

Preliminary communication

DIMETHYLSILYLENE TRANSFER FROM HEXAMETHYLSILIRANE TO OLEFINS

DIETMAR SEYFERTH and DENNIS C. ANNARELLI

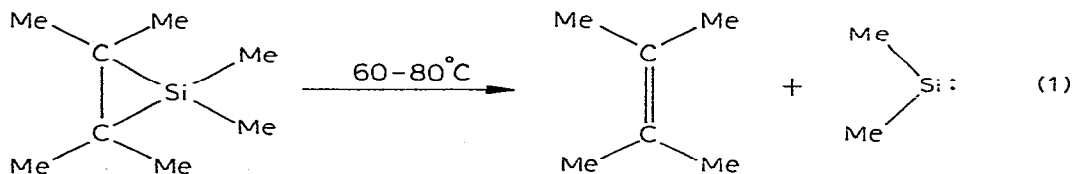
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received May 21st, 1976)

Summary

The thermolysis of hexamethylsilirane in the presence of *cis*- and *trans*-4-octene, cyclooctene, propenyltrimethylsilane and trimethylethylene resulted in dimethylsilylene transfer and formation of the respective silacyclopropanes. In contrast, silacyclopentane derivatives were formed when such thermolysis was carried out in the presence of styrene and α -methylstyrene. This is believed to be a result of the interception of the intermediate diradical from hexamethylsilirane ring opening by the styrene.

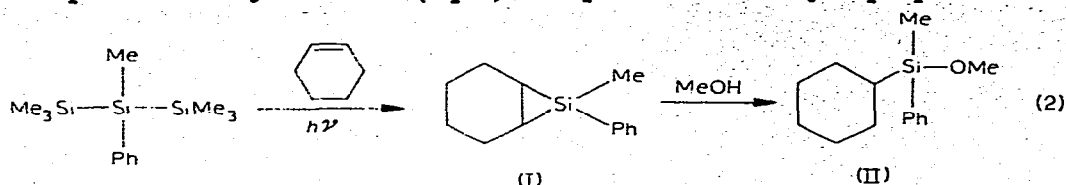
Recently we reported that hexamethylsilirane undergoes thermal decomposition at 60–80°C with extrusion of dimethylsilylene and formation of tetramethylethylene [1] (eq. 1). If appropriate substrates were present during the



thermolysis of hexamethylsilirane, dimethylsilylene transfer chemistry was observed, e.g., insertion into Si—H and Si—OMe bonds and formal 1,4-addition to 2,3-dimethylbutadiene [1]. We have been able to effect thermal dimethylsilylene transfer from hexamethylsilirane to other olefins to form new silacyclopropanes and have obtained results which may have a bearing on the Me_2Si transfer mechanism.

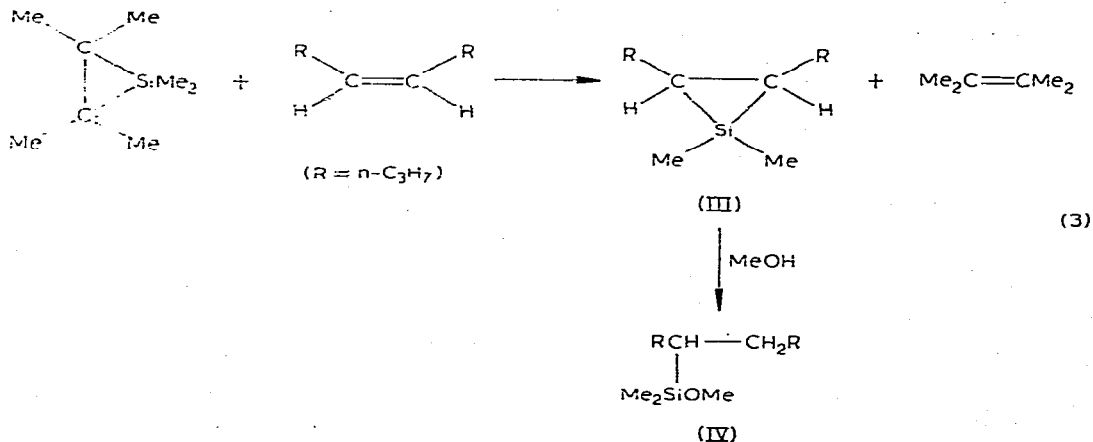
All earlier efforts to prepare silacyclopropanes by addition of a silylene to a C=C bond or even to obtain conclusive evidence for the intermediacy of a silacyclopropane in such a reaction had been unsuccessful [2] until in 1974 Ishikawa and Kumada [3] provided chemical evidence that a silacyclopropane had been formed when MePhSi was generated by photolysis of $\text{Me}_3\text{SiSiMePhSiMe}_3$

