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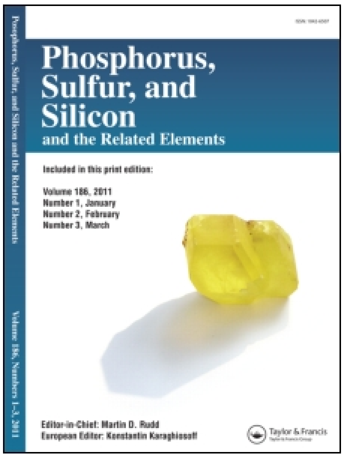

Phosphorus, Sulfur, and Silicon and the Related Elements

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To cite this Article Jenkner, Peter K. and Hengge, Edwin(1992) 'Properties and Reactions of Octadecamethylbicycl0[4.4.0]Decasilane', Phosphorus, Sulfur, and Silicon and the Related Elements, 64: 1, 25 — 31

To link to this Article: DOI: 10.1080/10426509208041124

URL: http://dx.doi.org/10.1080/10426509208041124

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Phosphorus, Sulfur, and Silicon, 1992, Vol. 64, pp. 25–31
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PROPERTIES AND REACTIONS OF OCTADECAMETHYLBICYCLO[4.4.0]DECASILANE

PETER K. JENKNER AND EDWIN HENGGE

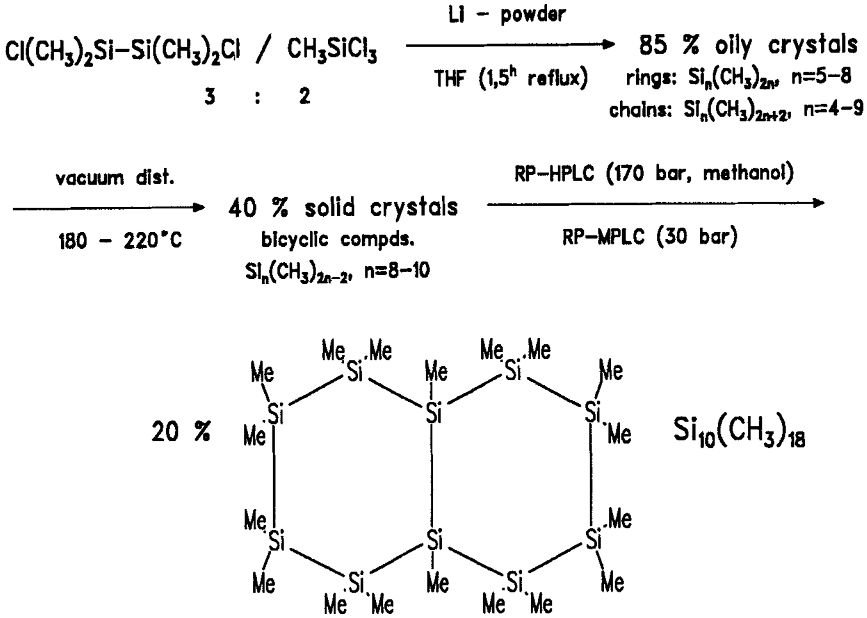
Abstract The title compound was synthesized by a Wurtz-type condensation of dichlorotetramethyldisilane and trichloromethylsilane under selected conditions. Isolation from a mixture of several other permethylated cyclic, catenated and cage oligosilanes was achieved by RP-HPLC and RP-MPLC methods. ESR - investigations upon chemical reduction were carried out at different temperatures. Reactivity is shown to be distincly different to that of medium-sized monocyclic permethyloligosilanes. The isomeric bi(nonamethylcyclopentasilanyl) was also prepared and pathways to other oligocyclic methylsilanes are shown, starting from monofunctional cyclopentasilanes.

INTRODUCTION

Presumably, octadecamethylbicyclo[4.4.0]decasilane had been synthesized by West and coworkers [1] in a small amount but the exact structure could not be assigned as several structural and stereo isomers are possible. Anellated and bicyclic oligosilanes are of interest in terms of determining the geometry of electron delocalization and as model structures for two- and threedimensional polysilane high polymers.

