

Preliminary communication

SULFUR AND SELENIUM INSERTION INTO THE SILICON—SILICON BOND IN DECAMETHYLCYCLOPENTASILANE

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Summary

Decamethylcyclopentasilane reacts with elemental sulfur or selenium in decalin at 190°C to give the six-membered ring products, cyclo-(Me₂Si)₅S and cyclo-(Me₂Si)₅Se. Dodecamethylcyclohexasilane is unreactive towards sulfur or selenium under the same conditions.

In our continuing studies of permethylcyclopolysilanes [1], we have noted that decamethylcyclopentasilane (Me₂Si)₅ reacts quite rapidly with chlorine and bromine, undergoing Si—Si bond cleavage to form the 1,5-dihalopermethylpentasilanes [2,3]. We now find that (Me₂Si)₅ reacts with sulfur or selenium at 180°C yielding the new six-membered ring compounds, cyclo-(Me₂Si)₅E (E = S, Se).

In these experiments 1 mmol of (Me₂Si)₅, admixed with an equimolar amount of the six-membered ring (Me₂Si)₆, was dissolved in 10 ml of decalin containing 1.1 mmol of sulfur or selenium, and the mixture was heated to reflux at 190°C. Disappearance of (Me₂Si)₅ and formation of the products were followed by gas chromatography. The reactions with S and Se required 6 and 10 h respectively for completion, producing quantitative yields in both cases.

The products were isolated as colorless liquids by preparative gas chromatography and identified by their spectroscopic properties. The ¹H NMR for each compound shows three resonances with relative intensities 2/2/1 with one of the more intense peaks shifted downfield, consistent with the assigned structure. For (Me₂Si)₅S, δ 0.404 (2H, s), 0.200 (2H, s), 0.204 ppm (1H, s); and for (Me₂Si)₅Se, δ 0.496 (2H, s), 0.172 (2H, s) and 0.200 ppm (1H, s). The mass spectra (70 eV) were characteristic, showing strong parent ion peaks and other fragments assignable on the basis of the structures given. Significant mass spectral peaks, with assignments and relative intensities, were: For (Me₂Si)₅S, 322 (*P*, 30%), 307 (*P* - CH₃, 25), 263 (*P* - SiMe₂H, 25); 116

(Me_4Si_2 , 100), 73 (Me_3Si , 95); For (Me_2Si)₅Se, 370 (*P*, 20), 355 (*P* - CH_3 , 20), 311 (*P*- SiMe_2H , 30), 116 (Me_4Si_2 , 100), 73 (Me_3Si , 95). Ultraviolet spectral bands were, for (Me_2Si)₅S, λ_{max} (nm) 202, 207 (sh), 227 ($\epsilon = 12,200$), and for (Me_2Si)₅Se, 202, 217 (sh), 240 ($\epsilon = 10,250$).

No change was observed in the amount of (Me_2Si)₆ present in the reaction mixture, showing that it does not react with S or Se under these conditions. Recent experiments show that (Me_2Si)₅ is approximately 18 kcal/mol less stable than (Me_2Si)₆ [4], presumably because of greater H-H repulsions in the five- than in the six-membered ring. Relief of this repulsion energy can account for the reactivity of (Me_2Si)₅ toward halogens and chalcogens.

This is apparently the first report of sulfur or selenium insertion into Si-Si bonds, but it is likely that similar reactions will take place with other strained polysilanes. The related oxygen insertion to form a five-membered ring takes place for (Me_2Si)₄ [5] and for disilacyclobutenes [6-9]. The insertion of sulfur into strained Si-C bonds has also been observed [10,11].

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