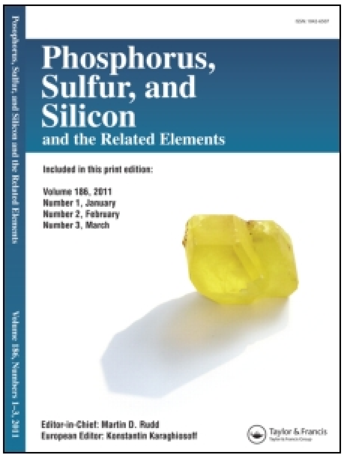

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A NEW APPROACH TOWARDS ORGANOPHOSPHORUS SULFENYL AND SELENYL HALIDES

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Abstract We describe new highly effective methods leading to compounds of general formula 1 and 2 including chiral diastereoisomeric systems 1 (Y=S, X=Cl) containing the asymmetric phosphorus center. Some aspects of the reaction between organophosphorus dithioacids and halogens are also discussed.

This work has its origin in anticipation that compounds of general formula 1 and 2 may find a wide range of important application in the organophosphorus-sulfur-selenium chemistry including the synthesis of analogues of naturally occuring phosphates and novel structures useful as agrochemicals. They can also serve as models in the studies of addition reaction to unsaturated systems. With this in mind diastereoisomeric compounds 1 (Y=S, X=Cl) are described.

RR'P(Y)SX 1 RR'P(Y)SeX 2 (Y=O,S,Se; X=Cl,Br)

Both types of compounds have electrophilic sulfur or selenium centers in contrast to other classes of organophosphorus compounds containing sulfur or selenium, in which these heteroatoms exhibit nucleophilic properties. Until recently, only the oxophosphoranesulfenyl chlorides RR'P(O)SCl 3 were readily available and employed as versatile reagents and intermediates.[1] The known synthetic procedure for the thioxaphosphoranesulfenyl chlorides RR'P(S)SCl 4 (1,Y=S,X=Cl) provides compounds of low purity.[2] Other types of sulfenyl and selenyl halides 1 and 2 were not available or accessible in mixture with non-separable by-products until our recent studies.

Numerous attempts in the past to obtain thioxaphosphoranesulfenyl chlorides 4 from commercially available dithioacids 5 by direct chlorination deserves special attention. It is known that the reaction of one equivalent of the elemental chlorine with two equivalents of the dithioacid 5 affords the disulfide 6.

$$RR'P(S)SH\ \ \underline{5} + Cl_2 \longrightarrow RR'P(S)SSP(S)RR'\ \ \underline{6} + 2HCl$$

When excess of chlorine is used, this reaction is a basis for the industrial process for thionochlorides 7 which are important starting materials in the synthesis of organophosphorus pesticides.[3,4] In the reaction leading to the disulfides 6, intermediacy of the thioxaphosphoranesulfenyl chlorides 4 seems certain. By employing low temperature ^{31}P NMR spectroscopy, we were able to demonstrate that the chlorides 4 are indeed formed in these reactions, but they are very susceptible towards further attack by the elemental chlorine which proceeds via the sulfonium 8 and phosphonium 8a intermediates.

$$\underset{\underline{4}}{RR'P(S)SCl} \xrightarrow{Cl_2} \underset{\underline{8}}{RR'P(S)\overset{+}{S}Cl_2}\ \ Cl^- \rightleftharpoons \underset{\underline{8a}}{RR'\overset{+}{P}(SCl)_2}\ \ Cl^- \xrightarrow{-SCl_2} \underset{\underline{7}}{RR'P(S)Cl}$$

This reaction is even more complex since the sulfur chlorides also act as chlorinating reagents. The essential difference in the synthesis of the chlorides 4 and the thioxaphosphoranesulfenyl bromides 9 is that the latter are formed with high efficiency from the thioacids 5 and the disulfides 6 by the action of elemental bromine.[5] This difference is due to low nucleophilicity of the Br^- and Br_3^- anions towards the tetracoordinate phosphorus atom. Trimethylsilyl esters of phosphorus dithioacids 10 can also be used as starting materials in the preparation of bromides 9. The reaction between silyl ester 10 and elemental chlorine affords the sulfenyl chlorides 4 in low yield. However, when elemental chlorine is replaced by sulfuryl chloride fluoride under properly chosen reaction conditions, moderate yield of 4 is observed.

