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Preliminary communication

PYROLYSIS OF HEXAMETHYLCYCLOTRISILTHIANE AND TETRAMETHYLCYCLODISILTHIANE IN THE PRESENCE OF CYCLIC SILOXANES: EVIDENCE FOR THE INTERMEDIACY OF DIMETHYLSILATHIONE [>*Si*=*S*]

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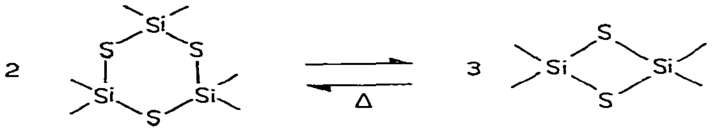
Summary

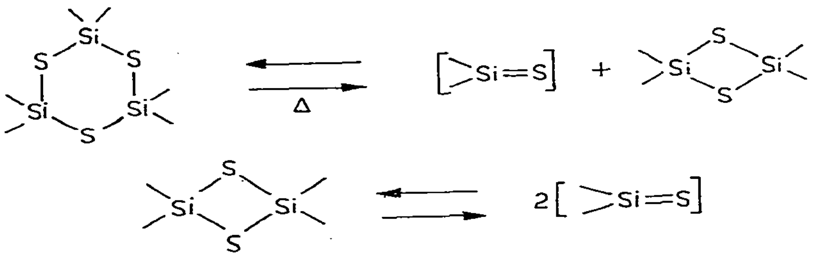
Copyrolysis of hexamethylcyclotrisilthiane and hexamethylcyclotrisiloxane yields 1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxo-1,3,5,7-tetrasila-8-thiacyclooctane. Likewise, copyrolysis of hexamethylcyclotrisilthiane or tetramethylcyclodisilthiane with 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane yields 1,1,3,3,5,5-hexamethyl-2-oxa-1,3,5-trisila-4-thiacycloheptane. Possible mechanisms are discussed.

The existence of an easily established equilibrium between hexamethylcyclotrisilthiane (I) and tetramethylcyclodisilthiane (II) has been known for some time [1,2]:

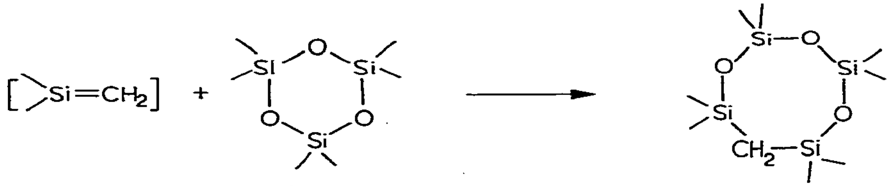


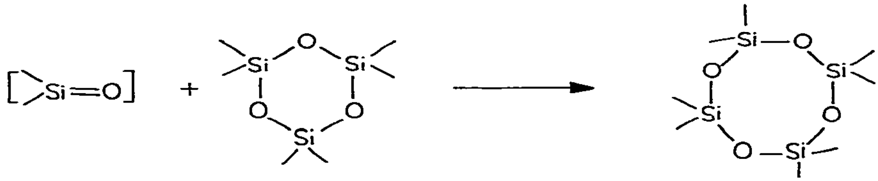
(I) (II)

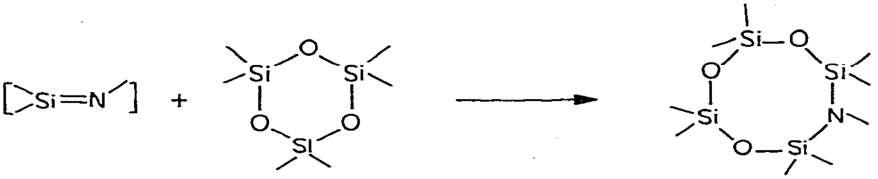
We were interested in the possibility that the mechanism for this equilibration might be as illustrated below and thus involve an intermediate possessing a silicon—sulfur double bond:



