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ONE THING LEADS TO ANOTHER — FROM SILYLCARBINOLS TO SILAETHYLENES

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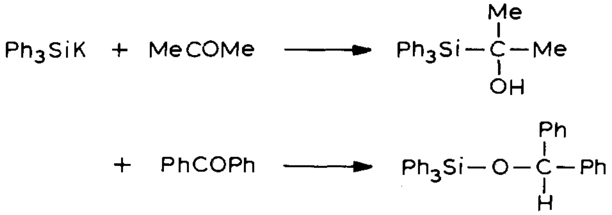
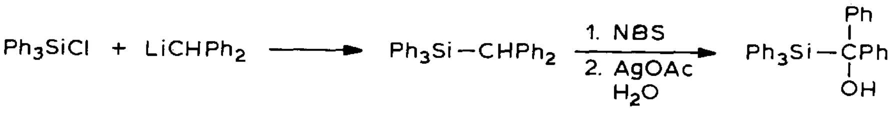
I became involved in organosilicon chemistry in 1952 as a result of a year's post-doctoral research with a distinguished gentleman and organometallic chemist, Henry Gilman, the North American father of organometallic chemistry, a man who probably made compounds of a wider variety of elements than anyone else, before or since. I learned a lot that year about chemistry and the excitement of research, and returned to Toronto in possession of two observations discovered while I was in the middle of the Iowa cornfields that Gilman indicated I was free to follow up if I wished. These arose from the investigation of the behaviour of triphenylsilylpotassium [1], the first discovered silylmetallic reagent, where it had been noted by Gilman's group [2] that with aliphatic aldehydes or ketones (exemplified by acetone below) the expected carbinol from normal addition to the carbonyl group was obtained, whereas with aromatic aldehydes or ketones (exempified by benzophenone) the isomeric silyl ether was obtained. What was the explanation of this anomaly: abnormal addition to the carbonyl group, or normal addition followed by some new kind of rearrangement?



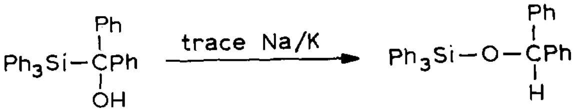
$$Ph_3SiK + MeCOMe \longrightarrow Ph_3Si-\underset{OH}{\overset{Me}{C}}-Me$$

$$+\ PhCOPh \longrightarrow Ph_3Si-O-\underset{H}{\overset{Ph}{C}}-Ph$$

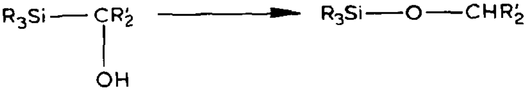
This led to our synthesizing the expected carbinol by an alternative route [3] and finding that this perfectly stable compound, when treated with a trace of sodium/potassium alloy, an expected impurity in the triphenylsilylpotassium as prepared in those days, underwent a rapid and clean rearrangement to the isomeric silyl ether.



$$Ph_3SiCl + LiCHPh_2 \longrightarrow Ph_3Si-CHPh_2 \xrightarrow[\substack{2.\ AgOAc\\ H_2O}]{1.\ NBS} Ph_3Si-\underset{OH}{\overset{Ph}{C}}Ph$$



Indeed it was eventually shown that this was a completely general reaction for all silylcarbinols, catalyzed by virtually any basic reagent, usually employed in only trace amounts [5].



R = aryl , alkyl
R' = aryl , alkyl hydrogen

Isomerizing agents : Na/K , Na , NaH ,
RLi , Et_2NH , R_3N

This novel rearrangement captured our interest and led to a lot of further study. Thus the rearrangement is characterized by having a low energy of activation, and a very large negative entropy of activation, characteristic of a process involving a cyclic transition state. In addition the Hammett σ–ρ relationship was studied and ρ was found to be very large and positive, indicative of a transition state having considerable carbanionic character on the benzylic carbon [6] (Table 1).

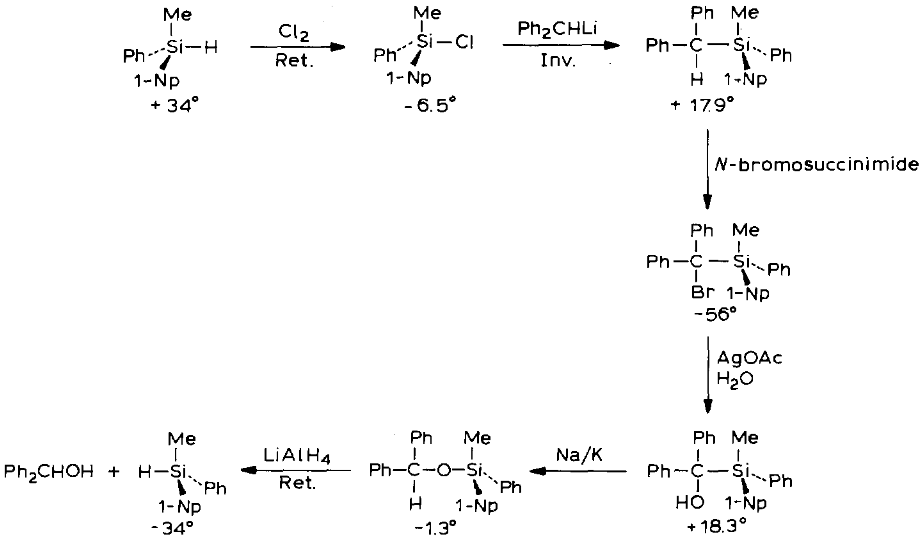
TABLE 1

ACTIVATION PARAMETERS AND HAMMETT σ–ρ RELATIONSHIPS FOR SILYLCARBINOLS

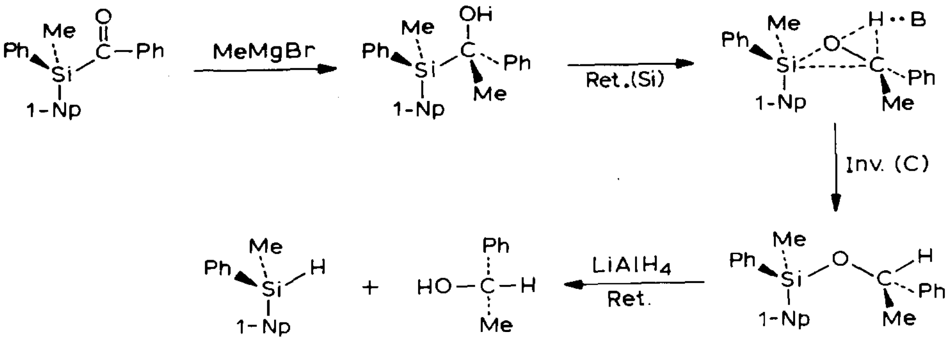
	E_{act} (kcal/mole)	ΔS^* (eu)	Solvent
$Ph_3SiCMePhOH$	11.2	−34	DMSO
$Ph_2MeSiCPh_2OH$	8.65	−46	$CHCl_3$
Hammett σ–ρ relationships			
$Ph_3SiCHOHC_6H_4X$		$\rho = 3.7$	
$Ph_3SiCOHMeC_6H_4X$		$\rho = 4.6$	
$Ph_3SiCOH(CH_2Ph)C_6H_4X$		$\rho = 3.4$	

