Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

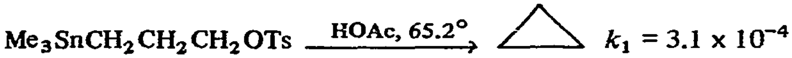
Fragmentation of the silacyclohexane ring. Solvolysis of 4-tosyl-1,1-dimethyl-1-silacyclohexane

STEPHEN S. WASHBURNE and RAM R. CHAWLA
Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122 (U.S.A.)

(Received June 10th, 1971)

The recent reports by Davis, Chambers, and Johnson concerning the thionyl chloride-induced elimination of γ-stannyl alcohols[1]:

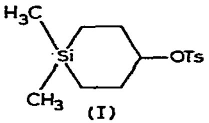
and Kuivila and Scarpa concerning the acetolysis of γ-tosyloxytrimethyltin[2]:

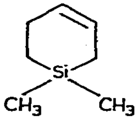
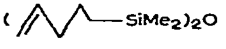
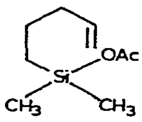
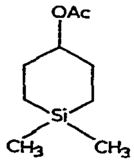


prompt us to communicate our finding of a similar fragmentation in the silacyclohexane series.

When 5mmol of the tosylate of 4-hydroxy-1,1-dimethyl-1-silacyclohexane(I)[3] was solvolysed in glacial acetic acid at 70° for 13 h using the procedure of Winstein and Holness[4] 0.65 g. (66%) of liquid product was obtained. GLC (DEGS, 85–90°) of the latter showed the presence of four products (II–V) (Table 1).

TABLE 1

PRODUCTS FROM SOLVOLYSIS OF  (I)

Product	 (II)	 (III)	 (IV)	 (V)
Yield (%)	13	7	53	27
GLC retention time (min)	1.0	5.5	8.0	13.0

J. Organometal. Chem., 31 (1971) C20–C22

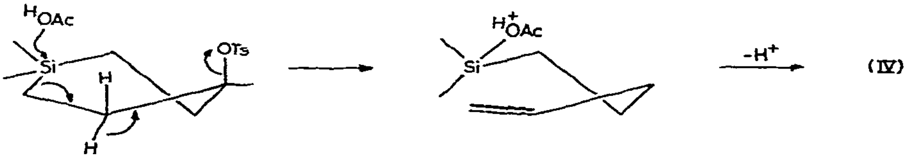
1,1-Dimethyl-1-sila-3-cyclohexene (II) was identified by its spectra: IR 1645, 1250, 850 cm^{-1}, NMR τ 4.3–4.5 (2H, q), τ 7.6–8.0 (2H, m), τ 8.75–8.95 (2H, m), τ 9.35 (2H, t), τ 9.95 (6H, s), which were similar to those reported for 1,1-dichloro-1-sila-3-cyclohexene[5], and identical to those of the olefin produced by pyrolysis (450°) of V.

1,3-Bis (4-pentenyldimethyl)disiloxane (III), IR 1650, 1255, 1060, 840 cm^{-1}, NMR τ 4.1–5.3 (6H, vinyl pattern), τ 7.95 (4H, q), τ 8.3–8.8 (4H, m), τ 9.3–9.7 (4H, m), τ 9.9 (12H, s), was identical in all respects with the product obtained by hydrolysis of the reaction mixture obtained by adding the Grignard reagent from 1-bromo-4-pentene to an excess of dimethyldichlorosilane.

4-Acetoxy-1,1-dimethyl-1-silacyclohexane(V) was characterized by its identity with an authentic sample synthesized by treatment of the corresponding alcohol with Ac_2O/Pyridine.

Attempted collection of IV by GLC afforded only III and acetic anhydride, however solution spectra supporting the assigned structure were obtained by bubbling the column effluent directly into CCl_4. Conversion of acetoxysilane IV into disiloxane III is an expected result in protic media[6], and supporting this it was noted that the yield of III increased at the expense of IV if workup did not immediately follow the solvolysis.

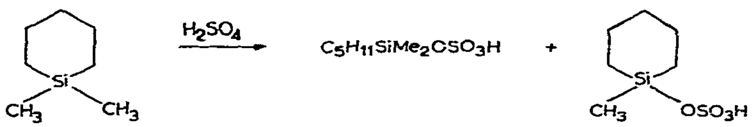
The primary solvolysis products are thus II, IV, and V. Conducting the solvolysis at 90° for 7 h gave increased yields of the normal products: II, 23% and V, 34%, but less fragmentation products: III, 14% and IV, 29%. Speculation on the mechanism of the fragmentation leading to IV is unwarranted at this time, but it is interesting to note that in the twist-boat conformation VI both the C–Si bond to be broken and the leaving group are anti-peri-planar to the hydrogen which migrates.



