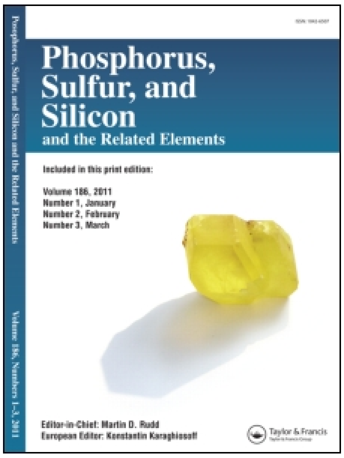

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reaction of Nucleophilic Polyhalogenalkylation in Two and Three-Component Systems

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To cite this Article Pinchuk, A. M. , Marchenko, A. P. and Koidan, G. N.(1990) 'Reaction of Nucleophilic Polyhalogenalkylation in Two and Three-Component Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 195 — 198

To link to this Article: DOI: 10.1080/10426509008038939

URL: http://dx.doi.org/10.1080/10426509008038939

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 195–198
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REACTION OF NUCLEOPHILIC POLYHALOGENALKYLATION IN TWO-AND THREE-COMPONENT SYSTEMS

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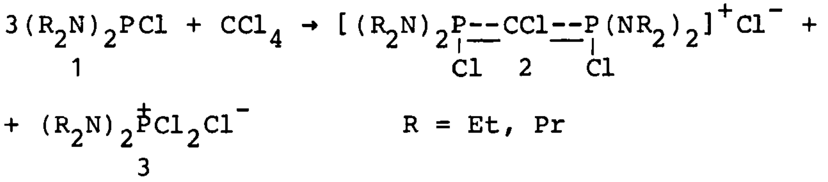
The halophilic reactions of the derivatives of P^{III} R_3P (R = R_2N, Alk, Ar) with CCl_4, having preparative significance, are studied thoroughly. As far as the compounds of R_2PHlg type are concerned, at the beginning of our researches there was was an opinion that the interaction of R_2PHlg with CCl_4 cannot be possible because of the low nucleophility of phosphorus. We determined for the first time that diamidochlorophosphites 1 react with CCl_4 at the temperature 20°C and form the compounds 2, 3.[1]



$$\underset{1}{3(R_2N)_2PCl} + CCl_4 \rightarrow \underset{2}{[(R_2N)_2\underset{Cl}{P}\text{--}CCl\text{--}\underset{Cl}{P}(NR_2)_2]^+Cl^-} + \underset{3}{(R_2N)_2\overset{+}{P}Cl_2Cl^-} \qquad R = Et,\ Pr$$

The scheme of their formation includes on the first stage the generation of threechloromethylide-ion, then threechloromethylation of the starting compound 1 with the formation of phosphonite 4, which transforms into P-Cl ylid 5, the latter connecting the compound 1 and forming the compound 2. Less nucleophilic diamidochlorophosphites 7 interact with

$$1 + CCl_4 \rightarrow (R_2N)_2\overset{+}{P}Cl_2\ CCl_3^- \xrightarrow[-(R_2N)_2\overset{+}{P}Cl_2\ Cl^-]{1} \underset{4}{(R_2N)_2PCCl_3} \rightarrow$$

$$\rightarrow \underset{6}{(R_2N)_2P(Cl){=}CCl_2} \xrightarrow{1} 2$$

CCl_4, forming chlorophosphines 8 and threeamidochlorophosphonium of the chlorides 9. It is established that the compounds 8, 9 are formed as the result of the interaction of

CCl_4 with the products of disproportionality of the compounds 7. Thus diamidochlorophosphites, depending on the nature of the radicals of the atoms of nitrogen interact with

$$\underset{7}{2(RR'N)_2PCl} \rightleftharpoons RR'NPCl_2 + (RR'N)_3P \xrightarrow{CCl_4} RR'NPCl_2 +$$

$$+ (RR'N)_3\overset{+}{P}Cl\ CCl_3^- \longrightarrow \underset{8}{(RR'N)P(Cl)CCl_3} + \underset{9}{(RR'N)_3\overset{+}{P}Cl\ Cl^-}$$

R=R'=Me; R=Et, R'=Ph

CCl_4 in two principally different directions. The reactions of the nucleophilic substitution of atoms of chlorine of P^{III} on threechloromethylic group under the conditions of two and three component systems form the basis for these transformations. The third direction is characteristic of the reaction of diamidofluorophosphites 10 with CCl_4, at the result of which P-F ylids 12 and diamidofluorochlorophosphonium chlorides 13 are formed.^{2} Like diamidochlorophosphites 1 the reaction apparently starts with the formation of threechloromethylide-ion, but the peculiarity of this process is that the nucleophilic substitution of a fluorine atom on the CCl_3-group in the compounds 10 is not the result of high durability of P-F bond. This leads to the formation of the intermediate compounds 11 with dechloration of which by diamidofluorophosphites 10 the ylids 12 are formed.

$$\underset{10}{(R_2N)_2PF} + CCl_4 \rightarrow (R_2N)_2\overset{+}{P}FCl\ CCl_3^- \rightarrow \underset{11}{(R_2N)_2\overset{+}{P}(F)CCl_3Cl^-}$$

