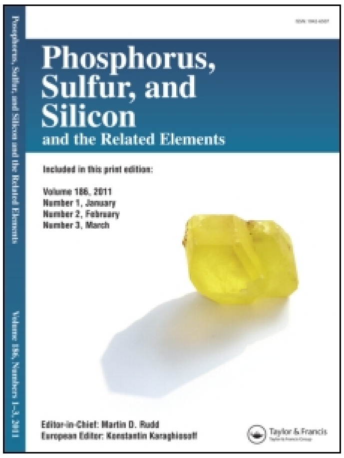

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A NOVEL METHOD FOR THE SYNTHESIS OF POLYCYCLIC PHOSPHORUS CHALCOGENIDES

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Abstract With pyridine as activating solvent and depolymerization catalyst and tris(trimethylsilylchalcogeno)phosphane $P(ESiMe_3)_3$ (E: S (**1a**), Se (**1b**)), we succeeded in synthesizing α-$[P_4E_7]M_2$ (M: $[Me_3Si\text{-}NC_5H_5]^+$; E: S (**2a**), Se (**2b**)), the first bicycles consisting of phosphorus chalcogen anions with a norbornane skeleton. The constitution of (**2a, 2b**) was determined by the analysis of their ^1H-, ^{31}P- and ^{77}Se-nmr spectra. By variation of the reaction conditions, two P_6-sulfur-heterocycles are obtained as the main products. The ^{31}P-nmr spectrum indicates two isomers of $P_6S_7M_2$ (**3a, 4a**) with a tricyclic structure related to the hydrocarbon brexan. In addition, the reactions of $tBuP(ESiMe_3)_2$ (E: S (**5a**), Se (**5b**)) in pyridine are reported.

INTRODUCTION

The chemistry of polycyclic phosphides[1] and organophosphanes[2] is well developed and a lot of data and synthetic routes are described in the literature. Although there has been made great progress during the last decades, our knowledge about polycyclic phosphorus chalcogenides is, in comparison with appropriate phosphides and organophosphanes, relatively poor. It might be, that in some cases the synthesis of phosphorus chalcogenides seems to be difficult, because of their low solubility and their trend to polymerization. To get deeper insights into the chemistry of molecular phosphorus chalcogenides, it seems to be necessary to look for new preparation methods.

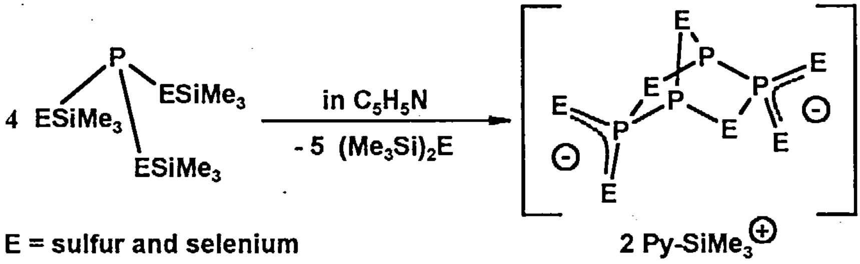
RESULTS AND DISCUSSION

From the orthophosphoric- via the phosphorotetrathioic- to the phosphorotetraselenoic acid the stability is decreasing i. e. the balance of the formal equation

$$2n\,H_3PE_4 \rightleftharpoons \text{" } 2\,(E{=}PE_{3/2})_n \text{ "} + 3n\,H_2E$$

is shifting to the right.

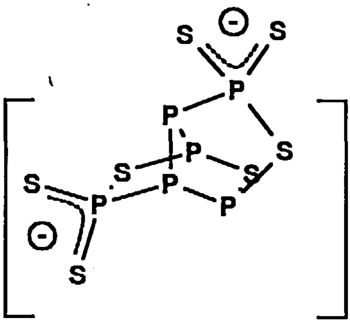
It was our intention to prove, if the family of phosphorus- or phosphonous chalcogeno acid esters with trimethylsilyl as a *"bulky proton"* could be used for the synthesis of phosphorus chalcogenides. Thus, we started to investigate the chemistry of tris-(trimethylsilylchalcogeno)phosphane $P(ESiMe_3)_3$ (E = S (**1a**), Se (**1b**)), because up to now our attempts failed to isolate $Se{=}P(SeSiMe_3)_3$ in pure form. Using (**1**) as a reactive starting material and pyridine as a base and solvent, the new compounds α-$P_4E_7M_2$ (M: $[C_5H_5N\text{-}SiMe_3]^+$; E: S (**2a**), Se (**2b**)) were found in a nearly quantitative reaction. In comparison with the well known α-$P_4E_3(R)_2$ (R = halogen or pseudohalogen) series, these are the first examples where the substituent carrying phosphorus is completely oxidized. In



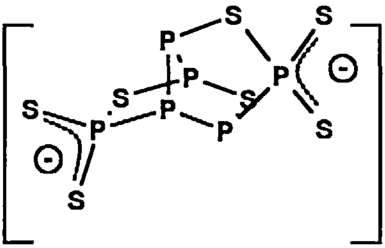
(1) (2)

pyridin the nmr data reveal (2b) as an α-$[P_4Se_7]^{2-}$ bicyclic anion, because the direct $^1J_{PSe}$ coupling constants between phosphorus and selenium in the exo and endo position were comparable and quite strong ($^1J_{(P=Se)}$≈ -650 Hz). In the ^{1}H-nmr spectrum one sharp singlet due to $(Me_3Si)_2Se$ and a broadened one for the Me_3Si-group (ratio of intensities: $(Me_3Si)_2Se$ / Me_3Si = 5 / 1 as expected) were visible.

