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Preliminary communication

CHEMISTRY OF A 1-SILACYCLOPROPENE. THERMAL PRODUCTION OF 1,4-DISILACYCLOHEXA-2,5-DIENES

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Summary

Thermolysis of 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene in the presence or absence of an alkyne such as diphenylacetylene or ethyldimethylsilylphenylacetylene gave a mixture of 1,1,4,4-tetramethyl-2,5-diphenyl-3,6-bis(trimethylsilyl- and 1,1,4,4-tetramethyl-2,6-diphenyl-3,5-bis(trimethylsilyl) -1,4-disilacyclohexa-2,5-diene in high yield. The formation of the 1,4-disilacyclohexa-2,5-diene system can be best rationalized in terms of a mechanism involving direct dimerization of the 1-silacyclopropene.

A perplexing problem in organosilicon chemistry is the formation of 1,4-disilacyclohexa-2,5-dienes in the reaction of silylenes with acetylenes. To account for their formation, Barton and Kilgour [3] proposed a mechanism involving the intermediacy of a 1,4-disilabuta-1,3-diene which undergoes a Diels—Alder addition to an acetylene.

Recently we have reported that photolysis of phenyl(pentamethyldisilanyl) acetylene (I) affords 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (II) in solution [1], and that treatment of the resulting solution with a catalytic amount of $PdCl_2(PEt_3)_2$ causes its dimerization with high stereoselectivity [2]. We report here some evidence that thermolysis of II proceeds to give its dimer by a direct σ-dimerization mechanism.

The silacyclopropene (II) was obtained pure in the following way. A solution of 2.2 mmol of I in 80 ml of dry benzene was photolyzed by irradiation with a low-pressure mercury lamp having a Vycor filter for 2.5 h. The conversion of the starting disilane I was ca. 100%. The solvent benzene was evaporated and the residue was distilled under reduced pressure to give a colorless liquid boiling up to 90°C/3 torr. GLC analysis of the distillate using a glass column showed a 41% yield of II and a 10% yield of trimethylsilylphenylacetylene. Pure II*

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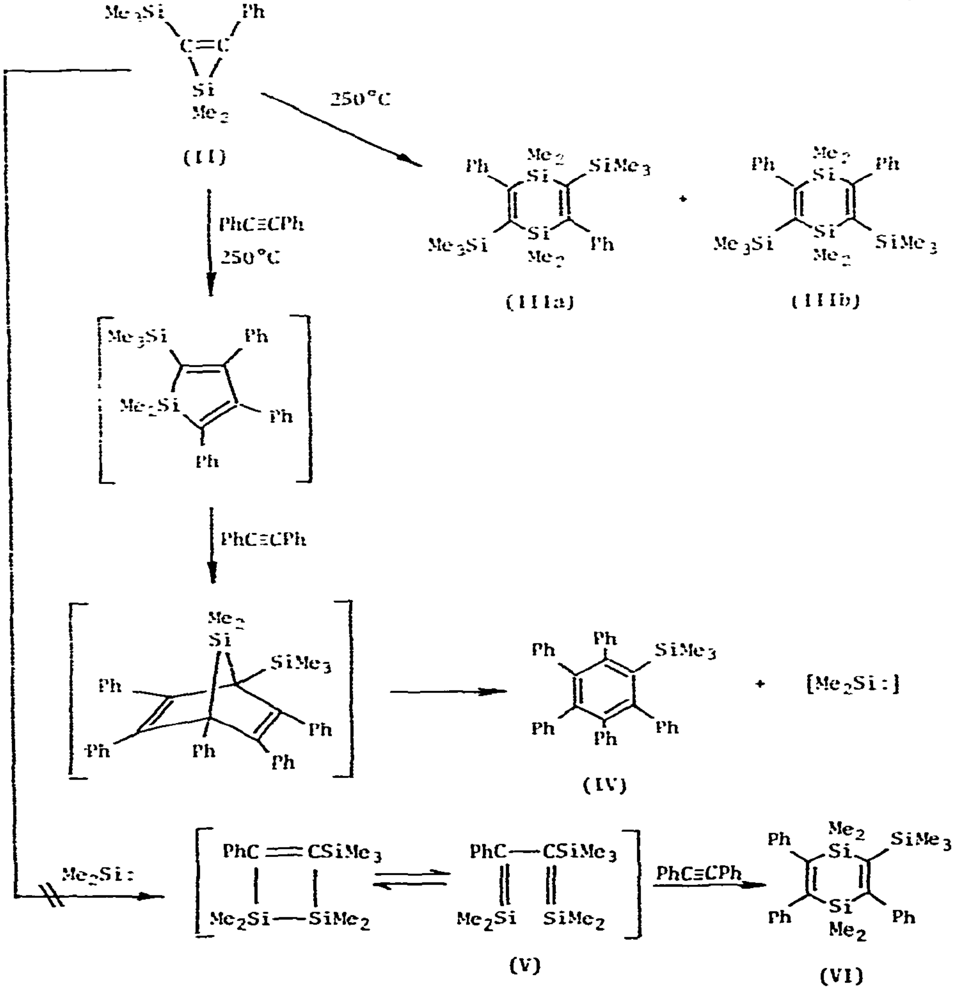
* The formation and reactions of the silacyclopropenes recently have been reported (see ref. 1,2,4—8).