$$\underset{\underline{10}}{\mathrm{RR'P(S)SSiMe_3}} + \mathrm{SO_2ClF} \longrightarrow \underline{4} + \mathrm{Me_3SiF} + \mathrm{SO_2}$$

The sulfenyl bromides 9 are convenient starting materials for the synthesis of the sulfenyl chlorides 4. The bromides 9 react with methanol in the presence of 2,6-lutidine to give methylsulfenates 11.

$$\underset{\underline{9}}{\mathrm{RR'P(S)SBr}} \xrightarrow[\text{2,6-lutidine}]{\mathrm{MeOH}} \underset{\underline{11}}{\mathrm{RR'P(S)SOR}} \xrightarrow{\mathrm{Me_3SiCl}} \underline{4} + \mathrm{Me_3SiOMe}$$

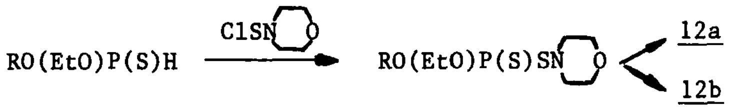
The sulfenate 11 react smoothly with trimethylsilyl chloride in methylene chloride to give 4 in nearly quantitative yield. A four center transition state is, most probably, responsible for this clean transformation. The synthesis of the chloride 4 from the sulfenyl bromide 9 can be performed as "one pot" reaction without isolation of the sulfenate 11.

In search for a more general method leading to the compounds 1 and 2 we discovered that the readily available mixed anhydrides derived from phosphorus thio- and selenoacids and acetic acid of general formula RR'P(Y)-X-C(O)Me (Y=O,S,Se; X=O,S),[6,7] undergo reaction with the elemental chlorine (sulfuryl chloride) and bromine to give compounds of the type 1 and 2.

$$\begin{array}{lll}
\mathrm{RR'P(S)OCOMe} & \xrightarrow{\mathrm{X_2}} \mathrm{RR'P(O)S\text{-}X} + \mathrm{MeCOX} & \mathrm{(X{=}Br,Cl)} \\
\mathrm{RR'P(Se)OCOMe} & \xrightarrow{\mathrm{Br_2}} \mathrm{RR'P(O)SeBr} + \mathrm{MeCOBr} & \\
\mathrm{RR'P(S)SCOMe} & \xrightarrow{\mathrm{X_2}} \mathrm{RR'P(S)SX} + \mathrm{MeCOX} & \mathrm{(X{=}Br,Cl)} \\
\mathrm{RR'P(Se)SCOMe} & \xrightarrow{\mathrm{Br_2}} \mathrm{RR'P(S)SeBr} + \mathrm{MeCOBr} &
\end{array}$$

All these reactions proceed below ambient temperature in neutral solvents in almost quantitative yield affording the sulfenyl and selenyl halides 1 and 2 of higher purity and stability than those prepared by other methods.

The diastereomeric sulfenyl chlorides 13a,b are obtained from resalved sulfenamides 12a,b .



12a $\xrightarrow{\text{R'Cl+EtOH}}$ RO(EtO)P(S)SCl R = L-Menthyl
$\delta^{31}P$ 94 13a
m.p. 85°; $[\alpha]_D$ 27.5° $\delta^{31}P$ 72; $[\alpha]_D$ -89.5°

12b $\xrightarrow{\text{R'Cl+EtOH}}$ RO(EtO)P(S)SCl R'= Me_3Si
$\delta^{31}P$ 92 13b
m.p. 82°; $[\alpha]_D$ -52.1° $\delta^{31}P$ 76; $[\alpha]_D$ 54.1°

When the sulfenamides 12a and 12b are treated with equivalent amount of trimethylsilyl chloride-ethanol in methylene chloride solution the corresponding sulfenyl chlorides 13a and 13b are formed.[8] The diastereoisomeric sulfenyl chlorides do not undergo stereochemical changes at the phosphorus center when stored at room temperature under dry argon. It can be therefore concluded that there is no fast halogen exchange between sulfur centers. The possibility of symmetrical bonding between halogen and sulfur atoms is also excluded.

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