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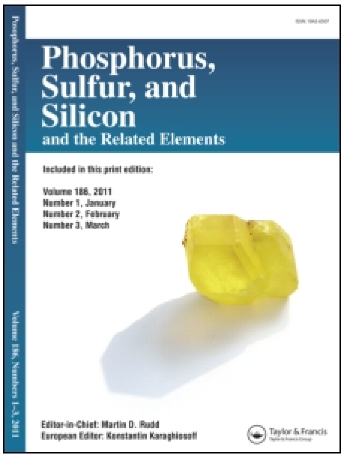

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Reactivity of Conjugated Bases of Hydridophosphoranes. Synthesis of Unusual Phosphoranes Bearing P-S$^-$, P-Se$^-$, P-P-S$^-$ and P-N- as Exocyclic Bonds

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REACTIVITY OF CONJUGATED BASES OF HYDRIDOPHOSPHORANES. SYNTHESIS OF UNUSUAL PHOSPHORANES BEARING P-S^-, P-Se^-, P-P-S^- AND P-$\bar{N}$- AS EXOCYCLIC BONDS

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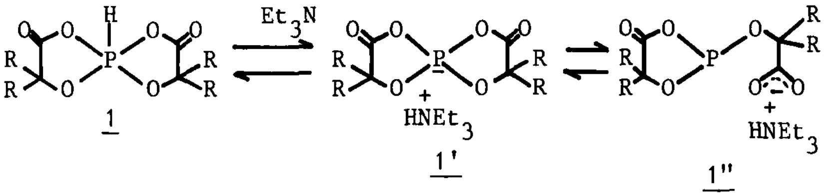
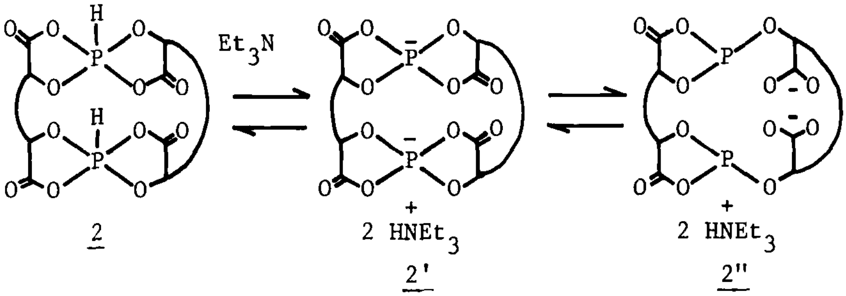
Abstract : Triethylammonium salts of spirophosphoranes having P-SH, P-SeH, P-P-SH and P-NH- bonds were prepared by reaction, in presence of triethylamine, of hydridophosphoranes on sulfur, selenium, Lawesson's reagent, tosylazide. With trimethylchlorosilane, trico-ordinated compounds was obtained instead of pentaco-ordinated derivatives.

INTRODUCTION

Hydridophosphoranes 1 and 2 are deprotonated by medium bases as pyridin or triethylamine, according to the schemes 1, 2[1]. Parent system was recently related[2,3].



Scheme 1



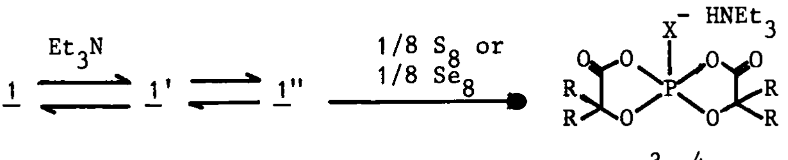
Scheme 2

The conjugated bases 1', 1", 2', 2" show nucleophilic properties which can be attributed to phosphoranides 1' , 2'. With alkylhalides, carbon disulfide and phenylazide, reactions were observed while phosphoranes 1, 2 are inert towards these reagents. Corresponding phosphoranes with exocyclic P-R, $P-CS_2^-$ or P-NH-Ph bonds were isolated.[3] Following these researchs, we studied the reaction of the systems 1, 2 with sulfur, selenium, Lawesson's reagent, tosylazide and trimethylchlorosilane.

RESULTS AND DISCUSSION

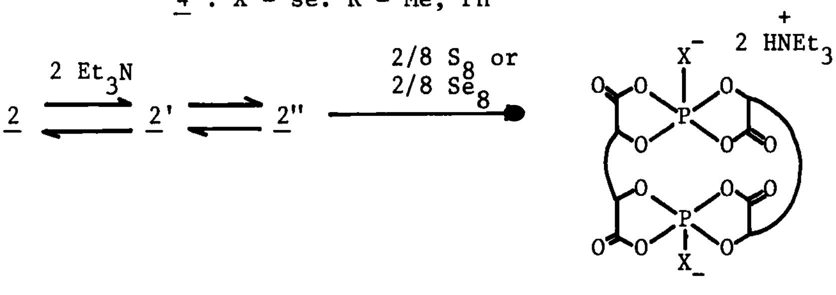
1. Sulfur and selenium

Fast and slightly exothermic reactions take place. Phosphoranes 3 - 6 are isolated as colourless, crystalline and hygroscopic powders.Spirophosphoranic structure has been established by means of NMR (^{31}P, ^{13}C, ^{1}H), infrared spectroscopy and elemental analysis (schemes 3 and 4).