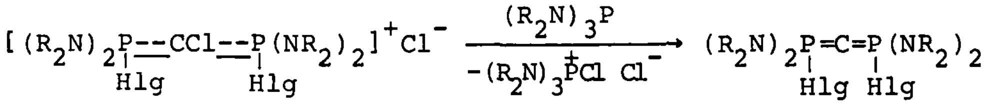
$$\underset{12}{(R_2N)_2P(F){=}CCl_2} + \underset{13}{(R_2N)_2\overset{+}{P}FCl\ Cl^-} \xleftarrow{(R_2N)_2PF} \mathbf{11}$$

R = Et, Pr, i-Pr

Like diamidofluorophosphites 10 di-t-butylphosphine 14 interacts with CCl_4. These data testify that the reaction of R_2PHlg with CCl_4 compounds open new approaches to the synthesis of the number of the key compounds of phosphorus, for example, derivatives of P^{III}, P-Hlg ylids. For the first time the accessibility of the compounds

$$\underset{14}{2t\text{-}Bu_2PF} + CCl_4 \rightarrow t\text{-}Bu_2P(F){=}CCl_2 + t\text{-}Bu_2\overset{+}{P}FCl\ Cl^-$$

15 makes it possible to obtain bis(halogenotetraalkyldiamidophosphanylidene)methanes 16, valuable starting reagents.[3] The reaction of threechloromethylation of halo-



$$[(R_2N)_2\underset{Hlg}{P}\text{---}CCl\text{---}\underset{Hlg}{P}(NR_2)_2]^+Cl^- \xrightarrow[-(R_2N)_3\overset{+}{P}Cl\ Cl^-]{(R_2N)_3P} (R_2N)_2\underset{Hlg}{P}{=}C{=}\underset{Hlg}{P}(NR_2)_2$$

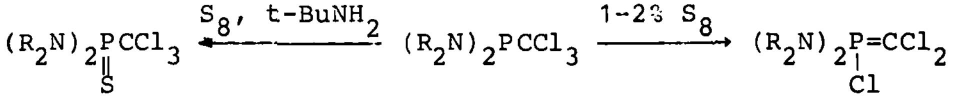
15 16

genides P^{III} under the conditions of three component system, which was discovered by us, has an independent preparatory significance. Only this method allows to obtain sterically difficult derivatives of threechloromethyldichlorophosphone and to synthesize compounds P^{III}, non-stable in ordinary conditions, containing CCl_2X group of 17 type. This makes it possible to investigate the peculiarities of their transformation which are connected with the increase of the coordinated figure and valency of phosphorus. It is

$$R_2PHlg + (Et_2N)_3P + CCl_3X \xrightarrow[Et_2O]{-40^oC} \underset{17}{R_2PCCl_2X} + (Et_2N)_3\overset{+}{P}Cl\ Cl^-$$

R = n-Alk$_2$N, i-Pr$_2$N, t-Bu; X = Cl, CF$_3$, CN; Hlg = Cl, J

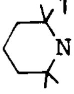
established that regrouping of phosphonites 17 in P-C ylids is accelerated by catalytic addition of chlorine, oxygen, sulphur, and inhibitorated by t-butylamin.[4]



$$(R_2N)_2\underset{\| \atop S}{P}CCl_3 \xleftarrow{S_8,\ t\text{-}BuNH_2} (R_2N)_2PCCl_3 \xrightarrow{1\text{-}2\%\ S_8} (R_2N)_2\underset{Cl}{P}{=}CCl_2$$

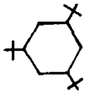
The reaction of nucleophilic threechloromethylation turns out to be suitable for the synthesis of different derivatives of chlorothreechloromethylphosphines 18. Unlike the compounds 17 the chlorophosphines 18 react with the R_3P compounds as galogenophilic agent. In this case the stabilization of carbanion is realized through β-elimination

$$RPCl_2 + (Et_2N)_3P + CCl_4 \xrightarrow[Et_2O]{-60^oC} \underset{18}{RP(Cl)CCl_3} + (Et_2N)_3\overset{+}{P}Cl\ Cl^-$$

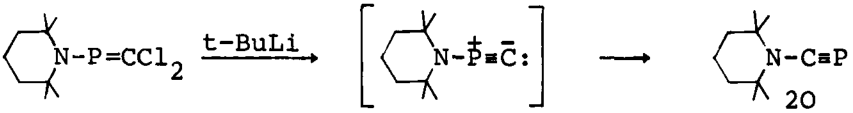
R = n-Alk$_2$N, i-Pr$_2$N, t-Bu$_2$N, N, t-Bu

of the atom of chlorine from phosphorus with the formation of λ^3-phosphaethylene. The single-stage method of obtaining λ^3-dihalogenophosphaethylene 19, the important starting reagents for the synthesis of two- and one-coordinated phosphorus derivatives, is being worked out.[5]

$$RPCl_2 + CHlg_4 + 2\ t\text{-}Bu_3P \rightarrow \underset{19}{R\text{-}P{=}CHlg_2} + 2\ t\text{-}Bu_3\overset{+}{P}Hlg\ Cl^-$$

R = i-Pr_2N, t-Bu_2N,  ; Hlg = Cl, Br, J

The first representative of dialkylaminoethine 20 was synthesized using the accessibility of these compounds 19.



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