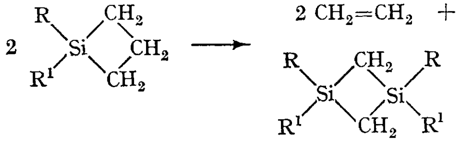
The Thermal Decomposition of 1,1-Dimethyl-1-silacyclobutane and Some Reactions of an Unstable Intermediate containing a Silicon–Carbon Double Bond

By L. E. GUSEL'NIKOV and M. C. FLOWERS*

(*Institute of Petrochemical Synthesis of the Academy of Science U.S.S.R., Moscow, and *Department of Chemistry, The University, Southampton*)

IT has been observed[1,2] that pyrolysis of 1,1-disubstituted-1-silacyclobutanes gives the corresponding substituted 1,3-disilacyclobutanes and ethylene.

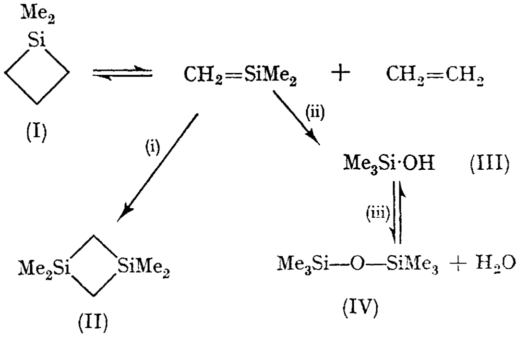


In the later investigations of this reaction,[2] it was suggested that the reaction proceeded *via* the initial formation of an unstable intermediate containing a silicon–carbon double bond and that dimerisation of this species resulted in the formation of 1,3-disilacyclobutanes. Here we present new data which support such a mechanism.

A kinetic study in a static system of the gas-phase thermal decomposition of 1,1-dimethyl-1-silacyclobutane (I) was undertaken between 400 and 460° and at pressures of 8—60 mm. Hg. The reaction rate has been followed by both pressure change and gas chromatography. The reaction is first order and has Arrhenius parameters very similar to the decomposition of alkyl-substituted cyclobutanes.[3]

The decomposition of 1,1-dimethylsilacyclobutane is inhibited by ethylene and propene. The magnitude of this inhibition is in agreement with the supposition that the initial step of the reaction giving $Me_2Si{=}CH_2$ and ethylene is reversible and the inhibition is not believed to be due to the suppression of radical reactions. Thus the reaction is comparable to the reversible decomposition of octafluorocyclobutane to tetrafluoroethylene.[4] More detailed studies of the reaction are currently being examined.

The addition of water to the reaction mixture has provided more concrete support for the intermediate formation of $Me_2Si{=}CH_2$. Water inhibits the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (II). In the static system with equimolar amounts of water and the silacyclobutane (I), and in a flow system with somewhat higher water concentrations, formation of compound (II) is completely suppressed. Under the same conditions water and the disilacyclobutane (II) do not react. On addition of water to the reaction mixture, the only additional products formed are trimethylsilanol (III) and hexamethyldisiloxane (IV). (III) was



Reagents: (i) $CH_2 = SiMe_2$, (ii) H_2O, (iii) Me_3SiOH.

identified by gas chromatographic retention time and by reaction with sodium, which removed all traces of the chromatographic peak, and subsequent acid hydrolysis of the trimethylsilanolate to hexamethyldisiloxane. (IV) was identified by gas chromatographic retention time, i.r. and mass spectrometry. The mass spectrum of hexamethyldisiloxane shows a very small parent peak but a large peak at *m/e* **147** (parent—Me fragment).

The results may be explained by the reaction scheme opposite in which the dimerisation of $Me_2Si{=}CH_2$ and its reaction with water are much faster than reaction with ethylene. Hexamethyldisiloxane results from the condensation of two molecules of trimethylsilanol with the elimination of water.

We thank Professor N. S. Nametkin and Dr. V. M. Vdovin for 1,1-dimethyl-1-silacyclobutane and for discussion of the results of this work.

(*Received, July* 18*th,* 1967; *Com.* 741.)

---

[1] N. S. Nametkin, V. M. Vdovin, L. E. Gusel'nikov, and V. I. Zavyalov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1966, 584.

[2] N. S. Nametkin, L. E. Gusel'nikov, V. M. Vdovin, P. L. Grinberg, V. I. Zavyalov, and V. D. Oppengeim, *Doklady Akad. Nauk S.S.S.R.*, 1966, **171**, 630; L. E. Gusel'nikov, P. L. Grinberg, V. M. Vdovin, and N. S. Nametkin, Symposium on "Structure, reactivity and reaction mechanism of compounds with multiple bonds and small rings." April 1967, Leningrad.

[3] H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 4884.

[4] J. N. Butler, *J. Amer. Chem. Soc.*, 1962, **84**, 1393.