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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## New Phosphorus – Tellurium Heterocycles in the Quasi – Binary System RP/Te

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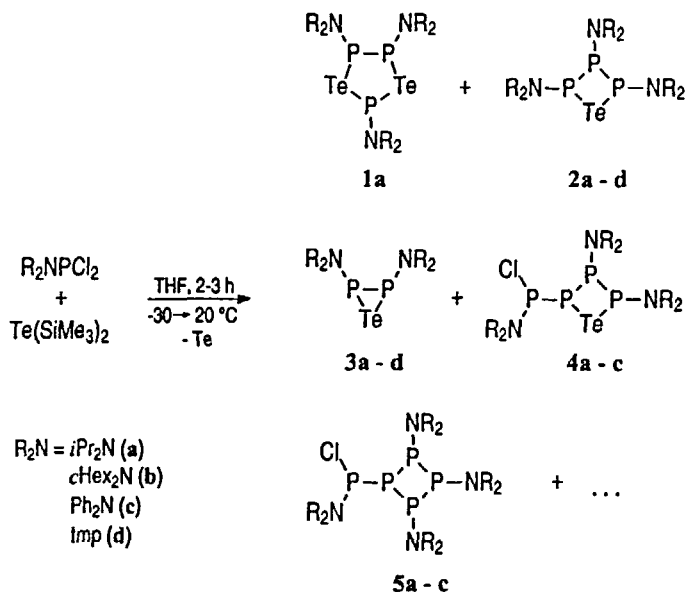
Condensation of amino dichlorophosphanes  $R_2NPCL_2$  with  $Na_2Te$  or  $Te(SiMe_3)_2$  yields the new P,Te-heterocycles **1** – **4** and the phosphino substituted cyclotetraphosphanes **5**. The new compounds are fully characterized by  $^{31}P$  and  $^{125}Te$  NMR spectroscopy. Using a triphenylphosphonium ylidyl dichlorophosphane unexpectedly orange yellow crystals of  $(Ph_3P)_2Te$  are isolated, the structure of which is determined by X-ray crystallography.

**Keywords:** 1,3-ditelluratriphospholanes; telluratriphosphetanes; telluraphosphiranes; triphenylphosphane telluride;  $^{31}P$  and  $^{125}Te$  NMR spectroscopy; X-ray structure determination

Compounds  $(RP)_nCh_m$  ( $Ch = O, S, Se, Te$ ) can be classified between cyclophosphanes  $(RP)_n$  and elemental chalcogens. The number of known examples with different  $n/m$  ratios and the variety of the structures observed increase rapidly in going from oxygen to sulfur and to selenium derivatives.<sup>[1-3]</sup> Only a few heterocycles  $(RP)_nTe_m$  are reported in the literature, however; all of them have *tert*-butyl substituents at phosphorus.<sup>[4]</sup>

Heterocycles  $(RP)_nS_m$  and  $(RP)_nSe_m$  are readily prepared either by oxidation of a cyclophosphane  $(RP)_n$  with elemental sulfur or selenium or by condensation of dichlorophosphanes  $RPCl_2$  with an alkali metal (poly)sulfide or -selenide  $M_2Ch_x$  ( $M = Li, Na, x = 1, 2$ ).<sup>[2,3]</sup> These

syntheses can only in part be applied to the analogous phosphorus tellurium heterocycles. In fact, the cyclophosphane oxidation does not work with elemental tellurium. We find, that the condensation of amino dichlorophosphanes  $R_2NPCl_2$  with  $Na_2Te$  or, more conveniently with  $Te(SiMe_3)_2$ , provides a general route to new aminosubstituted P,Te-heterocycles  $(R_2NP)_nTe_m$ :

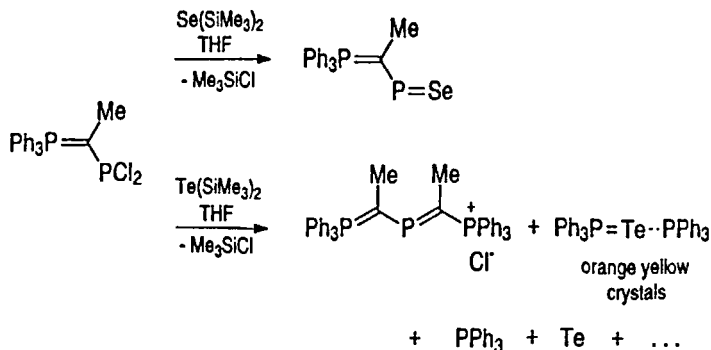


In all cases in addition to condensation also reduction of the dichlorophosphane by the telluride with formation of PP-bonds and elemental tellurium takes place. Thus only heterocycles  $(R_2NP)_nTe_m$  with  $n > m$  are obtained. Their structures result unambiguously from the  $^{31}P$ - and  $^{125}Te$  NMR spectra.

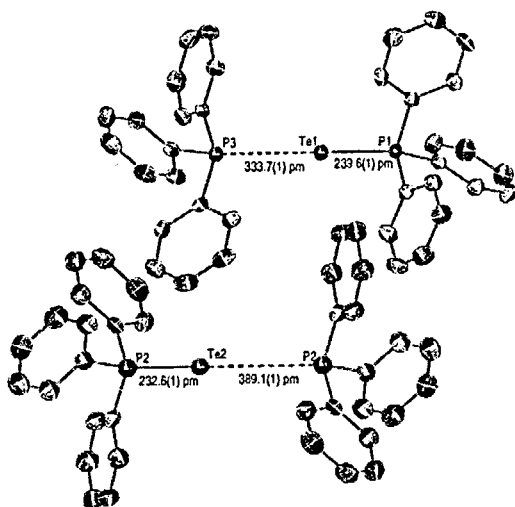
The 1,3-ditelluratriphospholane **1** is the heterocycle with the highest tellurium content in this system and is observed only for  $R_2N = iPr_2N$ . **1a** spontaneously eliminates tellurium and gives the telluratriphosphetane **2a**. With the bulky tmp substituent the telluradiphosphirane **3d** is the main product. The new phosphino substituted telluratriphosphetanes **4** and tetraphosphetanes **5** are formed in all cases except for  $R_2N = tmp$ .

[illegible]

Reaction of triphenylphosphonium ylidyl dichlorophosphanes with  $\text{Se}(\text{SiMe}_3)_2$  yields ylide substituted selenoxophosphanes, which are monomeric in solution and in the solid state.<sup>[5]</sup> The condensation with  $\text{Te}(\text{SiMe}_3)_2$ , however, results in the formation of a complex mixture of products. No analogous telluroxophosphane or heterocycles  $(\text{RP})_n\text{Te}_m$  were detected. Surprisingly, orange yellow crystals of  $(\text{Ph}_3\text{P})_2\text{Te}$ , a compound first described by T. Austad et al.<sup>[6]</sup>, could be isolated.



(Ph<sub>3</sub>P)<sub>2</sub>Te crystallizes in the space group P3 with two independent molecules in the unit cell. Each of the two linear P-Te-P units shows two different PTe distances: the short ones (232.6 and 239.6 pm) can be compared to that in phosphane tellurides (e.g. 136.5 pm in *i*Pr<sub>3</sub>PTe), the long ones (337.1 and 389.1 pm) are clearly below the sum of the van der Waals radii of phosphorus and tellurium (410 pm).



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