Stereochemical studies, involving the chiral methylphenyl-1-naphthylsilyl system developed by Leo Sommer [7], revealed that the rearrangements occurred with extremely clean retention of configuration at chiral silicon as revealed by the recovery of essentially optically pure silane after the Walden cycle shown in Scheme 1 [8,9], in which thanks to Sommer's work, the only step of unknown stereochemistry was that involving the rearrangement.

When a chiral centre was created at the carbinol carbon we were able to show that under our conditions, using only a catalytic amount of base, clean inversion of configuration occurred [10] (Scheme 2) (although subsequent studies by others [11] under very different conditions have shown that retention of configuration may occur in some cases).

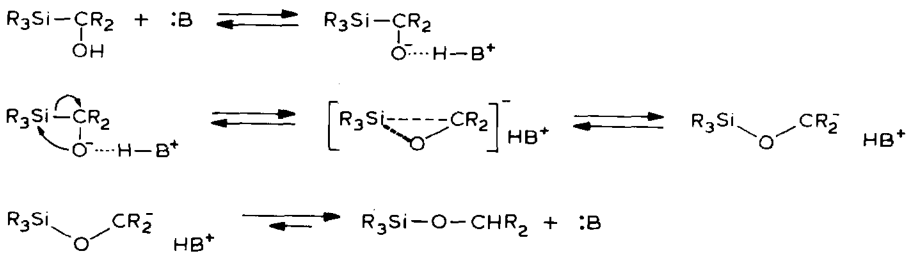


SCHEME 1. Np = naphthalene; Ret. = retention of configuration; Inv. = inversion of configuration.



SCHEME 2

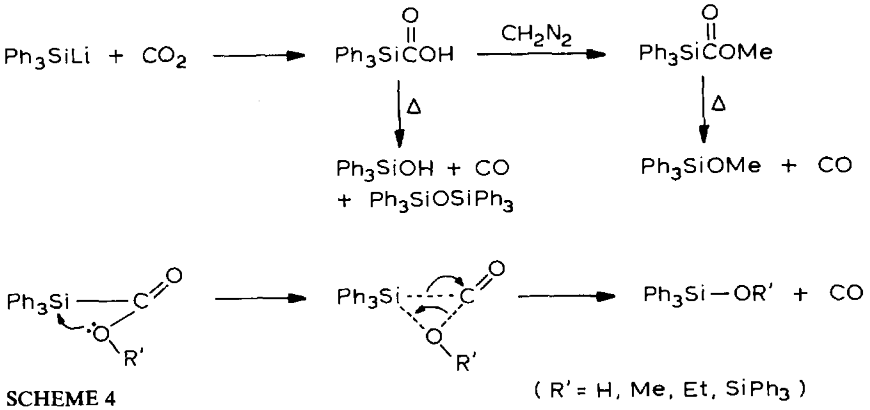
Integration of these findings led to the proposal of a mechanism to account for the details of the rearrangement as shown below, the key steps being an oxyanion-to-carbanion isomerization, undoubtedly facilitated by the formation of the very strong silicon–oxygen bond [9] (Scheme 3).



SCHEME 3

The above was one of the first in-depth studies of a class of carbon-functional organosilicon compounds, and it set the direction of future studies. More recently it has been shown that related rearrangements can occur when there are several carbon atoms between the carbon bearing the OH group and the silyl group which migrates, which in addition to being attached to carbon may also be attached to silicon [12]. Also in recent years synthetic applications of this rearrangement have been developed, as I will show later.

Having been brought up in the organometallic tradition (my Ph.D. Thesis was on Oxymercuration) I knew that one should see if a new organometallic could be carbonated. Hence the triphenylsilyl-potassium or -lithium reagents were treated with Dry Ice and it was found that the derived silanecarboxylic acids showed unusual behaviour, in that on heating to their melting points they eliminated carbon monoxide, as did their derived esters when heated to 150–200°C, behaviour shown to be due to an intramolecular process [13,14] (Scheme 4). In addition, in solution

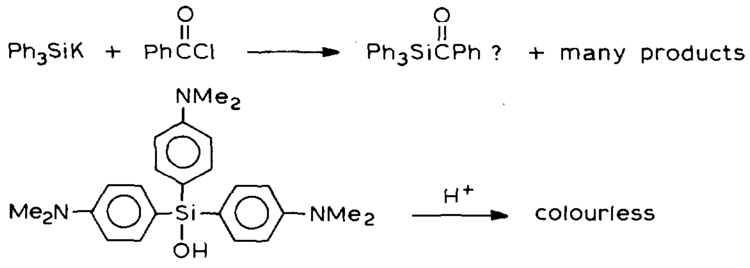


SCHEME 4

both the acids and their esters were exceedingly sensitive toward base-catalyzed decarbonylation [15], another reflection of the susceptibility of silicon to nucleophilic attack by oxygen.

Having found unusual behaviour for both silylcarbinols and silanecarboxylic acids it was a logical step to attempt to synthesize the hitherto unknown class of compounds corresponding to ketones, the acylsilanes (often poorly named as silyl ketones), where a carbonyl group is adjacent to silicon.