SYNTHESIS

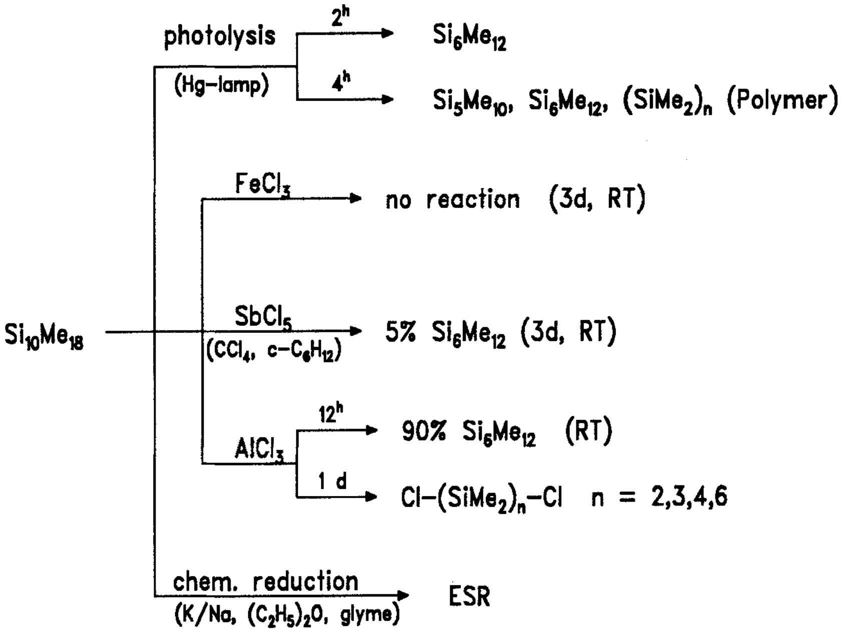
We succeeded in developing a Wurtz-type condensation method (Scheme 1) yielding preparative amounts of bicyclic compounds with a majority of $Si_{10}(CH_3)_{18}$ followed by a convenient work-up and purification. ^{29}Si-NMR-investigations (INEPT-INADEQUATE) revealed the [4.4.0]-bicyclic structure and only one isomer to be present in solution. $Si_{10}(CH_3)_{18}$ was recrystallized from benzene and a crystal structure was carried out.



SCHEME 1

REACTIONS

Photolytical degradation proceeds slowly via Si_6Me_{12} and after a longer period of irradiation small amounts of Si_5Me_{10} and $(SiMe_2)_n$ were detected. This is in contrast to the fast degradation of the permethylated monocyclic rings (n = 5 - 7). Reactions with various metal halides of different Lewis acidity lead to monosubstitution at Si_5Me_{10} [2] and to mono-, di- and trisubstituted species starting from Si_6Me_{12} [3]. However, no substitution products from $Si_{10}Me_{18}$ could be prepared; treatment with chlorides of increasing Lewis acidity gave only Si_6Me_{12} and subsequently led to scission of the ring; the α,ω-dichloropermethylpolysilanes $Cl\text{-}(SiMe_2)_n\text{-}Cl$ (n = 2,3,4,6) were found.



SCHEME 2

ESR

Chemical reduction of $Si_{10}Me_{18}$ with Na/K in a 3:1 mixture of diethylether/glyme was carried out at 130 K. ESR monitoring was done every 10 K starting from 150 K. The spectra up to 170 K show an overlap of two distinct species, $Si_6Me_{12}^-$ and $Si_5Me_{10}^-$ with diminishing intensity of the lines ascribed to $Si_6Me_{12}^-$ at 170 K. The spectra from 180 K to 220 K indicate the presence of only $Si_5Me_{10}^-$. It is well known that chemically generated $Si_6Me_{12}^-$ forms $Si_5Me_{10}^-$ at about 150 to 190 K [4]. Therefore we assume an initial reduction to $Si_6Me_{12}^-$ from $Si_{10}Me_{18}$ and no bicyclic anionic species can be observed at temperatures that were accessible during the experiments.