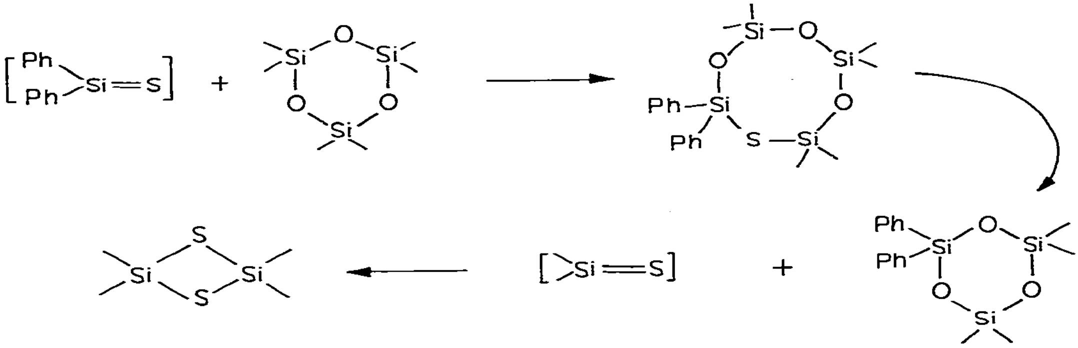
Hexamethylcyclotrisiloxane (III) has been used to trap intermediates possessing silicon—carbon [3,4], silicon—oxygen [4,5], silicon—nitrogen [6], and even silicon—sulfur [7] double bonds.


(III)

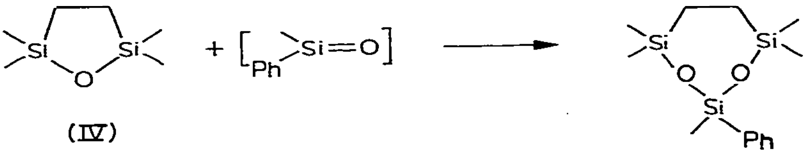




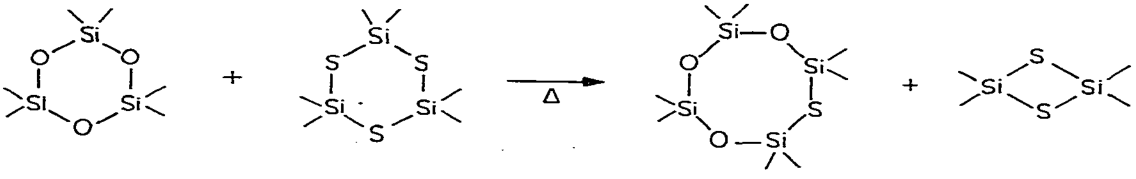
However, in this latter case the initial adduct was apparently unstable at the high reaction temperature (600°C) [7].



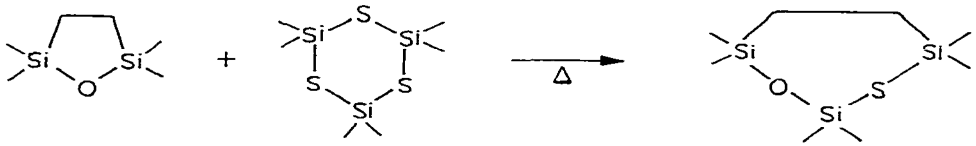
1,1,3,3-Tetramethyl-2-oxa-1,3-disilacyclopentane (IV) has also proved a useful trapping agent for silicon—oxygen doubly bonded intermediates [8].


(IV)

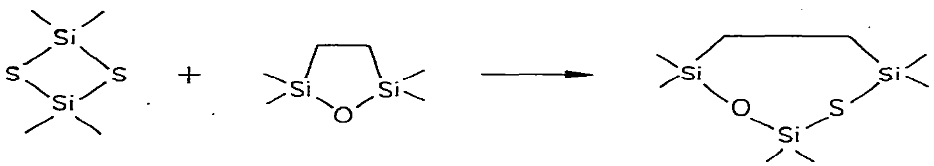
With these ideas in mind, we heated a 10/1 mixture of I and III at 200°C in a sealed pressure bottle for 7 h. This led to formation of 1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxa-1,3,5,7-tetrasila-8-thiacyclooctane (V) (31%)*, II (23%), and a non-volatile residue. The yields are based on the number of equivalents of available $[{>}Si{=}S]$ and are corrected for recovered starting material.