in the presence of cyclohexene (eq. 2). The presence of silacyclopropane I was



inferred on the basis of its reaction with methanol to give II in 22% yield. It could not be isolated or even detected spectroscopically.

Our procedure based on the thermolysis of hexamethylsilirane can give excellent results, as illustrated by its use in Me_2Si transfer to *cis*-4-octene. Hexamethylsilirane was prepared in THF solution [3]. The THF was removed at 65–70 mmHg during a 3 h period at room temperature from a sample of the solution. Analysis [1] showed that 1.70 mmol of the silirane remained behind in the 25 ml one-necked reaction flask which then was equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring unit. (In view of the high reactivity of hexamethylsilirane to oxygen and moisture, all operations must be performed under an inert atmosphere). 5 ml of *cis*-4-octene was added to the silirane and the resulting solution was stirred and heated at 75°C under nitrogen for 15 h. The solution was cooled to room temperature and 0.5 ml of anhydrous methanol added. An exothermic reaction resulted. GLC analysis showed that one product had been formed in 69% yield. This was collected by GLC and identified (analysis, IR, NMR) as IV. Tetramethylethylene was produced in high yield. The results are summarized in eq. 3. In a separate

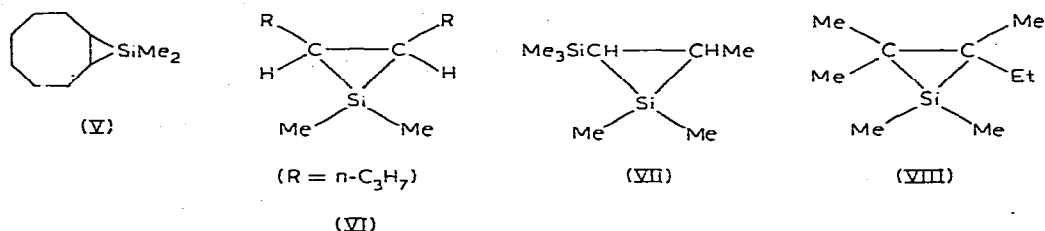


experiment, a portion of the reaction mixture was transferred to an NMR tube before methanolysis and a ^{29}Si FT NMR spectrum was obtained. With proton decoupling, a resonance at 59.8 ppm upfield from tetramethylsilane was observed*. A ^{29}Si NMR resonance in the region 50–60 ppm upfield from TMS is characteristic of silacyclopropanes [4] and thus provides good direct evidence that III was present. It is of interest to note that an attempt to transfer Me_2Si from III back to tetramethylethylene was not successful. After a heating

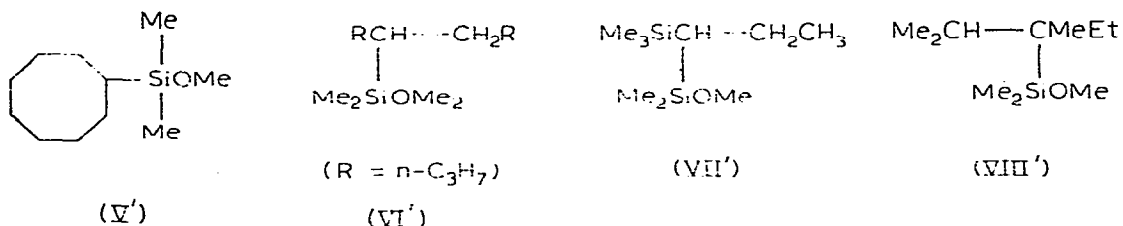
* A ^{29}Si NMR spectrum of the reaction mixture prior to heating showed the 49.5 ppm resonance characteristic of hexamethylsilirane [3].

period of 42 h at 66°C, 32% of III still was present, but no hexamethylsilirane had been formed, according to the results obtained on methanolysis of the reaction mixture. Evidently, not all siliranes decompose by a silylene extrusion pathway, a point that is receiving more detailed study.

