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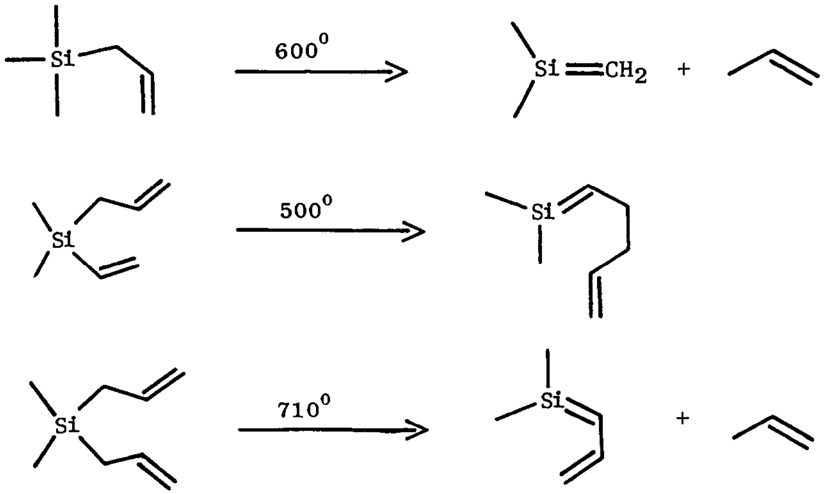
ON THE MECHANISM OF THE ALLYLSILANE-TO-VINYLSILANE REARRANGEMENT[1,2]

Susan M. Neider, Gregory R. Chambers,[3] and Maitland Jones, Jr.*
Department of Chemistry, Princeton University, Princeton, New Jersey 08544

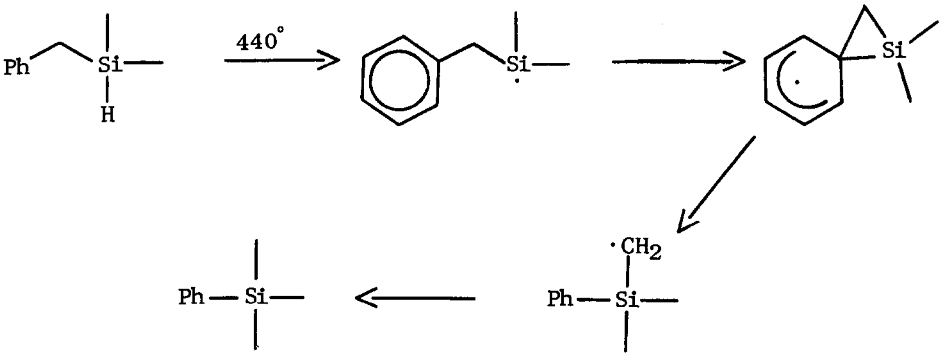
SUMMARY: The mechanism of the thermal conversion of allyltrimethylsilane to trimethylvinylsilane does not involve methylene extrusion. Rather, a methyl group originally bound to silicon is lost.

The heating of substituted allylsilanes results in an extraordinary variety of reactions. In addition to the "simple" [1,3]trimethylsilyl shift,[4] retro "ene" reactions in both simple allylsilanes[5] and diallylsilanes[6] have been claimed. Allylvinylsilane equilibrates with a silene through a Cope rearrangement.[7]

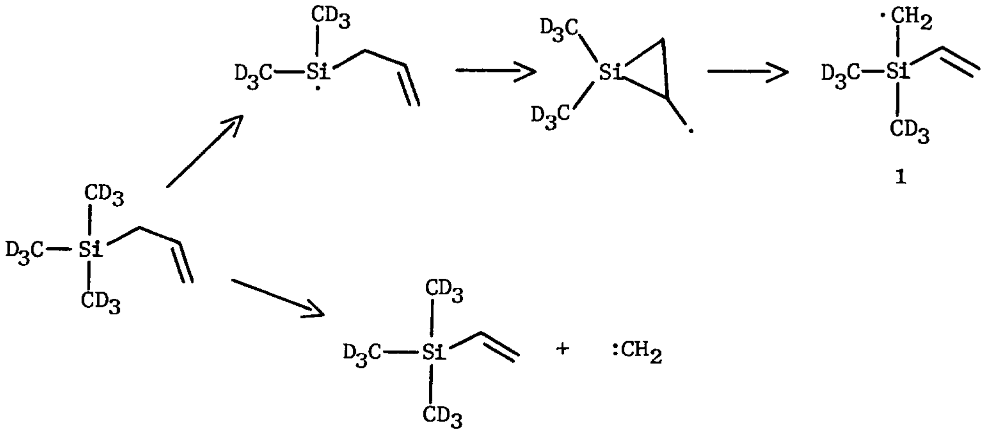


Superimposed upon this already complex chemistry is the report by Sakurai, Hosomi, and Kumada[8] that allyltrimethylsilane undergoes conversion to trimethylvinylsilane under conditions rather similar to those of ref. 5. A mechanism involving loss of methylene from the previous mechanism, this process requires loss of a methyl carbon and its attendant hydrogens. Cleavage of a silicon-allyl bond would lead ultimately to trimethylsilane and propylene. Recombination of methyl and trimethylsilyl radicals would give tetramethylsilane, the remaining major product reported.[8]

