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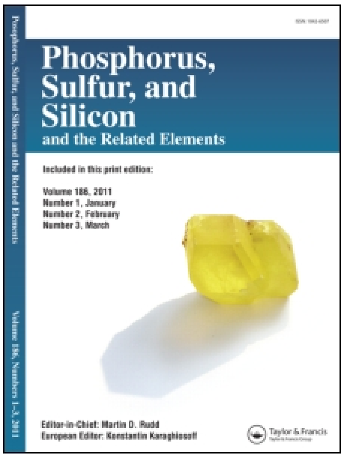

Phosphorus, Sulfur, and Silicon and the Related Elements

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To cite this Article Lönnecke, Peter and Meisel, Manfred(1997) 'Polycondensation of Tris(Trimethylsilylseleno)Phosphane', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 505 — 508

To link to this Article: DOI: 10.1080/10426509708545670

URL: http://dx.doi.org/10.1080/10426509708545670

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Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 505–508
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POLYCONDENSATION OF TRIS(TRIMETHYLSILYLSELENO)PHOSPHANE

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Abstract Tris-(trimethylsilyl)phosphane and their organo substituted derivatives $(Me_3Si)_{3-n}P(Me_3C)_n$ (n: 0, 1, 2) (**1a-c**) had been found suitable for the insertion of selenium into the phosphorus-silicon bond. At deep temperatures all silylselenophosphanes of the series $(Me_3SiSe)_{3-n}P(Me_3C)_n$ (**2a-c**) are formed in a nearly quantitative reaction, if no excess selenium is present. $(Me_3C)(Me_3SiSe)_2P{=}Se$ (**3b**) and $(Me_3C)_2(Me_3SiSe)P{=}Se$ (**3c**) are detectable in small quantities as the only by-products of the reaction of (**1b-c**) , whereas (**1a**) end in the formation of (**2a**) and traces of the dimer $(Me_3SiSe)_2P\text{-}P(SeSiMe_3)_2$ (**4**). On exposure to light or at elevated temperatures (**2a**) undergoes a disproportionation, forming $Se{=}P(SeSiMe_3)_3$ (**3a**), and the heterocycles $P_3Se_4(SeSiMe_3)$ (**5**) and $\alpha\text{-}P_4Se_3(SeSiMe_3)_2$ (**6**). $(Me_3Si)_2Se$ is split off as a condensation product. After further irradiation or prolonged standing at room temperature, an insoluble oligomer is formed. The constitutions of (**2-6**) were determined by the analysis of their ^{31}P- and ^{77}Se-nmr spectra.

INTRODUCTION

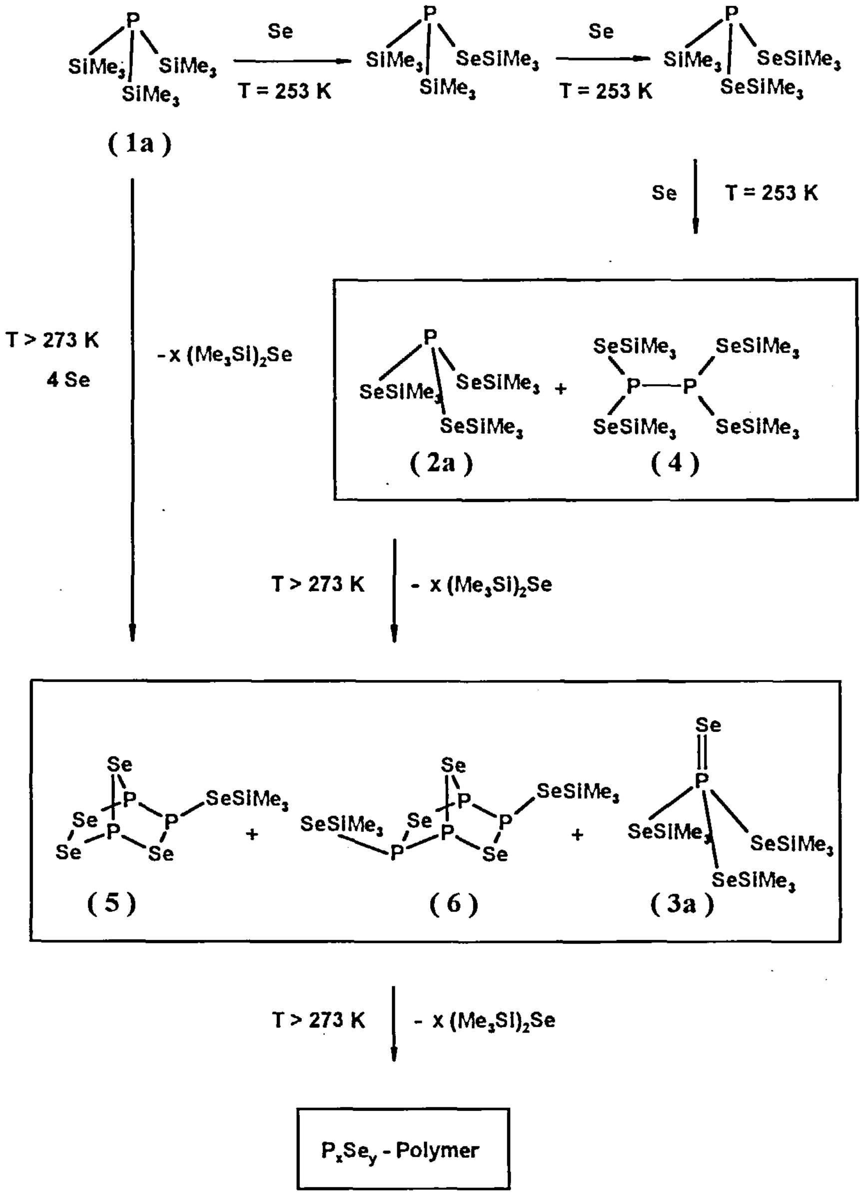
With pyridine as a proton acceptor, we had recently isolated the phosphorotetraselenoic acid in pure crystalline form[1]. Because of its low solubility and the poor yield it was difficult to study the chemical behaviour of this compound. To evade this problem we decided to investigate the analogous family of phosphorus selenium esters, using the trimethylsilyl group as a *"bulky proton"*.

