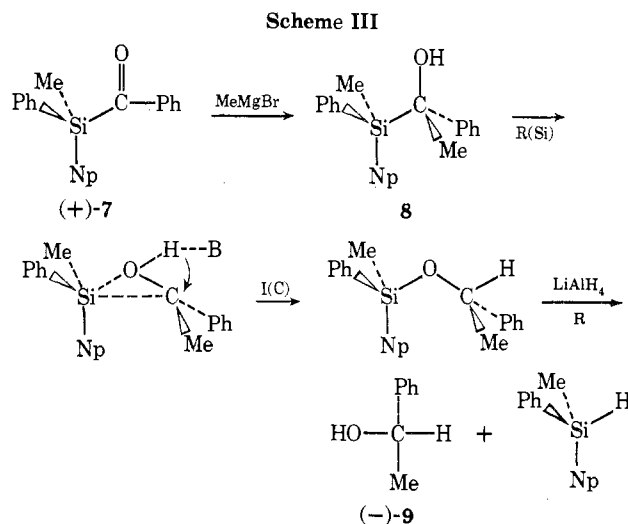
(15) In our early work[14] it was assumed that Cram's rule of asymmetric induction held, and that the sequence 1-naphthyl > phenyl > methyl applied, so that the diastereomer shown was postulated to be the *minor* product. Subsequently, related research communicated by H. S. Mosher[16] indicated this assumption was probably incorrect and led us to determine the configuration of the predominant diastereomer through the crystal structure of its *p*-bromobenzoate.[17] This indicated the major diastereomer had the configuration shown in Scheme III.
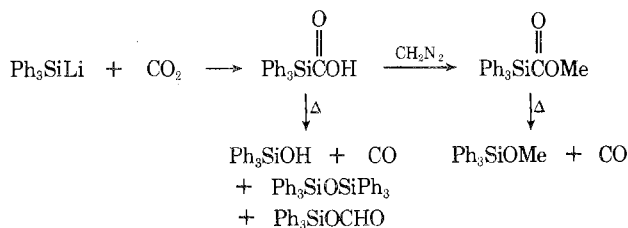
(16) M. S. Biernbaum and H. S. Mosher, *Tetrahedron Lett.*, 5289 (1968).

(17) S. C. Nyburg, A. G. Brook, J. D. Pascoe, and J. T. Szymanski, *Acta Crystallogr., Sect. B, 28,* 1785 (1972).
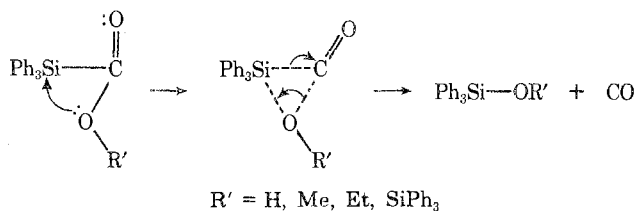
pected, optically active R₃Si*H which had retained configuration at chiral silicon during the rearrangement, and an 80:20 mixture of the enantiomeric 1-phenylethanols, **9**, with the (−) enantiomer, with absolute configuration as shown, predominating. This showed unambiguously, contrary to our original conclusion,[14] that highly stereospecific *inversion* of configuration was involved at the chiral carbon center during the rearrangement.[18] This was in accord with the findings of Mosher from related studies[16,19] and consistent with minimal movement of the proton from the O–H group to the adjacent carbon, as well as with the concept of a close association of BH⁺ with the three-membered transition state (intermediate), as suggested by the observed very large and negative entropy of activation.

A number of rearrangements, closely related in detail to that described above, have been observed among the reactions of α-substituted organosilicon compounds.

A number of years ago Benkeser,[20] and then Brook and Gilman,[21] showed that silylmetallic reagents could be carbonated to give silanecarboxylic acids, **10**, in good yield. These,[22] and their esters **11**,[23] were unusual in that at temperatures of 150–230°, they readily decarbonylated, the acids giving a mixture of silanol and CO, with some disiloxane and water due to thermal dehydration, as well as the isomeric silyl formate, while the silanecarboxylate esters smoothly and quantitatively gave only alkoxysilane and CO.

