

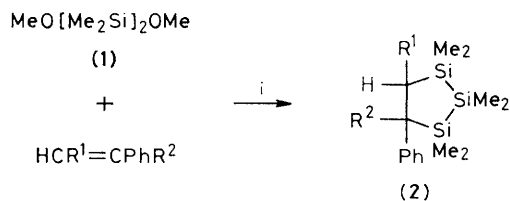
Formation of a New Silicon-containing Ring System; Preparation of 1,1,2,2,3,3-Hexamethyl-1,2,3-trisilacyclopentanes

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Reaction of 1,2-dimethoxytetramethyldisilane with stilbene (*cis* and *trans*) and with α -methylstyrene in the presence of NaOMe catalyst afforded derivatives of the new 1,2,3-trisilacyclopentane ring system.

While the chemistry of five-membered carbocycles containing one or two silicon atoms has been actively studied for a long time^{1,2} little is known about the trisilacyclopentane systems and it is only recently that 1,2,4-trisilacyclopentanes have been obtained.³ The formation of 1,2,3-trisilacyclopentanes was suggested by Kumada and coworkers,⁴ but a detailed investigation was not reported. We now report the formation and characterization of derivatives of the new 1,2,3-trisilacyclopentane ring system,[†] which can be generated as the major



Scheme 1. *i*, NaOMe (cat.), THF, room temp.

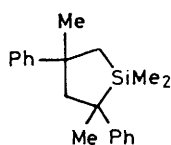
a; R¹ = Ph, R² = H
b; R¹ = H, R² = Me

products from the reaction of 1,2-dimethoxytetramethyldisilane (**1**) with phenylethenes in the presence of a catalytic amount of NaOMe (Scheme 1).

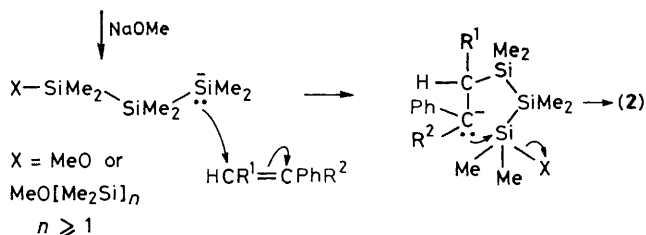
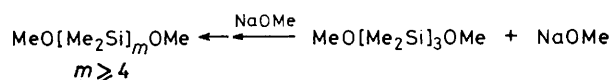
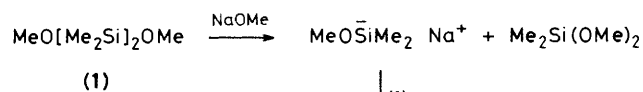
The reaction can be conveniently carried out under mild conditions. Typically, to a stirred suspension of NaOMe (1.2 mmol) in tetrahydrofuran (THF; 4 ml) was added a solution of 1,2-dimethoxytetramethyldisilane (**1**) (11.2 mmol) and *cis*-stilbene (9.6 mmol) in THF (10 ml) under argon. The mixture was stirred at room temperature for 24 h and quenched with NH₄Cl (0.5 g). After filtration and evaporation, a viscous liquid was obtained which, on trituration with cyclohexane, gave crude colourless crystals of the trisilacyclopentane (**2a**) (m.p. 197–201 °C; ‡ 30% yield based on the disilane). Recrystallization from THF–EtOH gave an analytical sample (m.p. 199–202 °C ‡). Its ¹H n.m.r. spectrum showed two different methine singlets at δ 2.67 and 2.83 in a 1 : 1 ratio, consistent with (**2a**) being a (1 : 1) *cis*–*trans*-mixture. We assigned the resonance at δ 2.67 to the *trans*-isomer and that at δ 2.83 to the *cis*-isomer, and these assignments were confirmed following partial separation of the isomers during recrystallization. The reaction with *trans*-stilbene gave similar results.

[†] These compounds were fully characterized by their i.r., n.m.r., and mass spectra and also by elemental analysis.

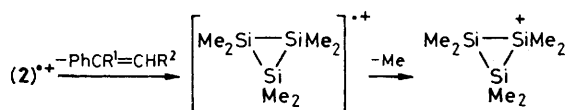
[‡] Sealed capillary.



(3)



Scheme 2



a; m/z 354 (15%)	m/z 174 (100%)	m/z 159 (20%)
b; m/z 292 (15%)	m/z 174 (100%)	m/z 159 (29%)

Scheme 3

The reaction with α -methylstyrene gave the trisilacyclopentane (2b) in low yield,[§] the monosilacyclopentane deriva-

[§] Styrene did not afford an appreciable amount of the corresponding trisilapentane, but gave mainly 1,1-dimethyl-2,4-diphenyl-1-silacyclopentane.

tive (3) being the major product. We suggest that the trisilacyclopentanes (2) are formed by a mechanism involving polysilyl anionic intermediates⁵ (Scheme 2).

The electron-impact mass spectra (20 eV) of (2a) and (2b) showed that the dominant mode of decomposition appears to be loss of a neutral phenylethene molecule giving permethylcyclotrisilane from which a methyl group was subsequently removed (Scheme 3). It is interesting that Masamune and co-workers have recently reported the first synthesis of the cyclo-trisilane system that was fully substituted by the sterically crowded 2,6-dimethylphenyl groups.⁶

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan.

Received, 25th May 1982; Com. 595

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