(*m/e* found 232.1095, calcd. 232.1104; IR (neat) (cm^{-1}) 1573, 1950; NMR (δ,ppm in C_6D_6) 0.23 (Me_2Si, s, 6H), 0.30 (Me_3Si, s, 9H), 7.0—7.7 (ring protons, m, 5H)) was isolated by preparative GLC using a glass column containing 30% Silicone SE-30 on Chromosorb W (5 mm X 1.5 m; column temperature 130°).

When a mixture of 300 mg (1.3 mmol) of II and 0.66 mmol of n-cetane as internal standard was heated at 250°C for 18 h in a sealed glass tube, a crystalline substance was obtained in 80% yield. GLC analysis of the crystals under various conditions showed a single peak, the retention time of which coincided with that of 1,1,4,4-tetramethyl-2,5-diphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (IIIa), which had been reported previously [2]. However, the ^1H NMR spectrum of the product indicated it to be a mixture of IIIa and its isomer (IIIb) in the ratio of 3/1. The assignment of IIIb is based on the

SCHEME 1



following facts. (1) Three different Me—Si resonances with relative intensities of 1/3/1 appear at δ (ppm) —0.20,—0.18 and 0.42. (2) The fragmentation pattern of the mixture in the mass spectrum is exactly the same as that of pure IIIa.

In order to learn whether the 1,4-disilacyclohexa-2,5-diene could be formed by the Barton's mechanism, we carried out the thermolysis of II in the presence of a 3-fold excess of diphenylacetylene at 250°C for 18 h. Distillation of the reaction mixture afforded IIIa and IIIb in the ratio of 3/1 in 62% combined yield, and phenyltrimethylsilylacetylene in 15% yield. Thin layer chromatography of the distillation residue gave small amounts of pentaphenyltrimethylsilylbenzene (IV) (5% yield) (*m/e* 530 (M^+), NMR (δ, ppm) 0.07 ($\mathrm{Me_3Si}$, s, 9H), 6.3—7.5 (ring protons, m, 25H), 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,4-diene (trace) [9,10] and hexaphenylbenzene (trace), in addition to recovered diphenylacetylene. 1,1,4,4-Tetramethyl-2,3,6-triphenyl-5-trimethylsilyl-1,4-disilacyclohexa-2,5-diene (VI), which might arise from the Diels—Alder reaction between 1,3-disilacyclobuta-1,3-diene (V) and diphenylacetylene [3], could not be detected by mass and ^{1}H NMR spectroscopic analysis, as well as by GLC analysis. These results strongly indicate that the formation of IIIa and IIIb could occur by direct dimerization of the silacyclopropene even in the presence of diphenylacetylene, as shown in Scheme 1. The production of IV can be explained in terms of the Diels—Alder reaction between the silacyclopentadiene and diphenylacetylene, followed by decomposition. Insertion of an acetylene into a silacyclopropene to give a silacyclopentadiene has recently been found by Seyferth et al. [11].

Furthermore, the thermolysis of II in the presence of ethyldimethylsilylphenylacetylene (VII) provided no positive evidence for involvement of intermediate V. Thus, a mixture of 203 mg (0.87 mmol) of II* containing 38 mg (0.22 mmol) of trimethylsilylphenylacetylene as impurity, 99 mg (0.44 mmol) of n-cetane and 655 mg (3.48 mmol) of VII was heated at 250°C for 18 h. Again IIIa and IIIb, in the ratio of 3/1 were produced in 32% combined yield. In addition, the following three products of insertion of VII into silacyclopropenes were obtained along with a 15% yield of trimethylsilylphenylacetylene (see Scheme 2): 20% yield of VIIIa (M^+ 420; NMR (δ, ppm in $\mathrm{CCl_4}$),—0.20 ($\mathrm{Me_2Si}$, s, 6H),—0.18 ($\mathrm{Me_3Si}$, s, 9H), 0.25 ($\mathrm{CH_2Si}$, m, 2H), 0.39 ($\mathrm{Me_2Si}$, s, 6H), 0.86 ($\mathrm{CH_3}$—C, m, 3H), 6.1—7.3 (ring protons, m, 10H), 9% yield of VIIIb [M^+ 420; NMR—0.52 ($\mathrm{Me_3Si}$, s, 9H),—0.21 ($\mathrm{Me_2Si}$, s, 6H), 0.2 ($\mathrm{CH_2Si}$, m, 2H), 0.24 ($\mathrm{Me_2Si}$, s, 6H), 1.8 ($\mathrm{CH_3}$—C, m, 3H), 6.7—7.4 (ring protons, m, 10H)], and 4% yield of IX (M^+ 434; NMR—0.18 ($\mathrm{Me_2Si}$, s, 12H), 0.07 ($\mathrm{Me_2Si}$, s, 6H), 0.2 ($\mathrm{CH_2Si}$, m, 2H), 1.8 ($\mathrm{CH_3}$—C, m, 3H), 6.7—7.4 (ring protons, m, 10H).
ful analysis of the reaction mixture indicated that Xa and Xb (*m/e* found 478.2391, calcd. 478.2364; NMR (δ, ppm in $\mathrm{CCl_4}$)—0.23/0.21/0.12 = 2/3/4 for Xa,—0.17/—0.15/0.13/0.44 = 2/3/2/2 for Xb, Xa/Xb = 4/1) were formed in only 4% combined yield. At present we feel that these compounds can also be formed from cross dimerization of II and XI. The production of compound IX clearly indicates that intermediate XI could be involved in this thermolysis.