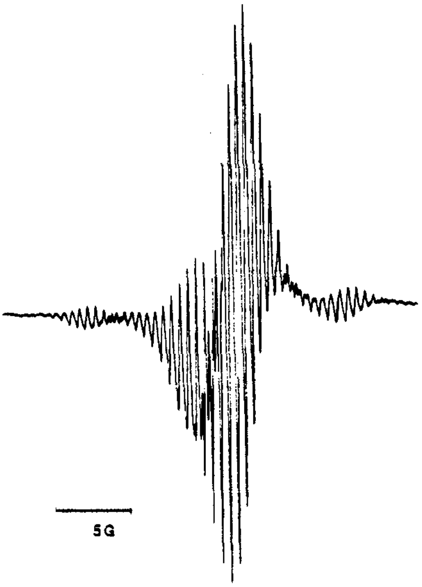


FIGURE 1 ESR at 150 K

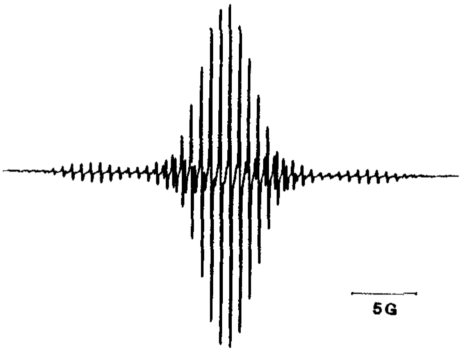


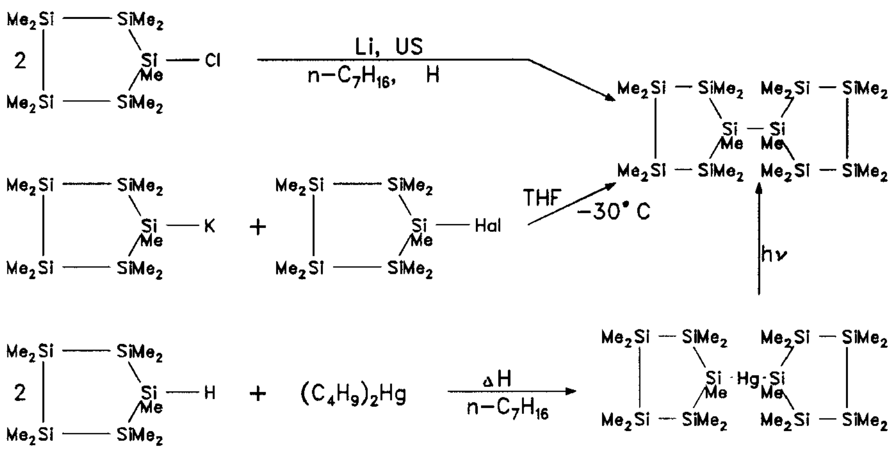
FIGURE 2 ESR at 180 K

CRYSTAL STRUCTURE

Data were collected by a STOE 3-circle diffractometer with MoKα-radiation (λ = 0,71069 Å, graphite monochromator). 11105 reflections were read of which 10400 were unique and 5692 observed. The data were corrected for absorption by means of an empirical method (Nigel & David (1983)). The solution with direct methods proceeded via anisotropic refinement of silicon atoms. The hydrogen atoms of the methyl groups were included at calculated positions, with their isotropic temperature coefficients refined.

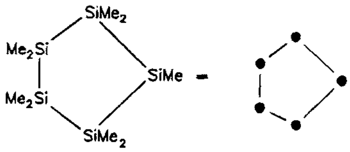
The crystal structure confirms the *trans* geometry of the fused two cyclohexasilane systems which adopt a regular chair conformation with a center of symmetry. The asymmetric unit contains two molecules which are crystallographically independent and have the same conformation. The average Si-Si distance of 2,347 Å agrees with the Si-Si covalent bond (2,34 Å). The Si-Si bond which connects the two rings (2,370 Å) appears to be 0,023 Å longer than the others. The molecular packing revealed discrete molecules with no intermolecular contacts.