Analogy for this mechanism exists in the work of Sakurai, Hosomi and Kumada, who noted the conversion of benzyldimethylsilane to phenyltrimethylsilane[10] at 440° C. The most likely mechanism is shown below:



Pyrolysis of allyltrimethylsilane, fully deuterated in the methyl groups, allows a distinction between the two mechanisms. Loss of CH_2 from the allyl group would lead to



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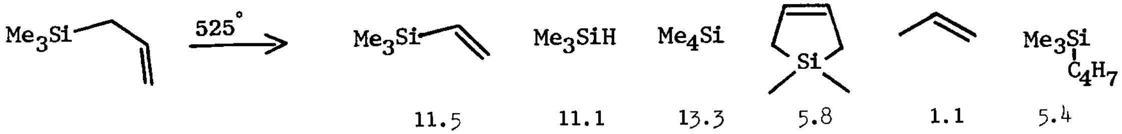
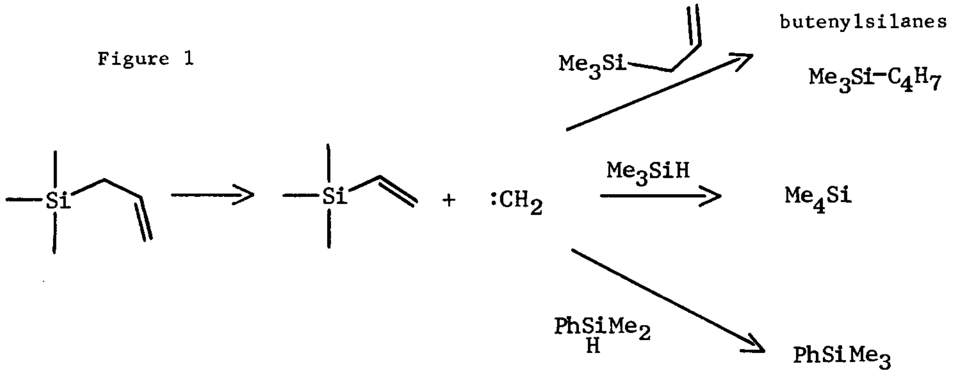


allyl group was proposed[8] (Figure 1). Tetramethylsilane and the butenylsilanes were claimed to be the result of reaction of CH_2 with starting material or trimethylsilane. Photolysis in the presence of added "methylene traps" such as dimethylphenylsilane led to other apparent reactions of CH_2.

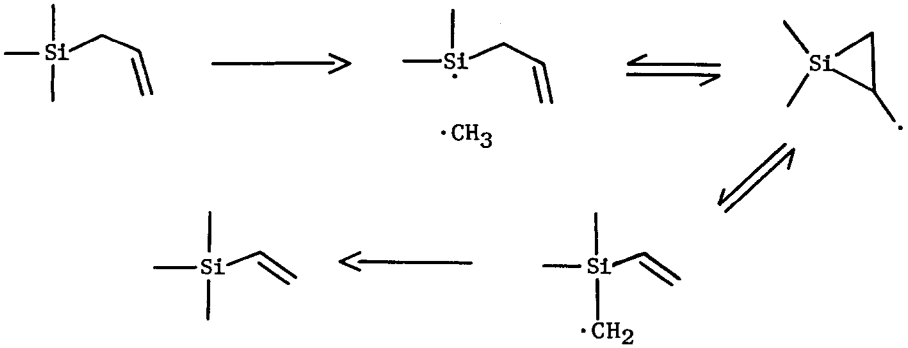
Figure 1



The thermal extrusion of CH_2, occasionally proposed, but as yet undemonstrated,[9] aroused our interest and prompted an appropriate labeling experiment, the results of which we describe here.

A reasonable alternative to CH_2 extrusion is shown below in Figure 2. Unlike the

Figure 2



trimethylvinylsilane fully deuterated in the methyl positions. The alternate mechanism (Fig. 2) leads to radical **1** and requires at least two protons in the final product. *A priori* we felt unable to predict whether **1** would abstract yet another proton from the environment or a deuteron from starting material, but in either event, the distinction between the two mechanisms would be clear.

We were able to reproduce the results of Sakurai *et al.*[8,11] Pyrolysis at 600° C through a quartz tube packed with aged quartz chips using nitrogen as carrier gas (30 ml/min) led to small conversions to trimethylvinylsilane. Pyrolysis of allyltrideuteriomethylsilane ($>$95% deuterated) led to trimethylvinylsilane containing 2.67 protons in the methyl position. Analysis of recovered starting material showed that only *ca.* 0.67 H had been incorporated into the methyl groups. Thus a minimum of two protons appears in the methyl groups of product. When trideuteriomethylvinylsilane was exposed to the reaction conditions, no exchange was found.

Thus no extrusion of methylene is required, and the evidence is solidly in favor of the mechanism postulated in Figure 2.

REFERENCES AND NOTES

1. Support from the National Science Foundation through Grant CHE 77-24625 is gratefully acknowledged.
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3. Allied Chemical Fellow, 1978-9.
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11. The implications of this regarding the work of Bailey[5] are unclear. Perhaps the geometry of the pyrolysis apparatus or contact time is responsible for the disparate results.

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