$$Ph_3SiLi + CO_2 \longrightarrow Ph_3Si\overset{\displaystyle O}{\overset{\|}{C}}OH \xrightarrow{CH_2N_2} Ph_3Si\overset{\displaystyle O}{\overset{\|}{C}}OMe$$

$$\downarrow \Delta \qquad\qquad\qquad \downarrow \Delta$$

$$Ph_3SiOH + CO \qquad Ph_3SiOMe + CO$$
$$+ Ph_3SiOSiPh_3$$
$$+ Ph_3SiOCHO$$

The ester decarbonylation was shown to be intramolecular, both from the thermolysis of mixtures of esters, where no "crossed" products could be detected, and from kinetic studies.[24] These results strongly suggest a similar type of reaction mechanism where lone pairs of electrons on oxygen attack at silicon, displacing carbon, and where the nature of the R group on oxygen has little effect on the reaction (except perhaps if R′ = H, when a 1,2-hydrogen shift occurs accounting for the silyl formate).

$$Ph_3Si\!-\!\!\overset{:O}{\overset{\|}{C}} \longrightarrow Ph_3Si\!\cdots\overset{O}{\overset{\diagup}{C}} \longrightarrow Ph_3Si\!-\!OR' + CO$$
$$\underset{R'}{\overset{\diagdown}{O}} \qquad\qquad \underset{R'}{\overset{\diagup}{O}}$$

R′ = H, Me, Et, SiPh₃

Related behavior is found in the thermolysis of the ketals of acylsilanes, **12**, in which again silicon–oxy-

gen bond formation yields an alkoxysilane.[25] From an optically active ketal of known absolute configuration, the 1-naphthylphenylmethylmethoxysilane isolated was 95% optically pure and was formed, as expected, with retention of configuration. The byproduct from the thermolysis is an alkoxycarbene, **13**, which has been trapped in a variety of ways including insertion into an Si–H bond, and by addition to an alkyne yielding a cyclopropene.
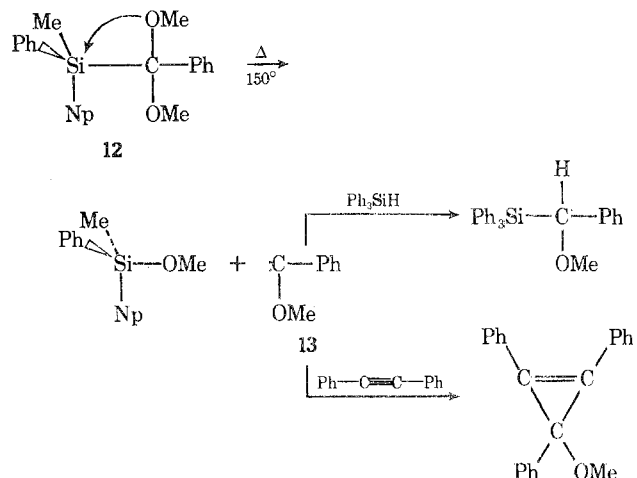
These rearrangements parallel closely the findings of Atwell and Weyenburg[26,27] who employed similar types of rearrangement as routes to silylenes **14** or carbenes.
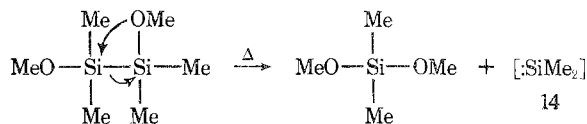
It is quite evident that there is a great similarity in all of these rearrangements, each of which is derived from intramolecular interaction between silicon and oxygen attached to an intervening carbon atom.

The acylsilanes, R₃SiCOR′, are themselves dramatic examples of compounds in which there are strong interactions between silicon and an adjacent functional group.

As has been described in detail elsewhere,[28,29] these compounds show remarkably long wavelength carbonyl stretching absorption in the infrared (6.08–6.18 μ; 1645–1618 cm⁻¹) as well as abnormally strong n–π* carbonyl ultraviolet absorptions at unusually long wavelengths, in the ranges 370–385 nm for acetylsilanes and 420–440 nm for benzoylsilanes. They are also more basic than the corresponding carbon analogs.[30]

With the strong n–π* absorption in the near ultraviolet, or visible, it might be anticipated that the acylsilanes would show interesting photochemistry. When photolyzed in halogenated solvents, the compounds readily undergo Norrish type I cleavage to

(18) A. G. Brook and J. D. Pascoe, *J. Amer. Chem. Soc.*, 93, 6224 (1971).
(19) M. S. Biernbaum and H. S. Mosher, *J. Amer. Chem. Soc.*, 93, 6221 (1971).
(20) R. A. Benkeser and R. G. Severson, *J. Amer. Chem. Soc.*, 73, 1424 (1951).
(21) A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 77, 2322 (1955).
(22) A. G. Brook, *J. Amer. Chem. Soc.*, 77, 4827 (1955).
(23) A. G. Brook and R. J. Mauris, *J. Amer. Chem. Soc.*, 79, 971 (1957).
(24) A. G. Brook, unpublished studies.