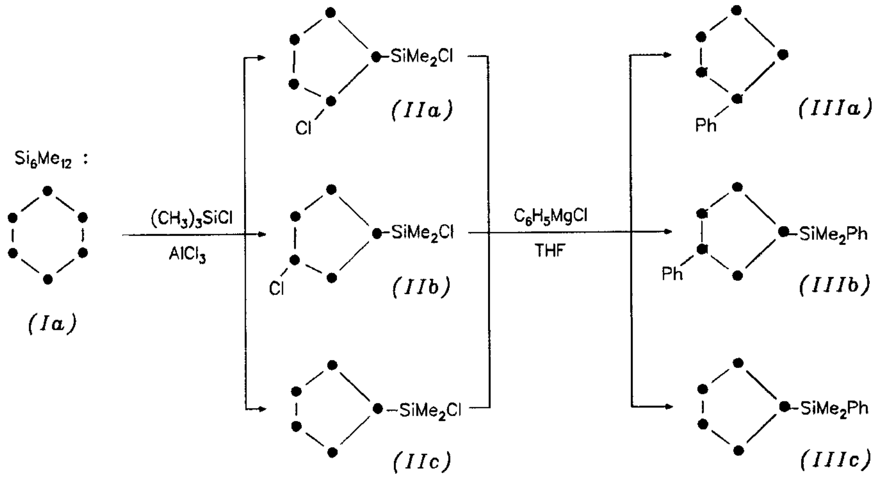
Synthesis of Bi(nonamethylcyclopentasilanyl) :



