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Preliminary communication

INSERTION OF METHYLPHENYLSILYLENE INTO CYCLIC SILOXANES, EFFECT OF RING SIZE ON SILOXANE REACTIVITY

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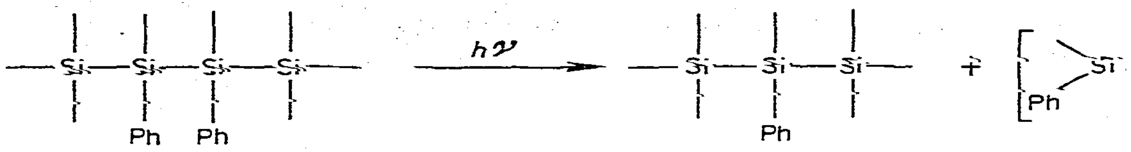
Summary

Insertion reaction of methylphenylsilylene into Si—O single bonds of cyclic siloxanes have been studied. Methylphenylsilylene is less reactive than dimethylsilylene. 1,1,3,3-Tetramethyl-2-oxo-1,3-disilacyclopentane is a more reactive silylene trapping reagent than hexamethylcyclotrisiloxane.

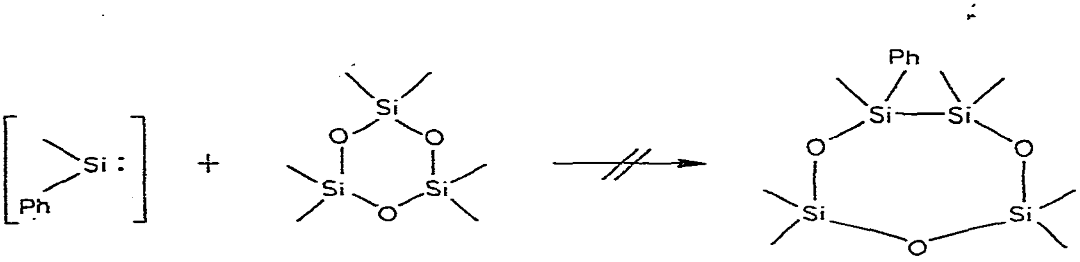
Dimethylsilylene has been shown to insert into a Si—O single bond of hexamethylcyclotrisiloxane (I) to yield 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxo-1,2,4,6-tetrasilacycloheptane (II) [1] and into a Si—O single bond of dimethoxydimethylsilane to yield *sym*-dimethoxytetramethyldisilane [2, 3]. We were interested in whether similar reactivity would be observed for methylphenylsilylene. Photolysis of octamethyl-2,3-diphenyltetrasilane (III) has been shown to yield heptamethyl-2-phenyltrisilane (IV) and methylphenylsilylene [4], while photolysis of IV has been shown to yield hexamethyldisilane (V) and methylphenylsilylene [5, 6].

Photolysis of a deoxygenated solution composed of I (3 mmol), III (1 mmol), and dioxane (20 mmol) with a 450 W medium pressure Hanovia lamp for 20 min resulted in 56% consumption of III and production of IV (60%) and V (20%). Yields are corrected for recovered starting material. No 1,2,2,4,4,6,6-heptamethyl-1-phenyl-3,5,7-trioxo-1,2,4,6-tetrasilacycloheptane, the expected product of insertion of methylphenylsilylene into a Si—O single bond of I, was obtained. Clearly, methylphenylsilylene is less reactive toward insertion into Si—O single bonds of I than dimethylsilylene.

A similar reaction was attempted in which I was replaced by 1,1,3,3-tetramethyl-2-oxo-1,3-disilacyclopentane (VI), as the methylphenylsilylene trapping reagent. Nine mmol of VI were used in place of 3 mmol of I since VI has only one reactive Si—O—Si functionality compared to three such groups in I. The following results were obtained: recovered III (36%), IV (53%), V (19.5%). and 1,1,2,4,4-pentamethyl-2-phenyl-3-oxo-1,2,4-trisilacyclohexane (VII)

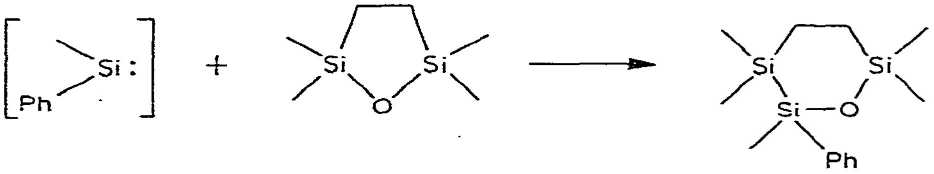


(III) (IV)