(25) A. G. Brook and P. J. Dillon, *Can. J. Chem.*, 47, 4347 (1969).
(26) W. H. Atwell and D. R. Weyenburg, *J. Amer. Chem. Soc.*, 90, 3438 (1968).
(27) W. H. Atwell, D. R. Weyenburg, and J. G. Uhlmann, *J. Amer. Chem. Soc.*, 91, 2025 (1969).
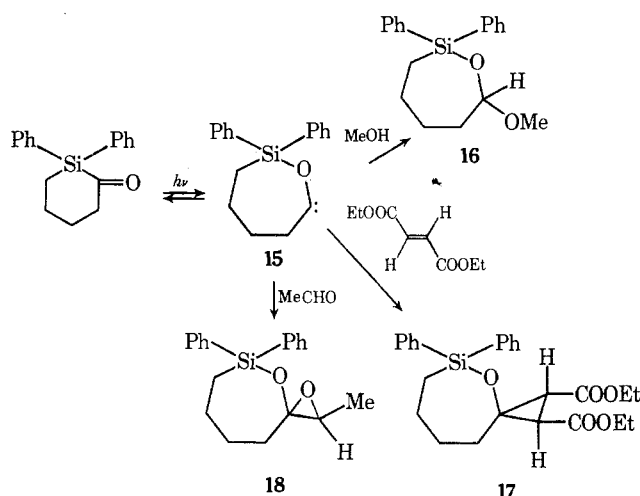(28) A. G. Brook, P. F. Jones, and G. J. D. Peddle, *Can. J. Chem.*, 46, 2119 (1968).
(29) A. G. Brook, *Advan. Organometal. Chem.*, 7, 95 (1968).
(30) K. Yates and F. Agolini, *Can. J. Chem.*, 44, 2229 (1966).

silyl and acyl radicals, the former yielding chlorosilane as the only silicon-containing product and the latter yielding acyl chloride, acyltrichloromethane ($RCOCl_3$), and hexachloroethane.[31] It was of particular interest to find that a chiral acylsilane, such as (−)-acetyl-1-naphthylphenylmethylsilane, gave a chiral radical which evidently was able to abstract halogen from the solvent more rapidly than it collapsed to a planar structure, since the (+)-1-naphthylphenylmethylchlorosilane isolated had largely retained its configuration, being about 80% optically pure.[32,33] Similar results were observed by Kumada who generated the chiral radical by treatment of the silane R_3Si^*H with peroxide.[34]
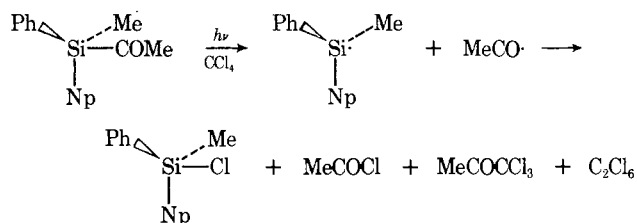
Under other conditions and especially in the presence of polar solvents such as alcohols, acylsilanes are photoisomerized to siloxycarbenes 15, another type of process involving Si–O bond formation and Si–C bond cleavage. These siloxycarbenes may revert to the parent acylsilanes, but in the presence of other reagents, especially those having marked kinetic acidity, the siloxycarbenes can be trapped, by insertion into polar bonds giving acetals[35] 16, by addition to electron-deficient carbon–carbon double bonds like diethyl fumarate to give cyclopropanes[36] 17, or in some cases by reaction with carbonyl groups[37] to give oxiranes 18. From these and other results[33] it can be demonstrated that the siloxycarbenes are nucleophilic in character. We have not as yet unambiguously established the multiplicity of the carbenes, or of the excited states which appar-

ently lead sometimes to radicals but under other conditions to siloxycarbenes.

Some of the reactions of the acylsilanes also involve interesting molecular rearrangements. Thus, when acylsilanes are treated with diazomethane, in anticipation of forming homologous ketones, two products are usually obtained,[38] one being the homologous β-ketosilane and the second the isomeric siloxyalkene.