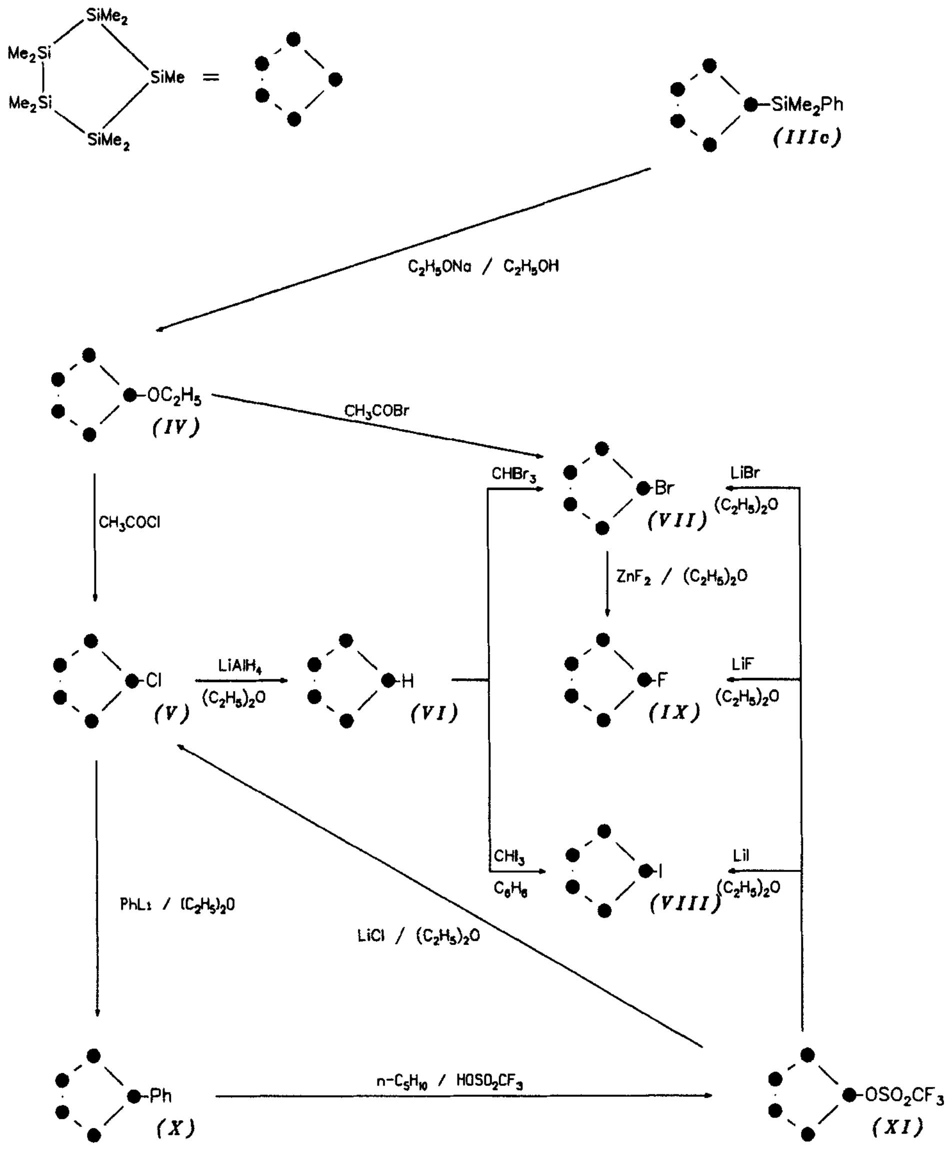
SCHEME 3

NEW MONOCYCLIC DERIVATIVES





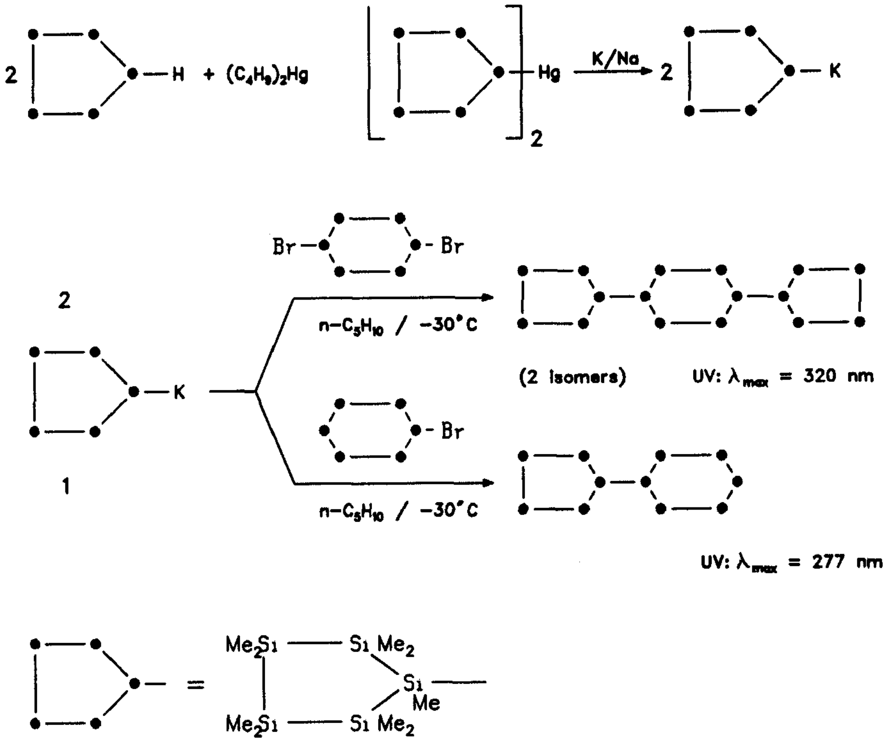
SCHEME 4



SCHEME 5

As we concentrate on further preparative work towards oligocyclic silicon structures starting from functional derivatives of Si_5Me_{10} and Si_6Me_{12}, a number of compounds have been made (X = -F, -Cl, -Br, -I, -H, $-C_6H_5$, $-O(C_2H_5)$, $-OSO_2CF_3$) according to scheme 4 and 5.

Advantages of Si_5Me_9- substituted mono- and oligosilanes (scheme 6) are a good solubility and low melting points, allowing to purify them easily via vacuum sublimation:



SCHEME 6

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