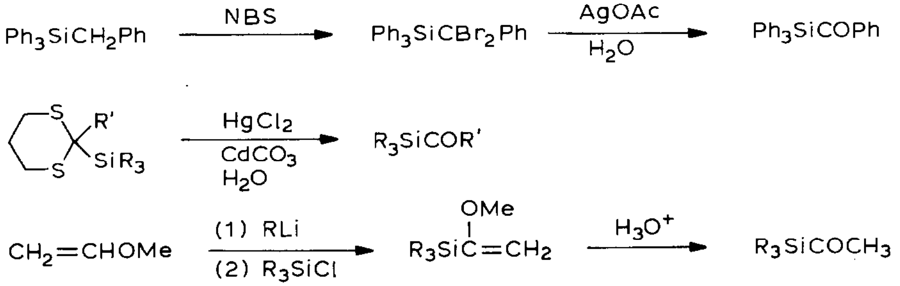
Our first efforts to make benzoyltriphenylsilane involved the attempted coupling



SCHEME 5

of triphenylsilylpotassium with benzoyl chloride, in what turned out, not surprisingly, to be a very messy reaction (Scheme 5). All the major products were identified as things not wanted and the only unusual product was about a 3% yield of a high boiling yellow oil of whose identity we had no idea. It certainly could not have been the desired benzoylsilane because it was well known at that time that silicon compounds could not be coloured-after all silicon did not form double bonds, and even the silicon analog of crystal violet, which should have been coloured if there was even a little bit of π-conjugative interaction, was colourless in acid media, unlike its carbon analog! So we put the yellow oil aside and looked for more promising reactions.

Sometime later when we did develop a route to benzoyltriphenylsilane [16] it turned out to be yellow coloured, and in the meantime the yellow oil had crystallized and was shown to be identical by mixed melting point, so that in fact a little of the first acylsilane had been made by the coupling reaction: nowadays there are a wide variety of much better routes to acylsilanes [17] (Scheme 6).

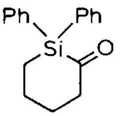


SCHEME 6. NBS = *N*-bromosuccinimide.

The acylsilanes turned out to be compounds of great interest both because of their extraordinary spectroscopic properties as well as their chemical behaviour [18]. As shown in Table 2 they have both unusual carbonyl infrared absorption and unusual ultraviolet absorption when compared with their carbon analogs, which clearly reveals a strong interaction between the silicon atom and the adjacent

TABLE 2

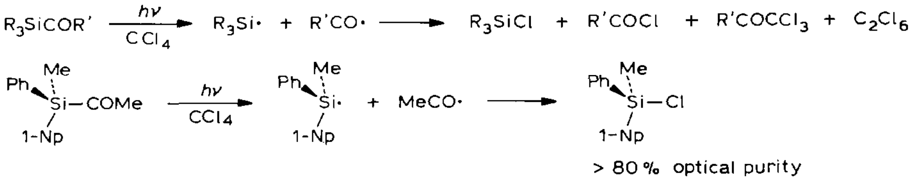
SPECTRAL PROPERTIES OF SOME ACYLSILANES AND KETONES

	IR C=O	stretch	UV C=O $\sigma-\pi^*$	$\lambda_{max}(\epsilon)$	$\pi-\pi^*(\epsilon)$
Me_3CCOMe	5.85μ	(1709 cm^{-1})	278 nm	(15)	186 (1100)
$Me_3SiCOMe$	6.08	(1645)	327 [a]	(126)	195 (4200)
	6.08	(1645)	383 [a]	(284)	
Ph_3CCOPh	5.91	(1692)	329	(299)	251 (11,600)
$Ph_3SiCOPh$	6.18	(1618)	424 [a]	(292)	257 (16,200)
$Me_3SiCOSiMe_3$	6.40	(1563)	537 [a]		

[a] Band has fine structure.

carbonyl group, an interaction that has been the subject of considerable discussion and investigation. Without going into great detail the interaction appears to be a combination of inductive electron release by silicon toward the carbonyl group, together with strong mixing of the silicon–carbon σ orbital with the lone pair electrons on the carbonyl oxygen giving considerable σ–π^* character to the long-wavelength electronic transition (Table 2) [19].

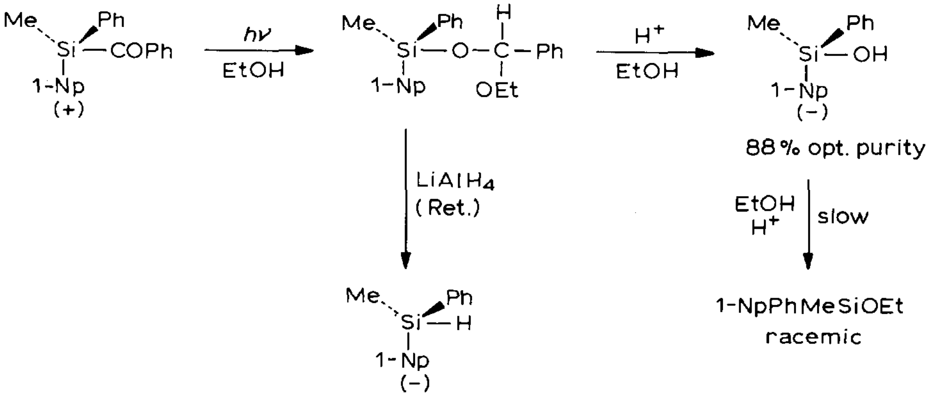
The long wavelength UV absorption led us rapidly into photochemical studies of the acylsilanes, in no small part because we began to realize that they were reacting while standing in solution on the lab bench illuminated by the fluorescent room lighting. Two types of photochemistry predominate. In non-polar solvents radical reactions occur forming silyl and acyl radicals where, in CCl_4 for example, the silicon cleanly and exclusively abstracts chlorine to yield a chlorosilane [20]. With a chiral acylsilane we were able to generate chiral silyl radicals and show that they had a much greater lifetime than their carbon analogs since they were captured as chiral chlorosilanes which had suffered only about 10% racemization [21]. Analogous carbon radicals undergo complete racemization under similar circumstances (Scheme 7).



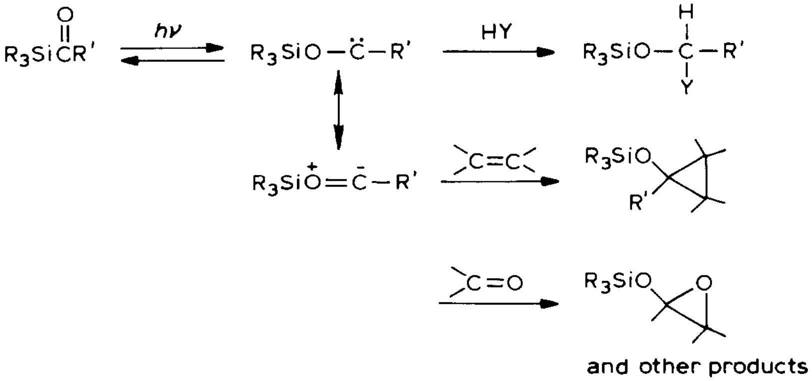
SCHEME 7

In polar solvents, particularly alcohols, a totally different photochemistry occurred yielding mixed acetals as the chiral example in Scheme 8 shows, the result of a rearrangement of a then unknown type which again involved complete retention of configuration at silicon [22]. The acetal products subsequently slowly undergo a variety of solvolysis reactions some of which involve racemization.