(VI)

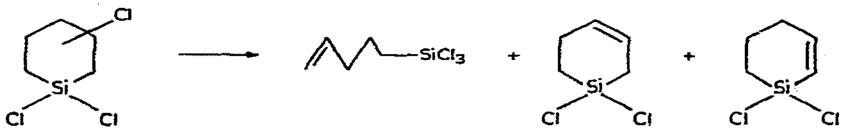
Further study will hopefully show whether the formation of IV is concerted or occurs in discrete steps. Frangomeric assistance[7] could be provided by the formation of a strong Si–O bond[8].

It should be noted that this fragmentation proceeds under far milder condition than any previously reported in γ-functional silicon compounds. In contrast to the facile opening of the Si–C_3 and Si–C_4 rings, dimethylsilacyclohexane undergoes ring-opening only under conditions of protodesilylation, and then competitively with methyl group cleavage[9]. Heating $Me_3SiCH_2CH_2CH_2OH$ with Cu at 300° gave small



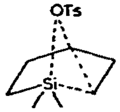
quantities of propylene[10], while formolysis of $Ph_3SiCH_2CH_2CH_2OTs$ (70°, 48h) gave $Ph_3SiOSiPh_3$ as a minor product together with $Ph_3SiCH_2CH_2CH_2OH$[11].

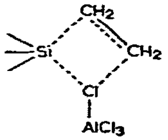
Chloride VII, closely related to I, underwent ring-opening only with quinoline at 240°, $FeCl_3$ at 235°, or pyrolysis at 540° [12].

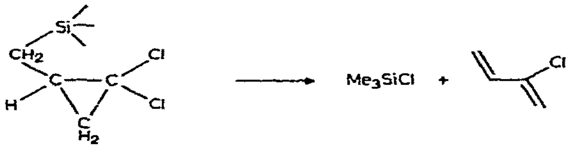


(VII)

The non-formation of cyclopropane products in acetolysis of I or pyrolysis of V is explainable when one considers the strain involved in the required transition state VIII for a concerted elimination. A similar transition state (IX) has been proposed for the Lewis acid-catalysed elimination of halosilane from β-haloethyl- and γ-halopropylsilanes[13], but olefinic products, *e.g.* X→XI [14], are formed in cases where the transition state would be strained. Studies of related silicon eliminations are under active investigation in these laboratories.







(VIII) (IX) (X) (XI)

REFERENCES

1 D.D. Davis, R.L. Chambers and H.T. Johnson, *J. Organometal. Chem.*, 25 (1970) C13.
2 H.G. Kuivila and N.M. Scarpa, *J. Amer. Chem. Soc.*, 92 (1970) 6990.
3 R.A. Benkeser and E.W. Bennett, *J. Amer. Chem. Soc.*, 80 (1958) 5414.
4 S. Winstein and N.J. Holness, *J. Amer. Chem. Soc.*, 77 (1955) 5562.
5 R. Benkeser and R.F. Cunico, *J. Organometal. Chem.*, 4 (1965) 284.
6 R.O. Sauer and W.I. Patnode, *J. Amer. Chem. Soc.*, 67 (1945) 1548.
7 E.M. Kosower, *An Introduction to Physical Organic Chemistry*, Wiley, New York, 1968, p. 95.
8 E.A.V. Ebsworth in A.G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Marcel Dekker, New York, 1968, p. 46.
9 A.F. Plate, N.A. Belikova and Y.P. Egorov, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, (1965) 1085; *Chem. Abstr.*, 51 (1957) 5085.
10 G.V. Goludnikov and A.A. Khalutina, *Zh. Obshch. Khim.*, 32 (1962) 2302. *Chem. Abstr.*, 58 (1963) 7963.
11 H. Gilman and O.L. Marrs, *J. Org. Chem.*, 30 (1965) 2096.
12 R. Benkeser, S.D. Smith and J.L. Noe, *J. Org. Chem.*, 33 (1968) 597.
13 R.W. Bott, C. Eaborn and B.M. Rushton, *J. Organometal. Chem.*, 3 (1965) 455.
14 D. Seyferth and T.F. Jula, *J. Amer. Chem. Soc.*, 90 (1968) 2938.