The Vapour-phase Thermolysis of Allyltrimethylsilane to Vinyltrimethylsilane: a Novel Methylene-transfer Reaction[1]

By HIDEKI SAKURAI* and AKIRA HOSOMI
(*Department of Chemistry, Faculty of Science, Tohoku University, Sendai* 980, *Japan*)
and MAKOTO KUMADA
(*Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto* 606, *Japan*)

Summary Allyltrimethylsilane was thermolysed to vinyltrimethylsilane at 500° with loss of the methylene group, the latter being inserted into an Si–H bond of $RMe_2Si–H$ by forming $RMe_2Si–Me$.

IN a previous paper,[2] a ($p\rightarrow d$) homoconjugation effect was suggested to explain an enhanced reactivity of allyltrimethylsilane towards the addition of trichloromethyl radicals. Subsequent investigation to explore such an intramolecular interaction between a silicon atom and a non-adjacent π-electron system led to the discovery of a new type of rearrangement.[3]

$$Ph[CH_2]_nSiMe_2H \rightarrow H[CH_2]_nSiMe_2Ph$$

We now report another example of such an interaction, leading to an unusual thermal degradation of allyltrimethylsilane to vinyltrimethylsilane accompanied by methylene transfer.

After allyltrimethylsilane was thermolysed at 500° by passing it through a glass tube mounted in a thermostatted furnace with nitrogen as a carrier gas, the products were collected in a trap immersed in a Dry Ice–methanol bath. Trimethylsilane, tetramethylsilane, vinyltrimethylsilane, and unchanged allyltrimethylsilane were detected in the reaction mixture together with small amounts of other products. These products were separated from the mixture by g.l.c. and the structures were unequivocally determined by i.r. and n.m.r. spectra. The results are listed in the Table.

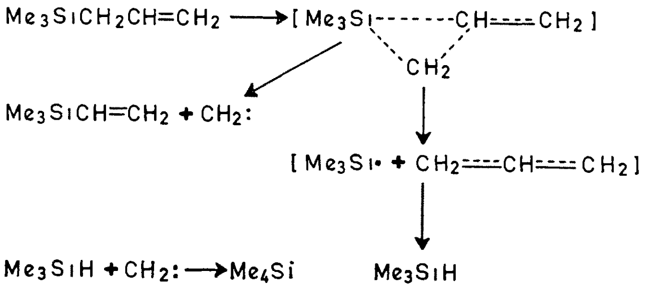
An important primary reaction would be one to give trimethylsilyl and allyl radicals and subsequently products such as trimethylsilane and propylene may result from hydrogen abstraction. However, as seen in the Table, vinyltrimethylsilane was a characteristic main product whose formation is very difficult to explain only by standard radical reactions.

We suggest the mechanism shown in the Scheme for formation of vinyltrimethylsilane

Thermolyses of allyltrimethylsilane[a]

Reaction temp (°)	500	525
Allyltrimethylsilane, treated (g)	5 00	6 00
Mixture, recovered (g)	4 70	5 90
Products (g l c area %)		
$MeCH{=}CH_2$	trace	1 09
Me_3SiH	4 30	11 06
Me_4Si	6 12	13 28
$Me_3SiCH{=}CH_2$	8 27	11 54
$Me_3SiCH_2CH{=}CH_2$	74 96	54 79
1 1 Dimethyl 1 silacyclopent 3 ene	3 90	5 83
Unidentified[b]	2 43	5 42

[a] Typical results of numerous experiments are listed
[b] Presumably butenyltrimethylsilanes (by g l c)



SCHEME

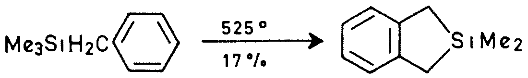
Formation of methylene and its subsequent insertion into an Si–H bond[4] were further supported by the fact that thermolysis of allytrimethylsilane at 525° with an excess of phenyldimethylsilane or (trimethylsilylmethyl)dimethylsilane in otherwise the same conditions gave phenyltrimethylsilane or hexamethyldisilylmethylene, respectively, in about 10% yield, at the expense of tetramethylsilane as product

$$Me_3SiCH_2CH{=}CH_2 + RMe_2SiH \rightarrow Me_3SiCH{=}CH_2 + RSiMe_3$$

$$(R{=}Ph \text{ or } Me_3SiCH_2)$$

When methylene was produced, it would also react with allyltrimethylsilane Since methylene would contain an excess of internal energy in addition to the thermal energy, the products would decompose to various compounds We could detect only butenyltrimethylsilanes as such products (by g l c)

The formation of 1,1-dimethyl-1-silacyclopent-3-ene[5] may be explained by the cyclization of allyldimethylsilylmethyl radicals This type of reaction represents the main course of the thermolysis of benzyltrimethylsilane Thus, thermolysis of benzyltrimethylsilane by the same procedure afforded mainly 2,2-dimethyl-2-silaindane



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