It was at about this time that my colleague Professor Peter Yates at Toronto was studying the photochemistry of some small fused ring compounds in alcohols and



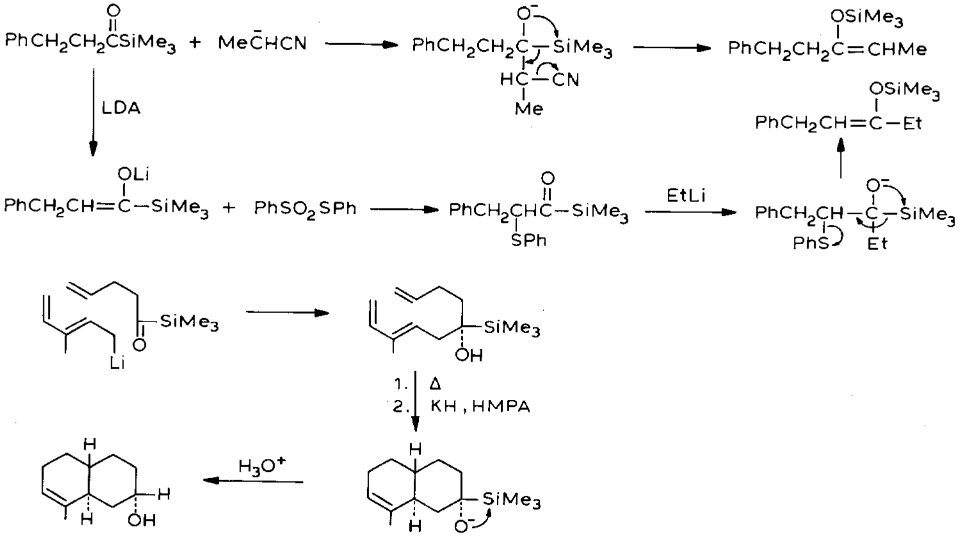
SCHEME 8



SCHEME 9

proposed the intermediacy of oxacarbenes to account for the observed products [23]. A similar type of intermediate appeared to nicely account for our results also. We proposed an intramolecular rearrangement of the acylsilane to a siloxycarbene, forming again the very stable silicon–oxygen bond, at the expense of the weaker silicon–carbon bond, and the reaction obviously terminated with insertion of the siloxycarbene into the polar H–Y bond of the alcohol or other kinetically-acidic trapping agent present [22]. We also trapped the carbene (or carbene-like species) with carbonyl groups [24] and an electron-deficient alkene [25], suggesting that the reaction intermediate had nucleophilic character (Scheme 9).

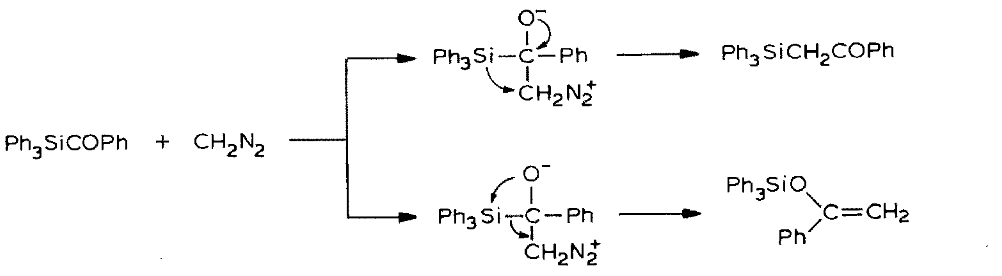
Acylsilanes also undergo a number of chemical reactions of interest, some of which have synthetic applications. One involves both acylsilanes and the silyl-carbinol-to-alkoxysilane rearrangement in a useful route to silyl-enol ethers and other reagents, routes that have been developed in recent years by Hans Reich [26], S. Wilson [27], and others, as shown below. In the first case addition of an anionic



SCHEME 10. LDA = lithium diisopropylamine; HMPA = hexamethylphosphoramide.

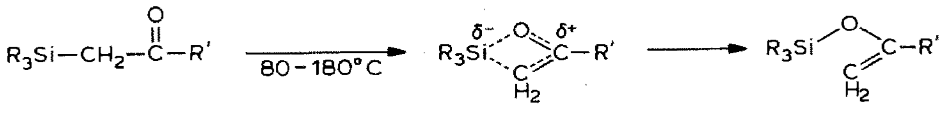
reagent to an acylsilane establishes the requirements for the silylcarbinol to alkoxysilane rearrangement, the unfavourable equilibrium being overcome by the presence of a good leaving group either on the attacking reagent or on the acylsilane. Using the two alternative routes shown, regioisomerically-pure silyl enol ethers can be synthesized. In the second example it was found that addition of the allyllithium reagent to the γ,δ-unsaturated acylsilane shown gave only the desired carbonyl adduct to be used for Diels–Alder ring formation, whereas use of the related γ,δ-unsaturated aldehyde (Me_3Si replaced by H), the more obvious and accessible reagent, gave a poor yield of the initial alcoholic adduct accompanied by much isomeric material difficult to separate (Scheme 10).

Another reaction of acylsilanes, that with diazomethane, led us to another functional group class. When acylsilanes are treated with diazomethane two products are formed in proportions which depend fairly predictably on the nature of the R group of the acylsilane [28]. On the one hand, normal 1,2-rearrangement of a group, always the silyl group in practice, to the CH_2 group of the diazomethyl group yields a β-ketosilane. Alternatively the reaction intermediate takes the oxyanion-to-carbanion rearrangement pathway yielding the isomeric silyl enol ether. Both processes take place with complete retention of configuration at silicon (Scheme 11).



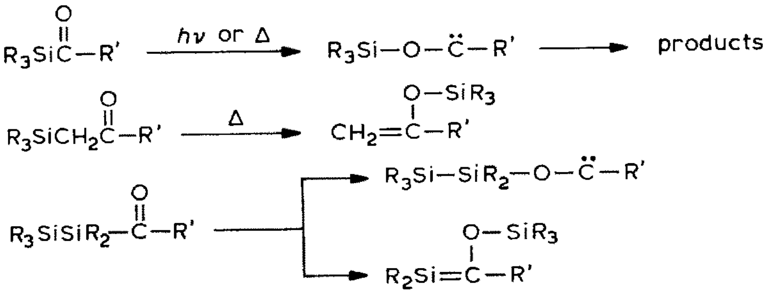
SCHEME 11

In investigating the β-ketosilanes it was found that although they did not have any interesting photochemistry they readily underwent an intramolecular thermal rearrangement under quite mild conditions to give silyl enol ethers. While this is not a sensible way to prepare silyl enol ethers it was a reaction of some interest mechanistically, involving a dipolar intermediate and retention of configuration at silicon [29], and considerable information about the details of the rearrangement was acquired (Scheme 12).