$$R_3SiCOR' + CH_2N_2 \longrightarrow R_3SiCH_2COR' + R_3SiOC{=}CH_2$$
$$\underset{R'}{|}$$
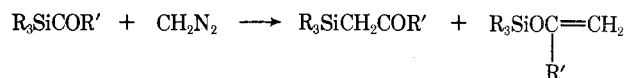
The intermediate formed in the reaction of diazomethane with benzoyltriphenylsilane, for example, may behave conventionally by re-forming the carbonyl group with accompanying migration of the silyl group to the electron-deficient center, yielding the β-ketosilane. (In all cases studied, only silyl migration has been observed regardless of the nature of the other groups attached to the carbonyl carbon.)
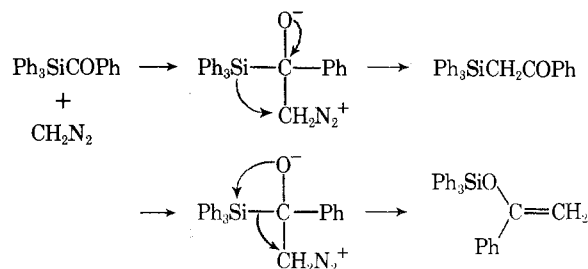
Alternatively the intermediate, which has an oxyanion adjacent to silicon, can undergo a silylcarbinol–alkoxysilane type rearrangement, forming a silicon–oxygen bond and releasing electrons toward carbon leading to the carbon–carbon double bond of the siloxyalkene. This latter process occurs most readily when the group on carbon (Ph in this case) is able to delocalize negative charge; in these cases the yields of siloxyalkene are often 40–50%. When an alkyl group is attached to carbon, which would tend to localize charge on carbon and thus disfavor cleavage of the carbon–silicon bond, the yields of siloxyalkene are usually in the range of 0–5%, and the major product is the β-ketosilane.

Similar behavior is observed in reactions with Wittig reagents.[39] With alkylacylsilanes 19 (R' = alkyl)

(31) A. G. Brook, P. J. Dillon, and R. Pearce, *Can. J. Chem.*, **49**, 133 (1971).

(32) A. G. Brook and J. M. Duff, *J. Amer. Chem. Soc.*, **91**, 2118 (1969).

(33) A. G. Brook and J. M. Duff, unpublished studies.

(34) H. Sakurai, M. Murakami, and M. Kumada, *J. Amer. Chem. Soc.*, **91**, 519 (1969).

(35) A. G. Brook and J. M. Duff, *J. Amer. Chem. Soc.*, **89**, 454 (1967).

(36) A. G. Brook, H. W. Kucera, and R. Pearce, *Can. J. Chem.*, **49**, 1618 (1971).
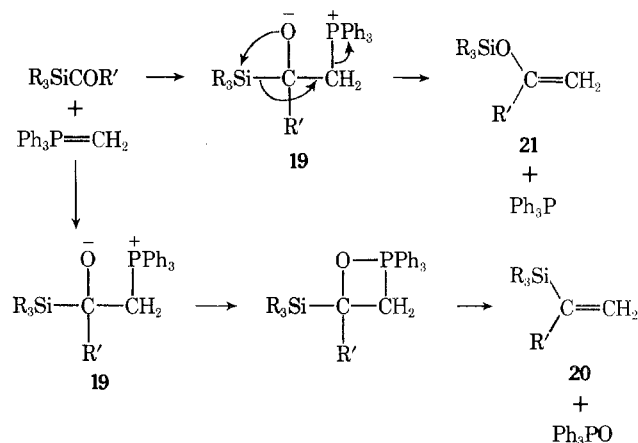
(37) A. G. Brook, R. Pearce, and J. B. Pierce, *Can. J. Chem.*, **49**, 1622 (1971).

(38) A. G. Brook, W. W. Limburg, D. M. MacRae, and S. A. Fieldhouse, *J. Amer. Chem. Soc.*, **89**, 704 (1967).
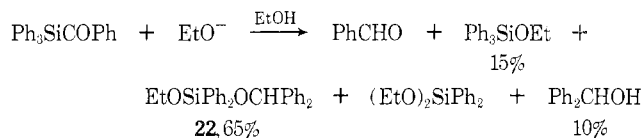
(39) A. G. Brook and S. A. Fieldhouse, *J. Organometal. Chem.*, **10**, 235 (1967).

only the normal product, the alkene **20**, is observed. With arylacylsilanes **19** (R' = aryl) an alternative process occurs, again involving a rearrangement leading to silicon–oxygen bond formation, the formation of a siloxyalkene, **21**, and triphenylphosphine.