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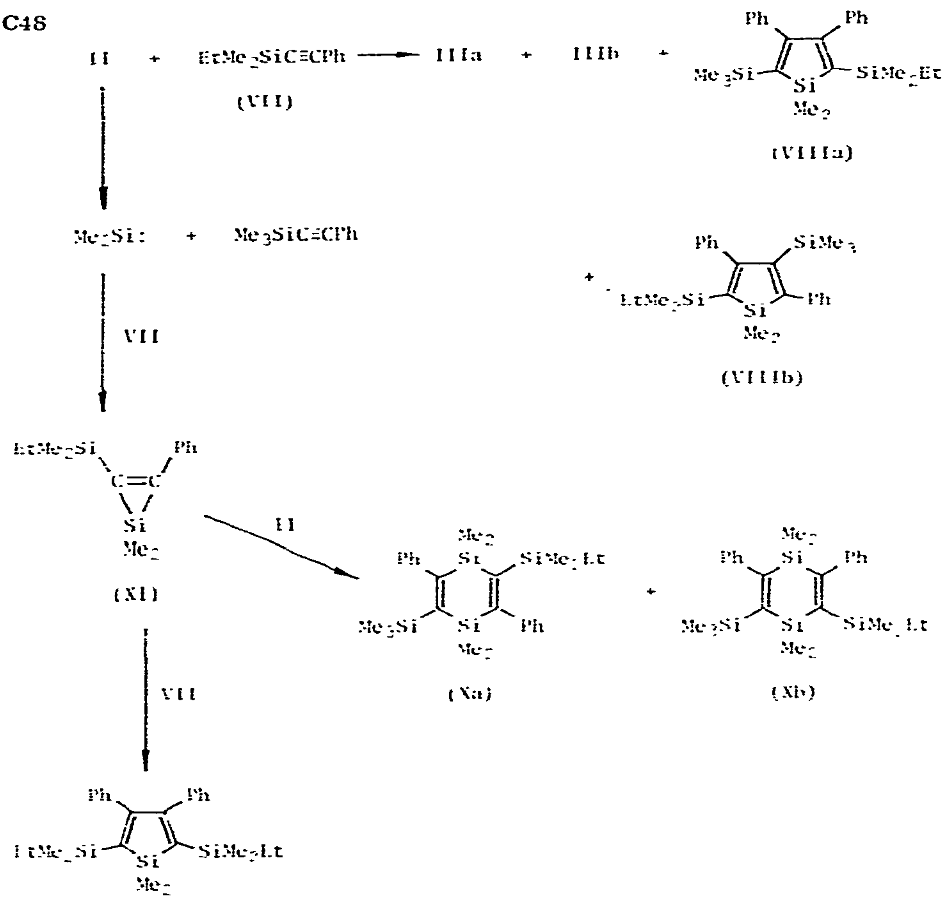
* This sample was what was obtained by distillation from the photoproduct of I.



SCHEME 2

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References

1 M. Ishikawa, T. Fuchikami and M. Kumada, J. Amer. Chem. Soc.,99 (1977) 245.
2 M. Ishikawa, T. Fuchikami and M. Kumada, J. Chem. Soc. Chem. Commun., (1977) 352.
3 T.J. Barton and J.A. Kilgour, J. Amer. Chem. Soc.,98 (1976) 7746.
4 (a) W.H. Atwell and D.R. Weyenberg, Angew. Chem., Int. Ed. Engl.,8 (1969) 469; (b) W.H. Atwell and D.R. Weyenberg, Intra-Sci. Chem. Rep.,7 (1973) 139.
5 R.T. Conlin and P.P. Gaspar, J. Amer. Chem. Soc.,98 (1976) 3715.
6 D. Seyferth, D.C. Annarelli and S.C. Vick, J. Amer. Chem. Soc.,98 (1976) 6382.
7 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 131 (1977) C15.
8 H. Sakurai, Y. Kamiyama and Y. Nakadaira, J. Amer. Chem. Soc.,99 (1977) 3879.
9 R. West and R.E. Bailey, J. Amer. Chem. Soc.,85 (1963) 2871.
10 W.H. Atwell and D.R. Weyenberg, J. Amer. Chem. Soc.,90 (1968) 3438.
11 D. Seyferth, D.P. Duncan and S.C. Vick, J. Organometal. Chem.,125 (1977) C5.