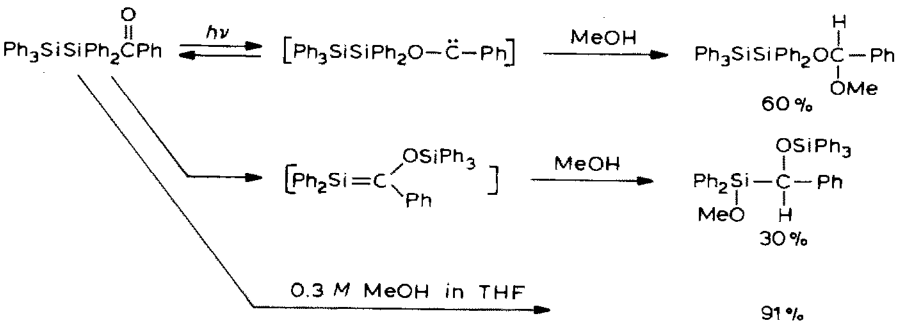
SCHEME 12. R' = alkyl, aryl, COOH, COOR; E_{act} 26–33 kcal/mol; ΔS^{*} −4 to −17 eu.

With the evidence that oxygen could interact either photochemically or thermally [30] with silicon located at the α position to give a siloxycarbene, or with silicon at the β position to give the silyl enol ether, we asked the question of what would happen with an acyldisilane. Reaction at the α silicon would be expected to yield the disilyloxycarbene, which was unlikely to be of great interest, but if the reaction occurred at the β silicon this might be a reaction of some interest, since the product should be a silaethylene (Scheme 13).



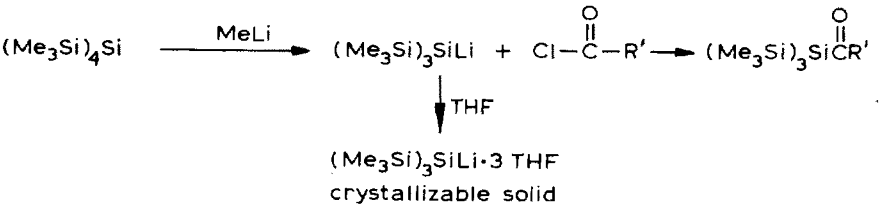
SCHEME 13

At this time, despite efforts stretching over decades, there had never been any evidence that silicon could form double bonds to itself, carbon or to any other element. However, in 1967 Gusel'nikov and Flowers [31], at the University of Bristol, produced evidence that silaethylenes, or silenes as they are now most commonly called, were produced as transient and highly reactive intermediates when silacyclobutanes were pyrolyzed at 400°C or higher. These were obviously awful conditions to use to try to study a reactive intermediate, and we hoped that the photolysis of an acyldisilane using long-wavelength low-energy radiation, perhaps at low temperatures, might serve as a better source of this elusive species. Early experiments suggested we were right, since photolysis of the acyldisilane in methanol, as shown below, gave products of methanol addition to both the disilyloxycarbene and to the anticipated silene. Modification of the conditions allowed formation of only the silene adduct (Scheme 14) [32,33].

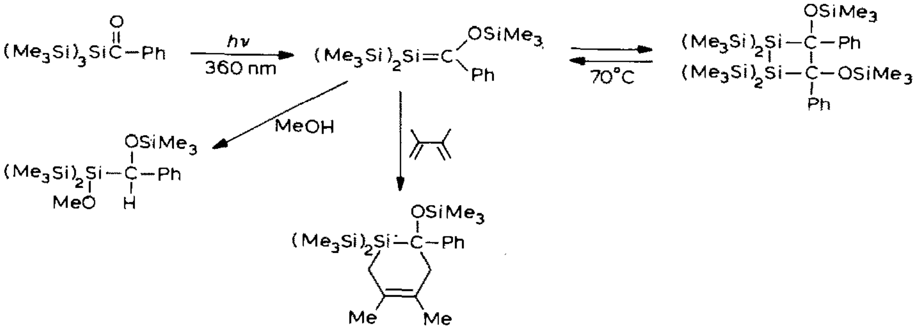


SCHEME 14

A change to tris(trimethylsilyl)acylsilanes, suggested by one of my research group, led to further success. The acylpolysilanes were made from tris(trimethylsilyl)silyllithium [34], which usually coupled cleanly with acid chlorides.

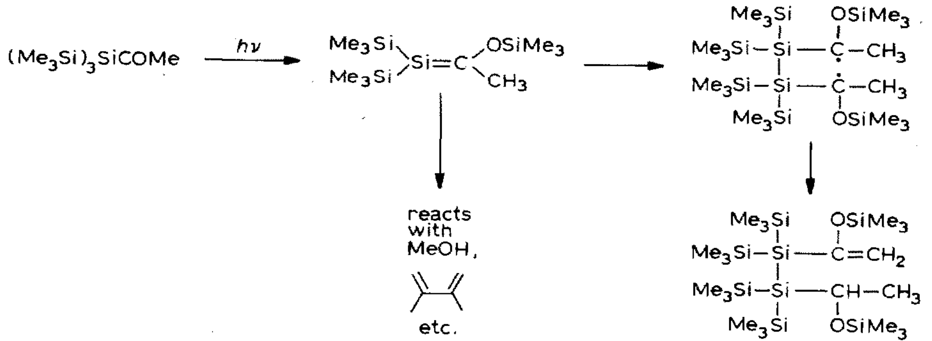


Photolysis of the benzoylpolysilane in alcohol gave the silene adduct and photolysis in the presence of dimethylbutadiene gave the expected Diels–Alder adduct of the silene. When photolyzed in inert solvent a dimer was formed, but what was surprising and unique was that the dimer was not the usual head-to-tail dimer formed by simple silenes consistent with the expected bond-polarization, but was instead the head-to-head dimer. The dimer evidently reverted to silene under mild conditions since warming at 70°C gave the expected silene adducts (Scheme 15) [33].