Several different synthetic routes to acylsilanes have been described,[29,40,41] the most general and useful being modeled after the Corey route to ketones using 1,3-dithianes. The chief difficulty with the reaction lies in the hydrolysis of the 2-silyl-1,3-dithiane, since the acylsilane is itself sensitive to hydrolysis, giving aldehyde and silanol, particularly in the presence of base. While silicon compounds are well known for their susceptibility to nucleophilic attack, in this case such a cleavage could imply the unfamiliar behavior of an acyl anion acting as a leaving group.

$$R_3SiCOR \xrightarrow{H_2O} R_3SiOH + RCHO$$
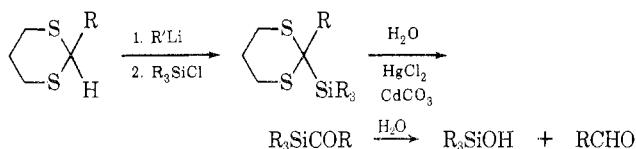
In the hope of learning more about this "solvolysis" process, we treated benzoyltriphenylsilane with ethoxide ion in ethanol. Under these conditions "solvolysis" became a minor pathway, and a new rearrangement, involving transfer of phenyl from silicon to carbon, occurred yielding ethoxybenzhydryloxydiphenylsilane, **22**, as the major product, together with minor by-products.[42]

$$Ph_3SiCOPh + EtO^- \xrightarrow{EtOH} PhCHO + Ph_3SiOEt +$$
$$15\%$$

$$EtOSiPh_2OCHPh_2 + (EtO)_2SiPh_2 + Ph_2CHOH$$
$$22, 65\% \qquad\qquad\qquad\qquad 10\%$$

This reaction must involve nucleophilic attack by ethoxide ion on silicon, yielding a five-coordinate transition state or intermediate **23**, which subsequently undergoes a 1,2 migration of phenyl to the adjacent carbonyl group. This new species, **24**, an
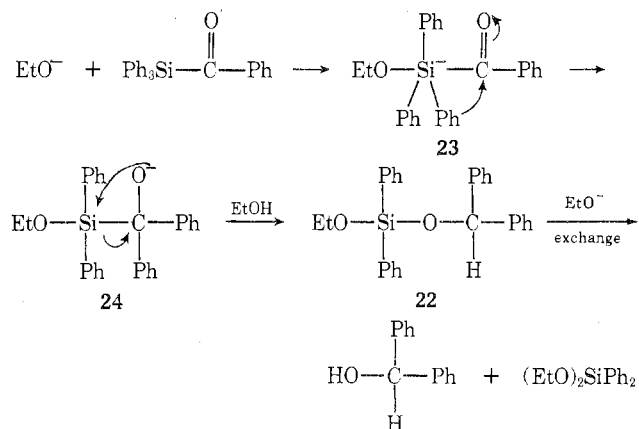
α-silyl oxyanion, subsequently rearranges in the usual manner, yielding the observed dialkoxysilane **22**, which can undergo alkoxide exchange, yielding

(40) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Amer. Chem. Soc.*, 89, 431 (1967), and references contained therein.

(41) A. G. Brook, H. W. Kucera, and D. M. MacRae, *Can. J. Chem.*, 48, 818 (1970).

(42) A. G. Brook and N. V. Schwartz, *J. Org. Chem.*, 27, 2311 (1962).

the observed diethoxydiphenylsilane and benzhydrol. This kind of rearrangement was found to occur with all acylsilanes and with a variety of alkoxides.
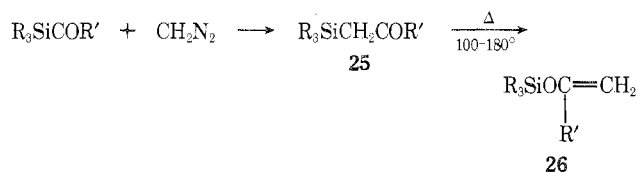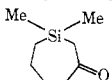
Finally, further studies of the "solvolytic" cleavage of acylsilanes suggest that this involves nucleophilic attack by alkoxide at the carbonyl group of the acylsilane; the resulting oxyanion then rearranges in the usual manner to give an acetal which subsequently undergoes alkoxide exchange, yielding the "solvolysis" products, as illustrated with benzoyltriphenylsilane and ethoxide ion.[43]
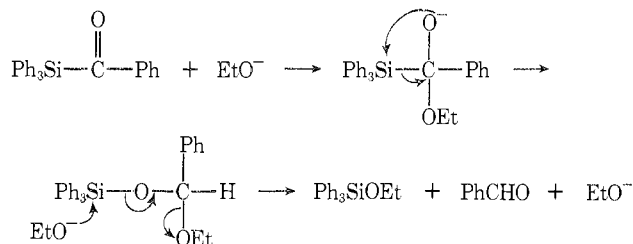
The above material clearly establishes both that a strong interaction occurs between silicon and various forms of oxygen attached to an intervening carbon atom and also that such systems have a pronounced tendency to undergo 1,2 rearrangements of silicon from carbon to oxygen, effecting silicon–oxygen bond formation and silicon–carbon bond cleavage.