3, 4

Scheme 3 : 3 : X = S. R = Me, Ph
4 : X = se. R = Me, Ph



5, 6

Scheme 4 : 5 : X = S. 6 : X = Se.

Phosphoranes 3 - 6 are only stable as salts. They are, in our opinion, the first isolated thiolo, selenophosphoranes. They can represent good models of intermediate thiolo, selenophosphoranes in nucleophilic reactions involving thio, selenophosphoric esters.

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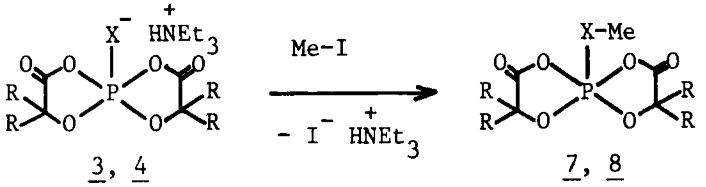
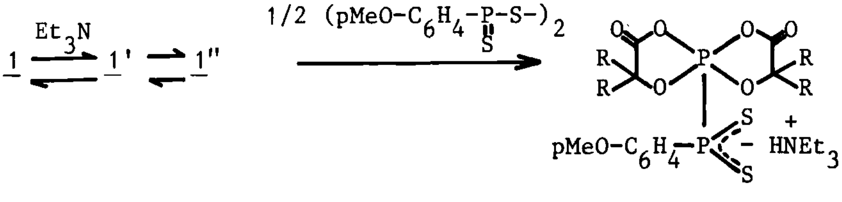
Compounds 3 - 6 react with alkyl halides (e.g. methyl chloride) giving the corresponding alkyl thiolo (seleno) phosphoranes (scheme 5), which are less stable than the corresponding ionic phosphoranes.



Scheme 5 : 7 : X = S, R = Me. 8 : X = Se, R = Me.

2. Lawesson's reagent

Lawesson's reagent easely reacts with systems 1. Unstable compounds have been obtained bearing P-P bonds. Nevertheless, the phosphorane 9 has been isolated as an hygroscopic powder (scheme 6).

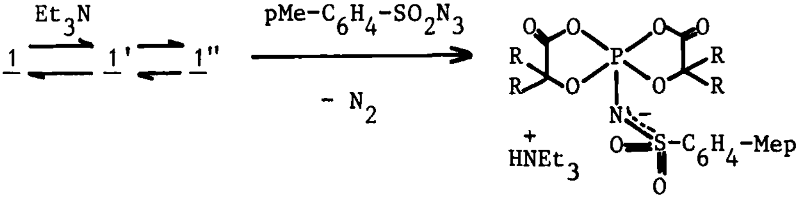


Scheme 6

9 : R = Me

3. Tosyl azide

Conjugated bases of phosphoranes 1 fastly react on tosyl azide leading to hygroscopic crystals whose NMR parameters and elemental analysis are consistent with the phosphorane salt 10 (scheme 7).



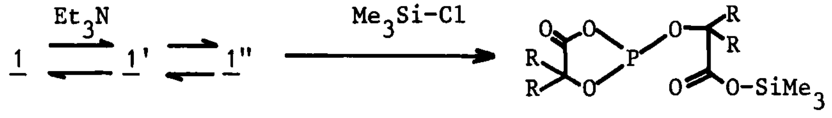
Scheme 7

10 : R = Me

These results show that phosphorane 10 is relatively strong acid. The chemical shift, in ^{31}P NMR suggests that the electronic charge is delocalized between nitrogen and sulfur atoms.

4. Trimethylchlorosilane

In contrast with the preceeding experiments, the trimethylchlorosilane reacts on the carboxylate group of the open form 1'' , and not on the phosphorus atom of the phosphoranide 1', giving the phosphorous ester 11 (schem 8). This result underlines the silicium hardness which attacks an hard basic center, the carboxylate group, rather than the soft basic phosphorus atoms of 1', 1'' forms.



11

Scheme 8

CONCLUSION

The reactivity of conjugated bases of phosphoranes 1, 2 led us to isolate new spirophosphoranic salts stabilized by their spirocyclic structure and electron delocalization. Thus, we could prepare thiolo and seleno phosphoranes which would be unstable compounds without these stabilizing factors.

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