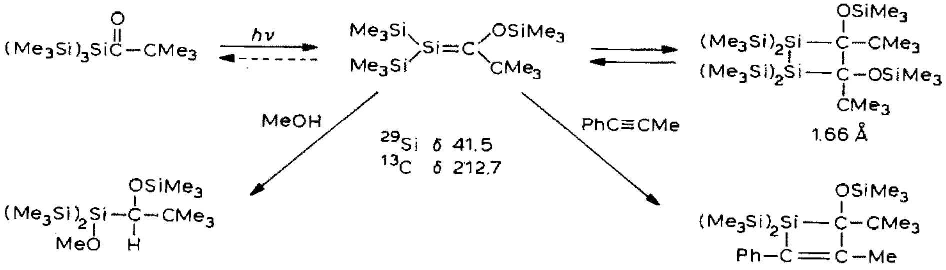
SCHEME 15

While all the silenes of this family have the unique property of forming head-to-head dimers, not all of these are 1,2-disilacyclobutanes. Thus the acetylpolysilane (and other related species with α hydrogen) forms a silene which couples head-to-head at silicon, possibly passing through a 1,4-diradical which subsequently disproportionates to the linear dimer saturated at one end and unsaturated at the other (Scheme 16).



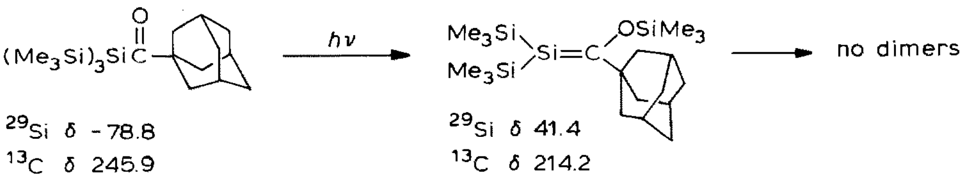
SCHEME 16

When we photolyzed the colourless solution of the t-butylacylsilane in inert solvent a yellow solution was formed whose NMR spectrum gave clear evidence not only for the presence of the head-to-head dimer but also another species, present in about a 4/1 excess, to which we attributed the structure of the silene monomer [33], based in particular on absorption attributable to an sp^2-hybridized carbon atom as well as a ^{29}Si NMR signal at 41 ppm below TMS, a very unusual position for a silicon atom to which silyl groups are attached, but consistent with its being due to sp^2-hybridized silicon [35]. This was the first silene produced and observed at room temperature, and it had a lifetime of about 2 weeks, totally unprecedented. This dimer was also of interest both because on dissolution it immediately formed an equilibrium mixture of monomer and silene dimer, and because the crystal structure revealed that the ring carbon–carbon bond was 1.66 Å long. This suggested that there was severe steric strain because of the bulky groups on carbon, causing the bond-lengthening, and further that perhaps if the steric bulk on carbon was increased even further it might be possible to inhibit dimer formation completely and thus make possible the isolation of the silene monomer (Scheme 17).



SCHEME 17

We chose to make the adamantoylsilane and this compound fulfilled our wildest expectations. Photolysis yielded a yellow solution, and the NMR spectrum indicated the total absence of dimers but the presence of the silene. Careful work-up led to the isolation of the first stable crystalline silene, a sample of which is unchanged after several years although if exposed to air the compound immediately disappears in a puff of smoke [36] (Scheme 18).

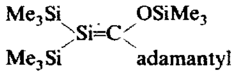


SCHEME 18

We have been successfull in acquiring a lot of data about the silene, which among other things indicated that the π-bond had appreciable strength since the silyl groups on silicon remained non-equivalent in the NMR spectra when heated to

TABLE 3

SPECTRAL DATA FOR



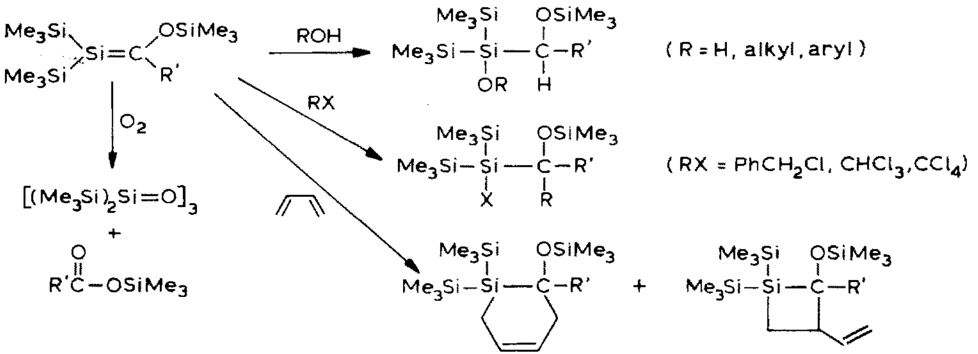
$(Me_3Si)_2Si{=}C(OSiMe_3)(\text{adamantyl})$

		Me_3Si	$C_{10}H_{15}$	other
NMR	^{1}H	δ 0.51, 0.47, 0.41	1.6–2.2 (br) ppm	
	^{13}C	δ 3.7, 2.7, 2.0	45.2, 42.7, 37.3, 29.4	=C< 214.2
	^{29}Si	δ −12.3, −12.6, 13.4 (Me_3SiO)		>Si= 41.4
UV		340 nm (ε 7400), very broad		
IR		1135 cm^{-1} (8.91 μm)		
MS	(CI)	m/z 411 $(MH)^+$		
IP	(PES)	7.7 eV (Courtesy Prof. H. Bock, Frankfurt)		

60°C, the highest temperature we could go without driving the silene back to the parent acylsilane. Some of these data are given in Table 3 [36,37].

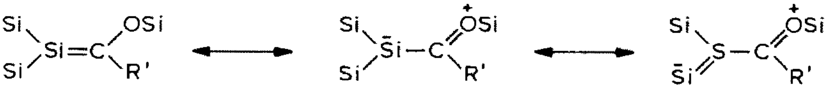
Thanks to the assistance of Professor Stanley Nyburg of our deparment we were able to determine the crystal structure of the silene. Two features were of particular interest. One was the length of the silicon–carbon double bond, 1.764 Å, rather longer than the best calculations suggested it should be, namely about 1.70–1.71 Å. Secondly, as Fig. 2 shows, the molecule has a twist of about 14.5° and considerable angle distortion at the sp^2-hybridized atoms, typical features for a highly sterically hindered molecule [36].

