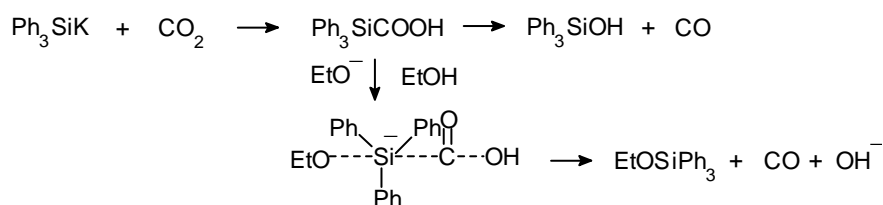
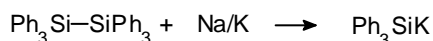


The Si=C Story: How It Happened.

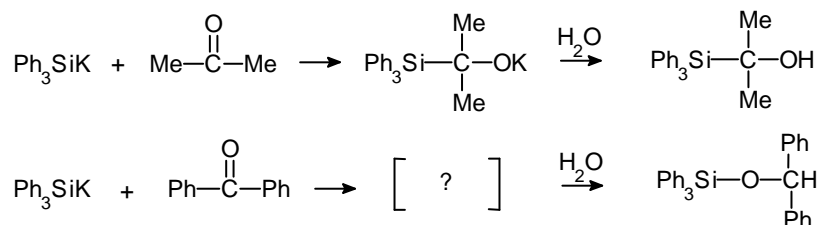
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I first got involved with organosilicon chemistry in 1952, when I spent a year as post-doctoral fellow with Professor Henry Gilman at what is now known as Iowa State University. Gilman's group had just learned how to make triphenylsilylpotassium, the first organosilylmetallic reagent and were investigating its properties. One of my contributions was to carbonate it to get pure triphenylsilanecarboxylic acid for the first time.

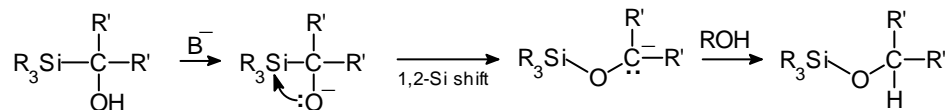


The acid showed unusual properties in that at its melting point it frothed vigorously, evolving carbon monoxide! In solution in a protic solvent such as ethanol containing a little base, it again evolved carbon monoxide vigorously at room temperature, strange behavior for a carboxylic acid.

It was also found that when the silylmetallic reagent was treated with simple carbonyl compounds such as acetone the expected alcohol was obtained, whereas treatment with an aromatic carbonyl compound gave the isomeric silyl ether.

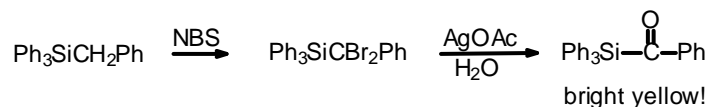


Over the years I investigated this behavior in detail and established that silylcarbinols underwent a base-catalyzed rearrangement to their isomeric silyl ethers, a process that became known as the Brook rearrangement.



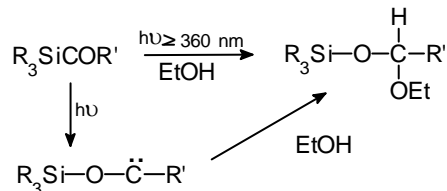
This was a second example of unusual behavior of a common functional group when it was adjacent to silicon.

A logical extension of this study was to make a ketone analog with the skeleton Si-CO-C, a species which we erroneously called silylketones for a while, but which are properly named acylsilanes.

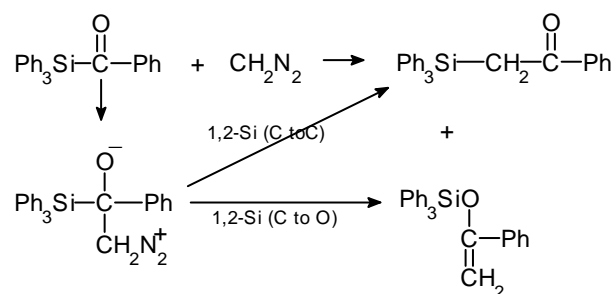


The first one we made, benzoyltriphenylsilane, was coloured yellow, although its carbon analog beta-benzpinacolone was colourless. That an organosilicon compound could be coloured was unheard of at the time, and I well remember Cecil Frye, during a visit to Dow Corning, trying to persuade me that I had a coloured impurity in my material. After all, silicon didn't form double bonds, so conjugation and resonance contributions were impossible, and hence silicon analogs of coloured carbon compounds wouldn't be coloured if silicon were part of the chromophoric system. Well acylsilanes can be coloured, due to interactions of silicon with the adjacent carbonyl group.