(V)

Likewise, we found that heating a 1/5 mixture of I and IV at 200°C for 7 h gave 1,1,3,3,5,5-hexamethyl-2-oxa-1,3,5-trisila-4-thiacycloheptane (VI) (31%), II (26%), and a non-volatile residue.


(VI)

Heating a 1/5 mixture of II and IV at 200°C for 7 h produced VI (8.5%), a small amount of recovered II, and a non-volatile residue.



The lower yield of VI isolated from reaction of II with IV, compared with reaction of I with IV, may be due to the availability of other reaction pathways for II.

Nevertheless, we believe these experiments suggest that the thermal equilibrium of I and II at 200°C involves an intermediate possessing a silicon—sulfur double bond, $[(CH_3)_2Si{=}S]$. In addition, they provide a new direct synthesis of heterocyclic compounds containing silicon—oxygen and silicon—sulfur bonds [10,11].

Further studies to clarify the mechanism and scope of these novel reactions are in progress.

Experimental

I (0.270 g, 1 mmol), IV (0.800 g, 5 mmol)*, and a Teflon-covered magnetic stirring bar were placed in a dry, nitrogen-filled pressure bottle. The mixture was stirred and heated to 200°C for 7 h. A white solid found to be II (0.069 g,

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*This result is in contradiction to Hailey and Nickless [9], who report that heating III and I at 180°C for several weeks resulted in no change.

*Available from Silar Laboratories (III and IV).

0.38 mmol, 26%) was collected from the neck of the flask. The liquid mixture was dissolved in cyclohexane and analyzed by GLPC on a 72″ × ¼″ DCQF-1 on Chromosorb W 60/80 mesh column at 100°C. The only volatile products were VI (0.225 g, 0.9 mmol, 31% based on number of equivalents of available $[{>}Si{=}S]$ and recovered I (0.011 g, 0.04 mmol). Properties of 1,1,3,3,5,5-hexamethyl-2-oxo-1,3,5-trisila-4-thiacycloheptane: NMR ($CDCl_3$, δ, ppm): 0.10 (s, 3H), 0.32 (s, 3H), 0.36 (s, 3H), 0.65—1.05 (m, 4H). IR (CCl_4): 1035 cm^{-1} (Si—O—Si). UV (cyclohexane): end absorption only. Mass spectrum: Parent *m/e* 250 (22%). Calculated for $C_8H_{22}OSSi_3$ 250.070, found 250.072. $P - 15$ *m/e* 235 (100%).

I (0.270 g, 1 mmol) and III (2.22 g, 10 mmol) were treated and analyzed as above to yield V (0.150 g, 0.48 mmol, 31%), II (0.030 g, 0.17 mmol, 23%). These yields are corrected for recovered hexamethylcyclotrisilthiane (0.129 g, 0.48 mmol, 48%). Properties of 1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxa-1,3,5,7-tetrasila-8-thiacyclooctane: NMR ($CDCl_3$, δ, ppm): 0.18 (s, 12H), 0.50 (s, 12H). IR (CCl_4): 1070 and 1020 cm^{-1}. UV: transparent. Mass spectrum: Parent *m/e* 312 (3%). Calculated for $C_8H_{24}O_3SSi_4$ 312.053, found 312.053. $P - 15$ *m/e* 297 (100%).

II (0.180 g, 1 mmol) and IV (0.80 g, 5 mmol) were treated as above. Some unreacted II (0.012 g, 0.07 mmol, 7%) was collected from the neck of the bottle. The remainder of this reaction product was a viscous liquid. It was taken up in CH_2Cl_2 and bulb-to-bulb distilled. A polymeric residue of 0.32 g was obtained along with a volatile component which was analyzed as before to give recovered IV (0.56 g, 3.5 mmol, 70%) and VI (0.042 g, 0.17 mmol, 8.5%).

Acknowledgements

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