Similar Me_2Si transfer reactions were successful in preparing silacyclopropanes (V (35%), VI (25%), VII (48%) and VIII (68%)), as indicated by formation of

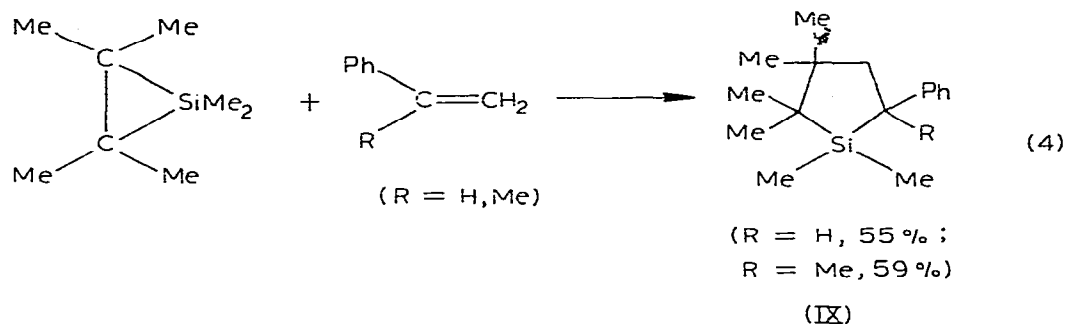


the appropriate methanolysis products, V', VI', VII' and VIII'. No methanolysis

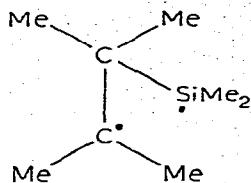


products were obtained from thermolyses of hexamethylsilirane in the presence of 1-decene and allyltrimethylsilane, although the tetramethylethylene yields were high. It is likely that the silacyclopropanes in question were formed but were too thermally labile to survive the reaction conditions.

The thermal decomposition of hexamethylsilirane in the presence of styrene and α -methylstyrene did not produce the expected silacyclopropanes. Instead, silacyclopentanes were formed (eq. 4). We suggest that these products resulted



from the trapping of a diradical intermediate involved in dimethylsilylene extrusion, X. In the case of the styrenes, which have a high reactivity toward radical reagents, the radical trapping reaction must be faster than the rate of Me_2Si release from X. With other olefins, this is not the case and silacyclopropanes are formed. It is the intermediacy of diradical X which would serve to explain the generally poor results obtained when hexamethylsilirane was thermolyzed in the presence of 1,3-dienes [1] and the fact that the thermal decomposition of the silirane in the presence of methyl acrylate initiates polymerization of the latter.



(X)

Our studies of this new silacyclopropane synthesis, of its scope and mechanism, are continuing.

Acknowledgments

The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC (Grant AF-AFOSR-76-2917) for generous support of this work and to Union Carbide Corporation for gifts of chemicals.

References

- 1 D. Seyferth and D.C. Annarelli, *J. Amer. Chem. Soc.*, **97** (1975) 7162.
- 2 (a) W.H. Atwell and D.R. Weyenberg, *Angew. Chem., Int. Ed.*, **8** (1969) 469; *Intra-Sci. Chem. Rep.*, **7** (1973) 139; (b) P.P. Gaspar and B.J. Herold, in W. Kirmse (Ed.), *Carbene Chemistry*, Academic Press, New York, 1971, p. 504-536.
- 3 M. Ishikawa and M. Kumada, *J. Organometal. Chem.*, **81** (1974) C3.
- 4 D. Seyferth and D.C. Annarelli, *J. Amer. Chem. Soc.*, **97** (1975) 2273.
- 5 D. Seyferth, *J. Organometal. Chem.*, **100** (1975) 237.