In the course of studying this family of more than a dozen silenes we have learned much about their chemistry: a few reactions are described below, where addition across the ends of the reactive double bond dominates the behaviour. Most reagents that add to alkenes add to silenes, which also react with a number of other types of reagent often under very mild conditions. Thus alcohols and water add rapidly across the double bond, as do HX and some alkyl halides such as benzyl chloride, chloroform and carbon tetrachloride. Dienes undergo both Diels–Alder [2 + 4] cycloaddition and also [2 + 2] cycloaddition in the dark, suggesting the possibility that some of these reactions are occurring by radical pathways under very mild conditions. Under controlled conditions oxygen cleaves the silicon–carbon double bond, yielding the trimer of the expected silanone and the silyl ester (Scheme 19).



SCHEME 19

It is pertinent to consider why these silenes are so much more stable than simpler less-substituted species. It seems clear that this is due to a combination of steric effects, which inhibit dimerization or other reactions, and substituent effects. Calculations by Apeloig [38] and others have shown that the combination of oxygen on carbon and silicon on silicon mutually assists in stabilizing the double bond, and contributions from structures such as shown below can help to explain the abnormally long double bond. In support of this description is the remarkably deshielded sp^2-hybridized carbon, which absorbs at about 214 ppm, and the shielded sp^2-hybridized silicon, which absorbs in the range 41–44 ppm (it is now known that sp^2-hybridized silicon may absorb in the range 40–144 ppm below TMS), consistent with positive charge on carbon and negative charge accumulation on silicon.



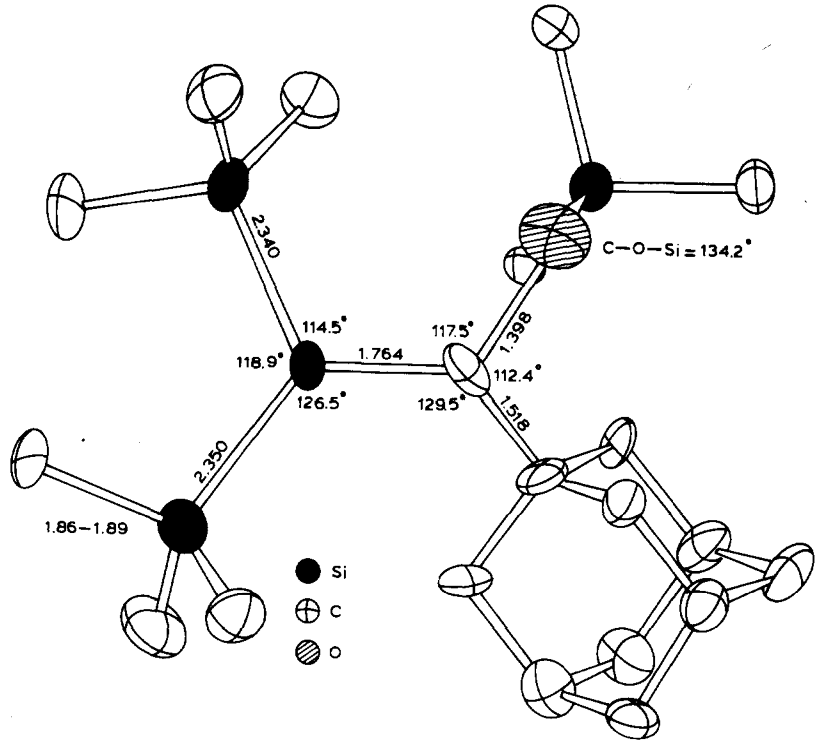


Fig. 1. Ortep diagram of adamantylsilene showing bond lengths and bond angles.

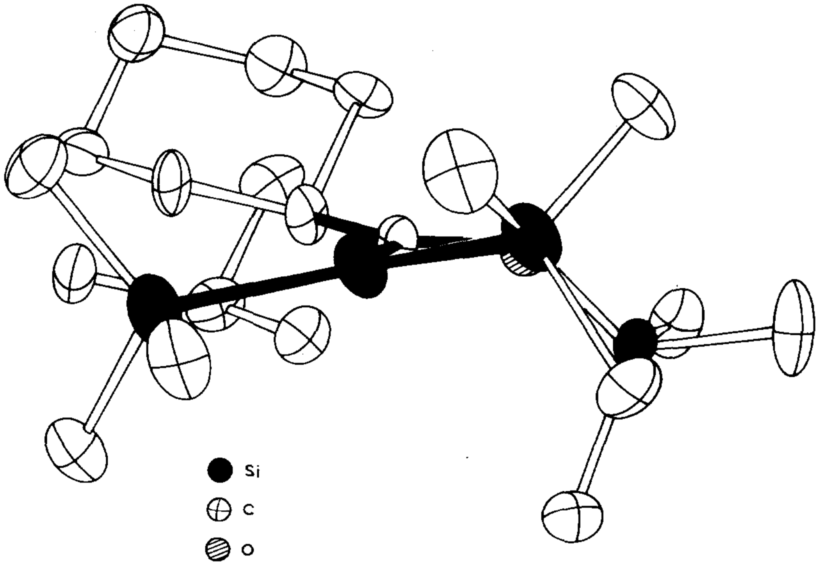
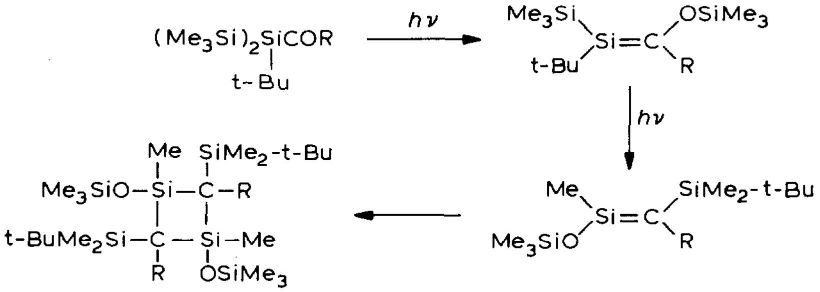


Fig. 2. Ortep diagram of adamantylsilene showing twist in silicon–carbon double bond.