We spent a lot of time studying the spectroscopic and chemical properties of a variety of acylsilanes. One important reaction was their 1,2-photochemical isomerization to yield transient siloxycarbenes, Si-O-C:, using visible or near UV radiation: the siloxycarbenes were readily trapped by alcohols to yield mixed acetals.

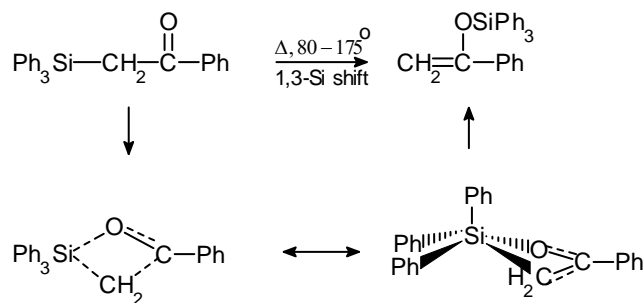


A second reaction of interest was with diazomethane where a mixture of two compounds was formed, an α -silylketone (or β -ketosilane), Si-C-CO-C, and also its siloxyalkene isomer, Si-O-C=C.



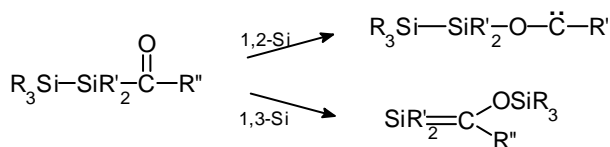
The β -ketosilane resulted from the relatively conventional C to C migration of the silyl group in an intermediary adduct, and the siloxyalkene arose from an analog of the Brook rearrangement, where the silyl group migrated 1, 2 to oxygen.

The β -ketosilanes had no unusual spectroscopic properties, but were found to undergo a thermal rearrangement under very mild conditions involving a 1,3-silyl carbon-to-oxygen migration, with retention of configuration at a chiral silicon centre, to yield siloxyalkenes.

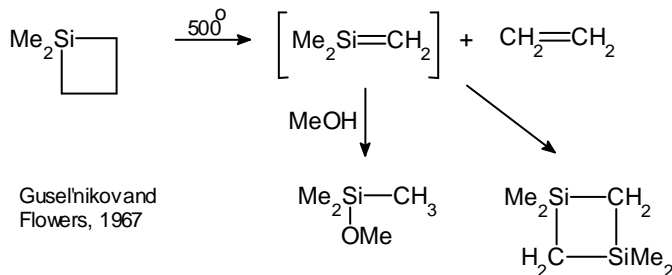


Recent findings by Kira¹ suggest that this rearrangement involves a distorted square pyramidal intermediate.

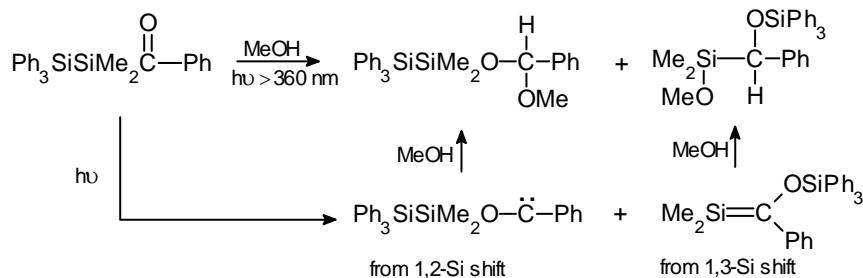
This result led us to wonder what would happen if an acyldisilane was photolyzed or thermolyzed.



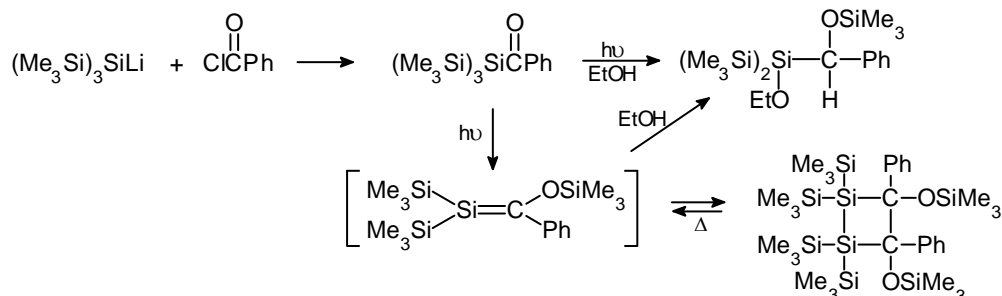
Would a 1,2-C to O silyl shift occur (as with a simple acylsilane) involving the adjacent α silicon atom to give a disilyloxycarbene, or would a 1,3-C to O silyl shift involving the β silicon atom occur (like a β -ketosilane) to give a compound containing a silicon-carbon double bond? This latter possibility was of great interest. The work of Gusel'nikov and Flowers² had recently shown convincingly that a silene was formed when dimethylsilacyclobutane was heated at about 500°C, the first compelling evidence that a silicon-carbon double bond could form.