Somewhat different but related behavior has been observed when the silicon atom and the functional group bear a β relationship.

Our entry into this field arose from the discovery that the β-ketosilanes **25**, which were formed from acylsilanes reacting with diazomethane, were thermally convertible in high yield at moderate temperatures to the isomeric siloxyalkenes **26**.[44] These ther-

$$R_3SiCOR' + CH_2N_2 \longrightarrow R_3SiCH_2COR' \xrightarrow[100-180°]{\Delta}$$
$$25$$

$$R_3SiOC{=}CH_2$$
$$\overset{|}{R'}$$
$$26$$

mal rearrangements were quite general, and it appeared worthwhile to investigate their mechanism. The reaction was shown to follow cleanly first-order kinetics over several half-lives. The data were reproducible, and there was no evidence of the rearrangement being catalyzed (*vide infra*). The rates of reaction of several compounds were determined at several temperatures and the reaction parameters determined are given in Table II.[45] The energies of activation are relatively constant despite large changs in structure of the reagents, and, with one exception, the ΔS* values, which are negative, are also relatively constant.

A Hammett ρ–σ study of several para-substituted-phenyl β-ketosilanes showed a good linear fit for the p-t-Bu, -H, -Cl, and Br derivatives, although the F and MeO compounds fell off the line. The slope of the line, −0.78, indicates the reaction to be quite insensitive to substituent effects and, more particular-

(43) A. G. Brook and T. Vandersaar, unpublished studies.

(44) A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Amer. Chem. Soc.*, 89, 5493 (1967).

(45) D. M. MacRae, Ph.D. Thesis, University of Toronto, 1972.

Table II
Summary of Activation Parameter Data for β-Ketosilanes

Compound	Solvent	Temp range, °C	E_A, kcal/mol	ΔS^*, eu
Ph₃SiCH₂COPh	Toluene	100–125	28.1 ± 0.4	-7.3 ± 1
Ph₃SiCH₂COPh	Decalin	105–125	28.4 ± 0.8	-6.4 ± 2
Me₃SiCH₂COPh	Neat	133–153	26.1 ± 0.7	-16.9 ± -1.6
Ph₃SiCH₂COMe	Melt	148–173	31.7 ± 0.9	-4.2 ± 2
Me₃SiCH₂COMe	Neat	159–180	30.1 ± 0.3	-9.8 ± 0.8
	Neat	175–195	33.0 ± 1.2	-6.4 ± 0.4

ly, that little if any charge is developed on the carbonyl carbon during the course of the reaction. These data are fully consistent with an intramolecular concerted four-center mechanism, as shown below, involving attack by carbonyl oxygen on silicon, with cleavage of the silicon–carbon bond.
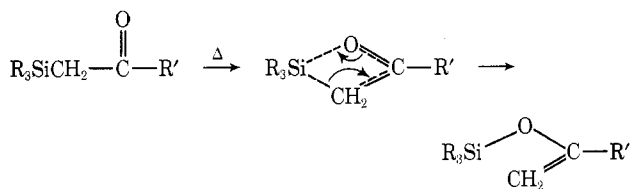
This mechanism can be contrasted to a related process reported by the Russian workers Litvinova, Baukov, and Lutsenko[46] at about the same time our work was published, which involved catalysis of the rearrangement of a variety of β-silylcarbonyl compounds (esters, ketones, etc.) by a variety of reagents including especially mercuric iodide or silyl iodides. These reactions are clearly bimolecular. Subsequently the Russian workers greatly extended their studies to include other classes of β-carbonyl silicon compounds and also to systems that, like ours, require no catalyst or other added reagent.[47] From our studies and the Russian work it is quite obvious that two mechanisms for these isomerizations are possible, one being an intramolecular noncatalyzed thermal process and the other a bimolecular (catalyzed) process.
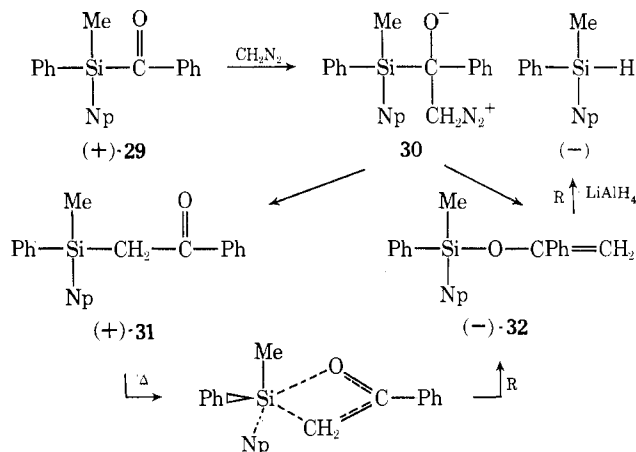
The stereochemistry of the β-ketosilane–siloxyalkene rearrangement was investigated[44] using optically active (+)-benzoyl-1-naphthylphenylmethylsilane (29) of known absolute configuration, as shown in Scheme IV. Treatment of the acylsilane with diazomethane gave, *via* adduct 30, the (−)-siloxyalkene 32, in a reaction expected to involve retention of configuration at silicon by analogy with the silylcarbinol to alkoxysilane rearrangement. This was confirmed by reduction of the siloxyalkene with LiAlH₄ under conditions known to involve retention of configuration at silicon, which, yielding (−)-R₃Si*H, indicated that there had been complete retention of configuration during the conversion of the acylsilane to the siloxyalkane.