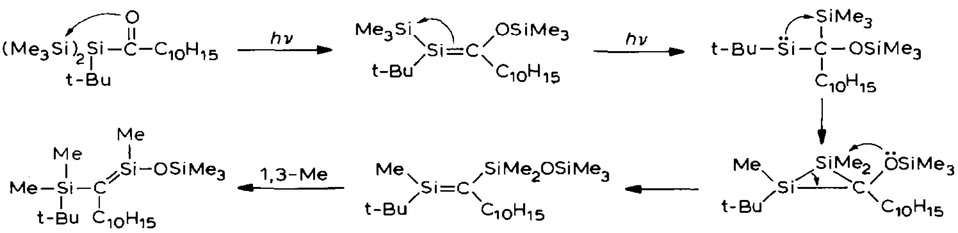
Some recent studies of the behaviour of other members of this silene family have indicated that there is still much interesting chemistry of the silicon–carbon double bond to be explored. It seemed likely that something could be learned about the role played by the silyl groups on silicon if they were replaced with groups like t-butyl or phenyl. The t-butylacylsilane shown below underwent normal photolysis to the silene as revealed by methanol trapping or NMR studies but on continued photolysis to remove the last of the acylsilane it was noted that the original silene signals disappeared and signals attributable to a new silene appeared. It was clear from the chemical shifts that this was a species with a very different structure. The new silene subsequently dimerized and a crystal structure confirmed that a head-to-tail dimer had formed from a silene which appeared to have three of the four groups originally attached to the double bond exchanged in some manner (Scheme 20) [39].



(R = $C_{10}H_{15}$)

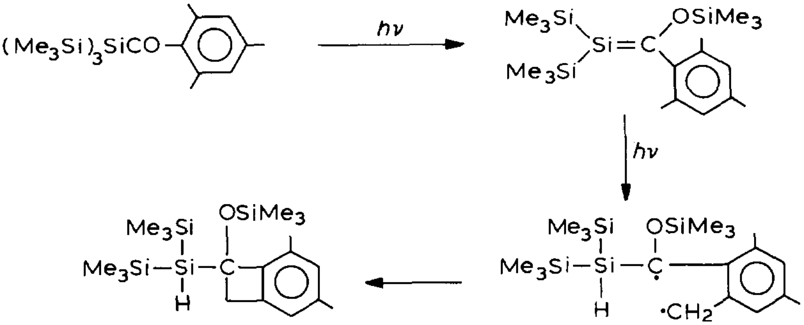
SCHEME 20

These results clearly indicate that there is a photochemistry of silenes to investigate. It is a challenge to explain what has occurred in this photochemical rearrangement and at present we can only propose as a working hypothesis a rather complex many-step pathway involving reactions for which some precedent is known. Thus silene-to-silylene rearrangements are known, although most commonly under thermal conditions, and thus trimethylsilyl group migration, followed by insertion of the silylene into a silicon–methyl bond, a reaction for which only limited precedent has been established, would lead to the disilacyclopropane shown. Photochemical ring-opening accompanied by trimethylsiloxy migration would lead to a new silene which, in accord with the recent findings of Eaborn [40] and of Wiberg [41], could be expected to undergo facile 1,3-methyl migration from silicon to silicon, leading to the silene which is clearly the precursor of the observed dimer. Considerable further effort will be needed before a full understanding of this behavior is gained (Scheme 21).



SCHEME 21

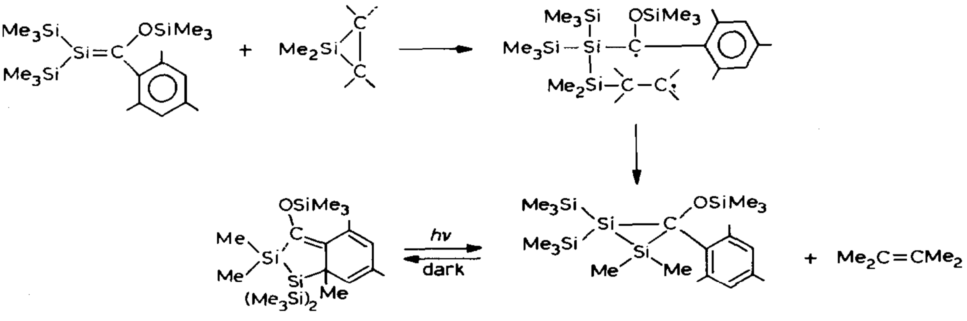
The possibility that a disilacyclopropane might be an intermediate in the above rearrangement led us to attempt the synthesis of an appropriate example by adding a silylene across the silicon–carbon double bond of a silene. In the belief that the adamantylsilene would be too sterically hindered, we made the mesitylsilene shown below, which was found to photochemically insert into one of the aromatic methyl groups to give the benzocyclobutene shown, somewhat surprising behavior since silenes do not normally insert into C–H bonds (Scheme 22).



SCHEME 22

When the same silene was allowed to react in the dark with hexamethylsilirane the elements of dimethylsilylene were added across the silicon–carbon double bond to form the disilacyclopropane shown (Scheme 23), although whether 'free' dimethylsilylene is involved, or whether the insertion into the double bond is a radical reaction, is not yet known. What is known, and is truly remarkable, is that on standing in the dark over a day or two the 3-membered ring undergoes ring expansion to give the bicyclic [4.3.0] ring system shown. This process can be reversed to regenerate the original disilacyclopropane by brief photolysis with radiation of > 360 nm and the system has been cycled back and forth several times without any major side reactions. This appears to be a remarkable case where ring strain in the 3-membered system just about balances the aromatic resonance energy lost as a result of the rearrangement [41]. Needless to say we are pursuing this interesting reaction further.

This brings me to the end of this personal account of how one thing has led to another, and in telling it I may have been remiss in not acknowledging the activities



SCHEME 23

of other research groups going on at more less the same time which, in some cases, may have had an important influence on our own efforts and conclusions: I seek the forgiveness of those so neglected. In the course of over thirty years research on organosilicon chemistry we have learned quite a bit about a number of new classes of carbon-functionalized organosilicon compounds. It is clear that silicon interacts very strongly with many neighbouring functional groups, especially those with oxygen or other electronegative elements, and that this interaction can be exploited to effect useful and interesting molecular rearrangements. Reference to the current chemical literature clearly reveals how organic chemists are exploiting this behavior in many ways to effect otherwise difficult syntheses, aided by the fact that silicon is generally very easy to remove from a molecule once its directing or protecting role is over. I believe our kind of research has helped to establish some of the ground rules of how this very abundant and interesting element can be profitably used in organic synthesis.

It goes without saying that this research could never have been accomplished but for the efforts, dedication, and enthusiasm of a large number of graduate and undergraduate students and post-doctoral fellows over the years whose stimulating suggestions for the conduct of our research have done much to lead us where we are today. I am exceedingly grateful to them. I am also very grateful for the support of my academic colleagues at the University of Toronto, and to the Natural Science and Engineering Council of Canada whose annual financial support, coupled with the Dow Corning Corporation's support over several years, has made it all possible.

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