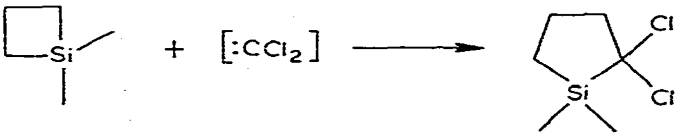
(I)

(40% yield based on methylphenylsilylene generated from photolysis of both III and IV). Clearly, VI is a much more reactive trapping reagent for methylphenylsilylene than I. We believe that this increased reactivity results from the greater angle strain of the Si—O—Si single bonds of VI. For comparison, the Si—O—Si bond angle of I is 125 ± 5° [7] while that of octamethylcyclotetrasiloxane (VIII) is 142.5° [8].

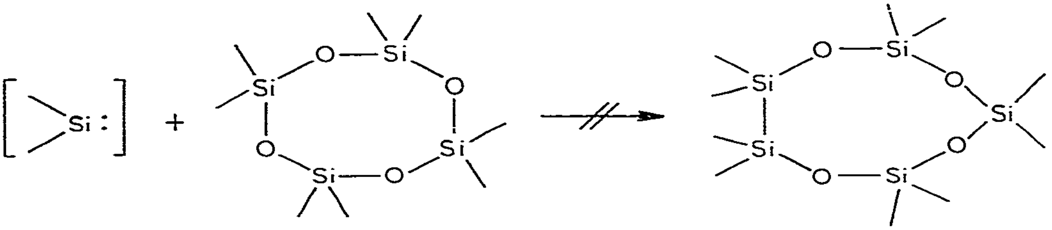


(VI) (VII)

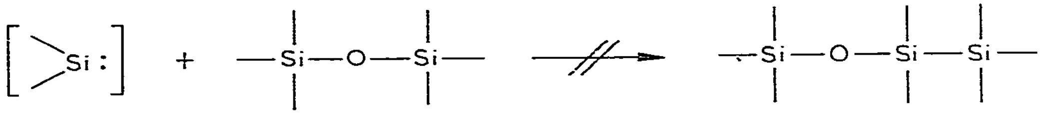
This effect of angle strain on insertion reactions has been previously observed in organosilicon chemistry. Thus dichlorocarbene is reported to insert into the Si—C single bond of 1,1-dimethylsilacyclobutane to yield 2,2-dichloro-1,1-dimethylsilacyclopentane. However, dichlorocarbene will not insert into the Si—C single bonds of larger silacycloalkanes [9].



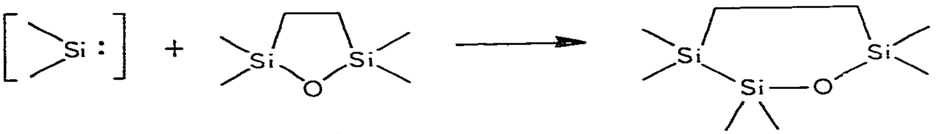
We have attempted to test further the validity of this idea by carrying out a number of photolysis reactions in the presence of various siloxanes. Photolysis of dodecamethylcyclohexasilane (IX) has been shown to yield dimethylsilylene and decamethylcyclopentasilane, which undergoes further photolysis to yield octamethylcyclotetrasilane and a second dimethylsilylene [2]. Photolysis of a deoxygenated solution composed of VIII (3 mmol), IX (1 mmol), and dioxane (80 mmol) gave no 1,1,2,2,4,4,6,6,8,8-decamethyl-3,5,7,9-tetraoxo-1,2,4,6,8-pentasilacyclononane, the expected product of insertion of dimethylsilylene into a Si—O single bond of VIII. (In both acid and base catalyzed polymerization reactions, VIII has been found to be less reactive than I [10].) An analogous experiment with hexamethyldisiloxane as the dimethylsilylene trapping reagent yielded no trimethylsiloxypentamethyldisilane.



(VIII)



On the other hand, photolysis of a solution composed of IX (0.5 mmol), VI (4.5 mmol), and dioxane (40 mmol) gave 1,1,2,2,4,4-hexamethyl-3-oxo-1,2,4-trisilacyclohexane (X) in slightly greater than 200% yield (1.07 mmol) based on IX. Thus the two dimethylsilylene groups being extruded by IX are efficiently captured by VI. Unreacted VI was recovered in greater than 95% yield (3.35 mmol).