RESULTS AND DISCUSSION

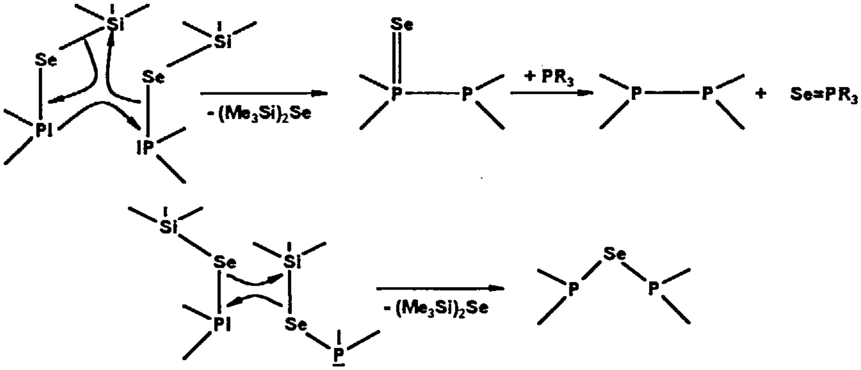
Synthetic methods for the preparation of Trimethylsilylselenophosphanes are rare and most procedures are only given for their sulphur analogues. Roesky[2] showed that the nucleophilic degradation of P_4S_{10} with $(Me_3Si)_2S$ is an efficient way for the synthesis of $S{=}P(SSiMe_3)_3$ and in 1995 a method was reported by Arnold[3], using the sterically demanding lithium tris(trimethylsilyl)tellurolate as a starting material. Mostly promising and simple was the possibility to insert a chalcogen into the P-Si-bond, as shown by Fritz[4] and Hahn et al[5].

Our results confirm the formation of tris-(trimethylsilylthio)phosphan $P(SSiMe_3)_3$ by treatment of **(1a)** with three equivalents of sulphur and its further oxidation to the appropriate thioxo-tris-(trimethylsilylthio)phosphan $S{=}P(SSiMe_3)_3$. The same reaction with selenium resulted in an insoluble polymeric reaction product. However, at lower temperatures the formation of tris-(trimethylsilylseleno)phosphan **(2a)** in nearly quantitative yield has been observed. Only traces of the dimer **(4)** are detectable as a by-product. Solutions of **(2a)** are stable at deep temperatures in the dark. Exposure to light or elevated temperatures resulted in the formation of the monomeric $Se{=}P(SeSiMe_3)_3$.**(3a)** and the phosphorus-selenium heterocycles $P_3Se_4(SeSiMe_3)$ **(5)** and α-$P_4Se_3(SeSiMe_3)_2$ **(6)**. After further irradiation or prolonged standing at room temperature an insoluble polymer is formed.

During the course of the relatively slow reaction, the selenium incorporation was monitored by ^{31}P- and ^{77}Se-nmr. All species given in the reaction scheme could unambiguously be identified by their typical nmr parameters e. g. coupling constants, spin systems, relative



intensities (P_kSe_m / $P_kSe_{m-n}{}^{77}Se_n$) and chemical shifts. At deep temperatures (2a) could not be oxidized by further addition of selenium. As it was pointed out for P_2Se_5[6], this behaviour and the diselenide bridge in (5) as a result of a rearrangement of the oxidized $Se{=}P(SeR)_2P(SeR)_2$ species demonstrate the unfavoured coordination of a $Se{=}PSe_{3/2}$-unit. The formation of (3a) at elevated temperatures can be explained by a disproportionation of (2a) into reduced (6), unchanged (5) and oxidized (3a). A possible mechanism is given below. For the transfer of the selenium, a direct chalcogen exchange seems to be very likely[7].



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