Journal of Organometallic Chemistry, 195 (1980) C1—C4

Preliminary communication

REARRANGEMENT OF BIS(TRIMETHYLSILYL)SILYLENE $(Me_3Si)_2Si$ IN THE GAS PHASE; NEW SILYLENE-TO-SILYLENE INTERCONVERSIONS

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(Received April 28th, 1980)

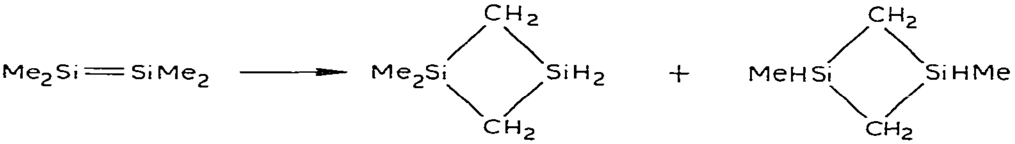
Summary

When bis(trimethylsilyl)silylene, $(Me_3Si)_2Si$, is generated in the gas phase by flow pyrolysis of methoxytris(trimethylsilyl)silane, $(Me_3Si)_3SiOMe$, or chlorotris(trimethylsilyl)silane, $(Me_3Si)_3SiCl$, the dominant reaction is rearrangement, producing as the major product in ca. 60% yield 1,1,4,4-tetramethyl-1,2,4-trisilacyclopentane.

The finding several years ago that dimethylsilylene can undergo dimerization in the gas phase [1]:

$$2\ Me_2Si: \rightarrow Me_2Si{=}SiMe_2 \rightarrow \text{rearrangement}$$

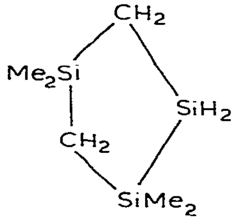
was followed by a renewal of interest in the mechanism of the rearrangement that converts tetramethyldisilene into isomeric dimethyl-1,3-disilacyclobutanes [2].



Wulff, Goure and Barton have recently proposed as an alternative to the radical-mediated rearrangements suggested by Roark and Peddle [2] a mechanism including an unprecedented silylene-to-silylene interconversion [3].

In this communication we report that bis(trimethylsilyl)silylene, $(Me_3Si)_2Si$, a molecule whose dimerization in solution has been reported [4], undergoes intramolecular reactions in the gas phase. The major product, a novel 1,2,4-trisilacyclopentane, can be rationalized by an extended sequence of silylene-to-silylene rearrangements.

When methoxytris(trimethylsilyl)silane, $(Me_3Si)_3SiOMe$, is subjected to flash vacuum pyrolysis at pressures below 30 millitorr and temperatures of 500 ± 5°C in a flow system, 73% decomposition occurs. At least nine products are detected by vapor chromatography, but all are produced in yields below 10% except for the major product, whose yield is 60% based on unrecovered starting material. Its structure, deduced from the nuclear magnetic resonance and mass spectrometric data (Table 1) is:



The PMR spectrum of this compound displays a pair of triplets of equal area, one in the Si—H region, the other upfield from TMS. This suggested the presence of a CH_2SiH_2 unit, and this was confirmed by comparison of the coupling constants, and by spin-decoupling. The other structural unit $XSiMe_2CH_2SiMe_2Y$ was suggested by the following spectroscopic features: 1. There is a second peak upfield from TMS, a singlet equal in area to the triplet. 2. There are two different peaks slightly downfield from TMS, each with an area three times that of the CH_2 and SiH_2 peaks. Independent evidence for the presence of four different kinds of carbon atoms in ratio 1/1/2/2 is provided by the decoupled ^{13}C NMR spectrum. The suggested structure is in accord with all these data.

TABLE 1

PHYSICAL PROPERTIES OF 1,1,4,4-TETRAMETHYL-1,2,4-TRISILACYCLOPENTANE

PMR (C_6D_6): δ 3.75 (Si—H, t, *J* 4.7 Hz, 2H), 0.25 (CH_3, s, 6H), 0.10 (CH_3, s, 6H), −0.16 (CH_2, t, *J* 4.7 Hz, 2H), −0.28 (CH_2, s, 2H).