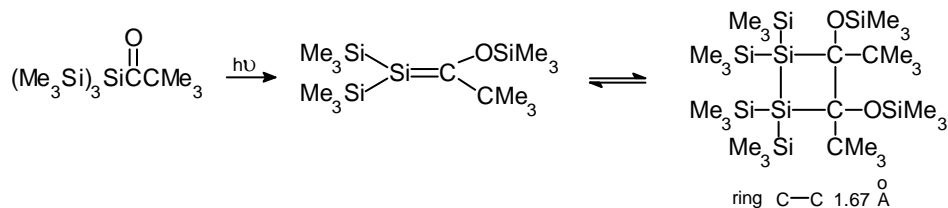
We hoped our approach to silenes using acyldisilanes, if it worked, would be a much milder method for the generation of silenes which might make their study easier. And it did work. When each of several acyldisilanes were photolyzed with long wavelength radiation in ethanol solution, mixtures of the ethanol-trapped disilyloxycarbene and ethanol-trapped silene were isolated. Some of this work was carried out by one of my graduate students under the supervision of my post-doc and colleague Alan Bassindale while I was absent on sabbatical leave.



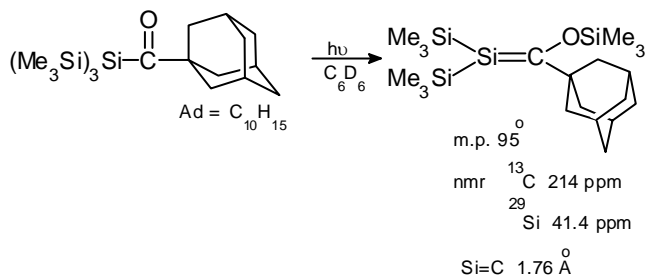
At this time we switched from acyldisilanes to acylpolysilanes, coupling the Gilman reagent tris(trimethylsilyl)silyllithium with various acid chlorides. With benzoyl chloride we got a yellow acylsilane which when photolyzed in ethanol gave the trapped product of the anticipated silene, or when photolyzed in inert solvent gave rise to a dimeric species which we showed to be the head-to-head cyclic dimer of an intermediate silene.



When we used pivaloyl chloride the acylsilane on photolysis in inert solvents gave NMR spectra that clearly showed the presence of three species – the starting polysilylacylsilane, the head-to-head cyclic dimer of an intermediary silene, and a third set of signals which we attributed to the silene itself, signals which persisted for days, indicating that we had a stable silene in solution³.



In hopes of discouraging dimer formation, and hence favouring silene formation, we decided to try and increase the steric bulk of the organic group attached to the carbonyl carbon and we replaced the t-butyl group by a 1-adamantyl group. Photolysis of that acylsilane gave rise to only one set of NMR signals, those of the silene, and careful workup in the absence of air or moisture gave rise to crystalline adamantylsilene, characterized spectroscopically, by analysis, and by an X-ray diffraction crystal structure^{4, 5}.



This work, together with the elegant work from Bob West's laboratory on the Si=Si bond, going on at the same time, clearly established by 1981 that, despite the synthetic efforts of numerous earlier workers, and the predictions of theoreticians, silicon could indeed form stable multiple bonds. However, since most of the functionally-substituted classes of organosilicon compound we used were not even known when we started this work, I could never have

predicted that by following what now appears to be a logical sequence of studies, we would end up with stable silenes. Subsequent work in our laboratory has revealed much about the chemical behavior of the silicon-carbon double bond, including the fact that it is stable enough for geometrical isomers of suitably substituted compounds to exist, and numerous other chemists have subsequently created other examples of stable silenes.

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- 1 M. Takahashi and M. Kira *J. Am. Chem. Soc.* **1999**, *121*, 8597
 - 2 L. E. Gusel'nikov and M. C. Flowers, *Chem. Commun.* **1967**, 864
 - 3 A. G. Brook *et al*, *Chem. Commun.* **1981**, 191.
 - 4 A. G. Brook *et al*, *J. Am. Chem. Soc.* **1982**, *104*, 5667.
 - 5 S. C. Nyburg, A. G. Brook *et al*, *Acta Crystallographica*, **1985**, *C41*, 1632.