Treatment of the chiral acylsilane with diazomethane also yielded the (+)-β-ketosilane 31. Here, too, retention of configuration at silicon was to be expected by analogy with Gutsche's findings with

Scheme IV

optically active 2-methylcyclohexanone.[48] This was confirmed by correlating the configurations of the β-ketosilane 31 with its germanium analog, 35. This was synthesized as shown in Scheme V, by reactions of known stereochemistry, from optically active (−)-R₃Ge*H 33, of known absolute configuration, *via* the germyllithium reagent and the β-carbinol 34 which was then oxidized to the (+)-ketone 35. The same (+)-β-ketogermane was obtained from the (+)-acylgermane 36 of known absolute configuration by treatment with diazomethane.[45] Hence this reaction necessarily involved retention of configuration. The (+)-rotating β-ketosilane 31 and -germane 35 had almost superimposable ORD spectra, confirming the identity of their absolute configurations and demonstrating that configuration at asymmetric sili-

Scheme V

con was retained during the formation of the β-ketosilane from the chiral acylsilane.

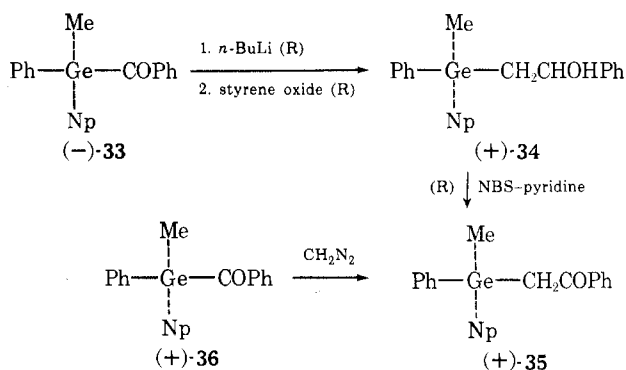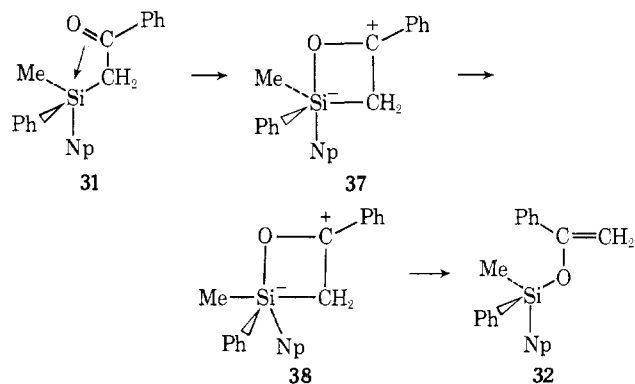(46) O. V. Litvinova, Yu. I. Baukov, and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, 173, 578 (1967), and references therein.

(47) I. F. Lutsenko, Yu. I. Baukov, A. S. Kostyuk, N. I. Savelyeva, and V. K. Krysina, *J. Organometal. Chem.*, 17, 241 (1969).

(48) C. Djerassi, B. F. Burrows, C. Overberger, T. Takekoshi, C. D. Gutsche, and C. T. Chang, *J. Amer. Chem. Soc.*, 85, 949 (1963).