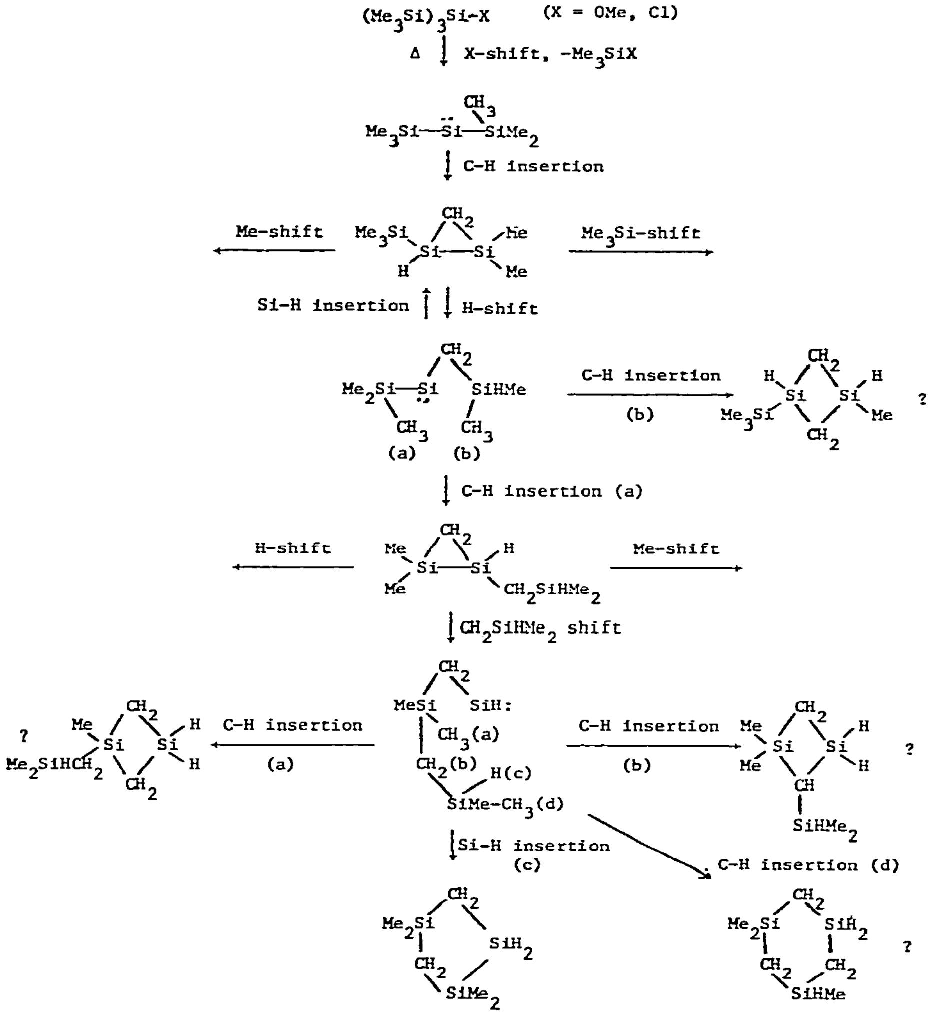
^{13}C NMR (C_6D_6): δ 1.410, 0.181, −0.754, −8.593 ppm (relative areas 1.0/1.7/1.6/1.0).

Mass spectrum: *m/e* 174 (parent), 159 (base).

The same product predominates when $(Me_3Si)_3SiCl$ replaces the methoxysilane as the silylene precursor. Reaction scheme 1 is proposed to account for its formation.

The reaction sequence is initiated by a conventional α-elimination forming bis(trimethylsilyl)silylene, a common thermal reaction of polysilanes [5]. This is followed by a series of intramolecular rearrangements including silylene C—H insertions to form disilacyclopropanes, α-eliminations that open these highly strained rings to β-silylsilylenes, and further intramolecular C—H and Si—H silylene insertions that can produce larger rings capable of surviving the reaction conditions.

The bis(trimethylsilyl)silylene system has many opportunities for rearrangement, and in Scheme 1 only those intermediates are shown that are required for



SCHEME 1

the formation of the major product. The predicted products indicated with queries but not yet identified are those expected to arise directly from these intermediates. Branches leading to other reactive intermediates are indicated by arrows. The full reaction scheme predicts the formation of eleven different cyclic structural isomers, six 1,3-disilacyclobutanes, three 1,2,4-trisilacyclopentanes and two 1,3,5-trisilacyclohexanes.

Work on the identification of the minor products continues in order to clarify the factors that lead to the predominant formation of 1,1,4,4-tetramethyl-1,2,4-trisilacyclopentane. It is clear that intramolecular rearrangement of bis(trimethylsilyl)silylene is rapid under conditions where dimethylsilylene undergoes dimerization. Silylene-to-silylene interconversions can give a preparatively useful yield of an unusual product, but the ability to control such reactions depends on the increased mechanistic knowledge toward which present studies are aimed.

Acknowledgments

We thank Professor Thomas J. Barton for helpful discussions, Mr. Jong Pyng Hsu for mass spectrometric analyses, and Mr. Gerard M. Sullivan for assistance with ^{13}C NMR spectroscopy. Financial support from the United States Department of Energy is gratefully acknowledged. This is technical report C00-1713-86.

References

1 R.T. Conlin and P.P. Gaspar, J. Amer. Chem. Soc., 98 (1976) 868.
2 D.N. Roark and G.J.D. Peddle, J. Amer. Chem. Soc., 94 (1972) 5837.
3 W.D. Wulff, W.F. Goure and T.J. Barton, J. Amer. Chem. Soc., 100 (1978) 6236.
4 Y. Nakadaira, T. Kobayashi, T. Otsuka and H. Sakurai, J. Amer. Chem. Soc., 101 (1979) 486.
5 W.H. Atwell and D.R. Weyenberg, Angew. Chem. Int. Ed., 8 (1969) 469.