For (2a) the ^{1}H- and ^{31}P-nmr spectrum also indicate an α-$[P_4S_7]^{2-}$ bicyclic anion. By variation of the reaction conditions, i. e. longer reaction times or using a mixture of $P(SSiMe_3)_3$ and $P(SiMe_3)(SSiMe_3)_2$ as starting material, two P_6-sulfur-heterocycles are detected as the main products. The symmetry of these two species can directly derived from their spinsystem observed in the ^{31}P-nmr spectrum (spinsystem: AA′BB′CC′ (3a), ABCDEF (4a)). A detailed analysis of these multiplets and a comparison with the nmr data of the known $P_6S_5(t\text{-}Bu)_2$[3] indicate two isomers of $P_6S_5(SM)_2$ with a tricyclic structure related to the hydrocarbon brexane. P_4S_3 and the new compound P_5S_4M are formed in small amounts as by-products. (2b) is stable in pyridin and (2a) disproportionates into reduced (3a), (4a) and presumably oxidized $(S_2PS_nPS_2)M_2$.



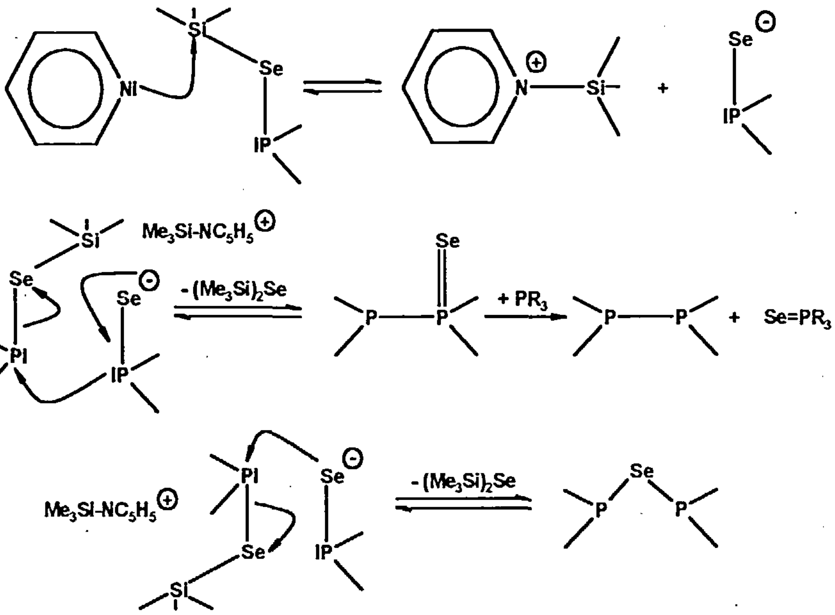
(3a)



(4a)

In addition, the condensation of $tBuP(ESiMe_3)_2$ (E: S (**5a**), Se (**5b**)) in pyridine was analyzed and found to yield the five and four membered monocycles $(tBuP)_3E_2(E)_n$ and $(tBuP)_3E(E)_n$ (double bonded chalcogen E in brackets; n: 0, 1), which had been already described by Karaghiosoff et al[4].

The reaction mechanism given below, explains the formation of the P-P- and P-E-P-units. Our results indicate, that every single step must be more or less an equilibrium and only the thermodynamically favoured compounds are formed. Especially the quantitative formation of (**2b**) and the rearrangement of (**2a**) into the tricycles (**3a**) and (**4a**) only can explained under this assumption. In addition $(Me_3Si)_2E$ and pyridine are well known to act as nucleophiles and they are able to attack electrophilic centers e. g. the phosphorus in P_4S_{10} under degradation of the cage molecule [5,6,7].



REFERENCES

[1] H. G. von Schnering, W. Hönle, Chem. Rev., **88**, (1988) 243
[2] M. Baudler, Angew. Chem., 94, (1982) 520
M. Baudler, Angew. Chem., 99, (1987) 429
[3] R. Blachnik P. Lönnecke, Z. anorg. allg. Chem., 620, (1994) 167
[4] K. Karaghiosoff, Postdoctoral Thesis, Munich (1997)
[5] M. Meisel, H. Grunze, Z. anorg. allg. Chem., 360, (1968) 277
[6] W. W. du Mont, R. Hensel, W. Mc Farlane, I. J. Colquhoum, M. L. Ziegler, O. Serhadli, Chem. Ber., **122**, (1989) 37
[7] H. W. Roesky. G. Remmers, Z. anorg. allg. Chem., **431**, (1977) 221