When the (+)-β-ketosilane **31** was thermolyzed at 110°, (−)-siloxyalkene **32** was obtained in quantitative yield and very high optical purity, indicating that, in the concerted 1,3 migration of silicon from carbon to carbonyl oxygen, there was virtually complete retention of configuration. This finding is consistent with the formation of a five-coordinate silicon intermediate involving d-orbital participation, and it can be rationalized in terms of a pseudorotation process.[49] Thus, axial attack of carbonyl oxygen on sili-

con in **31** would yield a trigonal bipyramid, **37**, as shown, which on pseudorotation would give a second trigonal bipyramid, **38**. Axial departure of the leaving methylene group then yields the siloxyalkene **32** with retained configuration at silicon. This description, of course, simply rationalizes the experimental findings, and does not prove that pseudorotation is involved.

Finally, several analogs of the β-ketosilane to siloxyalkene rearrangement have been observed. Silylacetic acids, **39**, formed by careful carbonation of silylmethylmetallic reagents,[50] can be converted either thermally or in the presence of base to the isomeric acetoxysilanes **40**. The thermal reaction is a
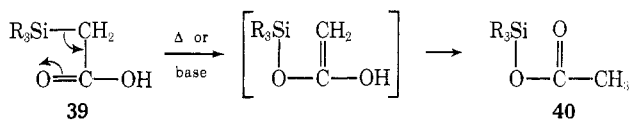
relatively clean process, but the base-catalyzed reaction may involve either unimolecular or bimolecular processes. However, under conditions of high dilution, which minimize bimolecular reactions, it has been shown that optically active silylacetic acids are converted to optically active acetoxysilanes with retention of configuration at silicon,[51] as observed with the β-ketosilanes. Thus a similar mechanism seems probable.

It was also found that β-silyl sulfoxides **41** were readily thermally isomerized,[52] initially presumably

to a sulfur ylide, **42** which was not isolated, but which subsequently must have undergone a Pummerer rearrangement, yielding the observed siloxymethyl sulfide **43**. Again these rearrangements appear to be members of a general family of 1,3 migrations of silicon from carbon to oxygen by concerted four-center pathways.
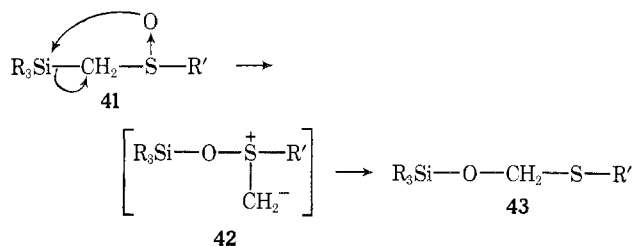
This Account has described only a few of the known molecular rearrangements of organosilicon compounds and has chiefly dealt with studies from the author's laboratory which have involved oxygen as the migration terminus. A number of other 1,2 rearrangements involving migration to nitrogen or sulfur have been described,[53,54] a 1,3-allylic rearrangement of silicon has recently been described,[55,56] 1,4 rearrangements of silicon involving oxygen–oxygen exchange have been observed on thermolysis of α-siloxy-β-ketosilanes,[57] and the rapid exchange of silicon between oxygens in a silylated acetylacetone involving 1,5 oxygen–oxygen rearrangements, with retention of configuration at asymmetric silicon, has recently been reported.[58,59]

Thus it is evident that organosilicon compounds having adjacent functional groups on carbon are a fertile source of molecular rearrangements, which frequently involve silicon–oxygen bond formation and concomitant silicon–carbon bond cleavage. In cases where the stereochemistry at silicon has been observed, the reactions have been found to involve retention of configuration with very high stereospecificity.

(49) F. H. Westheimer, *Accounts Chem. Res.,* 1, 78 (1968).

(50) A. G. Brook, J. M. Duff, and D. G. Anderson, *Can. J. Chem.,* 48, 561 (1970).

(51) A. G. Brook, J. M. Duff, and D. G. Anderson, *J. Amer. Chem. Soc.,* 92, 7567 (1970).

(52) A. G. Brook and D. G. Anderson, *Can. J. Chem.,* 46, 2115 (1968).

(53) R. West and M. Ishikawa, *J. Amer. Chem. Soc.,* 89, 4981 (1967), and references therein.

(54) A. Wright, D. Ling, P. Boudjouk, and R. West, *J. Amer. Chem. Soc.,* 94, 4784 (1972).

(55) H. Kwart and J. Slutsky, *J. Amer. Chem. Soc.,* 94, 2515 (1972).

(56) We believe the prediction that the stereochemistry of these reactions involves inversion of configuration at silicon will be found to be wrong.

(57) A. G. Brook and D. M. MacRae, unpublished research.

(58) T. J. Pannovia, W. T. Collins, and J. J. Howe, *J. Amer. Chem. Soc.,* 92, 4544 (1970).

(59) J. Lindemulder, A. Schwartz, and T. J. Pannovia, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, Abstract INOR-20.