(VI)

(X)

Since dimethylsilylene will react with both VI and I, a competition experiment to determine their relative reactivities as silylene trapping reagents was possible. Photolysis of a solution composed of I (2.25 mmol), VI (2.25 mmol), IX (0.25 mmol), and dioxane (20 mmol) resulted in recovery of I (100%, 2.25 mmol), VI (73%, 1.64 mmol), and formation of X (240%, based on IX, 0.6 mmol). On the basis that we could detect a 1% yield of II [1] by GLPC, the reactivity of VI for dimethylsilylene must be at least 100 times greater than I.

Experimental

IR spectra were determined as neat liquids on a Perkin—Elmer 261. NMR spectra were recorded on a Varian T-60 or XL-100 spectrometer. Spectra were taken using 10% solutions in CCl_4 with an internal standard of cyclohexane. Samples of all compounds for spectral and elemental analysis were purified by preparative vapor phase chromatography on a Hewlett—Packard F&M 700. Yields of various products were determined by GLPC. *sym*-Tetramethyldiphenyldisilane [11] was added as an internal standard. Mass spectra were determined on a duPont 21-492 at 70 eV. Microanalysis was performed by the Cal Tech Microanalytical Laboratory, Pasadena, CA.

Most of the starting materials and products are known compounds. They had physical and spectral properties in full agreement with literature values. In those cases where NMR spectra have not been previously reported, we have included these data. Hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexamethyldisilane, hexamethyldisiloxane and 1,1,3,3-tetramethyl-2-oxo-1,3-disilacyclopentane: Silar Laboratories. Heptamethyl-2-phenyltrisilane [12, 13].

Octamethyl-2,3-diphenyltetrasilane [4]: NMR (δ, ppm): 0.05 (s, 9H), 0.08 (s, 9H), 0.10 (s, 3H), 0.13 (s, 3H), 6.93—7.40 (m, 10H).

1,1,2,4,4-Pentamethyl-2-phenyl-3-oxo-1,2,4-trisilacyclohexane: NMR (δ, ppm): −0.06 (s, 3H), 0.16—0.18 (br s, 9H), 0.41 (m, 3H), 0.84 (m, 4H), 7.84 (m, 5H). IR (neat): 1005 cm^{-1}. Mass spectrum: Parent m/e 280 (100%), calcd. 280.113, found 280.112. $P - 15$ m/e 265 (35%), calcd. 265.090, found 265.088. UV (cyclohexane): λ_{max} 234, ϵ 7500.

1,1,2,2,4,4-Hexamethyl-3-oxo-1,2,4-trisilacyclohexane: NMR (δ, ppm): 0.04 (s, 6H), 0.07 (s, 6H), 0.14 (s, 6H), 0.94 (m, 4H). IR (neat): Si—O—Si 996 cm^{-1}. Mass spectrum: Parent m/e 218 (50%), calcd. 218.098, found 218.096. $P - 15$ m/e 203 (63%), calcd. 203.074, found 203.074.

Dioxane was purified by distillation from lithium aluminum hydride immediately prior to use.

Photolysis of octamethyl-2,3-diphenyltetrasilane (III) with 1,1,3,3-tetramethyl-2-oxo-1,3-disilacyclopentane (VI): The following is a typical procedure. A mixture of III (386 mg, 1 mmol), VI (1.440 g, 9 mmol), and dioxane (1.76 g, 20 mmol) was placed in a quartz NMR tube. The solution was deoxygenated by bubbling purified nitrogen through it for 20 min prior to irradiation with a 450 W medium pressure Hanovia Hg lamp for 30 min at 15°C in a water bath. GLPC analysis of the resulting solution on a 1/4" × 30" 20% SE-30 (Column 1) and on a 1/4" × 54" 20% polyphenyl ether (Column 2) on Chromosorb P 60/80 mesh resulted in recovered III (36%) and the formation of IV (53%), V (19.5%) and VII (40%). Product yields are corrected for recovered starting material. All products were collected by preparative GLPC on column I after bulb to bulb distillation under reduced pressure (1 mmHg). IV and V were identified by comparison of their IR and NMR spectra and GLPC retention times with those of authentic samples. VII is a new compound and was further characterized by high resolution mass spectra.

Acknowledgements

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